Non-photochemical synthesis of Re(diimine)(CO)₂(L)Cl (L = phosphine or phosphite) compounds

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Abstract

The synthesis and characterization of a series of compounds of the type Re(diimine)(CO)₂(L)Cl (where L = P(OEt)₃, PMe₃) is reported. The non-photochemical ligand substitution (non-PLS) utilizes the trans-labilizing effect of phosphorus ligands to facilitate carbonyl replacement. The non-PLS pathway leads to good yields (>60%) of single isomer products, comparing favorably to the lower yield, mixed isomer products of analogous PLS pathways. The substitution of a carbonyl group by a phosphine/phosphite ligands shifts absorption further into the visible region without diminishing molar absorptivity. The synthesis presented provides a general facile ligand substitution pathway for related light-sensitive neutral rhenium/manganese carbonyl halide compounds.

Introduction

Rhenium/manganese (I) diimine tricarbonyl halide complexes have been studied extensively for their photophysical properties,¹ as photo-activated CO releasing moieties (photoCORMs),² and as electrocatalysts³ and photocatalysts⁴ for the reduction of carbon dioxide to carbon monoxide,⁵ on the path to fuel formation.⁶ The initial ReCl(bpy)(CO)₃ (bpy = 2,2'-bipyridine) electrocatalyst⁷ has been improved on by the addition of alkyl substituents on the bipyridine ligand.⁸ Variation of the electron-donating ability of ligand-groups in electrocatalysts is commonly probed in order to tune the electronics of the metal center.⁹ Variation of the electron density on the metal center may also be affected by the use of σ -donor ligands, namely phosphite and phosphine ligands. Rhenium (I) diimine tricarbonyl complexes with phosphorous ligands have been reported¹⁰ and more recently, photochemical ligand substitution (PLS) of one of the carbonyl ligands has been widely explored,¹¹ alongside photochemical isomerization.¹² The synthesis of Re(bpy)(CO)₂(L)(L') compounds (where L and L' are N-donor ligands) utilizing a PLS pathway has been reported with the formation of mixed isomer products (and hence lower yields than reported herein).¹³ An alternate non-PLS route to rhenium(I) diimine dicarbonyl halide compounds is presented; that should be generally applicable to ligand substitution reactions for light-sensitive rhenium/manganese diimine carbonyl compounds.

Results and Discussion

Scheme 1. Complexes **1a-d** and **2a-d** were synthesized using a non-PLS pathway, with full characterization of novel compounds **2b-d**. This pathway yields only the *cis,trans*-isomer (as drawn above) in marked contrast to the isomeric mixtures of *cis,cis* and *cis,trans* seen in PLS approaches. TMAO = Trimethylamine *N*-oxide.

Synthesis. *fac*-ReCl(bpy)(CO)₃, *fac*-ReCl(bpy-Me)(CO)₃ (bpy-Me = 4,4'-dimethyl-2,2'-bipyridine), and *fac*-ReCl(bpy-tBu)(CO)₃ (bpy-tBu = 4,4'-di-tertbutyl-2,2'-bipyridine) were synthesized using known techniques.⁶ Complexes **1a-d** were synthesized with modifications to a known literature procedure.⁸ The tricarbonyl chloro complexes were refluxed with silver triflate (AgOTf) in THF for 3 hours, after which the AgCl was filtered off. 30 molar equivalents of the phosphorous ligand was added and refluxed over night. After the solvent was removed, a methanol solution of ammonium hexafluorophosphate (NH₄PF₆) was added. After H₂O and diethyl ether was added, the pale yellow solids were collected on a fritted funnel. Yields ranged from 70% to 88%. Spectroscopic data (¹H-NMR, IR, MS) match reported values and indicate the structures shown in scheme 1.

