A Phase Based Approach to Insulated Molecular Wires: Diplatinum Octatetraynediyl Complexes Bearing Fluorous Trialkylphosphine Ligands

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ABSTRACT: Reactions of [(tetrahydrothiophene)Pt(C₆F₅)μ-Cl]₂ and fluorous phosphines P((C-H₂)_mR_{fn})₃ (R_{fn} = (CF₂)_{n-1}CF₃; m/n = **a**, 2/8; **b**, 3/8; **c**, 3/10) afford the chloride complexes *trans*-(C₆F₅)((R_{fn}(CH₂)_m)₃P)₂PtCl (**8a-c**, 40-74%), which upon treatment with butadiyne and CuI (cat.) in HNEt₂/CF₃C₆H₅ give *trans*-(C₆F₅)((R_{fn}(CH₂)_m)₃P)₂Pt(C≡C)₂H (**9a-c**, 44-64%). Subsequent reactions with oxygen and CuCl/TMEDA in acetone yield the title complexes *trans,trans*-(C₆F₅)((R_{fn}(CH₂)_m)₃P)₂Pt(C≡C)₄Pt(P((CH₂)_mR_{fn})₃)₂(C₆F₅) (**10a-c**, 35-52%). All platinum complexes exhibit CF₃C₆F₁₁/toluene partition coefficients of >99:<1. The crystal structure of **8b** shows that the perfluoroalkyl groups segregate into fluorous domains. It was therefore thought that the perfluoroalkyl groups in **10a-c** would aggregate about the polyynediyl chain. However, these adducts could not be crystallized. Electrochemical oxidations of **10a-c** give radical cations that are much less stable than trialkyl and triarylphosphine analogs.

key words: fluorous; phosphine ligand; polyyne; platinum, molecular wire, crystal structure

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■ INTRODUCTION

There has been intense ongoing interest in complexes in which two metals are linked by a π conjugated, alkyne-containing bridge,¹ including a singular body of work by Jack Lewis, to whom this special issue is dedicated.² Such species are often viewed as prototypes for molecular wires. However, the "all alkyne" versions, polyynediyl complexes,^{1a,3} gradually diminish in stabilities as the carbon chains are lengthened.⁴ This trend is much more pronounced for paramagnetic analogs resulting from one electron oxidations or reductions.⁴ To address these problems and other issues, attention has been given to developing what are sometimes termed "insulated molecular wires".⁵

We have taken two distinct approaches to insulating or sterically protecting the sp carbon chains of polyynediyl complexes. One features termini spanning diphosphine ligands of the formula $Ar_2P(CH_2)_zPAr_2$, which can be introduced by substitution or metathesis reactions as illustrated in Scheme 1 for diplatinum complexes (**I**).^{6,7} The sp^3 chains adopt double helical conformations in the solid state. The other involves shielding the sp chain with a macrocycle, in the form

Scheme 1. Syntheses of helically protected polyynediyl complexes by coordination driven self assembly (top) and olefin metathesis followed by hydrogenation (bottom).

of a rotaxane assembled by an "active template" strategy⁸ as exemplified by **II** in Scheme 2.⁹

Scheme 2. Syntheses of polyynediyl complex rotaxanes by an "active template" strategy.

We wondered whether a third, architecturally simpler approach to sp carbon chain protection might complement those in Schemes 1 and 2. Specifically, a variety of fluororous trialkylphosphines are now readily available.¹⁰⁻¹² Most of these feature substituents of the formula $(\text{CH}_2)_m(\text{CF}_2)_{n-1}\text{CF}_3$, abbreviated $(\text{CH}_2)_m\text{R}_{fn}$. The $(\text{CH}_2)_m$ unit or "methylene spacer" dampens the electron withdrawing effect of the perfluoroalkyl segment, although far from completely when $m = 2$ or 3.¹³ Molecules or domains that are rich in perfluoroalkyl groups tend to phase separate from their non-fluorous counterparts, as evidenced by many types of phenomena in solution¹⁴ and seen in a variety of crystal structures.^{15,16}

Given that the families of diplatinum polyynediyl complexes depicted above carry two phosphine ligands on each terminus, it should be possible to introduce four fluororous phosphines with a total of twelve extended perfluoroalkyl groups. Although these could be arranged in a variety of motifs, contact between the fluororous domains would be maximized if as many as sterically feasible would adopt conformations that roughly parallel the sp carbon chain, as shown in **IV** in Scheme 3. Hence, there seemed to be a distinct possibility of "spontaneous self assembly" of insulating perfluorocarbon tubules.

In this paper, practical syntheses of a series of fluororous phosphine substituted diplatinum octatetraynediyl complexes are presented. A crystal structure of a precursor exhibits a high degree of perfluoroalkyl group segregation in the lattice. Their extremely high fluorophilicities and

the effect of the fluororous phosphine ligands upon redox properties are quantified.¹⁷

Scheme 3. Proposed phase separation (right, **IV**) of perfluoroalkyl groups in diplatinum octatetraynediyl complexes with fluororous aliphatic phosphine ligands

■ RESULTS

1. Platinum chloride complexes. The fluororous phosphines $P((CH_2)_mR_{fn})_3$ (**7**) in Scheme 4,¹⁰ which feature two or three methylene spacers and either perfluorooctyl or perfluorodecyl groups, are soluble in fluororous solvents and insoluble in most organic solvents with the exception of THF. They are stable in air as solids but readily oxidize in solution. As shown in Scheme 4, the phosphines were combined with the known diplatinum bis(tetrahydrothiophene) complex **6**¹⁸ in a ca. four to one molar ratio (i.e., two phosphines per platinum atom) in refluxing THF under an inert atmosphere. Workups afforded the platinum fluororous phosphine chloride complexes **8a-c** as air stable white powders in 40-74% yields.

Scheme 4. Syntheses of the fluororous platinum chloride complexes **8a-c**.

Complexes **8a-c** were insoluble in organic solvents such as CH_2Cl_2 and acetone. Thus, NMR spectra were recorded in perfluorobenzene (C_6F_6), using a small amount of $CDCl_3$ cosolvent for a deuterium lock. However, it should be emphasized in passing that perfluoroarenes are much more polar than perfluoroalkanes and are not considered fluororous.¹⁴ These and all new complexes below were characterized by NMR (1H , $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$) and IR spectroscop-

ies and microanalyses, as summarized in the experimental section. The $^{31}\text{P}\{^1\text{H}\}$ NMR signals (Table 1) show $^1J_{\text{PPt}}$ values that are diagnostic of *trans* geometries at platinum.¹⁹

Single crystals of **8b** were grown from C_6F_6 , and the X-ray structure determined as detailed in Table 2 and the experimental section. The molecular structure is shown in Figure 1. Three of the six $(\text{CH}_2)_3\text{R}_{\text{f8}}$ groups showed disorder (chains 2, 3, 6 as labeled in Figure 1); the dominant conformations were used for all analyses. Key bond lengths and angles are given in Table 3. A space filling representation of the lattice is provided in Figure 2. This illustrates the segregation of the fluororous and non-fluororous domains in the solid state. Packing diagrams are provided elsewhere.¹⁷

Figure 1. Thermal ellipsoid plots (50% probability level) of the dominant conformation of **8b**: top, view down the Cl-Pt axis; bottom, as above but with fluorine atoms omitted for clarity.

