Historic overview and new developments in synthetic methods for preparation of the rare-earth tetrapyrrolic complexes

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Keywords: rare-earth, porphyrin, phthalocyanine, naphthalocyanine, tetraazaporphyrin, synthesis

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Contents

1. Introduction
2. Synthetic approaches to single-decker complexes
 - 2.1. Template synthesis from phthalogens
 - 2.2. Rare-earth metal insertion reaction into free-base ligand
 - 2.3. Axial substitution at metal ion
3. Synthetic approaches to homoleptic double-decker complexes
 - 3.1. Template synthesis from phthalogens
 - 3.2. Metallation of free-base ligands
 - 3.3. Axial substitution at the metal center
4. Synthetic approaches to homoleptic triple-decker complexes
 - 4.1. Template synthesis from phthalogens
 - 4.2. Metallation of free-base ligand
 - 4.3. Monophthalocyanine based techniques
5. Synthetic approaches to heteroleptic and mixed-ligand double-decker complexes
 - 5.1. Phthalocyanine-metal-phthalocyanine complexes
 - 5.2. Phthalocyanine-metal-naphthalocyanine complexes
 - 5.3. Phthalocyanine-metal-porphyrin complexes
 - 5.4. Naphthalocyanine-metal-porphyrin complexes
 - 5.5. Porphyrin-metal-porphyrin complexes
6. Synthetic approaches to heteroleptic and mixed-ligand triple-decker complexes
 - 6.1. Heteroleptic phthalocyanine complexes
 - 6.2. Mixed-ligand phthalocyanine and porphyrin complexes

6.3. Mixed-ligand naphthalocyanine and porphyrin complexes

7. Conclusions

Acknowledgement

List of Abbreviations

Tetrapyrrole macrocyclic ligands

DAP	2,8,12,18-tetramethyl-3,7,13,17-tetraethyl-5,15-diazaporphyrinate(2-)
Nc	general abbreviation for naphthalocyaninate(2-)
OEP	2,3,7,8,12,13,17,18-octaethylporphyrinate(2-)
Pc	general abbreviation for phthalocyaninate(2-)
PnP	5,10,15,20-tetrapentylporphyrinate(2-)
Por	general abbreviation for porphyrinate(2-)
TAP	general abbreviation for tetraazaporphyrinate(2-)
^{Ph} TAP	2,3,7,8,12,13,17,18-octaphenyltetraazaporphyrinate(2-)
^{Pr} TAP	2,3,7,8,12,13,17,18-octapropyltetraazaporphyrinate(2-)
TFcP	5,10,15,20-tetraferrocenylporphyrinate(2-)
TPP	5,10,15,20-tetraphenylporphyrinate(2-)
TPyP	5,10,15,20-tetra(4-pyridyl)porphyrinate(2-)
TTP	5,10,15,20-tetra(<i>p</i> -tolyl)porphyrinate(2-)

General Abbreviations

acac	acetylacetonate(1-)
BNT	boron neutron therapy

btfa	benzoyl-1,1,1-trifluoroacetate(1-)
<i>n</i> -Bu	<i>n</i> -butyl
<i>t</i> -Bu	<i>tert</i> -butyl
CD	circular dichroism
1-CIN	1-chloronaphthalene
dbm	dibenzoylmethanate(1-)
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
<i>o</i> -DCB	1,2-dichlorobenzene
DFT	density functional theory
β -dik	β -diketonate(1-)
DMAE	<i>N,N</i> -dimethylaminoethanol
DNA	deoxyribonucleic acid
dpm	dipivaloylmethanate(1-)
FAB	fast atom bombardment (MS method)
fod	2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedionate(1-)
hfbc	3-heptafluorobutyryl- <i>d</i> -camphorate(1-)
HOMO	highest occupied molecular orbital
HOPG	highly oriented pyrolytic graphite
Ln	lanthanides and yttrium
LUMO	lowest unoccupied molecular orbital
MALDI-TOF	matrix-assisted laser desorption–ionization, time-of-flight (MS method)
MCD	magnetic circular dichroism
MS	general abbreviation for mass-spectrometry or mass-spectrum

NIR	near infrared spectral region
NPN	general abbreviation for naphthalonitrile
PDT	photodynamic therapy
PN	general abbreviation for phthalonitrile
QN	quinoline
SOMO	singly occupied molecular orbital
STM	scanning tunneling microscopy
TCB	1,2,4-trichlorobenzene
TfO ⁻	triflate anion (CF ₃ SO ₂ O ⁻)
UV-vis	ultraviolet-visible spectral region

Abstract: New developments as well as a historic overview on synthetic strategies for preparation of the rare-earth complexes with porphyrins, phthalocyanines, naphthalocyanines, tetraazaporphyrins, and related systems are discussed in detail with emphasis on selective synthetic pathways for preparation of single-, double, and triple-decker architectures.

1. Introduction

After their discovery almost 100 years ago, phthalocyanines (Pcs) were predominantly investigated because of their industrial applications as dyes, pigments, and catalysts [1-3]. Similarly, historically, porphyrins (Pors) were intensively studied because of their importance in mimicking biologically relevant atom- and electron-transfer processes as well as light-harvesting mechanisms associated with living cells [4-6]. In addition, porphyrins, phthalocyanines, and their analogues were found to be useful in applications such as redox-driven fluorescence markers and biomarkers, light-harvesting antennas for organic photovoltaics and dye sensitized solar cells, charge carriers for copiers and printers, materials for molecular electronics, as well as redox-active components in environmental, biological, and industrial sensors as well as active components in photodynamic therapy (PDT) and boron neutron therapy (BNT) of cancer [7-19]. In their initial attempts, researchers focused on rich coordination, redox, and magnetic properties of the metal-free, main-group, and especially transition-metal porphyrinoids. It was soon realized, however, that the rare-earth ions can form unusual systems when coupled with the phthalocyanine ligand.

The first rare-earth Pcs were reported by Russian scientists Kirin and Moskalev in 1965 [20]. Kirin and Moskalev also pointed out that because of the large ionic radii and high coordination numbers of the rare-earth ions, the formation of the double-decker rare-earth phthalocyanine compounds could be achieved under specific reaction conditions [20,21]. During the next 50 years, it was confirmed that rare-earth ions are capable of the formation of phthalocyanine single-, double, and triple-decker complexes and their analogues [22-33]. One of the interesting recent discoveries was the preparation and characterization of heteronuclear (rare-earth / cadmium) multiple-decker complexes, which contain up to six Pc ligands [34-42].

However, these compounds include no more than two rare-earth ions located at the periphery of such "super-sandwiches". As a result, electronic coupling between the rare-earth centers in these multiple-decker compounds decreases with an increase in the number of Pc ligands and their magnetic properties start to resemble classic rare-earth double-decker systems. These multiple-decker systems, with rare-earth ion size-dependent intramolecular electronic coupling between macrocycles, as well as metal-metal interactions (in the case of multinuclear rare-earth compounds), open potential applications for such compounds in electrochromic modules [30,43,44], gas sensors [30, 44-50], metal ion sensors [51], and bio-sensors [51-54], as well as active components of molecular magnets [33, 55-60], materials for multi-bit information storage [61-64], molecular electronics [33,65-67], and non-linear optics [30,68-70].

Synthetic approaches for the high-yield, selective formation of heteroleptic, mixed-ligand, and heteronuclear rare-earth multiple-decker complexes could potentially result in the preparation of new systems with exciting properties [41,42,71–81]. The most common strategies for the preparation of rare-earth Pcs are: (i) tetramerization reactions of phthalic acid derivatives (usually – PNs) in the presence of respective rare-earth ions (template synthesis) and (ii) metal insertion reactions into pre-formed metal-free macrocyclic system(s). The last method is particularly interesting for the preparation of asymmetric rare-earth multiple-decker systems with different macrocyclic ligands. In this review, we will discuss specific synthetic strategies for the preparation of rare-earth Pcs and their analogues and highlight their advantages and pitfalls. Although several high-quality reviews on rare-earth porphyrinoids are available in the literature, to the best of our knowledge, there is no published comprehensive overview on synthetic methodologies for preparation of such systems. This contribution compiles the work developed on the rare-earth porphyrinoids reported by several groups around the world.

In order to avoid confusion in terminology [23,25,29], the following definitions will be used in this review: (i) multiple-decker homoleptic complexes are those with identical ligands; (ii) multiple-decker heteroleptic complexes are those that have the same type of ligands (i.e. Pcs) with different substituents, as well as Pc–naphthalocyanine (Nc) and Pc–tetraazaporphyrin (TAP) ligands; (iii) mixed-ligand multiple-decker complexes are those that contain macrocycles with different meso-substituents, *i.e.* Pc-Por type complexes; (iv) heteronuclear multiple-decker systems are those containing different metals; (v) the definition of dimers and trimers will be used both for multiple-decker systems as well as systems with covalently bridged oligomers; and (vi) the Ln abbreviation will be used for lanthanides and yttrium.

Electronic absorption spectroscopy is known as the most commonly used characterization technique for porphyrinoids. It represents a simple, yet very effective tool and therefore deserves a short introduction, especially since rare-earth planar and sandwich-type tetrapyrrole complexes demonstrate unique features in their absorption spectra depending on the nature, number, and combination of their constituent ligands and metal ions, which affirms this method as the primary one both for identification and purity control purposes.

In this review, we exemplify spectral properties of the rare-earth tetrapyrrolic systems by the generalized Pc- and Nc-containing compounds. UV-vis spectra of the single-decker rare-earth Pcs and Ncs characterized by the intense *Q*- and *B*-(Soret) bands. In the case of tetrapyrrolic systems with effective four-fold symmetry, *Q*-band usually represents the first excited state and predominantly originates from the HOMO → LUMO, LUMO+1 single electron excitations. For instance, planar metal-containing Pcs and Ncs reveal a single *Q* band due to the LUMO degeneracy resulting from higher (D_{4h}) symmetry of the complex. The LUMO and LUMO+1 degeneracy usually holds in the case of single-decker rare-earth Pcs and Ncs, which

have effective C_{4v} symmetry. As a result, these complexes also have a single Q -band in their UV-vis spectra. Lowering effective symmetry in Pcs and Ncs results in non-degenerate LUMO and LUMO+1, which leads to splitting of the Q -band, similar to free-base Pcs with D_{2h} effective symmetry (Figure 1). Double-decker compounds are typically formed as stable neutral π -radicals of general formula $[\text{Pc}^{2-}\text{Ln}^{3+}\text{Pc}^{\cdot-}]^0$ and the unpaired electron occupies the ligand-centered SOMO level (Figure 2). Single-electron HOMO $\rightarrow$ SOMO transition contributes significantly to the BV (blue valence) band in the 450–500 nm region and the IV (inter-valence) band observed in the 1200 - 2100 nm region. In addition, SOMO $\rightarrow$ LUMO single-electron excitation provides a major contribution to the RV (red valence) band near 900 nm. The spectra of the redox-active species of the double-decker compounds demonstrate significant difference in comparison with their neutral forms (Figure 2). The oxidized double-decker systems have general formula $[(\text{Pc}^-)_2\text{Ln}^{3+}]^+$ and consist of two antiferromagnetically coupled phthalocyanine cation-radical ligands. Not surprisingly, the UV-vis spectrum of the oxidized form, $[(\text{Pc}^-)_2\text{Ln}^{3+}]^+$, shows a series of the typical for phthalocyanine cation-radical absorption bands with the broad band in 800–1000 nm region having predominantly $2b_1(\text{HOMO}) \rightarrow 2a_2(\text{LUMO})$ character and higher energy bands at ~ 750 and ~ 470 nm (Figure 2). In the reduced state, $[(\text{Pc}^{2-})_2\text{Ln}^{3+}]^-$, the SOMO ($2a_2$) orbital of the neutral, radical $[\text{Pc}^{2-}\text{Ln}^{3+}\text{Pc}^{\cdot-}]^0$ form becomes HOMO, giving rise to the $2a_2(\text{HOMO}) \rightarrow 6e_1(\text{LUMO})$ single-electron transition, which mainly contributes to the Q_2 low-energy component of the Q -band. While the higher-energy Q_1 band remains predominantly induced by the $2b_1 \rightarrow 6e_3$ single-electron transition as in the case of both the neutral and oxidized forms. The UV-vis spectra of the triple-decker rare-earth complexes are similar to those of single-electron reduced forms of the respective double-decker systems due to the same electronic configuration of the constituting ligands (Figure 1). Extension of the π -system (Figure

3), increase of the ionic radius of lanthanide, and introduction of the donor substituents typically lead to the low-energy shift of the main absorption bands. Finally, the spectra of heteroleptic compounds generally show intermediate character compared to the corresponding homoleptic relatives (Figure 3). The spectral properties of the sandwich-type tetrapyrrole complexes have already been reviewed in detail along with other common characteristics [26,27,30,33]. Herein, we will discuss UV-vis spectra of the rare-earth complexes only in content of purity of the target compounds.

2. Synthetic approaches to single-decker complexes

The main characteristics of the single-decker rare-earth Pcs (as compared to the multiple-decker systems) is their ability to complete the coordination sphere with a variety of different solvents to form complexes of general formula $[\text{Pc}^{2-}\text{Ln}^{3+}\text{X}^-](\text{Solv})_n$, where X^- is a counterion and Solv is an additional solvent molecule(s). Thus, in order to enforce the reaction toward the formation of the rare-earth single-decker complexes, one should effectively solvate the Ln ion during such reaction to avoid the formation of unwanted multiple-decker systems. So far, existing methods for preparation of the single-decker rare-earth complexes with Pcs and their analogues can be divided into three groups discussed below.

2.1. Template synthesis from phthalogens

The simplest method for preparation of the rare-earth single-decker Pc complexes is the high-temperature template reaction between the respective unsubstituted or substituted PN and a rare-earth salt (Scheme 1, conditions 1). This method was used for synthesis of unsubstituted rare-earth single-decker Pcs **1** [82,83] as well as the corresponding crown-ether derivatives **2** and

ytterbium tetrachlorophthalocyanine **3** (Table 1) [84,85]. However, the yields of target compounds under these reaction conditions have not been reported, while it is currently generally accepted that the high temperatures used in the original reports could facilitate the formation of the double-decker complexes [85]. As a result, selectivity for the formation of single-decker Pcs is rather poor and the reaction mixtures require extensive purification. According to Smirnov and co-workers [86], up to 76% yields of tetrachloro- (**3**) and tetranitro- (**4**) substituted Pcs can be observed, while yield of the corresponding tetrabromo derivative **5** is significantly lower [87] (Table 1). It was suggested in two reports [88,89] that the reaction between sterically hindered PNs and rare-earth salts leads to the selective formation of the single-decker Pc complexes **6-9** (Table 1) in 53-84% yields with target compounds being characterized by UV-vis spectroscopy. Template synthesis method *1* (Scheme 1) was also employed in the preparation of rare-earth single-decker 1,2-Ncs of general formula 1,2-NcLnCl (**13**) [95] and the rare-earth octaphenyl-substituted TAPs of general formula ^{Ph}TAPLnCl (**14**) [96].

Table 1. Reaction conditions and yields in preparation of rare-earth single-decker Pc derivatives (Scheme 1).