Compounds **2a-d** were synthesized by combining the corresponding **1** compound with 15 molar equivalents of tetraethylammonium (NEt₄Cl) chloride in DCM. One molar equivalent of Trimethylamine *N*-oxide (TMAO)¹⁴ in a DCM/MeOH solution was added slowly and the reaction mixture was refluxed for 24 hours. The solvent was lowered in volume and washed three times with water. After drying the organic layer with anhydrous sodium sulphate, the DCM volume was lowered to ~1 mL. Pentane was added to precipitate a red solid, which was collected and dissolved in minimal MeCN. The MeCN solution was filtered through glass wool, and then allowed to evaporate slowly to afford large red crystals. Yields ranged from 60% to 72%.

Table 1. $\nu(\text{CO})$ frequencies (cm⁻¹) and MLCT absorption peaks (nm) of complexes **2a-d**.

Complex	$\nu(\text{CO})^a$	MLCT ^b
2a	1924, 1844	423
2b	1921, 1831	407
2c	1927, 1847	416
2d	1901, 1815	445

^a measurements taken in solid state on ATR-FTIR.

^b measurements taken in MeCN

Characterization. Compounds **1a**,¹⁵ **1b**¹⁶ and **2a**^{11, 15} have been previously reported, synthesized via photochemical methods. ¹H-NMR, FT-IR, and UV/vis spectroscopic data matched the previously reported data. Using the same synthetic route for all compounds, we conclude that novel compounds **2b-d** are of the structure shown in scheme 1. Indeed the crystal structure of compound **2c** (Fig. 1) also confirms the product as the *cis,trans*-isomer (X-ray quality crystals were grown by the diffusion of pentane in a solution of the compound in acetone). FT-IR spectra (Table 1) shows two sharp peaks of equal intensity in the $\nu(\text{CO})$ region, in a similar pattern to that of related rhenium dicarbonyl complexes.¹¹ The UV/vis spectra of **2a-2d** shows an absorption peak around 425 nm, as well as a more intense band around 290 nm. The peak at ~290 nm is assigned to the $\pi \rightarrow \pi^*$ transition of the diimine ligand while the lower energy peak is assigned to the metal to ligand charge transfer (MLCT)¹⁷ from the rhenium to the diimine ligand.¹⁸ The MLCT peaks (Table 1) for complexes **2a-d** reveal a bathochromic shift of as much as 50 nm compared to the analogous rhenium diimine tricarbonyl chloro complexes, yet with relatively undiminished molar absorptivities (Fig. 2).

Figure 1. X-ray crystallographic structure of **2c** (50% probability thermal ellipsoids). Full crystallographic details can be found in the supporting information.

Figure 2. UV/Vis spectra displaying the shift of absorption to lower energy wavelengths, upon ligand substitution of a carbonyl ligand with a phosphorus-based ligand, yielding compounds **2a-d**.

Advantages of non-PLS approach. Compounds of the type $\text{Re}(\text{diimine})(\text{CO})_3\text{Cl}$ are generally unreactive towards thermal, photochemical, or oxidative carbonyl substitution. A published PLS approach lead to replacement of one CO ligand by acetonitrile solvent, giving approximately equal amounts of *cis,cis* and *cis,trans* products, with a combined yield of ~55%.¹¹ The two-step process presented herein has an overall yield of >60% (based on a first-step yield that is ~90 % followed by one that is ~70%) of, crucially, a single geometric isomer, the *cis,trans*. Brown et al.¹⁹ indicated that there is a general guideline for carbonyl reactivity towards TMAO which can be measured with FT-IR to be around $\sim 2000\text{ cm}^{-1}$. Although compounds of the type $\text{ReCl}(\text{diimine})(\text{CO})_3$ have a $\nu(\text{CO})$ in the region of $2010\text{--}2015\text{ cm}^{-1}$, when these compounds are combined with TMAO under various conditions, there is no reaction. When the Cl⁻ ligand is replaced by a phosphorous ligand, however, the same $\nu(\text{CO})$ shifts roughly 15-20 wavenumbers to ~ 2030 , indicating a labilization of the *trans*-CO.