Torsion angles associated with the $(\text{CH}_2)_3\text{R}_{\text{f8}}$ groups are summarized in Table s1 (Appendix B, supplementary data). Most of the four carbon segments exhibited approximately *anti* conformations, as reflected by C-C-C-C torsion angles in the range of 162° to 175° (absolute values). However, in five chains there was one four carbon segment with an approximately *gauche*

Figure 2. Space filling model of the dominant configuration of **8b** with fluorine atoms in yellow-green, chlorine atoms in green, platinum atoms in pink, and carbon atoms in gray.

conformation, as indicated by torsion angles in the range of 54° to 95° . Many studies have shown that the lowest energy conformations of *n*-perfluoroalkanes and perfluoroalkyl groups exhibit C-C-C torsion angles that are somewhat less than those in *n*-alkanes (180°).²⁰ The typically 10 – 20° deviations propagate in the same directional sense to give chiral helical poly(difluoromethylene) segments. The torsion angles associated with anti and gauche F-C-C-F linkages are similarly distorted, and average data for the $\text{CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2$ segments in the non-disordered chains are summarized pictorially in Figure 3.

Figure 3. Average torsion angles associated with the $\text{CF}_2\text{-CF}_2\text{-CF}_2\text{-CF}_2$ segments in the dominant conformation of crystalline **8b** (excluding one gauche linkage).

2. Fluorous platinum butadiynyl and diplatinum octatetraynediyl complexes. The next objective was to replace the chloride ligands in **8a-c** with butadiynyl groups. Usually such substitutions are carried out with an excess of butadiyne, a copper(I) catalyst, and a mixed solvent comprised of the base HNEt_2 and CH_2Cl_2 .²¹ However, given the poor solubilities of **8a-c** in organic solvents, a "hybrid" organic/fluorous solvent,^{22,23} trifluorotoluene ($\text{CF}_3\text{C}_6\text{H}_5$), was used

in place of CH_2Cl_2 . Such media are capable of dissolving appreciable concentrations of both fluorophilic and lipophilic solutes. Accordingly, reactions as outlined in Scheme 5 gave the platinum butadiynyl complexes **9a-c** in 44-64% yields as air stable tan powders.

Scheme 5. Syntheses of the fluorinated platinum butadiynyl (**9**) and diplatinum octatetraynediyl (**10**) complexes.

The marked fluorophilicities of **9a-c** proved advantageous in the workups. The solvents were replaced with organic/fluorous biphasic mixtures. As shown in Figure 4 (left), the products preferentially partitioned into the denser fluorous phase, whereas the colored copper containing byproducts and other species remained in the lighter organic phase. The spectroscopic properties of **9a-c** were similar to those of **8a-c**, but with additional characteristic NMR and IR signals associated with the $\text{C}\equiv\text{C}$ and $\equiv\text{CH}$ moieties (experimental section).

Figure 4. Exploiting the fluorophilicities of **9a-c** and **10a-c** in organic/fluorous CH_2Cl_2 /perfluorohexanes biphasic workups (Scheme 5). Left: workup of **9a**. Right: workup of **10a**.

Oxidative homocouplings of the butadiynyl complexes **9a-c** were investigated. The Hay protocol, which involves a copper(I)/TMEDA catalyst and molecular oxygen,^{6a-c} was studied

first. The complexes dissolved upon mild heating (40 °C) in the customary solvent acetone, consistent with highly temperature dependent solubilities observed for most fluorosubstituted compounds.²⁴ Thus, no cosolvent was required, and the conditions in Scheme 5 afforded the title octatetraynediyl complexes **10a-c** in 35-52% yields as air stable tan or yellow solids. During workups, the solvents were again replaced with organic/fluorous biphasic mixtures, with the colored copper containing byproducts and other species partitioning into the lighter organic phase, as shown in Figure 4 (right).

The spectroscopic properties of **10a-c**, which were only soluble in fluorosubstituted solvents, hybrid solvents, or C₆F₆, were very similar to those of other diplatinum octatetraynediyl complexes.^{6a-c,21} The ³¹P{¹H} NMR spectra (Table 1) exhibited parallel chemical shift and coupling constant trends. The sp carbons showed diagnostic ¹³C{¹H} NMR chemical shift patterns (99.5-51.5 ppm, experimental section). Whereas **9a-c** gave one characteristic IR ν_{C≡C} band (2153-2152 cm⁻¹, m-w), **10a-c** afforded two (2160-2152 cm⁻¹, m-w; 2029-2037 cm⁻¹, w).

3. Physical Measurements. The CF₃C₆F₁₁/toluene partition coefficients²⁵ of the free phosphines **7a,b** had been previously reported.^{10a} Both are highly fluorophilic, with the ratio becoming less biased with increasing non-fluorous content (>99.7:<0.3 and 98.8:1.2, respectively). The partition coefficients of **7c** and the complexes **8a-c**, **9a-c**, and **10a-c** were measured as described in the experimental section. In all cases, values of >99:<1 were obtained. It has been noted that the partition coefficients of complexes that contains several fluorosubstituted ligands can be higher than those of the fluorosubstituted ligands alone, despite added non-fluorous content (such as the sp carbon chains or pentafluorophenyl ligands in **9-10**).²⁵

Next, electrochemical oxidations of **10a-c** were probed. Cyclic voltammograms were recorded in acetonitrile/CF₃C₆H₅ mixtures under the standard conditions detailed in Table 4 and the experimental section. The CF₃C₆H₅ cosolvent was required to solubilize **10a-c**. Each complex exhibited an oxidation or anodic peak as summarized in Table 5, but no follow-up reduction or cathodic peak, for an *i*_{c/a} value of zero. This indicates the rapid decomposition of the initial oxidation products.

To probe whether the solvent mixture might have contributed to the lack of reversibility, the non fluorous analog *trans,trans*-(C₆F₅)((*p*tol₃P)₂Pt(C≡C)₄Pt(P(*p*tol₃)₂)(C₆F₅) (**11**; Figure 5)²¹ was assayed under identical conditions. A modest cathodic peak was now observed, for a *i*_{c/a} value of 0.27. However, per data reported earlier, reversibility was superior in CH₂Cl₂ (*i*_{c/a} = 0.48). For comparison, data (in CH₂Cl₂) for related complexes with alkyl phosphine substituents, *trans,trans*-(C₆F₅)(Et₃P)₂Pt(C≡C)₄Pt(P(Et₃)₂)(C₆F₅) (**12**)²⁶ and *trans,trans*-(C₆F₅)(Ph₂(*n*-octyl)P)₂Pt(C≡C)₄Pt(P(*n*-octyl)Ph₂)₂(C₆F₅) (**13**),^{6a} are also provided in Table 4.

Figure 5. Reference compounds used for measurements.