Cmpd	R	R'	Ln	X	Conditions	Yield, % ^a	Ref.
			Sm, Gd, Yb, Lu, Y				[82]
1	H	H	Nd, Y	OAc	<i>1</i>	–	[83]
			Lu		<i>2a</i>	5	[90]
2	15-crown-5		Lu	OAc	<i>1</i>	–	[85]
			Yb			–	[84]
3	H	Cl	Sm, Ho, Lu	Cl	<i>1</i>	74–76	[86]
			Y, Er			32–34	[87]
4	H	NO ₂	Nd, Sm, Ho, Lu	Cl	<i>1</i>	66–74	[86]
			Y, Er			55–56	[87]
5	H	Br	Y, Er	Cl	<i>1</i>	29–31	[87]
6	Cl		Nd, Eu, Lu	OAc	<i>1</i>	53–83	[88]

7	H		Nd, Eu, Lu	OAc, HCO ₂	<i>1</i>	77–82	[89]
8	H		Nd, Eu, Lu	OAc, HCO ₂	<i>1</i>	70–84	[89]
9	H	Ph ₂ CHC(O)NH	Nd, Eu, Lu	OAc, HCO ₂	<i>1</i>	70–80	[89]
10	H	<i>cyclo</i> -C ₃ H ₇	Lu	OAc	<i>2b</i>	< 25	[91]
11	–OCMe ₂ O–		Sm, Eu, Tb, Dy, Yb, Lu	OAc	<i>2b</i>	22–75	[92]

^a The dash indicates that the yield is not given.

The reaction temperatures for the preparation of rare-earth single-decker Pcs can be reduced if alcohols are used as solvents in the presence of a strong organic base (*i.e.* DBU, Scheme 1, conditions 2). Lutetium complexes **1** and **10** with unsubstituted [90] and cyclopropyl group substituted [91] Pcs as well as a series of rare-earth isopropylidenedioxy substituted Pcs **11** [92] have been prepared under these reaction conditions in 5 - 75% yields.

Isoindolines can also be used as a starting material for the preparation of rare-earth single-decker Pcs (Scheme 2). Indeed, template reaction between isoindolines and rare-earth ions in DMF or DMAE leads to the formation of unsubstituted (**1**) [93] as well as propyloxy-substituted (**12**) [94] single-decker Pcs.

2.2. *Rare-earth metal insertion reaction into free-base ligand*

Direct template synthesis of single-decker Pc derivatives by the reaction between PN and the rare-earth ions at elevated temperatures has several disadvantages, with the major one being the relatively low yields on the target compounds and the necessity of further purification step(s). An increase in selectivity toward the formation of rare-earth single-decker Pcs could be achieved using the metal-free macrocyclic ligand or its dianion as a starting material (Scheme 3).

The *in situ* formation of the corresponding macrocyclic dianions is a key for preparation of the rare-earth single-decker Pcs in high yields. Indeed, short-time (1-5 minutes) reaction between the rare-earth chlorides or acetates and Pc dianion (prepared from the metal-free Pc and *n*-butyl lithium) in DMSO, results in the formation of the single-decker Pc derivatives **1**, **15**, and **16** (Table 2) in ~90% yields (Scheme 3, conditions 1) [97-99]. DBU or 1,10-phenanthroline were also used as bases in preparation of the rare-earth single-decker Pcs from the metal-free Pc

crown-ethers **2** [100,101] or octaalkylphthalocyanines **17**, **18** [102] in high yields (Scheme 3, conditions 2). If the rare-earth tris(β -diketonates) are used as the rare-earth ion source (Figure 4), their reaction with the metal-free Pc could be conducted in DMSO without any organic base (Scheme 3, conditions 3a). Unsubstituted rare-earth Pcs **1** were prepared under these conditions with high, up to 86%, yields (Table 2) [104]. DMSO can be replaced by *o*-DCB (Scheme 3, conditions 3b) to form erbium single-decker Pcs **16** and **20** in 59 and 61% yields, respectively [105].

Table 2. Reaction conditions and yields in preparation of the rare-earth single-decker Pcs using conditions outlined in Scheme 3.

Cmpd.	R	R'	M	Ln	X	Synthetic pathway	Yield, %	Ref.
1	H	H	H	Pr, Nd, Sm–Lu	Cl, OAc	<i>1</i>	> 90	[97,99]
				Sm, Eu, Gd, Lu	fod, btfa, hfbc	<i>3a</i>	≥ 86	[104]
				Eu–Yb, Y	dbm	<i>3c</i>	≥ 90	[106]
			Li	Eu–Tm, Lu, Y	dpm, acac	<i>3c</i>	60–90	[107,108]
				Lu			> 93	[100]
2	15-crown-5		H	Sm, Dy, Tm	OAc	<i>2</i>	> 95	[101]
15	Me	Me	H	Pr, Nd, Sm–Lu	Cl, OAc	<i>1</i>	> 90	[98]
16	H	<i>t</i> -Bu	H	Pr, Nd, Sm–Lu	Cl, OAc	<i>1</i>	> 90	[98]
				Er	acac	<i>3b</i>	59	[105]
17	Et	Et	H	Eu, Er Lu	OAc	<i>2</i>	89–96	[102]
18	<i>n</i> -Bu	<i>n</i> -Bu	H	Eu, Er, Lu	OAc	<i>2</i>	95–97	[102]

19	Ph	Ph	H	Eu, Er, Lu	OAc	2	60–94	[103]
20	H	<i>n</i> -C ₅ H ₁₁ O	H	Er	acac	<i>3b</i>	61	[105]

Alkaline-metal Pcs, and especially commercially available dilithium Pc, can be introduced in the reaction with a variety of the rare-earth derivatives to form the target mononuclear rare-earth complexes (Scheme 3, conditions 3c). High solubility of the dilithium Pc in THF, acetone, and other organic solvents allows the reaction to be conducted at relatively low temperatures and in homogeneous conditions. Indeed, a large number of single-decker Pc complexes **1** with a variety of β -diketones were prepared under these reaction conditions (Table 2) [106-108].

Choice of the solvent is crucial in preparation of rare-earth single-decker Pcs from rare-earth tris(β -diketonates). For instance, when methanol or DMSO are used as the reaction solvents, the major reaction products have a general formula of $\text{Pc}^{\text{R}}\text{Ln}(\beta\text{-dik})(\text{Solv})_n$ [104,106,107]. In some cases, similar complexes could be obtained in THF [107] or upon treatment of the $\text{Li}[\text{PcLn}(\text{acac})_2]$ complexes with water [108]. The $\text{Li}[\text{PcLn}(\beta\text{-dik})_2]$ and $\text{H}[\text{PcLn}(\beta\text{-dik})_2]$ complexes are the major products in the reaction between dilithium Pc and rare-earth diketone in acetone [106-109]. In addition, these complexes were also obtained in THF [107] or as a minor reaction product in DMSO [104,110]. Reaction between dilithium Pc and $\text{U}(\text{acac})_4$ or $\text{Th}(\text{acac})_4$ in THF leads to the formation of $\text{PcM}(\text{acac})_2$ ($\text{M} = \text{U}, \text{Th}$) complexes in ~40% yield, while a similar reaction with the MCl_4 ($\text{M} = \text{U}, \text{Th}$) does not result in the formation of the corresponding single-decker Pcs [111]. Reaction between dilithium Pc and $\text{Ln}(\text{dpm})_3$ in boiling THF, followed by the multi-step reaction mixture workup, resulted in the formation of rather unique binuclear single-decker Pcs of general formula $\text{PcLn}_2(\text{dpm})_4$ (**21**) with two Ln ions and four β -diketonate ligands per single Pc macrocycle (Figure 5) [107,112,113]. According to two other reports [104,110], the rare-earth single-decker Pcs of general formula $\text{Pc}(1\text{-})\text{Ln}(\beta\text{-dik})_2$

(**22**) can be prepared by the reaction between metal-free Pc and rare-earth tris(β -diketonates) with strong electron-withdrawing groups (fod, hfbc, btfa; Figure 4) in DMSO or TCB in low yields (up to 6.5%). These complexes are stable in the solid state and their solutions have the characteristic red color of the Pc radical-cations, and show strong EPR signals associated with the singly oxidized Pc ligand [104].

The synthetic approach mentioned above can be extended to the other Pc analogues. Indeed, the general reaction between metal-free Pc analogues or Pors with rare-earth chlorides, acetates, and β -diketonates results in the formation of the lutetium tetra(*t*-Bu)-substituted pyrazinoporphyrazine **23** [114], lutetium octaphenyl-, octaethylthio-, and octadecylthio-substituted TAPs **24** [114,115], lutetium 1,2-Nc **13** [116,117] and tetra(*t*-Bu)-substituted 2,3-Nc **25** [118], octaphenoxy- [119] and octaphenyl- [103] substituted 2,3-Ncs **26** and **27**, lutetium 1,2,3,4,19,20,21,22-octaphenyldipthalo-11(12),29(30)-di(*tert*-butyl) dinaphthalotetraazaporphyrin **28** [120] (Figure 6), as well as a variety of rare-earth *meso*-substituted single-decker Por complexes [121–124]. DMF [114], DMSO [114,115,118,120], or octanol [115] were used as solvents in these reactions. Interestingly, lutetium insertion into the octaalkyl-substituted TAP macrocycle resulted in the formation of complex **24** even at room temperature. The formation of single-decker Pcs **26** and **27** were reported with 77-88% yields at conditions similar to those used for the preparation of Pcs **17-19** (Scheme 3, conditions 2) [103,119]. Both change in the ratio of reactants and longer reaction time do not lead to the formation of the double-decker Pc complexes. This observation could be indicative of the influence of the temperature and/or coordinating ability of the solvent, which prevents the formation of the double-decker derivatives and thus allows the use of this method as a selective approach for preparation of rare-earth single-decker Nc compounds [29,125]. Thus, insertion of

the rare-earth ions into metal-free macrocycles and their dianions is, indeed, a highly selective method for preparation of the single-decker rare-earth complexes, which leads to the formation of the target compounds in high yield and purity.

2.3. *Axial substitution at metal ion*

Axial ligand(s) substitution reaction in rare-earth complexes of aromatic macrocycles was reported for Pors [126-129], N-confused Pors [130], and Pcs [131-137]. In the case of single-decker Pc derivatives similar reactions were also described for zirconium, hafnium [138,139], and indium [140-142] complexes. Besides the obvious reasons for axial ligand(s) functionalization, stability of the rare-earth single-decker Pcs can also be significantly improved using this method. In the case of rare-earth single-decker Pors, the tridentate ligand suggested by Kläui (Scheme 4) [126-129], as well as tris(1-pyrrazoly)borohyrides (Scheme 5) [127], are quite commonly used to stabilize a single-decker structure via saturation of the first coordination sphere of the central metal ion. Such axial ligand exchange reactions are usually conducted at room temperature and result in the formation of the target compounds in fairly high yield (30 - 96%). Notably, yields of the products generally tend to increase with the Ln ions contraction.

Since stability of rare-earth single-decker Pcs with tridentate axial ligands is very good, such complexes can be used for further transformation located at the Por macrocycle. Indeed, ytterbium complex **35** (Scheme 6) can be prepared using this synthetic approach in four steps with high yields (60-90%) in individual reactions [128].

Because of the presence of an additional transition-metal ion in heteronuclear complex **35**, its photophysics and specifically luminescent properties in the NIR region are significantly improved compared to the dinuclear ytterbium-containing starting material [128]. The low yield

(5%) of the starting asymmetric metal-free hydroxy-substituted Por, however, limits the potential use of complex **35** in imaging and bioimaging applications. Water-soluble dinuclear complexes **37** can be prepared by quaternization of the corresponding tetra-(4-pyridyl)-substituted Pors **36** (Scheme 7). Target compounds **37** can intercalate with DNA fragments similar to the other cationic water-soluble Pors [129].

A similar synthetic approach was used in transformation of the N-confused dinuclear Por **38** into water-soluble quaternized derivative **39** [130]. Starting compound **38** was prepared from the corresponding metal-free N-confused Pors in two steps in 40-78% yield (Scheme 8).

Axial ligand substitution reactions with Kläui's ligand can also be achieved in the case of rare-earth single-decker Pcs to form target dinuclear complexes **40** and **41** [131,132] (Scheme 9). Yield of the dinuclear complexes **40** (9-30%), however, are significantly lower compared to the dinuclear complexes **41** (63-66%), perhaps because of the low solubility of the former systems in common organic solvents. X-ray structures of symmetric dinuclear complexes **40** (Figure 7) have been correlated with their individual magnetic properties [132].

Synthetic strategies for the preparation of rare-earth mixed ligand (Schiff base / Pc) single-, double-, triple-, and quadruple-decker complexes **42-45** has been described recently [133-136] (Scheme 10). Although reactions can be easily conducted at room temperature, increasing the reaction temperature to 80 °C in a sealed vial allows better (up to ~40%) yields of the target compounds [135]. Polynuclear complexes **42-45** can be obtained in a pure form upon slow crystallization of the reaction mixture. Polynuclear complexes **42-45** have optical and magnetic properties close to those observed for the single-decker Pc systems, which is indicative of a weak inter-ligand electronic coupling (Figures 8 and 9). For instance, minor splitting of the low-energy *Q*-band and its energy, which is close to the *Q*-band energy in rare-earth single-

decker Pcs in the case of systems **42** and **44**, is indicative of effective C_{4v} symmetry in these compounds and degeneracy of the Pc-centered LUMO and LUMO+1.

Reaction between single-decker PcLuOAc or PcMCl_2 ($M = \text{Zr, Hf}$) complexes with iron(II) chlathrochelatate precursors in methanol/ CH_2Cl_2 mixture allows the preparation of the hybrid binuclear Pc-chlathrochelatate complexes of general formula of $\text{PcM}(\text{Clat})$ ($M = \text{Lu, Zr, Hf}$; $\text{Clat} =$ chlathrochelatate anion) [137,138]. UV-vis and MCD spectra of these complexes are a superposition of the UV-vis and MCD spectra of the corresponding Pcs and chlathrochelates, which is indicative of a lack of electronic interactions between them. Electro- and spectroelectrochemical data as well as DFT calculations are suggestive that the HOMO is Pc-centered MO [143].

Single-decker Pcs of general formula PcMCl_2 ($M = \text{Zr, Hf}$) can also be introduced into the axial ligand substitution reaction with a variety of β -diketones with the formation of the target $\text{PcM}(\beta\text{-dik})_2$ complexes [139]. The PcInCl complex can react under mild conditions with $\text{Bu}_4\text{N}^+\text{X}^-$ ($X = \text{F, Cl, Br, CN, HCOO}$) salts in CH_2Cl_2 or THF with the formation of single-decker $[\text{NBu}_4]^+[\text{PcInX}_2]^-$ compounds in high yield [140]. Organometallic indium Pc complexes of general formula $^R\text{PcInR}'$ can be prepared in 12-70% yields by the reaction between substituted chloroindium Pcs, namely $^R\text{PcInCl}$ ($R = \text{alkyl or alkoxy group}$), with Grignard reagents of general formula $\text{R}'\text{MgCl}$ ($\text{R}' = \text{Me, Ph, } p\text{-FC}_6\text{H}_4, p\text{-CF}_3\text{C}_6\text{H}_4, m\text{-CF}_3\text{C}_6\text{H}_4, \text{F}_5\text{C}_6$) in ether or THF [141,142]. Similarly, the pentaferrocene-containing $\text{FcIn}(\text{TFcP})$ complex ($\text{TFcP}^{2-} = 5,10,15,20\text{-tetraferrocenylporphyrinate}$), with one of the ferrocene groups located in the axial position, can be prepared by the reaction between $\text{ClIn}(\text{TFcP})$ and ferrocene lithium [144]. All five ferrocenes in the $\text{FcIn}(\text{TFcP})$ compound can be oxidized at different potentials and this organometallic Por can form highly ordered "channel" structures with the C_{60} fullerene.

3. Synthetic approaches to homoleptic double-decker complexes

The most common group of the double-decker rare-earth complexes belongs to double-decker Pc derivatives, which were first reported in 1965 by a group of Russian scientists [20]. Major synthetic approaches for preparation of the rare-earth double-decker Pcs can be classified based on the type of starting materials involved in their preparation. Following such classification, PN-based template synthesis and metal insertion reactions into metal-free Pc or its dianion will be discussed below.