When the TMAO is slowly added to a solution of **1a-d** and NEt_4Cl in DCM (pale yellow), the solution immediately starts to turn red/orange indicating the immediate formation of the corresponding **2** compound. MS and NMR show that there is also the simultaneous formation of $[\text{Re}(\text{diimine})(\text{CO})_2(\text{P}(\text{OEt})_3)(\text{N}(\text{CH}_3)_3)]\text{PF}_6$. Although the boiling point of trimethylamine is $3\text{--}7^\circ\text{C}$, it may dissolve in the DCM as soon as it is formed by the reaction of TMAO allowing it to act as a ligand at the free coordination site.²⁰ Refluxing the reaction mixture for 24 hours in the presence of 15 molar equivalents of Cl⁻ drives the elimination of the unwanted byproduct, resulting in pure **2**.

Electrochemistry. Cyclic voltammograms (CV) of the phosphite substituted series, **2a-c**, were collected in anhydrous acetonitrile²¹ (Fig. S1). $E_{1/2}$ values for **2b** and **2c** were nearly identical (-1.922 V and -1.927 V respectively, vs Fc/Fc^+), displaying the expected effect of the donating alkyl groups (attached to the diimine), where the $E_{1/2}$ values for **2a** was more anodic at -1.883 V . Compounds **2a** and **2c** display a lack of reversibility at 0.100 V/s , whilst compound **2b** is quasi-reversible. A comparison of $\text{ReCl}(\text{bpy-tBu})(\text{CO})_3$ ⁶ with novel compounds **1c** and **2c** shows an anodic shift (Fig. S2) in the first reduction even as the halide is replaced by the more electron-donating phosphite ligand, however the cationic nature of **1c** is clearly the larger effect (upon the ease of reduction). Subsequent replacement of one CO ligand with chloride to give the neutral **2c** compound, shows a large (almost 300 mV) cathodic shift in reduction, displaying the electron-donating effect of the phosphite ligand; the electron-rich metal center is harder to reduce. The initial reduction of $\text{ReCl}(\text{diimine})(\text{CO})_3$ type compounds has been ascribed to the reduction of the diimine group,²² acting as a non-innocent²³ electron reservoir.²⁴

Conclusion

An improved synthetic route for neutral compounds of the type $\text{ReCl}(\text{diimine})(\text{CO})_2(\text{L})$ (where L = phosphine, phosphite) is presented, yielding single-isomer products without the use of chromatographic purification. Three novel examples of this type of complex were produced in good yields, with each novel compound being fully characterized. Only one synthetic method of a $\text{Re}(\text{diimine})(\text{CO})_2(\text{L})(\text{L}')$ complex with L and L' being two different ligands (cationic compounds where L/L' are N, P or C-donor, requiring chromatographic purification) has been reported without the use of photochemical ligand substitution.²⁵

Experimental

bpy = 2,2'-bipyridine; OTf = trifluoromethanesulfonate; $\text{P}(\text{OEt})_3$ = triethyl phosphite; bpy-4-Me = 4,4'-dimethyl-2,2'-bipyridine; bpy-tBu = 4,4'-di-tertbutyl-2,2'-bipyridine; PMe_3 = trimethylphosphine; NEt_4Cl = tetraethylammonium chloride; TMAO = trimethylamine *N*-oxide. All reactions were performed under Ar(g) using standard Schlenk-line techniques and worked up under open-air atmospheric conditions.