DISCUSSION

Schemes 4-5 show the feasibility of accessing a variety of platinum complexes with *trans* disposed fluorous trialkylphosphine ligands, although in some cases standard reaction conditions must be adjusted due to the phase properties of the starting materials. However, these same phase properties can prove advantageous for workups (Figure 4). In earlier related efforts, Stibrany and Gorun described three syntheses of a platinum dichloride complex, *trans*-((R_{f6}CH₂CH₂)₃P)₂PtCl₂, which features two fluorous trialkylphosphines with slightly shorter R_{f6} segments.^{16b}

Crystal structures of three other square planar complexes with *trans* fluorous trialkyl phosphines have been reported, *trans*-((R_{f6}CH₂CH₂)₃P)₂PtCl₂,^{16b} *trans*-((R_{f6}CH₂CH₂)₃P)₂Rh(CO)Cl,^{15a,16a} and ((R_{f6}CH₂CH₂)₃P)₂Ir(CO)Cl.^{15a} All exhibit a packing motif analogous to that of **8b** (Figure 2). The platinum-phosphorus and platinum-chlorine bond lengths in the first structure (2.312(2)-2.318(3) and 2.293(3)-2.300(3) Å) are essentially identical to those in **8b** (Table 3). We were unable to find any structures of the formula *trans*-(C₆F₅)(PR₃)₂PtCl in the literature,

so the effect of introducing the fluorous phosphines cannot be examined. However, two *cis* isomers have been reported.²⁸

Another type of "insulated molecular wire" with a fluorous shielding group has been synthesized, namely the diplatinum octatetraynediyl complex **14** depicted in Figure 5.^{6c} This is an adduct of the type **I** shown in Scheme 1, and features (CF₂)₈ segments in the middle of two α,ω -diphosphine ligands with fourteen carbon linkers. Although **14** could be generated from **11** (Figure 5) and the α,ω -diphosphine and characterized in situ by NMR, it oligomerized upon attempted isolation. This precluded recording cyclic voltammetry data that would be helpful in interpreting the results in Table 4.

The cyclic voltammograms of **10a-c**, which are illustrated elsewhere,¹⁷ are disappointing in that the initial oxidation products rapidly decompose. The $i_{c/a}$ ratios (Table 4) show that this occurs much more rapidly than with "non-insulated" model compounds such as **11-13** (Figure 5). The CF₃C₆H₅ cosolvent seems to contribute to this behavior, but is not the entire story. In the syntheses of fluorous molecules, it is not uncommon to encounter side reactions involving HF elimination from CH₂CF₂ linkages.²⁷ Thus, perhaps these moieties initiate some type of rapid irreversible ECE process.

In summary, this study has provided another family of diplatinum polyynediyl complexes (**10a-c**) in which the sp carbon chains are sterically shielded to a greater degree than in model compounds such as **11-13**. However, in the absence of structural data for **10a-c**, the motif **IV** proposed in Scheme 3 remains a reasonably supported conjecture as opposed to an established fact. Furthermore, the cyclic voltammetry data suggest that phosphines with (CH₂)_{*m*}R_{*fn*} substituents yield *less* stable radical ions. In terms of future studies, it may be productive to investigate triarylphosphines with C₆H₄R_{*fn*} or C₆H₃(R_{*fn*})₂ substituents, which lack CH₂CF₂ junctures. In any event, it would be amiss to close without again recognizing the leadership of Jack Lewis, whose work with alkyne rich diplatinum and polyplatinum complexes has inspired so many through the years.²

■ EXPERIMENTAL

General: All reactions were conducted under inert atmospheres using standard Schlenk and vacuum line techniques. Workups were carried out in air. Chemicals were treated as follows: THF (Fisher Scientific, ACS grade), dried and degassed using a Glass Contour solvent purification system; acetone (BDH, ACS grade), distilled from CaSO₄; acetonitrile and CH₂Cl₂ (2 × EMD, ACS grade), toluene (Macron Chemicals, ACS grade), perfluorohexanes (Apollo Scientific, 98% mixed isomers), CF₃C₆F₁₁ (ABCR, 90%), CF₃C₆H₅ (Acros, 99+%), C₆F₆ (Oakwood), CDCl₃ and C₆D₆ (2 × Cambridge Isotope Laboratories), CuI and CuCl (2 × Alfa Aesar, 99.999%), HNEt₂ (99+%, Alfa Aesar), *n*-Bu₄N⁺ PF₆[−] (Oakwood), TMEDA (tetramethylethylenediamine, 99%, Acros), Ph₃PO (Aldrich, 98%), and silica (Acros, 60 Å), used as received.

NMR spectra were recorded on a Varian NMRS 500 MHz spectrometer at ambient probe temperatures and referenced as follows (δ, ppm): ¹H, residual internal CHCl₃ (7.26) or C₆D₅H (7.16); ¹³C, internal CDCl₃ (77.20) or C₆F₆ (138.80); ³¹P, external H₃PO₄ (0.00). IR spectra were recorded using a Shimadzu IRAffinity-1 spectrometer with a Pike MIRacle ATR system (diamond/ZnSe crystal). Melting points were recorded with a Stanford Research Systems (SRS) MPA100 (Opti-Melt) automated system. Microanalyses were conducted by Atlantic Microlab.

***trans*-(C₆F₅)((R_{f8}(CH₂)₂)₃P)₂PtCl (**8a**).** A Schlenk flask was fitted with a condenser and charged with P(CH₂CH₂R_{f8})₃ (**7a**, ^{10a} 0.6369 g, 0.4641 mmol), [(tetrahydrothiophene)Pt(C₆F₅)μ-Cl]₂ (**6**, ¹⁸ 0.1250 g, 0.1292 mmol), and THF (20 mL) with stirring. The mixture was refluxed. After 24 h, the solvent was removed by rotary evaporation. The residue was crystallized from CF₃C₆H₅ and washed with cold CF₃C₆H₅. The solid was dried by oil pump vacuum to give **8a** as a white powder (0.3238 g, 0.1030 mmol, 40%), mp 97-100 °C. Anal. Calcd. for C₆₆H₂₄ClF₁₀P₂Pt (3142.21): C, 25.23; H, 0.77. Found: C, 25.29; H, 0.61.

NMR (δ, ppm): ¹H (C₆F₆ + C₆D₆ capillary) 2.65-2.45 (m, 12H, CF₂CH₂), 2.37-2.26 (m, 12H, PCH₂); ¹H (C₆F₆ + CDCl₃) 2.75-2.38 (m, 12H, CF₂CH₂), 2.36-2.20 (m, 12H, PCH₂); ¹³C{¹H} ²⁹ (C₆F₆ + CDCl₃) 146.0 (dd, ¹J_{CF} = 218.2 Hz, ²J_{CF} = 18.2 Hz, *o* to Pt), 138.5-137.6 (2 m, *m* and *p* to Pt), 121.1 (t, ²J_{CF} = 33.6 Hz, CH₂CF₂), ³⁰ 118.8 (t, ²J_{CF} = 33.3 Hz, CF₃), 116.5 (t,

$^2J_{\text{CF}} = 33.2$ Hz, CF_2), 114.2 (t, $^2J_{\text{CF}} = 33.3$ Hz CF_2), 113.6-112.3 (m, CF_2), 111.6-110.2 (m, CF_2), 109.3-108.2 (m, CF_2), 107.1-106.2 (m, CF_2), 26.0-25.3 (m, CH_2CF_2),³¹ 17.1-16.8 (m, PCH_2);³¹ $^{31}\text{P}\{^1\text{H}\}$ (C_6F_6) 11.2 (s, $^1J_{\text{PPt}} = 2628$ Hz);³² $^{31}\text{P}\{^1\text{H}\}$ ($\text{C}_6\text{F}_6 + \text{CDCl}_3$) 12.2 (s, $^1J_{\text{PPt}} = 2632$ Hz).³² IR (cm^{-1} , powder film): 1512 (w), 1458 (w), 1365 (w), 1195 (s), 1149 (s), 1064 (m), 956 (m), 802 (m), 702 (m).