3.1. *Template synthesis from phthalogens*

Template synthesis of double-decker Pcs from derivatives of phthalic acid, and specifically PN is one of the most common synthetic strategies for preparation of the double-decker complexes. Although this method is simple, its selectivity is very sensitive to the reaction conditions as rare-earth ions can form stable single-, double-, and triple-decker compounds. The most important reaction parameters are the reaction temperature, reaction time, the type of precursor rare-earth salt or complex, the type of phthalic acid derivative (most commonly PNs), and the ratio of reactants. For instance, elevated temperatures, longer reaction time, and use of heavier Ln ions would favor the formation of the double-decker Pcs compared to the single-decker Pc derivatives. Introduction of bulky substituents into the PNs, however, will favor the formation of the single-decker Pc derivatives. The first rare-earth double-decker Pc complexes **46** (Table 3) were prepared by Kirin and Moskalev by the reaction between the rare-earth acetates and PN at 280-290 °C with 1 : 4-8 (mol/mol) ratio [20,21]. New double-decker complexes were obtained in 10-15% yields and characterized by UV-vis spectroscopy (Scheme

11, conditions 1). This method was further optimized by several research groups for preparation of a large variety of the rare-earth double-decker Pcs **46** with unsubstituted macrocyclic ligands [145-148] as well as substituted double-decker Pcs **47-57** [85,94,148-155].

Note that along with the regular double-decker Pc complexes **56** [85], one research group was able to isolate and characterize new Gd, Yb, and Lu double-decker complexes with covalent C-C bonds between α -pyrrolic atoms of neighboring macrocycles, although yields of these systems were quite low (~1%) [156]. Because of the direct C-C bonds between Pc ligands and thus the loss of the conjugation in the macrocyclic π -system, no usual low-energy *Q*-band was observed in these complexes. Similar covalently linked Pcs have also been reported for titanium [157] and niobium [158] ions.

Depending on the nature of the Ln ion, yields of the rare-earth double-decker Pcs **46** can vary between 5 and 60% when the template reaction was conducted at 300-310 °C followed by a vacuum sublimation of the crude product [146,147]. Under these conditions, yields of the target double-decker Pc increase and the yields of the reaction by-product (metal-free Pc) monotonically decrease (from 75 to 2%) with light to heavy Lns. In order to improve yields of the double-decker Pcs with the early rare-earth ions, it was suggested [148] to conduct the template reaction in a sealed tube applying chromatographic purification instead of sublimation. In this case, target double-decker complexes **46** were isolated in 50-60% yield. This reaction modification was used later for a template synthesis of double-decker complexes **47-51** (Table 3) [148-152]. It was also mentioned that although the first step in this reaction is the formation of the single-decker Pc derivative [148,153,159,160], the formation of double-decker Pcs could be achieved for the early Ln ions in 5-10 minutes, while late Ln ions require longer reaction time for preparation of target double-decker systems. Similar to Lns, zirconium(IV) and hafnium (IV)

double-decker Pcs can be obtained in 60-70% yields upon heating PN or 4-*tert*-butylphthalonitrile and the corresponding metal chlorides [168,169].

If template condensation between PN and rare-earth salt is conducted in the presence of an inorganic base (*i.e.* Na₂CO₃, KOH, or KOCH₃ *etc.*) at 270-280 °C, the formation of the ionic double-decker Pcs **46** of general formula M⁺[Pc₂Ln][−] (Ln = La, Pr, Nd, Sm–Lu, Y; M = Na, K) was documented in 36–41% yields [161–164]. Alkaline cations in these systems can be replaced by tetraalkyl ammonium cations using simple metathesis reactions with tetraalkyl ammonium bromides in quantitative yields. New systems of general formula of [NAlk₄]⁺[Pc₂Ln][−] are easily soluble in a variety of organic solvents, which significantly simplifies their characterization. Electrochemical oxidation of the anionic form of double-decker Pc derivatives in CH₂Cl₂ results in the formation of neutral radical double-decker compounds of general formula [Pc^{2−}LnPc^{1−}]. Similar oxidation of neutral double-decker Pcs from the corresponding anionic form can also be achieved under UV light irradiation of a solution of [NAlk₄]⁺[Pc₂Ln][−] in CH₂Cl₂/acetonitrile [165].

Ln metals can also be used for preparation of double-decker Pcs. For instance, heating a mixture of ytterbium, PN, and iodine (molar ratio of 1:8:2) in a sealed tube at 200 °C results in the formation of dark violet crystals of ytterbium double-decker **46** of formula [Pc₂Yb]I₂ [166]. In this case, both Pc ligands are present in the single-electron oxidized radical form (Pc^{1−}). Similar complexes have been obtained using these reaction conditions also for zirconium(IV) and indium(III) metals, although in the case of indium, it has to be introduced in the reaction as an indium/thallium alloy [167].

Microwave radiation has also been used for a template synthesis of rare-earth double-decker Pc complexes (Scheme 11, Table 3) [170]. The main advantage of microwave radiation

for template condensation of Pcs is that the reaction time is reduced from hours to minutes. For instance, unsubstituted Pc_2Ln complexes **46** ($\text{Ln} = \text{Tb}, \text{Dy}, \text{and Lu}$) were prepared in more than 70% yields upon microwave irradiation (650-700 W) of the reaction mixture of PN and the corresponding rare-earth salts for only 6-10 minutes [170]. However, respective *t*-Bu-substituted analogues **47** can only be obtained in low (less than 10%) yields under the same reaction conditions. In a more recent report [154], the reduction of the microwave power to 300-450 W as well as a shorter reaction time (5-8 minutes) resulted in improved yields of *t*-Bu-substituted rare-earth double-decker Pcs **54** (Table 3).

Table 3. Yields of the rare-earth double-decker Pcs under template condensation reaction conditions shown in Scheme 11.

Cmpd	R	R'	Ln	X	Synthetic route	Yield,%	Ref.
46	H	H	La, Pr, Nd, Sm–Lu	OAc	<i>1</i>	10–15	[20,21,145]
			Lu		<i>3a</i>	10	[90]
			Nd, Sm, Er, Lu		<i>1</i>	50–60	[148]
			Pr, Nd, Sm–Lu		<i>1</i>	5–60	[146,147]
			Tb, Dy, Lu		<i>2</i>	> 70	[170]
			La, Pr, Nd, Sm, Gd, Er, Lu		<i>1</i>	60–80	[148,149]
47	H	<i>t</i> -Bu	Er, Gd, Lu	HCOO, Cl	<i>1</i>	70	[150]
			Ce	OBz	<i>1</i>	52	[151]
			Er	acac	<i>3c</i> , 12h	24	[105]
48	H	(CF ₃) ₃ C	Lu	OAc	<i>1</i>	–	[152]
49	H	Ph	Lu	HCOO	<i>1</i>	up to 70	[150]
50	H	PhO	Lu	HCOO	<i>1</i>	70	[150]
51	Br	<i>t</i> -Bu	Lu	HCOO	<i>1</i>	70	[150]
52	H	PrO	Lu	OAc	<i>1</i>	–	[94]
53	H	(CH ₃) ₃ CCH ₂	Lu	OAc	<i>1</i>	–	[94]
54	C _n H _{2n+1} , n = 1	C _n H _{2n+1} , n = 1	Tb, Lu	OAc	<i>1</i>	–	[153]
	n = 2	n = 2	Eu, Dy, Lu	OAc, acac	<i>3b</i> , 15–20 h	11–53	[154]
	n = 4	n = 4	Eu, Dy, Lu	OAc, acac	<i>1</i> , 2–8 h	22–49	[154]

					$3b$, 15–20 h	6–46	
					2, min	5–8	16–23
	$n = 7$	$n = 7$	Eu, Gd Y	acac	$3c$, 13h	68–72	[171] [172]
	$C_nH_{2n+1}O$, $n = 1$	$C_nH_{2n+1}O$, $n = 1$	Lu	OAc	1	–	[153]
	$n = 3$	$n = 3$	Sm, Tm, Lu	HCOO, OAc	$3c$, 8h	61–66	[173]
	$n = 4$	$n = 4$	Er	OAc	$3a$, 20h	–	[174]
	$n = 5$	$n = 5$	Eu, Gd Y	acac	$3c$, 8h	75–79	[171] [172]
	$n = 6$	$n = 6$	Er	OAc	$3a$, 20h	–	[174]
			Er	OAc	$3a$, 20h	–	[174]
55	$n = 8$	$n = 8$	La–Nd, Sm–Tm, Y	acac	$3c$, 12h	9–63	[175]
	$n = 9$	$n = 9$	Er	OAc	$3a$, 20h	–	[174]
			Er	OAc	$3a$, 20h	24	[176]
	$n = 10$	$n = 10$	Lu	OAc	$3a$, 24h	20	[177]
			Lu	OAc	$3a$, 20h	20	[178]
			Nd, Eu, Er, Lu	OAc	$3a$, 20h	15–23	[176]
	$n = 12$	$n = 12$	Pr, Nd, Eu–Lu	OAc	$3a$, 20h	20–30	[174]
			Ce	acac	$3c$, 12h	22	[179]
	$n = 14$	$n = 14$	Er	OAc	$3a$, 20h	–	[174]

			Lu	OAc	3a, 24h	14	[177]
	n = 16	n = 16	Er	OAc	3a, 20h	–	[173]
			Lu	OAc	3a, 24h	11	[177]
	n = 18	n = 18	Er	OAc	3a, 20h	27	[176]
			Lu	OAc	3a, 24h	12	[177]
						–	[180]
56	15-crown-5		Lu	OAc	3a, 20h	19	[181]
					1	35	[85]
57	H		Pr, Nd, Eu–Lu	OAc	1, 1h	30–50	[155]
58	18-crown-6		Lu	OAc	3a, 20h	7	[181]
59	MeO[(CH ₂) ₂ O] _n (n = 1,2,3,4)	MeO[(CH ₂) ₂ O] _n (n = 1,2,3,4)	Lu	OAc	3a, 8–22h	6–12	[181,182]
	n = 2	n = 2	Eu	acac	3c, 8h	31	[183]
60			Lu	OAc	3a, 8h	20	[184]
	R ₁ = C _n H _{2n+1} , (n = 12,13)	R ₁ = C _n H _{2n+1} , (n = 12,13)					
61	BnO	BnO	Nd, Sm, Dy, Lu	HCOO, OAc	3a, 8h	37–55	[185]
62	C _n H _{2n+1} S (n = 8,10,12, 14,16,18)	C _n H _{2n+1} S (n = 8,10,12, 14,16,18)	Eu, Tb, Lu	OAc	3a, 22–44h	26–44	[186]
	n = 6	n = 6	Sm, Gd, Dy	OAc	3a, 48h	29–36	[187]

			Lu		3c, 48h	12	[188]
63	H	${}^n\text{C}_{12}\text{H}_{25}\text{S}$	Lu	OAc	3a, 20h	8.1	[189]
64	H	cyclo- C_3H_7	Lu	OAc	3b	< 25	[91]
65	H	${}^n\text{C}_5\text{H}_{11}\text{O}$	Er	acac	3c, 12h	30	[105]
66	PhO	PhO	Eu, Ho, Lu	acac	3c, 8h	36–43	[190]
67	PhS	PhS	Eu	acac	3c, 8h	42	[190]
68	Me ^(a)	Me ^(a)	Dy, Er, Tm, Lu	HCOO, OAc	3a	66–72	[191]
69	CN	CN	Nd	OAc	3d	–	[192]
70			Gd, Lu	OAc	3c ^(b) , 20–30h	2–17	[70]
	R = $i\text{C}_4\text{H}_9$	R = $i\text{C}_4\text{H}_9$					
71	H		Lu	OAc	3a, 6h	49	[69]
72	HO[(CH ₂) ₆ S]	HO[(CH ₂) ₆ S]	Eu, Yb, Lu	acac	3a, 8–10h	10–13	[51]
73	H		Lu	OAc	3a, 24h	27	[44]
74	H		Lu	OAc	3a, 24h	12	[193]

^(a) Substituents at 1,3,8,10,15,17,22,24 positions of Pc ligand;

^(b) Lithium alkoxide was used as a base.

The third synthetic strategy for preparation of the rare-earth double-decker Pcs using a template condensation reaction is boiling the mixture of the corresponding PN, rare-earth precursor, DBU (as a strong organic base), and a long-chain alcohols (usually pentanol or hexanol) as shown in Scheme 11, condition 3. The target double-decker compounds can be purified by standard column chromatography approaches. Yield of the unsubstituted (**46**) [90] as well as substituted (**47**, **54-75**, Table 3) [44,51,69,70,91,105,154,156,171–194] rare-earth double-decker Pcs prepared using this method depends on the nature of substituents in the Pc macrocycle as well as the type of Ln ion used for the reaction and varies between 2 and 79%. For instance, lutetium salts tend to result in the lowest yields, while the higher yields were observed for europium and gadolinium complexes. Similarly, the presence of bulky substituents in the Pc macrocycle leads to a reduction of the rare-earth double-decker Pcs yields (Table 3).

Template synthesis has also been used in preparation of a variety of the rare-earth double-decker Nc complexes (Scheme 12) [119,125,195–198]. For instance, high-temperature template condensation reaction between 5-bromo-7-*tert*-butylnaphthalonitrile [195] or 6,7-diphenoxynaphthalonitrile [119,196,197] (Scheme 12, condition 1) results in the formation of the rare-earth double-decker compounds **76** or **77** in 41-55% yields without any single-decker complexes formed as byproducts. Optimization of the reaction temperatures can significantly improve yields of the target compounds [199]. Europium and erbium double-decker Ncs **77** also can be prepared using microwave radiation (Scheme 12, condition 2) similar to a synthesis of double-decker Pcs **54** (Scheme 11) [154,171,172]. The best yields of europium and erbium

double-decker complexes **77** (39 and 33%, respectively) can be achieved using 700 W microwave power and 5-7 minutes reaction time [199].

High-boiling solvents can be utilized in template preparation of the double-decker Ncs. For instance, complexes **78** and **79** were prepared in 35-79% yield using the rare-earth acetylacetonates and the corresponding naphthalonitriles in boiling *n*-octanol in the presence of DBU (Scheme 12, condition 3). In this approach, yields of the target complexes decrease upon Ln ion contraction [125,198]. The choice of *n*-octanol as a solvent for this reaction is critical as its replacement with lower boiling point *n*-pentanol or *n*-hexanol as well as high boiling point chlorinated aromatic solvents (TCB or 1-CIN) did not result in the formation of the target compounds [125].