Preparation of 1a.¹² $\text{ReCl}(\text{bpy})(\text{CO})_3$ (0.207 g, 0.45 mmol) and AgOTf (0.116 g, 0.45 mmol) were added to THF (100 mL) and refluxed for 3h. The resulting AgCl was filtered off on a medium fritted funnel. The filtrate was returned to a flask, and excess $\text{P}(\text{OEt})_3$ (2.3 mL, 1.3 mmol) was added. The mixture was refluxed overnight, and the THF was removed by rotary evaporation. 5 mL of methanol and 5 mL of a saturated NH_4PF_6 methanol solution was added slowly. $\sim 50\text{ mL}$ of diethyl ether and $\sim 50\text{ mL}$ of DI H_2O was added and the resulting pale yellow solid (**1a**) was collected on a fritted funnel (87% yield). $^1\text{H-NMR}$ (δ , 400 MHz, acetone- d_6): 9.25 (bpy-6,6'), 8.86 (bpy-3,3'), 8.48 (bpy-4,4'), 7.92 (bpy-5,5'), 3.96 ($-\text{CH}_2-$), 1.07 ($-\text{CH}_3$). $^{31}\text{P-NMR}$ (δ , 400 MHz, acetone- d_6): 107.8. $\nu(\text{CO})$ (cm^{-1}): 2029, 1924. MS (m/z): 593.0846 ($[\text{M}]^+$)

Preparation of 1b.¹³ The procedure for **1b** was nearly identical to that of **1a** but using ReCl(bpy-4-Me)(CO)₃ (0.358 g, 0.73 mmol) instead of ReCl(bpy)(CO)₃ (all molar ratios were kept the same). The resulting off white solid (**1b**) was obtained in 82% yield. ¹H-NMR (δ, 400 MHz, acetone-d₆): 9.03 (bpy-6,6'), 8.71 (bpy-3,3'), 7.74 (bpy-5,5'), 3.94 (-CH₂-), 2.68 (bpy-CH₃), 1.07 (-CH₃). ³¹P-NMR (δ, 400 MHz, acetone-d₆): 108.3. ν(CO) (cm⁻¹): 2038, 1915. MS (^{m/z}): 621.1162 ([M]⁺)

Preparation of 1c. The procedure for **1c** was nearly identical to that of **1a** but using ReCl(bpy-tBu)(CO)₃ (0.305 g, 0.53 mmol) instead of ReCl(bpy)(CO)₃ (all molar ratios were kept the same). The resulting pale yellow solid (**1c**) was obtained in 88% yield. ¹H-NMR (δ, 400 MHz, acetone-d₆): 9.10 (bpy-6,6'), 8.88 (bpy-3,3'), 7.91 (bpy-5,5'), 3.94 (-CH₂-), 1.48 (tBu), 1.05 (-CH₃). ³¹P-NMR (δ, 400 MHz, acetone-d₆): 108.3. ν(CO) (cm⁻¹): 2032, 1947, 1913. MS (^{m/z}): 705.2097 ([M]⁺)

Preparation of 1d. The procedure for **1d** was nearly identical to that of **1a** but using ReCl(bpy-4-Me)(CO)₃ (0.200 g, 0.41 mmol) instead of ReCl(bpy)(CO)₃ and PMe₃ instead of P(OEt)₃ (all molar ratios were kept the same). The resulting pale yellow solid (**1d**) was obtained in 70% yield. ¹H-NMR (δ, 400 MHz, acetone-d₆): 9.05 (bpy-6,6'), 8.74 (bpy-3,3'), 7.75 (bpy-5,5'), 2.67 (bpy-CH₃), 1.27 (PMe₃). ³¹P-NMR (δ, 400 MHz, acetone-d₆): -27.2. ν(CO) (cm⁻¹): 2021, 1932, 1901. MS (^{m/z}): 531.0893 ([M]⁺)