***trans*-(C_6F_5)($\text{R}_{\text{f8}}(\text{CH}_2)_3\text{P}$) $_2\text{PtCl}$ (**8b**).** A Schlenk flask was fitted with a condenser and charged with $\text{P}(\text{CH}_2\text{CH}_2\text{CH}_2\text{R}_{\text{f8}})_3$ (**7b**;^{10a} 0.8120 g, 0.5741 mmol), **6** (0.1394 g, 0.1441 mmol),¹⁸ and THF (30 mL) with stirring. The mixture was refluxed. After 24 h, the solvent was removed by rotary evaporation. Then $\text{CF}_3\text{C}_6\text{H}_5$ (30 mL) was added, and the solution was passed through a silica gel plug. The plug was washed with additional $\text{CF}_3\text{C}_6\text{H}_5$ (50 mL). The solvent was removed from the combined filtrates by oil pump vacuum to give **8b** as a white solid (0.5115 g, 0.1585 mmol, 55%), mp 107-110 °C. Anal. Calcd. for $\text{C}_{72}\text{H}_{36}\text{ClF}_{107}\text{P}_2\text{Pt}$ (3226.37): C, 26.80; H, 1.12. Found: C, 26.71; H, 1.12.

NMR (δ , ppm): ^1H ($\text{C}_6\text{F}_6 + \text{CDCl}_3$ capillary) 2.35-2.22 (m, 12H, CH_2CF_2), 2.10-2.00 (m, 24H, PCH_2CH_2); $^{13}\text{C}\{^1\text{H}\}$ ²⁹ (C_6F_6) 145.9 (dd, $^1J_{\text{CF}} = 240.2$ Hz, $^2J_{\text{CF}} = 22.1$ Hz, *o* to Pt), 137.8-136.9 (2 m, *m* and *p* to Pt), 120.4-119.0 (m, CH_2CF_2),³⁰ 118.1-117.1 (m, CF_3), 116.0-114.9 (m, CF_2), 113.5-111.5 (m, CF_2), 111.1-109.0 (m, 2 CF_2), 108.8-107.0 (m, CF_2), 106.2-105.1 (m, CF_2), 31.4-30.7 (m, CH_2CF_2),³¹ 21.0-20.5 (m, PCH_2CH_2), 14.6 (s, PCH_2);³¹ $^{31}\text{P}\{^1\text{H}\}$ (C_6F_6) 9.6 (s, $^1J_{\text{PPt}} = 2550$ Hz).³² IR (cm^{-1} , powder film): 1504 (m), 1458 (m), 1334 (m), 1196 (s), 1149 (s), 1111 (s), 1064 (m), 1010 (m), 957 (m), 802 (m), 702 (w).

***trans*-(C_6F_5)($\text{R}_{\text{f10}}(\text{CH}_2)_3\text{P}$) $_2\text{PtCl}$ (**8c**).** A Schlenk flask was fitted with a condenser and charged with $\text{P}(\text{CH}_2\text{CH}_2\text{CH}_2\text{R}_{\text{f10}})_3$ (**7c**;^{10c} 1.7026 g, 0.9931 mmol), **6** (0.2474 g, 0.2557 mmol), and THF (40 mL) with stirring. The mixture was refluxed. After 24 h, the solvent was removed by rotary evaporation. The residue was dissolved in warm $\text{CF}_3\text{C}_6\text{H}_5$. The solution was kept at 3 °C for 18 h. The precipitate was collected by filtration, washed with cold $\text{CF}_3\text{C}_6\text{H}_5$, and dried by oil pump vacuum to give **8c** as a white solid (1.4403 g, 0.3764 mmol, 74%), mp 136-139 °C. Anal. Calcd. for $\text{C}_{84}\text{H}_{36}\text{ClF}_{131}\text{P}_2\text{Pt}$ (3826.46): C, 26.37; H, 0.95; F, 65.04. Found: C,

26.61; H, 0.83; F, 64.97.

NMR (δ , ppm): ^1H ($\text{C}_6\text{F}_6 + \text{CDCl}_3$) 2.44-2.30 (m, 12H, PCH_2), 2.16-2.09 (m, 24H, $\text{CH}_2\text{-CH}_2\text{CF}_2$); $^{13}\text{C}\{^1\text{H}\}$ ²⁹ ($\text{C}_6\text{F}_6 + \text{CDCl}_3$) 144.9 (dd, $^1J_{\text{CF}} = 229.1$ Hz, $^2J_{\text{CF}} = 20.1$ Hz, *o* to Pt), 139.1-137.9 (m, *m* and *p* to Pt), 121.1 (t, $^2J_{\text{CF}} = 36.9$, CH_2CF_2),³⁰ 118.8 (t, $^2J_{\text{CF}} = 31.5$, CF_3), 116.5 (t, $^2J_{\text{CF}} = 32.6$, CF_2), 114.2 (t, $^2J_{\text{CF}} = 32.6$, CF_2), 113.8-112.7 (m, CF_2), 111.8-110.6 (m, 2 CF_2), 109.7-108.3 (m, CF_2), 107.5-106.4 (m, CF_3), 100.7 (t, $^2J_{\text{CF}} = 27.5$, CF_2), 32.9-32.6 (m, CF_2CH_2),³¹ 32.4-29.9 (m, PCH_2CH_2), 16.2-15.7 (m, PCH_2);³¹ $^{31}\text{P}\{^1\text{H}\}$ ($\text{C}_6\text{F}_6 + \text{CDCl}_3$) 10.1 (s, $^1J_{\text{PPt}} = 2324$ Hz).³² IR (cm^{-1} , powder film): 1504 (w), 1458 (w), 1342 (w), 1203 (br s), 1149 (s), 1072 (m), 956 (w), 887 (w), 663 (w), 640 (w), 516 (s).

***trans*-(C_6F_5)($(\text{R}_{\text{f8}}(\text{CH}_2)_2)_3\text{P}$) $_2\text{Pt}(\text{C}\equiv\text{C})_2\text{H}$ (**9a**).** A Schlenk flask was charged with **8a** (0.6840 g, 0.2177 mmol), CuI (0.1067 g, 0.5603 mmol), HNet₂ (25 mL), and $\text{CF}_3\text{C}_6\text{H}_5$ (12 mL) with stirring and cooled to -45 °C (acetonitrile/ CO_2). A solution of $\text{H}(\text{C}\equiv\text{C})_2\text{H}$ (0.44 g, 8.7 mmol in 2.7 mL THF)³³ was added. After 1 h, the cold bath was removed. The solution turned reddish-brown. After 4 h, the solvents were removed by rotary evaporation. Toluene (20 mL) and CH_2Cl_2 (20 mL) were added. The mixture was extracted with perfluorohexanes (3×20 mL). The solvent was removed from the extracts by oil pump vacuum to give **9a** as a tan solid (0.4366 g, 0.1383 mmol, 64%) that yellowed at 117 °C and liquefied at 141 °C. Anal. Calcd. for $\text{C}_{70}\text{H}_{25}\text{F}_{107}\text{P}_2\text{Pt}$ (3155.81): C, 26.64; H, 0.80; F, 64.42. Found: C, 26.92; H, 0.84; F, 64.12.