3.2. Metallation of free-base ligands

Synthesis of the double-decker rare-earth Pcs using the corresponding metal-free Pc macrocycles avoids many unwanted side reactions, especially the formation of linear oligomers from the corresponding PNs. The formation of the target double-decker complexes using this method, however, is complicated by steric interactions between the initially formed rare-earth single-decker Pc and the incoming metal-free macrocycle. This results in lower yields of the target double-decker compounds compared to the template synthesis method, especially, for heavy Ln cations. Rare-earth acetates or acetylacetonates are usually used as the metal precursors in this approach (Scheme 13, Table 4). Reactions are carried out using lithium or sodium Pcs as well as metal-free Pc in QN, TCB, or *n*-octanol. A variety of the unsubstituted rare-earth double-decker Pcs **46** was prepared using this method in QN or TCB (Scheme 13, conditions *1a* and *1b*) in 9-33% yields [171,172,200,201], while alkoxy-substituted complexes **55** and **80** can be

synthesized using *n*-octanol (Scheme 13, condition *1c*) [202,203]. Attempts to prepare hexadeca-*n*-heptyl- and hexadeca-*n*-pentoxysubstituted double-decker europium and gadolinium Pcs **54** and **55** using *n*-octanol at 190 °C, on the other hand, (Scheme 13, conditions *1b*) completely failed [171]. The selective formation of double-decker alkylsubstituted Pcs **54** in high yields (R = Et, *n*-Bu, Table 4) can be facilitated by addition of the strong organic base (DBU) to *n*-hexanol (Scheme 13, condition *2a*), or by increase of the reaction temperature (Scheme 13, conditions *1d*) [102]. Combination of the alcohol and DBU allows the formation of the double-decker complexes of 1,4,8,11,15,18,22,25-octabutoxyphthalocyanine (**81**) as well as chiral tetrasubstituted (*D*)- and (*L*)-mentol compounds **82** (Scheme 13, conditions *2b* and *2c*) [204,205]. Moreover, the use of equimolar amounts of Pc and dibenzo-18-crown-6 increases yield of the target double-decker complexes **81** from 1-2% to 24-38% under the same reaction conditions [204]. An approach mentioned in this section was also used in preparation of the rare-earth double-decker complexes **83** with electron-withdrawing groups, which were used as model platforms for characterization of multi-electron reduced forms, although no detailed experimental conditions have been provided [206]. Proposed by Tomilova and co-workers, the synthetic approach for preparation of the single-, double-, and triple-decker rare-earth Pcs in an alcohol/TCB mixture allows the preparation of phenyl-containing double-decker Pcs **84** in 49-96% yields [103], which are higher than the most of the reported yields for similar systems.

Table 4. Yields of the rare-earth double-decker Pcs prepared using Scheme 13 reaction conditions.

Cmpd	R	R'	M	Ln	X	Rxn. Cond.	Yield, %	Ref.
46	H	H	H	Lu	OAc	1a, 22h	9	[200]
			Li	La, Pr, Nd, Sm–Lu	acac	1b, 4h	12–33	[201]
			Li	Eu, Gd	acac	1b, 10h	32, 25	[171]
			Li	Y	acac	1b, 10h	27	[172]
47	H	<i>t</i> Bu	H	La, Tb, Dy	OAc	3	61–63	[207,208]
54	<i>n</i> -C _n H _{2n+1} , n = 2, 4	<i>n</i> -C _n H _{2n+1} , n = 2, 4	H	Eu	OAc	2a	87–95	[102]
				Er, Lu		1d	85–90	
55	<i>n</i> = 8, 12, 18 <i>n</i> C ₄ H ₉ O	<i>n</i> = 8, 12, 18 <i>n</i> C ₄ H ₉ O	H	Lu	OAc	4	–	[214,215]
			H	Yb, Lu	OAc	1c	–	[202]
56	15-crown-5		H	Gd, Yb, Y	OAc	2d, 2h	15–35	[209–212]
			H	La	OAc	2d, 1h	70	[212,213]
			H	Sm, Dy, Tm	OAc	2d, 2h	40–45	[101]
80	(C ₂ H ₅) ₂ CHO ^(a)	H	H	Eu, Lu, Y	acac	1c, 9h	21–49	[203]
81	<i>n</i> C ₄ H ₉ O ^(c)	<i>n</i> C ₄ H ₉ O ^(c)	H	Eu, Y	acac	2c ^(d) , 10h	24–38	[204]
82		H	H	Eu, Lu, Y	acac	2b, 8–12h	9–10	[205]
83	<i>n</i> C ₃ F ₇ ; F ^(c)	<i>n</i> C ₃ F ₇ ; F ^(c)	H	Tb, Lu	–	–	–	[206]

84	Ph	Ph	Li	Eu, Er, Lu	OAc	$I^{(b)}$, 5–10 min	49–96	[103]
85			H	Lu	OAc	4	–	[216]
86	$C_nH_{2n+1}OCH_2$ (n = 8,12,18)	$C_nH_{2n+1}OCH_2$ (n = 8,12,18)	H	Lu	OAc	4	< 40	[217,218]

^(a) Substituents at 1,8,15,22-positions of Pc ligand;

^(b) Mixture of *n*-C₁₆H₃₃OH/TCB (1:1 v/v);

^(c) Substituents at 1,4,8,11,15,18,22,25-positions of Pc ligand;

^(d) Equimolar amount of crown-ether was used.

DBU is quite often used as a strong organic base in preparation of substituted double-decker rare-earth Pc complexes (Scheme 13, conditions 2a, 2d, and 3) [101, 207-213]. For instance, the preparation of octa-*t*-Bu-substituted complexes of lanthanum, terbium, and dysprosium **47** was suggested to produce target compounds in good (61-63%) yields using DBU under 240 W microwave radiation (Scheme 3, conditions 3; Table 4), although reported UV-vis spectra of the target compounds are close to those of the corresponding single-decker rare-earth Pcs [207,208]. On the other hand, Ln double-decker octa-15-crown-5-substituted Pcs **56** were prepared using the metal-free Pc, rare-earth precursor, and DBU (1.5:1:2 molar ratio) in 1-ClN as solvent (Scheme 13, conditions 2d) in 15-45% yield [101,209-212]. In this case, structures of the target compounds were confirmed by spectroscopic methods as well as crystallography [211]. Further optimization of the reaction conditions and specifically use of the 1:1.5:10 molar ratios between Pc ligand, rare-earth precursor, and DBU allowed the preparation of double-decker lanthanum octa-15-crown-5-substituted Pcs **56** (as a mixture of neutral radical and reduced anion forms) in 70% yield (Table 4) [212,213].

Several double-decker lutetium Pcs **54**, **85**, and **86** with long-chain substituents have liquid crystal properties [214-218]. These complexes were prepared in up to 40% yield using amyl alcohol as a solvent and generated *in situ* from potassium and alcohol alkoxide anion as a base (Scheme 13, conditions 4; Table 4). Asymmetric double-decker rare-earth Pcs **87** and **88** (Scheme 14) have been prepared using synthetic conditions [219] developed for systems **54** [102]. These complexes were further used as precursors for preparation of the nano-sized rare-earth systems.

Planar diphthalocyanines **89-91** with extended π -system can be transformed into the corresponding mono- as well as trinuclear double-decker "sandwich-planar" complexes **92-94** (Scheme 15) [220]. Mononuclear complex **94** was prepared from trinuclear **92** by demetalation reaction in acidic media. In the case of complexes **92-94**, both halves of the sandwich fragments have extended π -conjugation, which leads to unusual optical properties of the target compounds. Interesting "sandwich-clamshell" trinuclear tetraphthalocyanine-containing complex **96** was prepared from asymmetric zinc "clamshell" Pc **95** and lutetium acetate in *n*-hexadecanol using catalytic amounts of lithium methoxide in 45% yield (Scheme 16) [221].

Reaction of the metal-free "clamshell" asymmetric Pc **97** with the rare-earth ions resulted in the formation of the bridged "sandwich-clamshell" double-decker Pcs **98** (Scheme 17) [222]. Availability of the synthetic strategies for preparation of tetrabenzotriazoporphyrins [223-226] led to preparation of the first double-decker lutetium tetrabenzotriazoporphyrin complex **99** (Scheme 18) [227].

The first lutetium double-decker tetradiazepinoporphyrazine based complex **100** can be prepared using either template condensation of the dicyanodiazepine with lutetium acetate or by metallation of the metal-free diazepine-containing macrocycle (Scheme 19) [228]. Note that the formation of double-decker system **100** was achieved under conditions typical for preparation of the single-decker rare-earth Pcs (Scheme 3, conditions 2) [102].

Metal insertion reactions can be used in the formation of the double-decker systems, which contain not only rare-earth ions, but also actinides and titanium. For instance, reaction between UCl_4 or ThCl_4 with disodium Pc in 1-CIN results in the formation of the double-decker Pc_2M ($\text{M} = \text{U}, \text{Th}$) complexes **101** in 8 and 6% yields, respectively [229]. Similar reaction between TiCl_4

and PN or 4-*tert*-butylphthalonitrile in boiling DMSO results in the formation of $^R\text{Pc}_2\text{Ti}$ ($R = \text{H}$, *t*-Bu) complexes **102** in up to 40% yield [230].

Reaction between lutetium acetate and unsubstituted dilithium 2,3-Nc or 1,2-Nc in QN or 1-CIN leads to the formation of the corresponding double-decker systems **103** [231] and **104** [196] in 47 and 60% yields, respectively (Figure 10). In the case of 1,2-Nc derivatives, each of the individual macrocycles can form four positional isomers of C_{4h} , D_{2h} , C_{2v} , C_s symmetry and thus complex **104** should also consist of numerous positional isomers, which will be challenging to separate using conventional purification methods. Neodymium and europium double-decker 1,2-Ncs **104** are also discussed in [95], but synthetic conditions and yields of the target compounds were not clearly reported. Phenyl-substituted double-decker 2,3-Ncs **105** could be prepared in 55-63% yields [124] using a general method developed for the preparation of their unsubstituted analogues **84** (Table 4).

Interestingly, double-decker Pors **106-108** and TAPs (**109**, **110**) have so far only been prepared from the corresponding metal-free macrocycles and the corresponding metal salts (Figure 10). For instance, complexes **106** [232], **107** ($M = \text{La-Nd}$, Sm-Gd) [233,234], and **109** ($M = \text{Ce}$) [235] were prepared in up to 80% yields by the reaction of the metal-free Pors or TAPs with rare-earth acetylacetonates in boiling TCB. Similar reaction with $M(\text{NEt}_2)_4$ ($M = \text{Zr}$, Hf) in toluene leads to the formation of complexes **108** and **110** in 54-61% yields [236, 237]. The preparation of double-decker TAPs **109** ($M = \text{Eu}$, Lu) could be achieved using *n*-hexanol in 36 and 44% yields, respectively [235]. Finally, double-decker Por systems **107** ($M = \text{Tb-Lu}$, Y) can be prepared in 60-80% yields using the “raise-by-one-story” approach described in section 3.3 [234].

3.3. Axial substitution at the metal center

In this approach, the pre-formed single-decker complex reacts with an appropriate metal-free macrocycle to form the double-decker compound. It is commonly abbreviated as the “raise-by-one-story” method and usually used for the preparation of heteroleptic and mixed-ligand compounds discussed in the next chapters. However, it also was used in several cases for the preparation of homoleptic double-decker complexes. For instance, the reaction between tin(IV) single-decker Pc, PcSnCl_2 , and disodium Pc in boiling 1-CIN afforded a double-decker Pc_2Sn complex [238], while the reaction between $(\text{TPyP})\text{Ln}(\text{acac})$ ($\text{Ln} = \text{Sm}, \text{Eu}, \text{Gd}$; $\text{TPyP}^{2-} = 5,10,15,20\text{-tetra(4-pyridyl)porphyrinate}$) and $[\text{TPyP}]^{2-}$ in boiling TCB resulted in the formation of double-decker $(\text{TPyP})_2\text{Ln}$ complexes [239]. Octaethylporphyrin (OEP) $_2\text{Ln}$ derivatives **107** ($\text{Ln} = \text{Tb-Lu}, \text{Y}$) were also prepared using the corresponding single-decker rare-earth OEPs and dilithium OEP in 60-80% yields [234].

4. Synthetic approaches to homoleptic triple-decker complexes

4.1. Template synthesis from phthalogens

The first hypothesis on the formation of triple-decker rare-earth Pcs was reported by Russian scientists in 1967 [21,240]. The reaction between PN and rare-earth acetates at 280-290 °C led to the formation of not only double-decker complexes, but also compounds which, based on spectroscopic data and elemental analysis, were assigned as dinuclear triple-decker Pcs **111** of general formula Pc_3Ln_2 ($\text{Ln} = \text{Pr}, \text{Nd}, \text{Er}, \text{Lu}$; Scheme 20). Later on, this method was extended for the synthesis of all rare-earth and yttrium complexes **111** [241–243], as well as lutetium

system **112** with crown-ether substituents [85]. Despite the early findings, the structure of the rare-earth triple-decker compound was confirmed crystallographically only in 1999 for complex **112** (Figure 11) [244].

The preparation of triple-decker systems using the template condensation reaction is also reported for indium and bismuth complexes. For instance, the reaction between PN and indium/tin alloy at 210 °C results in the formation of triple-decker Pc_3In_2 complex [245], while heating of PN with bismuth selenide produces triple-decker Pc_3Bi_2 complex [246]. Although in both cases yields of the target compounds were not reported, structures of the final products were confirmed by X-ray crystallography. Pc_3Bi_2 complex was also prepared by the reaction between PN and bismuth acetate at the increased temperature of 310 °C [247]. In this case, the yield of Pc_3Bi_2 complex was reported as 63%.

4.2. *Metallation of free-base ligand*

Crown-ether substituted triple-decker Pcs **112** ($\text{Ln} = \text{Gd}, \text{Yb}$) were prepared using the reaction between metal-free macrocycles and the corresponding rare-earth acetates in the presence of DBU (1.5:1:2 molar ratio) in 1-CIN as a solvent in 10-15% yield (Scheme 21, conditions 1) [209,212]. Replacement of rare-earth acetates by the corresponding acetylacetonates and exclusion of DBU from the reaction mixture (with a 1:3 Pc to rare-earth precursor molar ratio), allows the preparation of triple-decker compounds **112** ($\text{Ln} = \text{Nd}, \text{Tb}$) in mild conditions and much better (62 and 68%) yields (Scheme 21, conditions 2a) [248]. This synthetic modification was later used for the preparation of unstable triple-decker lanthanum complexes **112** [249].

The preparation of butoxy-substituted triple-decker **113** can be achieved by the reaction between metal-free macrocycle and rare-earth acetates (1:2.6 molar ratio) in boiling *n*-octanol in 76-83% yield (Scheme 21, conditions 2*b*) [250,251]. The target compounds can be purified using column chromatography on silica gel [250] or basic alumina [248,251]. In addition, size exclusion chromatography can also be used for the purification of triple-decker complexes [250,251]. A similar synthetic strategy was used for the preparation of alkylsubstituted triple-decker systems **114** and **115** (Scheme 21) [102]. For instance, the reaction between the corresponding metal-free Pc and europium acetate (1:1 molar ratio) in boiling *n*-octanol results in the formation of **114** and **115** in 92 and 94% yields, respectively. Yields of the lutetium and erbium triple-decker systems are lower, which was attributed to the insufficient reaction temperature (ca. 190 °C) [102]. Indeed, a similar reaction in *n*-hexadecanol at 280 °C results in the formation of lutetium and erbium triple-decker complexes **114** and **115** in 88-93% yields (Scheme 21, conditions 2*c*). Triple-decker systems **115** were studied using X-ray crystallography [252] and NMR spectroscopy with ¹³C-labeled samples [253]. Aryl-substituted triple-decker complexes **116** [103] and **117** [254] were prepared in 67-80% yields using a *n*-C₁₆H₃₃OH/TCB (1:1 v/v) mixture or in pure TCB (Scheme 21, conditions 2*a*). Hexaphthalocyanines **118** were prepared as by-products in 7-14% yields during preparation of the double-decker complexes **98** (Scheme 17) [222].

A triple-decker complex **119** was prepared by the reaction between dilithium 1,2-Nc and lutetium acetate in 1-ClN in 55-60% yield (Scheme 22) [116,255]. It represents the only known example of a homoleptic triple-decker rare-earth system with the 1,2-Nc macrocycle. Similar to double-decker complex **104** (Figure 10), this compound was isolated as a mixture of all possible positional isomers, while only one of those is shown in Scheme 22.