Preparation of 2a.^{11, 15} **1a** (0.105 g, 0.14 mmol) and NeT₄Cl (0.360 g, 2.2 mmol) was dissolved in DCM (40 mL). A solution of TMAO (0.0175 g, 0.16 mmol) in DCM/methanol (50 mL/2 mL) was prepared. The **1a** solution was refluxed and the TMAO solution was added to it drop-wise over an hour. The solution was then refluxed for 24 additional hours. The DCM and methanol were removed by rotary evaporation. The residue was dissolved in 10 mL of DCM, which was washed 3 times with ~50-80 mL of DI H₂O. The organic layer was dried with anhydrous sodium sulfate, and the solvent was removed by rotary evaporator to afford a red solid. The residue was dissolved in minimal acetonitrile, filtered through glass wool, and the solvent was evaporated slowly to afford large red crystals, (**2a**), in 72% yield. ¹H-NMR (δ, 400 MHz, acetone-d₆): 9.04 (bpy-6,6'), 8.56 (bpy-3,3'), 8.19 (bpy-4,4'), 7.66 (bpy-5,5'), 3.75 (-CH₂-), 1.00 (-CH₃). ³¹P-NMR (δ, 400 MHz, acetone-d₆): 119.5. ν(CO) (cm⁻¹): 1924, 1844. Elemental analysis for C₁₈H₂₃N₂ClO₅Pre: Calculated; C, 36.03; N, 4.67; H, 3.86; Found; C, 36.27; N, 4.63; H, 3.84.

Preparation of 2b. The procedure for **2b** was nearly identical to that of **2a** but using **1b** (0.202 g, 0.26 mmol) instead of **1a** (all molar ratios were kept the same). The resulting red/orange solid was obtained in 70% yield. ¹H-NMR (δ, 400 MHz, acetone-d₆): 8.83 (bpy-6,6'), 8.38 (bpy-3,3'), 7.46 (bpy-5,5'), 3.74 (-CH₂-), 2.57 (bpy-CH₃), 1.00 (-CH₃). ³¹P-NMR (δ, 400 MHz, acetone-d₆): 120.7. ν(CO) (cm⁻¹): 1930, 1829. Elemental analysis for C₂₀H₂₇N₂ClO₅Pre: Calculated; C, 38.25; N, 4.46; H, 4.33; Found; C, 38.72; N, 4.45; H, 4.36.

Preparation of 2c. The procedure of **2c** was nearly identical to that of **2a** but using **1c** (0.176 g, 0.21 mmol) instead of **1a** (all molar ratios were kept the same). The resulting red/orange solid was obtained in 69% yield. ¹H-NMR (δ, 400 MHz, acetone-d₆): 8.90 (bpy-6,6'), 8.56 (bpy-3,3'), 7.67 (bpy-5,5'), 3.73 (-CH₂-), 1.45 (tBu), 0.97 (-CH₃). ³¹P-NMR (δ, 400 MHz, acetone-d₆): 120.2. ν(CO) (cm⁻¹): 1927, 1847. Elemental analysis for C₂₆H₃₉N₂ClO₅Pre: Calculated; C, 43.85; N, 3.93; H, 5.52; Found; C, 43.80; N, 3.91; H, 5.38.

Preparation of 2d. The procedure of **2d** was nearly identical to that of **2a** but using **1d** (0.106 g, 0.16 mmol) instead of **1a** (all molar ratios were kept the same). The resulting red solid was obtained in 60% yield. ¹H-NMR (δ, 400 MHz, acetone-d₆): 8.82 (bpy-6,6'), 8.40 (bpy-3,3'), 7.46 (bpy-5,5'), 2.58 (bpy-CH₃), 1.22 (PMe₃). ³¹P-NMR (δ, 400 MHz, acetone-d₆): -21.7. ν(CO) (cm⁻¹): 1901, 1815. Elemental analysis for C₁₇H₂₁N₂ClO₃Pre: Calculated; C, 37.95; N, 5.21; H, 3.93; Found; C, 38.14; N, 5.29; H, 3.90.

Supporting Information. CV of compounds **1a**, **1c** and **2a-c**, electrochemistry experimental details, and full crystallographic information on **2c**, can be found in the supporting information (available online).

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References

TOC synopsis

A generalized reaction is shown for the primary products of the paper. A light bulb is crossed-out to indicate that the synthesis is non-photochemical in nature. Below this are sample UV/Vis spectra (highlighting the bathochromic shift upon ligand substitution).