NMR (δ , ppm): ^1H ($\text{C}_6\text{F}_6 + \text{CDCl}_3$) 2.58-2.36 (m, 12H, CF_2CH_2), 2.33-2.19 (m, 12H, PCH_2), 1.70 (s, 1H, $\equiv\text{CH}$); $^{13}\text{C}\{^1\text{H}\}$ ²⁹ (C_6F_6) 149.3 (dd, $^1J_{\text{CF}} = 217.2$ Hz, $^2J_{\text{CF}} = 20.3$ Hz, *o* to Pt), 140.5-139.4 (m, *m* and *p* to Pt), 122.7-121.9 (m, CH_2CF_2),³⁰ 119.0-118.2 (m, CF_3), 116.7-116.0 (m, CF_2), 114.7-113.9 (m, CF_2), 113.8-112.7 (m, CF_2), 110.2-109.3 (m, CF_2), 109.2-107.9 (m, CF_2), 107.2-106.1 (m, CF_2), 98.5 (s, $\text{PtC}\equiv\text{C}$), 95.1 (s, $\text{PtC}\equiv\text{C}$), 71.2 (s, $\text{PtC}\equiv\text{CC}$), 59.0 (s, $\text{PtC}\equiv\text{CC}\equiv\text{C}$), 27.0-26.5 (m, CH_2CF_2),³¹ 17.9-17.4 (m, PCH_2);³¹ $^{31}\text{P}\{^1\text{H}\}$ (C_6F_6) 9.2 (s, $^1J_{\text{PPt}} = 2535$ Hz).³² IR (cm^{-1} , powder film): 3311 (w), 2153 (m, $\nu_{\text{C}\equiv\text{C}}$), 1505 (m), 1451 (m), 1327 (m), 1196 (s), 1142 (s), 1072 (m), 957 (s), 655 (s).

***trans*-(C_6F_5)($(\text{R}_{\text{f8}}(\text{CH}_2)_3)_3\text{P}$) $_3\text{Pt}(\text{C}\equiv\text{C})_2\text{H}$ (**9b**).** Complex **8b** (0.3225 g, 0.0999 mmol),

CuI (0.0285 g, 0.135 mmol), HNEt₂ (15 mL), CF₃C₆H₅ (7 mL) and H(C≡C)₂H (0.19 g, 3.9 mmol, in 1.2 mL THF)³³ were combined in a procedure analogous to that for **9a**. A similar workup (extraction: 50 mL perfluorohexanes; drying: oil pump vacuum) gave **9b** as a tan solid (0.1411 g, 0.04355 mmol, 44%) that yellowed at 115 °C and liquefied at 129 °C. Anal. Calcd. for C₇₆H₃₇F₁₀₇P₂Pt (3239.97): C, 28.17; H, 1.15; F, 62.74. Found: C, 27.90; H, 1.14.

NMR (δ, ppm): ¹H (C₆F₆ + CDCl₃) 2.49-2.28 (m, 12H, CF₂CH₂), 2.26-2.03 (m, 24H, PCH₂CH₂), 1.72 (s, 1H, ≡CH); ¹³C{¹H}²⁹ (C₆F₆) 150.2 (dd, ¹J_{CF} = 214.5 Hz, ²J_{CF} = 20.9 Hz, *o* to Pt), 141.6-140.0 (m, *m* and *p* to Pt), 124.1-122.8 (m, CH₂CF₂),³⁰ 122.1-120.8 (m, CF₃), 120.0-118.6 (m, CF₂), 117.1-115.5 (m, 2 CF₂), 114.7-113.3 (m, CF₂), 112.1-111.4 (m, CF₂), 109.8-109.0 (m, CF₂), 97.2 (s, PtC≡C), 94.5 (s, PtC≡C), 72.4 (s, PtC≡CC), 61.6 (s, PtC≡CC≡C), 35.6-34.3 (m, CH₂CF₂),³¹ 27.4-26.1 (m, CH₂CH₂CF₂), 18.8 (s, PCH₂);³¹ ³¹P{¹H} (C₆F₆) 8.0 (s, ¹J_{PPt} = 2470 Hz).³² IR (cm⁻¹, powder film): 3309 (w), 2152 (m, ν_{C≡C}), 1504 (m), 1458 (m), 1334 (m), 1195 (s), 1149 (s), 1111 (s), 956 (m), 825 (m), 702 (m).

trans-(C₆F₅)((R_{f10}(CH₂)₃)₃P)₂Pt(C≡C)₂H (9c). Complex **8c** (0.5569 g, 0.1455 mmol), CuI (0.0364 g, 0.1911 mmol), HNEt₂ (20 mL), CF₃C₆H₅ (10 mL), and H(C≡C)₂H (0.29 g, 5.8 mmol, in 1.8 mL THF)³³ were combined in a procedure analogous to that for **9a**. A similar workup (extraction: 2 × 15 mL perfluorohexanes; drying: oil pump vacuum) gave **9c** as a cream colored solid (0.3131 mmol, 0.08154 mmol, 56%) that yellowed at 112 °C, browned at 130 °C, and liquefied at 135 °C. Anal. Calcd. for C₈₈H₃₇F₁₃₁P₂Pt (3840.06 g/mol): C, 27.52; H, 0.97. Found: C, 26.83; H, 0.78.³⁴

NMR (δ, ppm): ¹H (C₆F₆ + CDCl₃) 2.37-2.23 (m, 12H, CH₂CF₂), 2.19-2.03 (m, 24H, PCH₂CH₂), 1.48 (s, 1H, ≡CH); ¹³C{¹H}²⁹ (C₆F₆) 147.8 (dd, ¹J_{CF} = 244.8 Hz, ²J_{CF} = 20.8 Hz, *o* to Pt), 139.0-138.2 (2 m, *m* and *p* to Pt), 121.0 (t, ²J_{CF} = 33.3 Hz, CH₂CF₂),³⁰ 118.8 (t, ²J_{CF} = 31.5 Hz, CF₃), 116.5 (t, ²J_{CF} = 33.3 Hz, CF₂), 114.2 (t, ²J_{CF} = 33.3 Hz, CF₂), 113.8-112.5 (m, CF₂), 111.7-110.0 (m, 2 CF₂), 109.7-108.2 (m, 2 CF₂), 107.3-106.4 (m, CF₂), 99.8 (s, PtC≡C), 92.8 (s, PtC≡C), 70.3 (s, PtC≡CC), 58.3 (s, ≡CH), 32.7-31.6 (m, CH₂CF₂),³¹ 21.8 (t, ²J_{CF} = 15.5 Hz, PCH₂CH₂), 15.7 (s, PCH₂);³¹ ³¹P{¹H} (C₆F₆) 9.7 (s, ¹J_{PPt} = 2835 Hz).³² IR (cm⁻¹, powder

film): 3310 (w), 2924 (w), 2854 (w), 2152 (w, $\nu_{C\equiv C}$), 1743 (w), 1505 (w), 1458 (w), 1373 (w), 1342 (w), 1204 (s), 1150 (s), 1072 (s), 957 (s), 894 (s), 802 (m), 710 (m).

***trans,trans*-(C₆F₅)((R_{f8}(CH₂)₂)₃P)₂Pt(C≡C)₄Pt(P((CH₂)₂R_{f8})₃)₂(C₆F₅) (10a).** A three neck round bottom flask was fitted with a gas dispersion tube and a condenser, and charged with **9a** (0.1021 g, 0.03235 mmol) and acetone (10 mL) with stirring. Then oxygen was aspirated through the mixture, which was heated to 40 °C. A solution of CuCl (0.0140 g, 0.141 mmol) and TMEDA (0.010 mL, 0.0078 g, 0.067 mmol) in acetone (10 mL; previously stirred for 30 min) was added. After 6 h, the solvent was removed by rotary evaporation. Toluene (20 mL) and CH₂-Cl₂ (20 mL) were added. The mixture was extracted with perfluorohexanes (3 × 15 mL). The solvent was removed from the extracts by oil pump vacuum to give **10a** as a light yellow solid (0.0534 g, 0.00847 mmol, 52%), which yellowed at 120 °C and liquefied at 135 °C. Anal. Calcd. for C₁₄₀H₄₈F₂₁₄P₄Pt₂ (6309.60): C, 26.65; H, 0.77; F, 64.42. Found: C, 26.37; H, 0.72; F, 64.16.