In addition to the systems mentioned above, rare-earth triple-decker Pors and TAPs were also reported in the literature (Figure 12). For instance, the reaction between metal-free (OEP)H₂ and cerium(III) acetylacetonate in boiling TCB produces cerium triple-decker (OEP)₃Ce₂ complex **120** in 12% yield [233]. Similar reaction with a metal-free diazaporphyrin platform leads to the formation of (DAP)₃Ln₂ complexes **121** [256]. TAP-containing (^{Pr}TAP)₃Eu₂ compound **122** was prepared in 9% yield using the reaction between europium(II) iodide and metal-free (^{Pr}TAP)H₂ in boiling *n*-hexanol [235]. Interesting lutetium triple-decker tetrathienotetraazaporphyrin complex **123** (Figure 12) was recently prepared in 36% yield as a mixture of possible positional isomers using *n*-C₁₆H₃₃OH/TCB (1:1 v/v) mixture as a reaction solvent [257].

4.3. *Monophthalocyanine based techniques*

Simple heating of single-decker lutetium PcLu(OAc)·2H₂O complex to 400 °C in vacuum (1 torr) produced triple-decker complex **111** in 40% yield (Scheme 23) [258]. A similar formation of the triple-decker systems under high vacuum (10⁻⁶ torr) sublimation at 300-420 °C of the reaction products obtained from template condensation between PN and a series of rare-earth acetates (Ln = La, Nd, Eu, Gd, Dy, Er, Yb, Lu) was suggested earlier [242], although ultimate structural assignment of new compounds was not provided.

A very similar approach was utilized by Cook and co-workers for the preparation of cadmium triple-decker Pc complex **124** (Figure 13) [259]. In this case, a triple-decker compound was obtained upon slow crystallization of a simple cadmium Pc in THF/MeOH mixture. Although the structure of triple-decker cadmium complex **124** was confirmed by X-ray crystallography, it has relatively low stability in solution as well as in the solid state. Later on,

the same research group extended the preparation of triple-decker cadmium complexes to soluble 2,3,9,10,16,17,23,24-octasubstituted Pcs [260] and proven their radical nature by EPR spectroscopy [261]. Both EPR and electrochemical data were suggestive of a reversible dissociation of these triple-decker systems in solution [261,262]. Work done by Cook and co-workers stimulated an additional interest toward the preparation of heteronuclear rare-earth/cadmium complexes with four or more tetrapyrrolic ligands [34-42].

5. Synthetic approaches to heteroleptic and mixed-ligand double-decker complexes

So far, three classes of heteroleptic (Pc "A" – Pc "B", Por "A" –Por "B", and Pc – Nc) and two classes of the mixed-ligand (Pc–Por and Nc–Por) double-decker rare-earth complexes were reported in the literature. All existing synthetic strategies for the preparation of these complexes can be classified into four following groups according to the type of reactants involved in the reactions: (i) reaction between two different PNs in the presence of rare-earth salt; (ii) reaction of the single-decker rare-earth complexes with PN or its analogues; (iii) reaction between two different metal-free or dilithium (disodium) Pc ligands with rare-earth salt; and (iv) reaction between single-decker rare-earth complexes and metal-free or alkali metal macrocycles. The first two methods could be associated with template synthesis, while two later methods belong to the direct synthetic methodology.

5.1. *Phthalocyanine-metal-phthalocyanine complexes*

The most simple, but the less selective method for the preparation of rare-earth heteroleptic complexes is a direct template condensation of rare-earth salt and two different PNs under appropriate reaction conditions. Indeed, if the reactivity and steric properties of equimolar

quantities of two different PNs in the reaction are similar, one might expect the formation of 21 rare-earth double-decker reaction products. Taking into account a possible formation of single-decker, triple-decker, and open-chain oligomeric products, separation of such reaction mixture seems to be very challenging.

Nevertheless, the reaction between lutetium acetate and an equimolar mixture of 4-propyloxyphthalonitrile and 4-*tert*-butylphthalonitrile at 270-280 °C for 4 h resulted in the formation of a lutetium double-decker tetra-*tert*-butyl-tetrapropyloxyphthalocyanine in 4.6% yield. FAB mass spectrum of the chromatographically isolated mixture of positional isomers was indicative of presence of four *t*-Bu and four propyloxy substituents in the target complex.

The steric hindrance strategy can also be used in the preparation of rare-earth double-decker complexes from two different PNs. This approach was used initially for preparation of asymmetric transition-metal Pcs and their analogues and consists of the template condensation between two different precursors (usually PNs), one of which is sterically crowded (*i.e.* 3,6-diphenylphthalonitrile or 3,4,5,6-tetraphenylphthalonitrile) [264-267]. When unsubstituted and 3,4,5,6-tetraphenyl-substituted PNs were condensed using lutetium acetate as a template, three homoleptic (**46**, **125**, and **126**) and three heteroleptic (**127-129**) double-decker complexes were isolated using preparative TLC approach and identified by UV-vis spectroscopy and elemental analysis (Scheme 24) [268].

A template condensation between unsubstituted and crown-ether containing PNs with lutetium acetate in boiling *n*-hexanol in the presence of DBU was studied by Ishikawa and co-workers (Scheme 25) [269,270]. Although the reaction mixture consisted of rare-earth single- and double-decker complexes along with the starting materials and oligomeric open-chain by-products, the authors were able to separate a target lutetium double-decker complex **130** in 3%

yield. A presence of crown-ether substituents in this compound is suitable for accommodation of different alkali metal ions [270].

Dinuclear, double-decker "sandwich-planar" complexes **131** were prepared in 4.3% (**131a**) and 2% (**131b**) yields using a template cross-condensation between a substituted Pn and bis(diiminoisoindoline) in boiling *n*-amyl alcohol in the presence of DBU (Scheme 26) [271]. Complexes **131a** and **131b** are biradical in nature and their NIR spectra resemble those observed in classic radical double-decker systems (Figure 14).

A reaction between rare-earth single-decker Pc and PN represents a more selective approach for the preparation of heteroleptic double-decker complexes. For instance, the reaction between single-decker europium Pc with a mixture of unsubstituted and crown-ether substituted PNs results in the formation of double-decker complex **130** in 13% yield (Scheme 27) [272]. Besides of the target complex **130**, new heteroleptic double-decker Pcs **132-135** were also isolated in 5-12% yields from the reaction mixture using conventional chromatography.

The reaction between single-decker rare-earth Pc and the corresponding PN was used for the preparation of heteroleptic complexes **135-150** (Scheme 28, Table 5). In the case of heteroleptic double-decker Pcs **135-142**, a large excess of the PN was applied as it was employed as a reactant and a solvent (Scheme 28, conditions 1) [86,87,89,98,273,274].

Table 5. Yields of the double-decker heteroleptic rare-earth Pcs prepared using conditions shown in Scheme 28.

Cm pd	R	R'	R ¹	R ²	R ³	Ln	X	Condit ions	Yield,%	Ref.
135	H	H	15-crown-5		H	Lu	OAc	<i>1</i>	14	[273]
		15-crown-5	H	H	H	Sm, Dy, Tm	OAc	<i>2c</i>	31–43	[101]
136	H	<i>t</i> -Bu	H	H	H	Lu	Cl	<i>1</i>	–	[98,274]
137	H	Cl	H	H	H	Sm, Ho, Er, Lu, Y	Cl	<i>1</i>	28–61	[86,87]
			H	Bu	H	Er				
138	H	Br	H	H	H	Er, Y	Cl	<i>1</i>	43–55	[87]
			H	Bu	H	Er				
139	H	NO ₂	H	H	H	Nd, Sm, Ho, Er, Lu, Y	Cl	<i>1</i>	31–57	[86,87]
140	H		H	H	H	Nd, Eu, Lu	OAc, HCOO	<i>1</i>	62–75	[89]
141	H		H	H	H	Nd, Eu, Lu	OAc, HCOO	<i>1</i>	52–67	[89]
142	H	Ph ₂ CHCONH	H	H	H	Nd, Eu, Lu	OAc, HCOO	<i>1</i>	56–71	[89]
143	H	H	C ₇ H ₁₅	C ₇ H ₁₅	H	Eu, Y	acac	<i>2b</i>	32, 28	[172,275]
144	H	H	C ₅ H ₁₁ O	C ₅ H ₁₁ O	H	Eu, Y	acac	<i>2b</i>	27, 25	[172,275]

145	H	H	PhO	PhO	H	Eu, Ho, Lu	acac	2 <i>b</i>	26–29	[190]
146	H	H	PhS	PhS	H	Eu	acac	2 <i>b</i>	30	[190]
147	15-crown-5		AlkO [*]	AlkO [*]	H	Lu	OAc	2 <i>a</i>	7.5	[181]
148	H	H	H	H	Alk'O [*]	Sm–Lu, Y	acac	2 <i>c</i>	15–31	[276,277]
149	H	H			H	Y	acac	2 <i>c</i> , 6 <i>h</i>	19	[194]
150	H	C ₃ H ₇ O	H	<i>t</i> -Bu	H	Lu	OAc	3	31.6	[263]

^{*} AlkO = MeO[C₂H₄O]₃; Alk'O = (C₂H₅)₂CHO.

This synthetic approach can be used for the preparation of double-decker heteroleptic complexes with electron-acceptor (**137-139**) as well as bulky (**140-142**) substituents in quite good yields (28 - 75%, Table 5) [86,87,89]. Note, however, that structures of the target compounds were decided on the basis of only UV-vis and IR spectra as well as elemental analysis, while NMR and mass spectra of these complexes were not reported. Moreover, since the typical *Q*-band shift for rare-earth double-decker complexes as a function of the rare-earth ion radius was not observed, the purity of target complexes remains unclear.

The combination of alcohol and DBU can also be used in the preparation of rare-earth heteroleptic double-decker complexes (Scheme 28, conditions 2). In particular, well characterized complexes **135**, **143-149** with alkyl- and alkoxy-substituents can be prepared using such reaction conditions [101,172,181,190,194,275-277]. Yields of the target compounds depend on the steric bulkiness of substituents and vary between 7.5 and 43% (Table 5). Double-decker Pcs **148** and **149** are examples of chiral systems [190,276,277]. Chirality of the complexes **148** arises from the nature of their substituents, which directed the formation of only the C_{4h} symmetry macrocycle, existing as an enantiomeric pair. Use of four biphenyl substituents in complex **149** dictates (by definition) its chirality [190]. Note that the CD spectra of enantiomers of **149** are fairly close to the CD spectra of the enantiomeric pair of symmetric system **75** with eight binaphthyl groups (Figure 15).

Lithium amylate generated *in situ* was used as a strong base in the preparation of lutetium double-decker complex **150** in 32% yield as a mixture of positional isomers (Scheme 28, conditions 3) [263]. An interesting synthetic route for preparation of the heteroleptic lanthanum double-decker complex **135** was developed by Gorbunova and co-workers [213]. First, because

of the low stability of single-decker Pc lanthanum complexes, preparation of **135** cannot be achieved at any standard conditions listed in Scheme 28. In addition, attempt to prepare this complex from $\text{La}(\text{acac})_3 \cdot \text{H}_2\text{O}$ in the presence of lithium Pc and lithium crown-ether containing Pc also failed. In order to overcome these problems, Gorbunova and co-workers first prepared lanthanum triple-decker complex $[(\text{R}_4\text{Pc}^{2-})\text{La}^{3+}(\text{Pc}^{2-})\text{La}^{3+}(\text{Pc}^{2-})]$ (R = 15-crown-5), which upon a prolonged stay in a chloroform solution dissociates to form double-decker **135** in 31% yield.

Rare-earth heteroleptic double-decker Pcs **151** (Figure 16) were prepared from A_3B type asymmetric single-decker Pcs in 10-20% yield using conditions *2a* in Scheme 28 [278]. As the starting A_3B single-decker compounds were synthesized in ~20% yield, the overall yield of the target **151** is quite low (2-4%).

In a series of publications, Bekaroğlu and co-workers discussed preparation and characterization of several interesting dinuclear double-decker complexes with conformationally flexible crown-thioether type bridging ligands (Scheme 29) [279,280]. Statistical condensation between diiminoisoindoline derivatives **152** and **153** in 1:6 molar ratio resulted in the formation of single-decker dinuclear complex **154**, which after chromatographic purification was introduced into reaction with two equivalents of the substituted lithium Pc to form target dinuclear double-decker system **155**. In spite of the presence of A_3B type macrocycle in single-decker complexes **154**, their UV-vis spectra resemble spectra of the regular single-decker rare-earth Pcs with symmetric macrocycles and effective C_{4v} symmetry (Figure 17). In particular, a single *Q*-band in complexes **154** is suggestive of close energies of the LUMO and LUMO+1 and nearly equivalent electronic properties of crown-thioether and thioalkyl substituents. Reported UV-vis spectra of double-decker complexes **155** resemble those observed in free-radical Pc_2Ln compounds except for a prominent low-energy shoulder observed next to the *Q*-band (Figure 17)

[279,280]. Later on, the same research group reported synthesis of dinuclear tetraphthalocyanine **158**, which was prepared using a similar strategy, *i.e.* reaction of dinuclear calix[4]arene precursor **156** with diiminoisoindoline **153** (Scheme 30) [281]. The reported MALDI-TOF spectrum of complex **158**, however, shows a very low intensity molecular ion and no peaks associated with double-decker fragments (Figure 18). The most intense peak in the MALDI-TOF spectrum belongs to the metal-free derivative of **157**, which can be formed by demetallation of dilutetium derivative **157** under reaction conditions. Such a hypothesis agrees well with the reported UV-vis spectrum of **158** (Figure 19), which has a split *Q*-band characteristic for the metal-free Pcs.

Further development of the above mentioned synthetic strategy for the preparation of double-decker multinuclear complexes resulted in reports on trinuclear single-decker complexes **159** and **160** as well as double-decker complexes **161** and **162** (Scheme 31) [282,283]. Reported UV-vis spectra of the target compounds **161** and **162** (Figures 20 and 21) could have an admixture of the metal-free derivatives of single-decker **159** and **160**, which (by analogy with complexes **157** [281]) could be formed during demetalation reaction of these single-decker complexes.

An interesting set of Por-substituted rare-earth double-decker complexes **163-165** was prepared using the synthetic approaches outlined in Scheme 32 [284]. In this case, 4-hydroxyphenyl-substituted Pors were introduced in the reaction with nitro-substituted PNs or 4,5-dichlorophthalonitrile to form PN-containing Pors. Further reaction of such PN-containing Pors with unsubstituted PN and europium PcEu(acac) precursor leads to the formation of Por-substituted europium double-decker complexes **163-165** in 31-40% yields [284]. In a separate study, the rare-earth double-decker Pcs were linked to a fullerene using an esterification reaction

between a double-decker hydroxymethyl Pc and a fullerene derivatized with a carboxylic acid functional group to form dyads **166** (Scheme 33) [285]. The compounds have interesting photophysical properties associated with intramolecular electron-transfer, which results in the formation of photoinduced charge-separation states.

Two different metal-free Pcs can react with the corresponding rare-earth salt in the presence of an organic base to form heteroleptic double-decker systems (Scheme 34). For instance, heteroleptic double-decker Pcs **136** and **167** were prepared using microwave radiation and DBU as a base [286-288]. The UV-vis spectrum of **136** prepared using this approach [286], however, is identical to the spectra of rare-earth single-decker Pcs and differ significantly from a previously reported spectrum of **136**, which was prepared using dilithium salts of unsubstituted and tetra-*t*-Bu-substituted Pcs and 1-CIN as a solvent in 20% yield (Scheme 34, conditions 2a) [287]. Change of 1-CIN to basic QN and use of prolonged reaction time allowed the formation of amphiphilic double-decker Pc **167** in 47% yield (Scheme 34, conditions 2b) [288].