NMR (δ , ppm): ¹H (C₆F₆ + CDCl₃) 2.60-2.42 (m, 24H, CF₂CH₂), 2.34-2.21 (m, 48H, PCH₂); ¹³C{¹H}²⁹ (C₆F₆) 145.6 (dd, ¹J_{CF} = 221.2 Hz, ²J_{CF} = 19.8 Hz, *o* to Pt), 137.8-136.9 (m, *m* and *p* to Pt), 117.7-117.0 (m, CH₂CF₂),³⁰ 115.3-114.3 (m, CF₃), 112.9-112.2 (m, CF₂), 109.9-108.1 (m, CF₂), 107.9-107.0 (m, 2 CF₂), 105.9-105.1 (m, 2 CF₂), 99.5 (s, PtC≡C), 88.5 (s, PtC≡C), 57.5 (s, PtC≡CC), 51.5 (s, PtC≡CC≡C), 25.7-25.1 (m, CH₂CF₂),³¹ 14.7-14.3 (m, PCH₂);³¹ ³¹P{¹H} (C₆F₆) 9.1 (s, ¹J_{PtP} = 2304 Hz).³² IR (cm⁻¹, powder film): 2160 (w, $\nu_{C\equiv C}$), 2029 (w, $\nu_{C\equiv C}$), 1975 (w), 1504 (m), 1458 (m), 1195 (s), 1149 (s), 1072 (s), 956 (m), 894 (m), 802 (m), 640 (s).

***trans,trans*-(C₆F₅)((R_{f8}(CH₂)₃)₃P)₂Pt(C≡C)₄Pt(P((CH₂)₃R_{f8})₃)₂(C₆F₅) (10b).** Complex **9b** (0.1037 g, 0.03201 mmol), acetone (10 mL), and a solution of CuCl (0.0145 g, 0.147 mmol) and TMEDA (0.010 mL, 0.0078 g, 0.067 mmol) in acetone (5 mL) were combined in a procedure analogous to that for **10a**. After 6 h, the solvent was removed by rotary evaporation. Toluene (10 mL) and CH₂Cl₂ (10 mL) were added. The mixture was extracted with perfluorohexanes (2 × 15 mL). The solvent was removed from the extracts by rotary evaporation. The residue was washed with toluene (10 mL) and CH₂Cl₂ (10 mL) and dried by oil pump vacuum to

give **10b** as a light yellow solid (0.0358 g, 0.00553 mmol, 35%) that darkened at 90 °C, liquefied at 107 °C, and blackened at 175 °C. Anal. Calcd. for C₁₅₂H₇₂F₂₁₄P₄Pt₂ (6477.92): C, 28.18; H, 1.12. Found: C, 28.05; H, 1.17.

NMR (δ , ppm): ¹H (C₆F₆ + CDCl₃) 2.45-2.37 (m, 24H, PCH₂), 2.22-2.04 (m, 48H, CH₂-CH₂CF₂); ¹³C{¹H}²⁹ (C₆F₆) 147.2 (dd, ¹J_{CF} = 216.4 Hz, ²J_{CF} = 24.1 Hz, *o* to Pt), 138.5-137.5 (m, *m* and *p* to Pt), 121.2-120.1 (m, CH₂CF₂),³⁰ 118.6-117.9 (m, CF₃), 116.6-115.5 (m, CF₂), 113.7-112.2 (m, CF₂), 111.3-110.0 (m, 2 CF₂), 109.1-108.0 (m, 2 CF₂), 106.9-105.6 (m, CF₂), 96.7 (s, PtC≡C), 92.0 (s, PtC≡C), 69.4 (s, PtC≡CC), 58.5 (s, PtC≡CC≡C), 35.6-34.3 (m, CH₂-CF₂),³¹ 27.4-26.1 (m, CH₂CH₂CF₂), 18.8 (s, PCH₂),³¹ ³¹P{¹H} (C₆F₆) 7.6 (s, ¹J_{PPt} = 2458 Hz).³² IR (cm⁻¹, powder film): 2152 (m, $\nu_{C\equiv C}$), 2029 (w, $\nu_{C\equiv C}$), 1504 (m), 1458 (m), 1365 (m), 1334 (m), 1195 (s), 1149 (s), 1111 (s), 1064 (m), 1018 (m), 956 (s), 817 (w), 786 (m).

trans,trans-(C₆F₅)((R_{f10}(CH₂)₃)₃P)₂Pt(C≡C)₄Pt(P((CH₂)₃R_{f10})₃)₂(C₆F₅) (10c). Complex **9c** (0.1212 g, 0.03156 mmol), acetone (10 mL) and a solution of CuCl (0.0151 g, 0.154 mmol) and TMEDA (0.010 mL, 0.0078 g, 0.067 mmol) in acetone (5 mL) were combined in a procedure analogous to that for **10a**. After 6 h, the solvent was removed by rotary evaporation, and CH₂Cl₂ (20 mL) was added. The mixture was extracted with perfluorohexanes (3 × 15 mL). The solvent was removed from the extracts by oil pump vacuum to give **10c** as a light yellow solid (0.0520 g, 0.00677 mmol, 43%) that yellowed at 115 °C and liquefied at 133 °C. Anal. Calcd. for C₁₇₆H₇₂F₂₆₂P₄Pt₂ (7678.10 g/mol): C, 27.53; H, 0.95. Found: C, 26.30; H, 0.73.³⁴

NMR (δ , ppm): ¹H (C₆F₆ + CDCl₃) 2.39-2.20 (m, 24H, PCH₂), 2.18-2.01 (m, 48H, CH₂-CH₂CF₂); ¹³C{¹H}²⁹ (C₆F₆) 147.0 (dd, ¹J_{CF} = 246.1 Hz, ²J_{CF} = 18.9 Hz, *o* to Pt), 138.2-137.5 (2 m, *m* and *p* to Pt), 120.2 (t, ²J_{CF} = 36.0 Hz, CH₂CF₂),³⁰ 118.0 (t, ²J_{CF} = 27.2 Hz, CF₃), 115.7 (t, ²J_{CF} = 27.2 Hz, CF₂), 113.9-112.1 (m, 2 CF₂), 111.3-109.6 (m, 2 CF₂), 108.7-107.9 (m, CF₂), 106.5-105.5 (m, CF₂), 99.3 (s, PtC≡C), 90.3 (s, PtC≡C), 73.7 (s, PtC≡CC), 60.3 (s, PtC≡C-C≡C), 31.7-30.9 (m, CH₂CF₂),³¹ 21.5-20.6 (m, PCH₂CH₂), 14.9-14.6 (m, PCH₂),³¹ ³¹P{¹H} (CF₃C₆F₅) 10.0 (¹J_{PPt} = 2581 Hz),³² ³¹P{¹H} (C₆F₆) 9.7 (¹J_{PPt} = 2600 Hz).³² IR (cm⁻¹, powder film): 2160 (w, $\nu_{C\equiv C}$), 2037 (w, $\nu_{C\equiv C}$), 1975 (w), 1859 (w), 1504 (m), 1458 (m), 1203

(s), 1149 (s), 1072 (m), 979 (m), 956 (m), 894 (m), 802 (m).