Several heteroleptic rare-earth double-decker complexes **168-170** were prepared by the reaction between dilithium salts of two different Pcs and lutetium acetate (Scheme 34, conditions 2a) [289]. The yields of the target double-decker complexes (24-31%) are significantly compromised by the formation of the homoleptic double-decker derivatives.

Use of the dilithium salts of two different Pc ligands was also explored in the preparation of terbium complex **171**, which has a pyrene substituent capable of forming non-covalent π - π conjugates with single wall nanotubes and possesses interesting magnetic properties [81]. A synthetic approach for the preparation of this complex requires synthesis of A₃B type macrocycle **171a** using a statistical template condensation of two different PNs and another statistical

reaction between dilithium salts of two different Pc ligands (Scheme 35). Not surprisingly, overall yield of the target complex **171** is quite low.

The last method for preparation of rare-earth heteroleptic double-decker complexes belongs to the interaction between a rare-earth single-decker Pc complex and a metal-free Pc macrocycle in a protic or an aprotic solvent (Scheme 36, conditions *1a* and *1b*). This approach was used for the first time in 1993 by Japanese researchers [290] and is now known as the “raise-by-one-story” method because it includes a single-step reaction for the preparation of double-decker systems. Double-decker heteroleptic compounds **135** [270,290,291], **148** [277], **172** [292,293] and **173** [205] were prepared using this methodology, but the yields did not exceed 32%. Again, similar to synthetic methodologies mentioned in Schemes 24-35, the formation of homoleptic double-decker Pcs is predominantly responsible for relatively low yields.

Use of a TCB/alcohol mixture with or without an organic base (Scheme 36, conditions *1c* and 2) allows for increased (71-85%) yields of the heteroleptic complexes **174** and **175** substituted with *n*-Bu groups and chlorine atoms [294]. Interestingly, optimal conditions for the formation of europium complexes **174** and **175** are conditions 2 (Scheme 36), while those for the formation of lutetium analogs are conditions *1c* (Scheme 36). Similar to the earlier mentioned (*R*)- and (*S*)-enantiomers of double-decker complexes **75** and **149** (Figure 15), chiral heteroleptic derivatives **173** with peripheral (*D*)- and (*L*)-mentol groups have close CD spectra with those observed in homoleptic double-decker compounds **82** [205].

Another interesting set of heteroleptic double-decker complexes **172** has eight butoxy groups at the α -positions of one Pc ligand. Oxygen atom of these substituents can be involved in secondary coordination with sodium cations to form a dimeric structure $\{[{}^{\text{R8}}\text{PcLnPc}]\text{Na}\}_2$ **176** in a solid state (Figure 22) [292]. This structure can be viewed as a pseudo quadruple-decker

complex in which two sodium cations are held by coordination bonds with oxygen atoms of butoxy-groups between the two double-decker Pc anions.

By analogy with the synthesis of heteroleptic double-decker complexes presented in Scheme 36, complex **177**, which has one Pc and one tetrabenzotriazoporphyrin ligand, was recently characterized in the literature (Scheme 37) [227].

5.2. *Phthalocyanine-metal-naphthalocyanine complexes*

Representatives of this class of compounds are relatively rare to date. This is largely due to the insufficient development of synthetic methods. Thus, the reaction between equimolar amounts of PN and 2,3-NPN in the presence of lutetium acetate and DBU in boiling *n*-hexanol produced [295] the following set of complexes by ratio of isoindole and benzoisoindole fragments with the yields (%) given in parentheses: 8:0 (1), 7:1 (5.5), 6:2 mixture of positional isomers (20), 5:3 mixture of positional isomers (37), 4:4 mixture of positional isomers (28), 3:5 mixture of positional isomers (7), 2:6 mixture of positional isomers (1.5). Note that the isolation procedure for the target heteroleptic complex NcLuPc (**178**) out of the mixture has not been described by the authors [295]. This compound was later obtained by the direct interaction of an alkali metal Nc with lutetium single-decker Pc [296] or with lithium Pc in the presence of lutetium acetate [231] (Scheme 38). However, in the first case, the authors do not provide the yield of the title compound. In the second case, the formation of significant amounts of the corresponding homoleptic product was observed; yield of the desired complex **178** in this case was 17%.

By analogy with the heteroleptic double-decker Pcs (Section 5.1, Scheme 28) substituted complexes **178–182** were prepared by the template condensation starting from single-decker rare-earth Pcs in a melt [274], or in *n*-hexanol [297] or *n*-octanol [298] solutions of NPNs

(Scheme 39, conditions 1–3). Selectivity of this approach is low as well and yields of compounds **178**, **180–182** are in the range of 25–59%, which is caused not only by the formation of the homoleptic products, but also by oligomerization and/or oxidative destruction of the initial NPNs. Note chirality of compounds **182**, which, by analogy with some double-decker Pcs (for example, **148**, Section 5.1), exists as a mixture of enantiomers [298].

5.3. *Phthalocyanine-metal-porphyrin complexes*

The main feature in the synthesis of the Por containing sandwich-type rare-earth complexes, including mixed-ligand derivatives, consists in the introduction of a Por moiety exclusively as a preformed free-base ligand. Both template and direct formation synthetic strategies are employed for the Pc–Por complexes (Schemes 40 and 41) as in the case of the heteroleptic double-decker Pcs (Section 5.1).

Thus, metallation of the free-base Pors with rare-earth salts in TCB or *n*-octanol as a solvent results in the formation of corresponding single-decker complexes, which further react with PN in alcohol media in the presence of DBU [172,299–303] to form compounds **183–195** (Scheme 40). Yields of the products depend both on the nature of rare-earth ion and substituents in the ligands, varying within the wide range from 2 to 69%. For example, maximum yields (up to 36%) were observed in the case of complexes **190** [301] for the mid-row elements, ionic radii of which, according to the authors, set optimal distance between the ligands, thereby causing the most effective stabilizing overlap of their π -orbitals. At the same time, an introduction of bulky substituents in the peripheral positions of macrocycles leads to an expected decrease in the yields of the target compounds [299].

Direct interaction of the single-decker rare-earth Pors with a free-base Pc or its lithium salt generally proceeds more efficiently in comparison with the template method and results in the formation of mixed-ligand complexes **183** [304], **188** [305], **196–203** [306–310] (Scheme 41) with yields varying in a wide range. Thus, compounds **183** and **188** were synthesized [304,305] in TCB in 60–85% yields, while complexes **196–199** were prepared in boiling *n*-octanol [74,306,307] with 24–61% yields (Scheme 41, conditions 1*a,b*). Using nanoporous anodized alumina as a template, authors [308] were able to use double-decker europium complex **196** for the preparation of nanotubes. Synthesis of compound **200** was carried out using microwave radiation (Scheme 41, conditions 2); the yield was 66% [309]. For obtaining compounds **201–203**, europium and cerium halogenides were initially treated with two equivalents of $\text{LiN}(\text{SiMe}_3)_2$ in diglyme to form salts of general formula of $\text{LnX}[\text{N}(\text{SiMe}_3)_2]_2$ ($\text{Ln} = \text{Ce}, \text{Eu}$; $\text{X} = \text{Cl}, \text{I}$), which reacted *in situ* with the free-base Pors to form the corresponding single-decker complexes [310]. Further interaction of the single-decker rare-earth Pors with unsubstituted or tetra-*t*-Bu-substituted lithium Pc in boiling diglyme allowed isolation of mixed-ligand products **201–203** in yields from moderate to high (38–94%) (Scheme 41, conditions 3).

An alternative way of the direct synthesis (Scheme 42) involves a reverse sequence of the complexation reactions. Thus, the reaction of lithium Pc with $\text{Ln}(\text{acac})_3$ leads to formation of the corresponding single-decker complexes, which further react *in situ* with free-base Pors forming the mixed-ligand derivatives. This method allowed obtaining compounds **183** [304,311] and **188** [179] for the elements of a first half of the Ln series ($\text{Ln} = \text{La–Nd}, \text{Eu}, \text{Gd}$) with yields of 36–69%. The described methodology (Scheme 41) also provided a basis for the synthesis of a series of low-symmetry complexes **204–208** (Figure 23, Scheme 43) [75,312–314], including **205**, which contain *N*-confused Por ligands [313], optically active complex **206** [314], and complex

208, which possesses interesting photophysical properties [75] due to the presence of a perylenediimide fragment.

Particularly noteworthy is the fact that during direct synthesis, double-decker complexes of trivalent metals are formed as the anionic species, which are gradually transformed into the neutral paramagnetic species oxidation with a variety of oxidizing agents, such as atmospheric oxygen. In addition, the stability of the anionic forms among the similar type of rare-earth complexes decreases with decreasing ionic radii of these elements [304]. In contrast, tetravalent metals exclusively form neutral diamagnetic double-decker compounds with Pcs and their analogues. Thus, a direct interaction of single-decker PorMCl_2 ($\text{M} = \text{U}, \text{Th}, \text{Zr}, \text{Hf}$) with sodium Pc in a boiling 1-CIN [229,315] produced complexes **183**, **201**, and **209** with tetravalent metals (Figure 24). In the case of uranium and thorium ions, the synthesis was carried out for 40 hours with the mixed-ligand products isolated in 20–45% yields [229], while zirconium and hafnium provided the desired compounds within only 3 hours with 25–69% yields [315].

5.4. Naphthalocyanine-metal-porphyrin complexes

The first double-decker complexes of this type, namely, compounds **210** and **211** were prepared by Jiang and co-workers in 1999 [316] by a template tetramerization of unsubstituted and 6,7-bis(dodecylthio)-substituted NPNs in the presence of single-decker europium Pors (Scheme 44) in 52 and 69% yields, respectively. Single-decker rare-earth Por complexes studied in the work [316] were prepared by metallation of the corresponding ligands with europium acetylacetonate in boiling TCB, which was then evaporated. After that, further reaction with the corresponding NPNs was carried out under conditions of Scheme 44. Later, these researchers have shown [179,317–319] that a direct reaction between the metal-free Por, NPN and rare-earth

salt (Scheme 44) leads to mixed-ligand complexes **212–214** in comparable yields ($\text{Ln} = \text{Eu}$). For compounds **212** [317] and **214** [319] the authors note a downward trend for yields along the rare-earth series with decreasing ionic radii from 73 to 29% and from 45 to 21%, respectively, and explained this fact by the increased influence of steric effects. Notably, all the studies of the rare-earth Nc–Por sandwich complexes hitherto belong to the same group of researchers, which can explain the use of only one synthetic approach for complexes of this type.

5.5. Porphyrin-metal-porphyrin complexes

Synthesis of the heteroleptic double-decker rare-earth Pors is based on the direct interaction of single-decker metal complexes with dianions of the respective ligands (Scheme 45). Thus, interaction between single-decker $(\text{TPP})\text{Ln}(\text{acac})$ and $(\text{OEP})\text{Li}_2$ obtained *in situ* by the reaction of butyllithium and $(\text{OEP})\text{H}_2$ [320] results in formation of compounds **215** in 5–35% yields [320,321] as well as the corresponding homoleptic derivatives $(\text{TPP})_2\text{Ln}$, $(\text{OEP})_2\text{Ln}$, and $(\text{OEP})_2\text{Ln}_3$. Separation of this mixture, also containing residues of the starting compounds, was carried out by a four-step chromatography on basic alumina using several types of eluents. The complexes of tetravalent metals $(\text{OEP})\text{M}(\text{TPP})$ ($\text{M} = \text{U}, \text{Th}$) [229] were obtained under similar conditions, and the yields of uranium and double-decker thorium Pors after chromatographic purification were 30 and 16%, respectively. A more complex sequence of the reactions (Scheme 46) allowed synthesizing low-symmetry heteronuclear compounds **216** [322], one of which contains a ferrocene moiety, that was further explored as molecular motor on the surface of HOPG by STM method.

The authors of [237] showed that Por-centered complexation proceeds more efficiently in the presence of silver triflate. Thus, ligand exchange reaction with $(\text{OEP})\text{ZrCl}_2$ afforded

zirconium single-decker (OEP)Zr(OTf)₂, which reacted in mild conditions with lithium octaethyl-substituted TAP forming compound **217** in 74% yield (Scheme 47).

6. Synthetic approaches to heteroleptic and mixed-ligand triple-decker complexes

Triple-decker rare-earth complexes containing different tetrapyrrolic ligands have been known for nearly twenty years, while a sharp rise in the number of papers on this topic was observed in the period from 2000 to 2007. Studies conducted in these years have shown that synthesis of the heteroligand and heteronuclear derivatives allows for the efficient managing of interligand π - π interactions and f - f interactions of metal ions in the triple-decker complexes, giving the last ones pronounced magnetic [323] and nonlinear optical [23,71] properties, as well as opening up the possibility of their application in high-capacity information storage devices [310,324].

Currently known systems of this type can be divided into three groups depending on the nature of their constituent ligands: (i) heteroleptic Pcs; (ii) mixed-ligand complexes of Pcs with Pors; and (iii) mixed-ligand complexes of Ncs with Pors. Synthetic approaches, with a rare exception, represent various modifications of the direct complexation method and are often characterized by a low selectivity. By analogy with Section 5, this part of the review is also classified by type of the target compounds.

6.1. Heteroleptic phthalocyanine complexes

The first triple-decker rare-earth complex containing different ligands, namely, heteroleptic lutetium system **218** was prepared (Scheme 48) by Ishikawa and Kaizu in 1994 [325]. The reaction was carried out using a three-fold molar excess of single-decker lutetium relative to the

tetra-crown substituted ligand, while the corresponding double-decker system **135** (Scheme 36) was prepared from an equimolar mixture of these reactants [290]. Complex **218** was isolated in an individual state as a result of repeated chromatography and characterized by elemental analysis, mass- (FAB method) and ^1H NMR spectra. Unfortunately, the yield of this compound was not specified by the authors [325].

The first series of heteroleptic triple-decker compounds for almost all rare-earth range (except La, Pm, and Lu) was obtained by Jiang and co-workers in 2000 [326]. They carried out reaction between the rare-earth acetylacetonates, lithium Pc and the corresponding double-decker Pcs in boiling TCB, which afforded compounds **219** (Scheme 49) in 26–79% yield. Along with the main products, the authors also isolated and characterized complexes **220** (except Ln = Pr) in 3–17% yield. They explain the formation of **220** by possible thermolysis of **219** to form heteroleptic complexes $^{\text{R}}\text{PcLnPc}$ ($\text{R} = \text{C}_8\text{H}_{17}\text{O}$), which further react with an excess of the initially formed single-decker $\text{PcLn}(\text{acac})$ systems. This assumption is supported by the fact that the final yield of **220** increases proportionally with the duration of the synthesis. Furthermore, a control experiment, comprising interaction of $\text{PcLn}(\text{acac})$ ($\text{Ln} = \text{Tb}$) and $^{\text{R}}\text{PcH}_2$ ($\text{R} = \text{C}_8\text{H}_{17}\text{O}$) in boiling TCB medium, resulted in complex **220** with 51% yield, while the yield of **219** was found to be 37%. Using the corresponding free-base ligand instead of lithium Pc, Ishikawa and co-workers carried out synthesis of heteroleptic homo- and heteronuclear complexes **221–223** under the similar conditions (Scheme 49) with yields of ~60% [323,327]. In this case, the formation of byproducts, analogous to **220**, was not mentioned by the authors. Compounds **221–223** were characterized by elemental analysis and ^1H NMR spectral data [328]. By analogy with the method of Ishikawa, amphiphilic complexes **224–227** [183,329–331] as well as triple-decker

system **228** [332] composed of two unsubstituted and one external 15-crown-5-substituted Pc ligands were obtained in 20–48% and 39–70% yields, respectively.