Partition Coefficients. A. The following is representative. A vial was charged with a fluororous compound (0.00090-0.00521 mmol), $\text{CF}_3\text{C}_6\text{F}_{11}$ (2.00 mL, delivered by syringe), toluene (2.00 mL, delivered by syringe), and a stir bar. It was tightly sealed and vigorously stirred for 24 h. Stirring was halted. After 10 min, aliquots (1.00 mL) were removed from each phase by syringe. The solvents were removed by rotary evaporation. A standard solution of Ph_3PO in CDCl_3 was prepared in a volumetric flask (0.0267 M). Then C_6F_6 (0.50 mL) and the standard solution (0.50 mL) were added to each residue by syringe. The CH_2 ^1H NMR signals of the fluororous compound were integrated versus the aryl signals of Ph_3PO . **B.** Worked example: The vial was charged with **10c** (0.0069 g, 0.00090 mmol) and $\text{CF}_3\text{C}_6\text{F}_{11}$ (2.00 mL) per A to give a 4.5×10^{-4} M solution. Addition of toluene gave a biphasic mixture. After stirring and workup, integration indicated 4.43×10^{-4} mmol of **10c** in the fluororous phase and 8.31×10^{-7} mmol in the toluene phase. After normalization for the aliquot volume, this indicated a total mass recovery of 99%.

Cyclic Voltammetry. A BASi Voltammetric Analyzer with the program EpsilonEC (version 2.13.77_USB) was utilized. Cells were fitted with platinum working and counter electrodes, and an Ag/AgCl reference electrode. Measurements were conducted with acetonitrile/ $\text{CF}_3\text{C}_6\text{H}_5$ solutions (1:1 v/v) that were $1.4\text{--}2.5 \times 10^{-4}$ M in substrate, 0.40 M in $n\text{-Bu}_4\text{N}^+ \text{PF}_6^-$, and prepared under nitrogen.

Crystallography. A C_6F_6 solution of **8b** was layered with toluene. After 12 d, colorless multi-faceted crystals were obtained. Data were collected as outlined in Table 2. Cell parameters were obtained from 180 data frames taken at widths of 0.5° . Integrated intensity information for each reflection was obtained by reduction of the data frames with the program APEX2.³⁵ Data were corrected for Lorentz and polarization factors, and using SADABS³⁶ for absorption and crystal decay effects. The structure was solved by direct methods using SHELXTL (SHELXS).³⁷ Three of the six fluororous chains were disordered. The hydrogen atoms were placed in idealized positions and were refined using a riding model. The disorder was successfully modeled using extensive restraints (EADP and EXYZ) to keep the thermal ellipsoids meaningful and for the re-

finement to converge. The chains designated C(E)/C(F) were modeled with a 66:34 occupancy ratio. The chains designated C(D)/C(I) were modeled with a 50:50 occupancy ratio. The chains designated C(G)/C(H) were modeled with a 69:31 occupancy ratio, except for C(9)-C(11) which were modeled with a 53:47 occupancy ratio. All non-hydrogen atoms were refined with anisotropic thermal parameters. The final refinement was restricted to 100 degrees as no reflections were observed above that angle. The parameters were refined by weighted least squares refinement on F^2 to convergence.³⁷

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Appendix A. Supplementary material

CCDC 1413648 contains the supplementary crystallographic data for **8d**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix B. Supplementary data

Supplementary data related to this article (table of torsion angles, representative NMR spectra) can be found at [http:// dx.doi.org/10.1016/j.jorganchem.2015.05.023](http://dx.doi.org/10.1016/j.jorganchem.2015.05.023).

■ REFERENCES

(1) (a) Bruce, M. I.; Low, P. J. *Adv. Organomet. Chem.* **2004**, 50, 179. (b) Wong, W.-Y.; Ho, C.-L.; *Coord. Chem. Rev.* **2006**, 250, 2627-2690. (c) Aguirre-Etcheverry, P.; O'Hare, D. *Chem. Rev.* **2010**, 110, 4839-4864.

(2) See, *inter alia*, (a) Davies, S. J.; Johnson, B. F. G.; Khan, M. S.; Lewis, J. J. *Chem. Soc., Chem. Commun.* **1991**, 187-188. (b) Khan, M. S.; Davies, S. J.; Kakkar, A. K.; Schwartz, D.; Lin, B.; Johnson, B. F. G.; Lewis, J. J. *Organomet. Chem.* **1992**, 424, 87-97. (c) Lewis, J.; Khan, M. S.; Kakkar, A. K.; Johnson, B. F. G.; Marder, T. B.; Fyfe, H. B.; Wittmann, F.; Friend, R. H.; Dray, A. E. *J. Organomet. Chem.* **1992**, 425, 165-176. (d) Khan, M. S.; Schwartz, D. J.;

Pasha, N. A.; Kakkar, A. K.; Lin, B.; Raithby, P.; Lewis, J. Z. *Anorg. Allg. Chem.* **1992**, *616*, 121-124. (e) Markwell, R. D.; Butler, I. S.; Kakkar, A. K.; Khan, M. S.; Al-Zakwani, Z. H.; Lewis, J. *Organometallics* **1996**, *15*, 2331. (f) Lewis, J.; Long, N. J.; Raithby, P. R.; Shields, G. P.; Wong, W.-Y.; Younus, M. *J. Chem. Soc., Dalton Trans.* **1997**, 4283-4288.

(3) (a) Szafert, S.; Gladysz, J. A. *Chem. Rev.* **2003**, *103*, 4175-4206. (b) Szafert, S.; Gladysz, J. A. *Chem. Rev.* **2006**, *106*, PR1-PR33.

(4) (a) Dembinski, R.; Bartik, T.; Bartik, B.; Jaeger, M.; Gladysz, J. A. *J. Am. Chem. Soc.* **2000**, *122*, 810-822. (b) Zheng, Q.; Gladysz, J. A. *J. Am. Chem. Soc.* **2005**, *127*, 10508-10509.

(5) One-two lead references from each of several active groups: (a) Klotz, E. J. F.; Claridge, T. D. W.; Anderson, H. L. *J. Am. Chem. Soc.* **2006**, *128*, 15374-15375. (b) Frampton, M. J.; Claridge, T. D. W.; Latini, G.; Brovelli, S.; Cacialli, F.; Anderson, H. L. *Chem. Commun.* **2008**, 2797-2799. (c) Schenning, A. P. H. J.; Arndt, J.-D.; Ito, M.; Stoddart, A.; Schreiber, M.; Siemsen, P.; Martin, R. E.; Boudon, C.; Gisselbrecht, J.-P.; Gross, M.; Gramlich, V.; Diederich, F. *Helv. Chim. Acta* **2001**, *84*, 296-334. (d) Kwan, P. H.; Swager, T. M. *Chem. Commun.* **2005**, 5211-5213. (e) Li, C.; Numata, M.; Bae, A.-H.; Sakurai, K.; Shinkai, S. *J. Am. Chem. Soc.* **2005**, *127*, 4548-4549. (f) Ajayaghosh, A.; Praveen, V. K.; Vijayakumar, C.; George, S. J. *Angew. Chem., Int. Ed.* **2007**, *46*, 6260-6265; *Angew. Chem.* **2007**, *119*, 6376-6381. (g) Leroux, Y. R.; Fave, C.; Zigah, D.; Trippe-Allard, G.; Lacroix, J. C. *J. Am. Chem. Soc.* **2008**, *130*, 13465-13470. (h) Sugiyasu, K.; Honsho, Y.; Harrison, R. M.; Sato, A.; Yasuda, T.; Seki, S.; Takeuchi, M. *J. Am. Chem. Soc.* **2010**, *132*, 14754-14756. (i) Terao, J.; Kimura, K.; Seki, S.; Fujihara, T.; Tsuji, Y. *Chem. Commun.* **2012**, *48*, 1577-1579. (j) Masai, H.; Terao, J.; Seki, S.; Nakashima, S.; Kiguchi, M.; Okoshi, K.; Fujihara, T.; Tsuji, Y. *J. Am. Chem. Soc.* **2014**, *136*, 1742-1745. (k) Parthey, M.; Gluyas, J. B. G.; Schauer, P. A.; Yufit, D. S.; Howard, J. A. K.; Kaupp, M.; Low, P. *J. Chem. Eur. J.* **2013**, *19*, 9780-9784.