The formation of the heteroleptic triple-decker compounds is also facilitated by protic solvents. Thus, a set of isomeric samarium, gadolinium, and lutetium complexes **229** (Scheme 49) was prepared [333] in boiling *n*-octanol with 40, 42, and 24% yields, respectively. The authors explain the lower yield of the lutetium complex by increased steric hindrance due to the smallest ionic radius of this ion. Synthesis of triple-decker system **220** and its heteronuclear analogues **230** was also carried out by Jiang and co-workers according to Scheme 50 by the reaction between the corresponding single-decker Pcs and heteroleptic double-decker complexes in boiling TCB [334]. Target compounds **220** and **230** were isolated in 8–15% yield, while the formation of even trace amounts of the alternative complexation products was not observed, which is quite unusual, taking into consideration the earlier studies of these authors [326].

An original approach to the synthesis of triple-decker Pcs **218** and **231** was proposed by Gorbunova and co-authors [335,336] (Scheme 51). Unstable double-decker lanthanum Pc utilized as the donor of the unsubstituted ligand reacted with the rare-earth acetylacetonates in the presence of tetra(15-crown-5)-substituted Pc leading to compounds **218** in 10–31% yield, while triple-deckers **231** were the major products and their yields varied between 31 and 53%.

One of the most spectacular examples of heteroleptic Pcs obtained to date is quintuple-decker tetranuclear complex **232** synthesized by Katoh and co-authors [337], which belongs to the "sandwich-planar" type (Scheme 52). This complex shows an absorption spectrum similar to the classic triple-decker Pcs (Figure 25), while considerable bathochromic shift of the Q_2 band to the 800–900 nm region should be noted, which is apparently reflects the presence of the "planar"

type ligand in the molecule of **232**. Unfortunately, the synthetic procedure selected by the authors allowed obtaining of the desired product in only a 2.3% yield.

The authors of [294] found conditions for the selective preparation of heteronuclear europium–lutetium complexes **233** and **234** starting from the corresponding mono- and double-decker Pcs in 70–89% yield (Scheme 53). Compounds **233b** and **234b** are the first triple-decker Pcs, which molecules contain ligands with both donor and acceptor substituents.

6.2. Mixed-ligand phthalocyanine and porphyrin complexes

This type of triple-decker complexes includes a much larger number of members as compared to the sandwich-type heteroleptic Pcs. The main reason for this is a generally better development of the Por chemistry, which expands opportunities to produce compounds with the desired properties. Nevertheless, the available synthetic approaches to the Por-containing heteroligand complexes, in most cases, are characterized by low selectivity and often lead to a mixture of compounds.

There are three types of triple-decker Pc–Por systems known to date, which differ in composition and internal arrangement of the ligands. Synthetic methods used for their preparation can also be divided into three major groups depending on the nature of the reacting substrates (Scheme 54). Table 6 summarizes data on the synthesis and yields of triple-decker complexes **235–265**, for which the symbols "a", "b" and "c" denote the type of product according to the Scheme 54.

Table 6. Yields of the triple-decker Ln complexes synthesized by Scheme 54.

No.	R	R'	R ¹	R ²	Ln	Ln'	X	Conditions	Yield, %	Ref.
235a					Sm, Eu, Gd*			1, 2	62–78	[311, 338]
235b			H	H			acac	1	15–17	[338]
236a					Gd, Lu, Y	Ce		3	64–79	[339]
237a	C ₆ H ₅	H			Y	La		3	69	
238a			Me	Me		Eu	acac	1	14	[324]
238b								1	8.9	
239a						Eu	acac	3	50	[300]
239b			15-crown-5					4	42	
240a								1	23	
240b			H	H		Eu	acac	1	10	[342]
240c								1	3	
241a						Eu	acac	1	42	[324]
241b			C ₈ H ₁₇ O	C ₈ H ₁₇ O				1	11	
242b	<i>p</i> -MeC ₆ H ₄	H			Ce	Eu	I	4	39	[310]
243a								1	13	
243b						Eu	acac	1	17	[324]
243c			H	<i>t</i> -Bu				1	2.7	
244a						Ce	I	1	13	[310]
245b					Ce	Eu	I	4	53	[310]
246a	<i>p</i> -MeOC ₆ H ₄	H	H	H		Eu	acac	1	49	[343]
246b								1	21	

					Nd, Eu, Gd		<i>I</i>	–	[344]
247a							<i>I</i>	63	[343]
								36	[324]
247b	<i>p</i> -Me ₃ CC ₆ H ₄	H	H	H	Eu	acac	<i>I</i>	30	[343]
								11	[324]
247c							<i>I</i>	0.7	[324]
					Eu		<i>I</i>	45	[343]
248a					Tb		5	35	[341]
					La,Pr,Nd,Sm–Er,Y		5	3	
	<i>p</i> -ClC ₆ H ₄	H	H	H		acac	<i>I</i>	5–48	[345]
					Eu		<i>I</i>	20	[343]
							5	31	
248b					Tb		5	28	[341]
					La,Pr,Nd,Sm–Er,Y		<i>I</i>	4–40	[345]
249a					La			47	
	4-C ₅ H ₄ N	H	H	H	Eu	acac	4	51	[340]
249b					La, Eu			–	
250a					Eu			35	
					Tb			4	
					Eu		5	32	
250b	<i>p</i> -C ₁₂ H ₂₅ OC ₆ H ₄	H	C ₈ H ₁₇ O	C ₈ H ₁₇ O	Tb	acac		21	[341]
251b					Eu	Tb		58	
252b					Tb	Eu	4	44	
253a								39	
253b	C ₅ H ₁₁	H	H	H	Eu	acac	<i>I</i>	30	[324]
254a			Me	Me				8	

254b									2	
255a									39	
255b			H	<i>t</i> -Bu					11	
256a						Ce	I		13	[310]
257a			Me	Me		Eu	acac	<i>I</i>	20	[324]
258c			C ₇ H ₁₅	C ₇ H ₁₅					18	
259b	H	Et				Eu	acac		76	
260b			H	<i>t</i> Bu	Ce	Eu	I	4	38	[310]
261b		H	H	H		Eu	acac	4	18	[74]
262a	<i>p</i> -MeOC ₆ H ₄	H		15-crown-5		La, Ce, Pr	acac	5	20–32	[302]
263a						La, Pr, Nd, Eu			42–63	[346]
	<i>p</i> -BrC ₆ H ₄	H		15-crown-5		Tb	acac	5	48	[303]
263b						Nd			4	[346]
						Tb			57	[303]
						Dy			50	
264b	<i>p</i> -ClC ₆ H ₄	H	PhO	PhO	Y Dy	Dy Y	acac	4	43 75	[347]
						Y			58	
						Eu			38	
265b		H	H	H			acac	4		[348]
						Y			36	
<i>(R)</i> -/ <i>(S)</i> -										

* here and further merging of columns corresponds to $L_n = L_{n'}$.

The first method (Scheme 54, conditions 1) consists of a consecutive reaction of the rare-earth salts with Por and Pc ligands. At the initial step, a $\text{Ln}(\text{acac})_3$ interacts with a free-base Por in TCB forming a single-decker complex, which further reacts with an excess of dilithium Pc resulting in the formation of a mixture of sandwich-type products of both double-decker and triple-decker nature. Triple-decker complexes synthesized by this method are presented in Table 6, and the yields of the target complexes tend to gradually decrease from the type "a" to the type "c" compounds. The formation of the latter was mentioned in only one work [324] with a maximum yield of 18% (**258c**), which is evidence of their relatively low stability. Varying the ratio of initial reagents allows to shift the equilibrium towards a particular product; however, substantial increase in the process selectivity can hardly be achieved following conditions 1 [324]. Reverse order of the reaction (Scheme 54, conditions 2) also has virtually no effect on the yields of the target compounds (**235a**, Table 6) [311,338].

The second method (Scheme 54) involves interaction of the *in situ* obtained single-decker rare-earth Por with the double-decker $(\text{R}^1\text{R}^2)\text{PcLnPor}$ (conditions 3) or $(\text{R}^1\text{R}^2)\text{Pc}_2\text{Ln}$ (conditions 4), complexes which leads to the type "a" and type "b" products, respectively, formed in good yields (Table 6). Scheme 54 (conditions 3) has also been used for the synthesis of heteronuclear triple-decker systems composed of different Por ligands, namely $(\text{TPP})\text{CePcGd}(\text{OEP})$ (**266**) and $(\text{PnP})\text{Ce}(t\text{-Bu}_4\text{Pc})\text{Eu}(\text{TTP})$ (**267**) [310]. Nevertheless, selectivity of this approach, as in the case of that discussed above (Scheme 54, conditions 1), strongly depends on the reaction conditions. Thus, compounds **249a** were obtained as the main products following Scheme 54 (Conditions 4) by refluxing the reagents in TCB, while expected triple-deckers **249b** were isolated only in trace amounts [340].

The third method, unlike the first two, is the template one and comprises the reaction between the single-decker rare-earth Por with PNs in the presence of DBU (Scheme 54, conditions 5). This approach was tested [341] for obtaining complexes **248a,b** and **250a,b**; the authors mentioned its low selectivity comparable to the synthesis by the conditions 1 (Table 6). Conditions 5 (Scheme 54) were also used [302,303,346] for the synthesis of crown-substituted complexes **262** and **263**.

The synthesis of a number of the triple-deckers containing asymmetrically substituted Por ligands was performed according to Scheme 54 as well. Thus, using conditions 1, complexes **268** and **269** [349], which include two A₃B-type Por moieties linked through the butadiyne bridge (Figure 26), were obtained in 33 and 17% yield, respectively. Likewise, a series of compounds **270–272** [63] containing triallyl fragments was synthesized (Figure 27). The introduction of these functional groups allowed the formation of the ordered triple-decker monolayers by adsorption onto Si(100) surface. Efficient binding of the Pc–Por complexes to the electrodes provides high concentration of the redox-active species on their surface, which increases density of the generated charge. High charge density is crucial for the development of molecular materials for large-volume information carriers [63].

The synthesis of the functionally substituted multi-decker systems, as well as a number of bridged structures, was carried out [62,324,342,350,351] using Pd(0) catalyzed cross-coupling reactions. Some examples are shown in Schemes 55 and 56. Thus, initial complexes **273–275** were prepared following Scheme 54 (conditions 4) and further reacted with terminal alkynes at Sonogashira coupling conditions (Scheme 55, conditions 1) forming thioacetyl derivatives **276–279** in 10–50% yield [62,324,342]. The authors observed the formation of considerable amounts of side products, mainly, as a result of homo-coupling of the initial alkynes that significantly

complicated isolation of the target complexes. Further optimization of the reaction conditions (Scheme 55, conditions 2) allowed minimization of the undesirable side processes [324,342]. However, yields of target products **276–279** were not improved.

Coupling of the terminal ethynyl groups by the modified Eglinton-Glaser reaction [342] led to the triple-decker complexes, linked through the butadiyne bridge. As an example, Scheme 56 shows a homo-coupling of compound **280** to form dimeric product **281** in 89% yield. Using a large variety of methods described above, synthesis of the more complex derivatives was performed [350,351] with some examples (**282–287**) shown in Figure 28.

6.3. *Mixed-ligand naphthalocyanine and porphyrin complexes*

Among the possible combinations of Ncs and Pors in the triple-decker complexes there are representatives of only one structural type synthesized to date (Scheme 57). Moreover, these compounds are still the only example of the sandwich-type tetrapyrrole triple-decker systems containing 2,3-Nc ligand. Their synthesis was carried out exclusively by the direct method (Scheme 57). first metallating the free-base Por by the rare-earth acetylacetonate to form the single-decker complex, which is then reacted with lithium Nc (conditions 1) or with the Nc–Por rare-earth double-decker (conditions 2). The first route afforded europium triple-decker complex **288** [324] by refluxing a mixture of the reagents in TCB in 3% yield. Yields of products **289** synthesized by the second route in boiling TCB amount to 46% and 63% for europium and neodymium, respectively [319].

7. Conclusions

Without reservations, there is a wide range of the rare-earth complexes with tetrapyrrole ligands of single-, double- and triple-decker nature known to date, including their heteroleptic, mixed-ligand and heteronuclear derivatives. Bisphthalocyanines are the most extensively studied representatives among the homoleptic complexes, and porphyrin–phthalocyanine double-deckers are the most explored among the heteroleptic and mixed-ligand compounds. Recent advances in the synthetic studies, including those made by the authors of this review, provide increased yields and selectivity, thus, contributing to the development of chemistry of the tetrapyrrole rare-earth compounds and enhancing their availability for practical use.

Acknowledgements

Generous support from the NSF CHE-1110455 and CHE-14010375, the Minnesota Supercomputing Institute to VNN is greatly appreciated. We also thank Presidium of the Russian Academy of Sciences, Ministry of Science and Education (Project No. 14.576.21.0029), Council under the President of the Russian Federation for State Support of Young Scientists and Leading Scientific Schools (Grant MD-3738.2015.3) and Russian Foundation for Basic Research (Grant Nos. 15-03-05890, 15-33-21012, 16-33-00097, 16-33-60031) for financial support.

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Fig. 1. UV-vis spectra of generalized free-base ligand PcH_2 (a), single-decker PcLnOAc (b) and triple-decker Pc_3Ln_2 (c) compounds in solution (for $\text{Ln} = \text{Lu}$).

Fig. 2. Left part: UV-vis spectra of generalized double-decker Pc_2Ln (for $\text{Ln} = \text{Lu}$) in neutral (a), one-electron oxidized (b) and reduced (c) states; inset shows the NIR part of the spectrum of the neutral form. Right part: schematic representation of the energetic levels and transitions with the main contributions to the corresponding absorption bands for the general Pc_2Ln neutral form in D_{4d} symmetry according to [26,27 and references therein].

Fig. 3. UV-vis spectra of generalized double-deckers Pc_2Ln (a), PcLnNc (b) and Nc_2Ln (c) in solution (for $\text{Ln} = \text{Lu}$).

$R^1 = R^2 = \text{Me}$ (acac), *tert*-Bu (dpm), Ph (dbm)

$R^1 = \text{tert-Bu}$, $R^2 = \text{C}_3\text{F}_7$ (fod)

$R^1 = \text{Ph}$, $R^2 = \text{CF}_3$ (btfa)

(hfbc)

Fig. 4. Structures and abbreviations of selected β -diketone anions.

Fig. 5. X-ray structure of binuclear samarium Pc **21** [113].

Fig. 6. Representative examples of the single-decker rare-earth Pc analogues.

Fig. 7. (a) X-ray crystal structure of binuclear complex **40** and (b) schematic representation of the first coordination sphere of the rare-earth ions Ln^{3+} ($\text{Ln} = \text{Dy}, \text{Tb}, \text{Ho}, \text{and Gd}$) [132].

Fig. 8. (a) X-ray crystal structure of complex **45** and (b) schematic representation of the first coordination sphere of Dy³⁺ ions [135].

Fig. 9. UV-vis spectra of mononuclear (**42**) and binuclear (**44**) dysprosium complexes in $\text{CHCl}_3/\text{DMSO}$ (9:1 v/v) system [133].

Fig. 10. Representative examples of double-decker rare-earth Pc analogues.

Fig. 11. X-ray crystal structure of triple-decker dilutetium Pc **112** [244].

Fig. 12. Representative examples of the rare-earth triple-decker Pors, DAPs, and TAPs.

Fig. 13. X-ray crystal structure of *n*-hexyl substituted triple-decker cadmium Pc **124** [259].

Fig. 14. UV-vis spectra of binuclear complexes **131**, their respective mononuclear analogues **55** (Ln = Dy, Y), and their reduced forms obtained by the reduction with $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ in the presence of NBu_4Br in CHCl_3 . Narrow bands at ~ 2350 nm are solvent overtones [271].

Fig. 15. UV-vis and CD spectra of homoleptic complexes **75** (a) and their heteroleptic analogues **149** (b). Black and red lines represent CD spectra of (*R*)- and (*S*)-enantiomers, respectively [194].

Fig. 16. Rare-earth heteroleptic double-decker complexes with A₃B type of asymmetric macrocyclic ligand [278].

Fig. 17. UV-vis spectra of **154** (---) and **155**(-) in CHCl₃ [279,280].

Fig. 18. MALDI-TOF spectrum of **158** in 3,5-dinitrobenzene matrix [281].

Fig. 19. UV-vis spectra of **157** (-) and **158** (···) in CHCl_3 [281].

Fig. 20. UV-vis spectra of **159** (···) and **161** (-) in CHCl_3 [282].

Fig. 21. UV-vis spectra of **160** (-) and **162** (···) in CHCl_3 [283].

Fig. 22. Structure of the pseudo tetra-decker heteroleptic samarium complex **176** [292].

Fig. 23. Representative examples of Pc–Por mixed-ligand complexes [312–314].

Fig. 24. Representative examples of double-decker Pc–Por mixed-ligand complexes of tetravalent ions **183**, **201**, and **209** [229,315].

Fig. 25. UV-vis spectrum of **232** in CHCl_3 ($8.2 \times 10^{-6} \text{ M}$, 298 K) [337].

Fig. 26. Representative examples of mixed-ligand triple-decker Pc-Por complexes with covalently linked Por substituents [349].

Fig. 27. Representative examples of mixed-ligand triple-decker Pc–Por complexes with terminal tri-allyl groups [63].

Fig. 28. Representative examples of triple-decker and expanded triple-decker Pc-Por complexes prepared by the cross-coupling reactions [350,351].

X = Cl, OAc, HCO₂

(i) 1: 200-300 °C, 2-3 h

2: DBU, *n*-C₆H₁₃OH (a) or *i*-C₅H₁₁OH (b), 130-160 °C, 2-7 h

Scheme 1.

R = H; Ln = Sm, Eu, Tb-Lu (**1**)

R = OPr; Ln = Lu (**12**)

(i) DMF or DMAE, 135-150 °C, 5-7 h

Scheme 2.

M = H, Li; X = Cl, OAc, β -diketonate

(i) 1: BuLi, Ca(OAc)₂, DMSO, 190 °C

2: DBU, DCB, 180 °C

3: DMSO (a), DCB (b), MeOH (c), 65-190 °C

Scheme 3.

$\text{Ln} = \text{Er}$ (**29-31**), Yb (**32**, **33**)

$\text{Ar} = 3,4,5\text{-(MeO)}_3\text{C}_6\text{H}_2$ (**29**), $4\text{-(MeO)C}_6\text{H}_4$ (**30**, **33**), C_6H_5 (**31**), $4\text{-MeC}_6\text{H}_4$ (**32**)

Scheme 4.

Scheme 5.

Scheme 6.

$\text{Ln} = \text{Er, Yb}$; $R^{1-4} = \text{Ph, 4-Py}$

(i) $[\text{Ln}\{\text{N}(\text{SiMe}_3)_2\}_3]$, toluene/ CH_2Cl_2 , reflux, 12 h

(ii) NaL , 20 °C, 12 h

Scheme 7.

Scheme 8.

Ln = Dy, Tb, Ho, Gd, Er, Yb; R = H (**40**), *tert*-Bu (**41**)

(i) $[\text{Ln}\{\text{N}(\text{SiMe}_3)_2\}_3][\text{LiCl}(\text{THF})_3]_x$, toluene, reflux, 12 h

(ii) NaL, 20 °C, 12 h

Scheme 9.

Scheme 10.

(i) 1: 250-350 °C, 0.5-4 h

2: MW (300-700 W), 5-10 min

3: DBU, YOH (Y = $n\text{-C}_6\text{H}_{13}$ (a), $i\text{-C}_5\text{H}_{11}$ (b), $n\text{-C}_5\text{H}_{11}$ (c)) or sulfolane (d), 130-160 °C, 5-48 h

Scheme 11.

R = *tert*-Bu, R' = H, R'' = Br; Ln = Lu; X = OAc (**76**)

R = R' = PhO, R'' = H; Ln = Eu, Er, Lu; X = OAc (**77**)

R = *tert*-Bu, R' = R'' = H; Ln = La, Ce, Pr, Nd, Eu, Gd, Tb, Er, Y; X = acac (**78**)

R = R' = C₁₂H₂₅S, R'' = H; Ln = Eu; X = acac (**79**)

(i) 1: 280-310 °C, 2-4 h

2: MW (700 W), 5-7 min

3: DBU, *n*-C₈H₁₇OH, 190 °C, >18 h

Scheme 12.

M = H, Li; X = OAc, acac

(i) 1: quinoline, 240 °C (a); TCB, 220 °C (b); *n*-C₈H₁₇OH, 190 °C (c); *n*-C₁₆H₃₃OH, 230 °C (d)

2: DBU, *n*-C₆H₁₃OH (a), *n*-C₅H₁₁OH (b), *n*-C₈H₁₇OH (c), 130-190 °C, 2-3 h; DBU, 1-CIN, 260 °C, 1-2 h (d)

3: DBU, MW (240 W), 10 min

4: *n*-C₅H₁₁OK, *n*-C₅H₁₁OH, 135 °C

Scheme 13.

Ln = Lu (**a**), Eu (**b**)

(i) $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ or $o\text{-C}_6\text{H}_4(\text{CH}_2\text{Br})_2$, NaH/DMF, 25 °C

(ii) $\text{Eu}(\text{acac})_3$, MeOLi, $n\text{-C}_{16}\text{H}_{33}\text{OH}$, 180 °C (A)

$\text{Lu}(\text{acac})_3$, $n\text{-C}_{16}\text{H}_{33}\text{OH}$, 210 °C (B)

(iii) 1. H_2SO_4 ; 2. H_2O (ice)

Scheme 14.

Scheme 15.

Scheme 16.

Ln = Lu (**a**), Dy (**b**), Eu (**c**)

(i) Ln(acac)₃, MeOLi, *n*-C₁₆H₃₃OH, 180-200 °C

Scheme 17.

Scheme 18.

(i) $\text{Lu}(\text{CHOO})_3$, DBU, $i\text{-C}_5\text{H}_{11}\text{OH}$, reflux, 19 h (5% yield)

(ii) $\text{Lu}(\text{CHOO})_3$, DBU, $o\text{-DCB}$, reflux, 4.5 h (30% yield)

(iii) $\text{Lu}(\text{acac})_3$, DBU, $o\text{-DCB}$, reflux, 3 h (85% yield)

Scheme 19.

Scheme 20.

Scheme 21.

Scheme 22.

Scheme 23.

Scheme 24.

Scheme 25.

Scheme 26.

Scheme 27.

(i) 1: 240-310 °C, 0.5-3 h

2: DBU, YOH ($\text{Y} = n\text{-C}_6\text{H}_{13}$ (a), $n\text{-C}_5\text{H}_{11}$ (b)), 130-160 °C, 6-20 h

2c: DBU, 1-CIN- $n\text{-C}_4\text{H}_9\text{OH}$ (1:1, vol.), reflux, 2 h

3: Li, $n\text{-C}_5\text{H}_{11}\text{OH}$, 130 °C, 17 h

Scheme 28.

Scheme 29.

Scheme 30.

Scheme 31.

Scheme 32.

Scheme 33.

M = H, Li

R = R' = H, R¹ = H, R² = *tert*-Bu, R³ = H (**136**)

R = H, R' = CH₃(OC₂H₄)₈O, R¹ = H, R² = C₁₂H₂₅O, R³ = H (**167**)

R = H, R' = *tert*-Bu, R¹ = Cl, R² = R³ = H (**168**)

R = H, R' = *tert*-Bu, R¹ = R² = Cl, R³ = H (**169**)

R = H, R' = *tert*-Bu, R¹ = R² = R³ = Cl (**170**)

(i) 1: DBU, MW (240 W), 10 min

2: 1-CIN (a), quinoline (b), 240-260 °C, 1-24 h

Scheme 34.

Scheme 35.

R-R' = 15-crown-5; R'' = R''' = R¹ = H; Ln = Lu (**135**); X = OAc

R = R' = R'' = R¹ = H; R''' = (C₂H₅)₂CHO; Ln = Sm-Lu, Y (**148**); X = acac

R = R' = R¹ = H; R'' = R''' = C₄H₉O; Ln = Sm, Eu, Gd (**172**); X = acac

R = *n*-Bu; R' = R'' = H; R¹ = H (**174**), Cl (**175**); Ln = Eu, Lu; X = OAc

(i) 1: *n*-C₈H₁₇OH (a), 1-CIN (b), 190-260 °C, 8 h; TCB-*n*-C₁₆H₃₃OH (50:1, vol.), 220 °C, 1 h (c)

2: DBU, TCB-*n*-C₁₆H₃₃OH (50:1, vol.), 220 °C, 2 h

Scheme 36.

Scheme 37.

Scheme 38.

$R = R' = R^1 = R^2 = R^3 = H$ (**178**); $Ln = Tb$; $X = OAc$

$R = H$; $R' = \textit{tert}\text{-Bu}$; $R^1 = R^2 = R^3 = H$ (**179**); $Ln = Lu, Sm$; $X = OAc$

$R = R' = H$; $R^1 = (C_2H_5)_2CHO$; $R^2 = R^3 = H$ (**180**); $Ln = Sm$; $X = acac$

$R = R' = H$; $R^1 = R^2 = C_8H_{17}O$; $R^3 = H$ (**181**); $Ln = Sm$; $X = acac$

$R = R' = R^1 = R^2 = H$; $R^3 = (C_2H_5)_2CHO$ (**182**); $Ln = Sm, Eu, Y$; $X = acac$

(i) 1: 250-270 °C, 1.5-2 h

2: DBU, $(NH_4)_6Mo_7O_{24}$, $n\text{-C}_6H_{13}OH$, reflux, 20 h

3: DBU, $n\text{-C}_8H_{17}OH$, 190 °C, 7 h

Scheme 39.

183-195

X = acac

R = C₆H₅; R' = H (**183**); Ln = Eu, Y

R = C₆H₅; R' = C₇H₁₅ (**184**); Ln = Eu, Y

R = C₆H₅; R' = 15-crown-5 (**185**); Ln = Eu

R = 4-MeOPh; R' = 15-crown-5 (**186**); Ln = La, Ce, Pr

R = 4-BrPh; R' = 15-crown-5 (**187**); Ln = Tb

R = 4-C₅H₄N; R' = H (**188**); Ln = Eu, Y

R = 4-C₅H₄N; R' = C₇H₁₅ (**189**); Ln = Eu, Y

R = *p*-ClC₆H₄; R' = H (**190**); Ln = La, Nd, Pr, Sm-Lu, Y

R = *p*-ClC₆H₄; R' = C₇H₁₅ (**191**); Ln = Eu

R = *p*-MeOC₆H₄; R' = H (**192**); Ln = Eu

R = *p*-MeOC₆H₄; R' = C₇H₁₅ (**193**); Ln = Eu

R = *p*-(*tert*-Bu)C₆H₄; R' = H (**194**); Ln = Eu

R = *p*-(*tert*-Bu)C₆H₄; R' = C₇H₁₅ (**195**); Ln = Eu

(i) TCB or *n*-C₈H₁₇OH, 190-220 °C, 4-6 h

(ii) DBU, YOH (Y = *n*-C₅H₁₁ or *n*-C₈H₁₇), 130-190 °C, 12 h

Scheme 40.

X = acac, OAc, Cl, I; M = H, Li

R = C₆H₅; R¹ = R² = R³ = H (**183**); Ln = La, Pr, Nd, Eu, Gd, Er, Lu, Y; X = acac

R = 4-C₅H₄N; R¹ = R² = R³ = H (**188**); Ln = Ce, Eu, Gd; X = acac

R = 4-ClC₆H₄; R¹ = (C₂H₅)₂CHO; R² = R³ = H (**196**); Ln = Sm, Eu, Y; X = acac

R = 4-ClC₆H₄; R¹ = R³ = C₄H₉O; R² = H (**197**); Ln = Y; X = acac

R = 4-(*n*-C₈H₁₇NH)C₆H₄; R¹ = (C₂H₅)₂CHO; R² = R³ = H (**199**); Ln = Ho, Y; X = acac

R = 4-(*tert*-Bu)C₆H₄; R¹ = R³ = H; R² = *tert*-Bu (**200**); Ln = Lu; X = OAc

R = 4-MeC₆H₄; R¹ = R² = R³ = H (**201**); Ln = Eu; X = Cl

R = 4-MeC₆H₄; R¹ = R³ = H; R² = *tert*-Bu (**202**); Ln = Ce, Eu; X = I, Cl

R = *n*-C₅H₁₁; R¹ = R³ = H; R² = *tert*-Bu (**203**); Ln = Ce; X = I

(i) 1: TCB (a) or *n*-C₈H₁₇OH (b), 190-220 °C, 8-12 h

2: DBU, MW (440 W), 10 min

3: LiN(SiMe₃)₂, diglyme, 160 °C, 18 h

Scheme 41.

Scheme 42.

Scheme 43.

R = 4-C₅H₄N; R' = R¹ = R² = H (**210**); Ln = Eu

R = 4-C₅H₄N; R' = H; R¹ = R² = C₁₂H₂₅S (**211**); Ln = Eu

R = 4-(*tert*-Bu)C₆H₄; R' = R¹ = R² = H (**212**); Ln = La, Ce, Pr, Nd, Sm-Tm, Y

R = 4-ClC₆H₄; R' = R¹ = H; R² = *tert*-Bu (**213**); Ln = Eu

R = R¹ = R² = H; R' = Et (**214**); Ln = La, Ce, Pr, Nd, Sm-Lu, Y

(i) DBU, *n*-C₈H₁₇OH, 190 °C, 18 h

Scheme 44.

Scheme 45.

Scheme 46.

Scheme 47.

Scheme 48.

(i) TCB or $n\text{-C}_8\text{H}_{17}\text{OH}$, 190-220 °C, 3-12 h

Scheme 49.

R = n -C₈H₁₇O; Ln' = Lu; Ln = Gd-Yb (**230**)

Scheme 50.

Scheme 51.

Scheme 52.

Scheme 53.

Scheme 54.

$\text{R} = p\text{-MeC}_6\text{H}_4$; $\text{R}^1 = \text{R}^2 = \text{H}$ (**273**); $\text{X} = \text{AcS}$ (**276**), $[p\text{-(AcSCH}_2\text{)C}_6\text{H}_4]_3\text{C}$ (**277**)

$\text{R} = n\text{-C}_5\text{H}_{11}$; $\text{R}^1 = \text{R}^2 = \text{Me}$ (**274**); $\text{X} = \text{AcS}$ (**278**)

$\text{R} = n\text{-C}_5\text{H}_{11}$; $\text{R}^1 = \text{H}$; $\text{R}^2 = \text{tert-Bu}$ (**275**); $\text{X} = \text{AcS}$ (**279**)

(i) 1: $\text{Pd(PPh}_3\text{)}_2\text{Cl}_2$, CuI , $(i\text{-Pr})_2\text{EtN}$, THF , $30\text{ }^\circ\text{C}$, 20 h

2: $\text{Pd}_2(\text{dba})_3$, $\text{P}(o\text{-tol})_3$, $(i\text{-Pr})_2\text{EtN}$, toluene , $35\text{ }^\circ\text{C}$, 44 h

Scheme 55.

R = *p*-MeC₆H₄

(i) Pd(PPh₃)₂Cl₂, CuI, I₂, (*i*-Pr)₂NH, toluene, 25 °C, 20 h

Scheme 56.

Scheme 57.

Graphical Abstract