(6) (a) Stahl, J.; Mohr, W.; de Quadras, L.; Peters, T. B.; Bohling, J. C.; Martín-Alvarez, J. M.; Owen, G. R.; Hampel, F.; Gladysz, J. A. *J. Am. Chem. Soc.* **2007**, *129*, 8282-8295. (b) de Quadras, L.; Bauer, E. B.; Mohr, W.; Bohling, J. C.; Peters, T. B.; Martín-Alvarez, J. M.; Ham-

pel, F.; Gladysz, J. A. *J. Am. Chem. Soc.* **2007**, *129*, 8296-8309. (c) de Quadras, L.; Bauer, E. B.; Stahl, J.; Zhuravlev, F.; Hampel, F.; Gladysz, J. A. *New. J. Chem.* **2007**, *31*, 1594-1604. (d) Owen, G. R.; Stahl, J.; Hampel, F.; Gladysz, J. A. *Chem. Eur. J.* **2008**, *14*, 73-87.

(7) (a) Horn, C. R.; Martín-Alvarez, J. M.; Gladysz, J. A. *Organometallics* **2002**, *21*, 5386-5393. (b) Horn, C. R.; Gladysz, J. A. *Eur. J. Inorg. Chem.* **2003**, 2211-2218.

(8) Crowley, J. D.; Goldup, S. M.; Lee, A.-L.; Leigh, D. A.; McBurney, R. T. *Chem. Soc. Rev.* **2009**, *38*, 1530-1541.

(9) (a) Weisbach, N.; Baranová, Z.; Gauthier, S.; Reibenspies, J. H.; Gladysz, J. A. *Chem. Commun.* **2012**, *48*, 7562-7564. (b) Sahnoune, H.; Baranová, Z.; Bhuvanesh, N.; Gladysz, J. A.; Halet, J.-F. *Organometallics* **2013**, *32*, 6360-6367. (c) Baranová, Z.; Amini, H.; Bhuvanesh, N.; Gladysz, J. A. *Organometallics* **2014**, *33*, 6746-6749.

(10) (a) Alvey, L. J.; Rutherford, D.; Juliette, J. J. J.; Gladysz, J. A. *J. Org. Chem.* **1998**, *63*, 6302-6308. (b) Emnet, C.; Weber, K. M.; Vidal, J. A.; Consorti, C. S.; Stuart, A. M.; Gladysz, J. A. *Adv. Synth. Catal.* **2006**, *348*, 1625-1634. (c) Gimbert, C.; Vallribera, A.; Gladysz, J. A.; Jurisch, M. *Tetrahedron Lett.* **2010**, *51*, 4662-4665 (see footnote 9 therein).

(11) (a) Emnet, C.; Tuba, R.; Gladysz, J. A. *Adv. Synth. Catal.* **2005**, *347*, 1819-1826. (b) Alvey, L. J.; Meier, R.; Soós, T.; Bernatis, P.; Gladysz, J. A. *Eur. J. Inorg. Chem.* **2000**, 1975-1983.

(12) (a) Bhattacharyya, P.; Gudmunsen, D.; Hope, E. G.; Kemmitt, R. D. W.; Paige, D. R.; Stuart, A. M. *J. Chem. Soc., Perkin Trans. I* **1997**, 3609-3612. (b) Langer, F.; Püntener, K.; Stürmer, R.; Knochel, P. *Tetrahedron: Asymmetry* **1997**, *8*, 715-738. (c) Vlád, G.; Richter, F.; Horváth, I. T. *Org. Lett.* **2004**, *6*, 4559-4561. (d) Vlád, G.; Richter, F.; Horváth, I. T. *Tetrahedron Lett.* **2004**, *6*, 8605-8608.

(13) Jiao, H.; Le Stang, S.; Soós, T.; Meier, R.; Kowski, K.; Rademacher, P.; Jafarpour, L.; Hamard, J.-B.; Nolan, S. P.; Gladysz, J. A. *J. Am. Chem. Soc.* **2002**, *124*, 1516-1523.

(14) *Handbook of Fluorous Chemistry*, Gladysz, J. A.; Curran, D. P.; Horváth, I. T. Eds.; Wiley/VCH, Weinheim, 2004

(15) (a) Guillevis, M.-A.; Rocaboy, C.; Arif, A. M.; Horváth, I. T.; Gladysz, J. A. *Organometallics* **1998**, *17*, 707-717 (b) Tuba, R.; Tesevic, V.; Dinh, L. V.; Hampel, F.; Gladysz, J. A. *Dalton Transactions* **2005**, 2275-2283. (c) Consorti, C. S.; Hampel, F.; Gladysz, J. A. *Inorg. Chim. Acta* **2006**, *359*, 4874-4884. (d) da Costa, R. C.; Hampel, F.; Gladysz, J. *Polyhedron* **2007**, *26*, 581-588. (e) Tuba, R.; Brothers, E. N.; Reibenspies, J. H.; Bazzi, H. S.; Gladysz, J. A. *Inorg. Chem.* **2012**, *51*, 9943-9949.

(16) (a) Fawcett, J.; Hope, E. G.; Kemmitt, R. D. W.; Paige, D. R.; Russell, D. R.; Stuart, A. M.; Cole-Hamilton, D. J.; Payne, M. J. *Chem. Commun.* **1997**, 1127-1128. (b) Stibrany, R. T.; Gorun, S. M. *J. Organomet. Chem.* **1999**, *579*, 217-221. (c) Malosh, T. J.; Wilson, S. R.; Shapley, J. R. *J. Organomet. Chem.* **2009**, *694*, 3331-3337. (d) Malosh, T. J.; Wilson, S. R.; Shapley, J. R. *Inorg. Chim. Acta* **2009**, *362*, 2849-2855.

(17) For additional details, see Clough, M. C. Doctoral Dissertation, Texas A&M University, 2012.

(18) Uson, R.; Fornies, J.; Espinet, P.; Alfranca, G. *Synth. React. Inorganic Met.-Org. Chem.* **1980**, *10*, 579-590.

(19) Grim, S. O.; Keiter, R. L.; McFarlane, W. *Inorg. Chem.* **1967**, *6*, 1133-1137.

(20) (a) Dunitz, J. D.; Gavezzotti, A.; Schweizer, W. B. *Helv. Chim. Acta* **2003**, *86*, 4073-4092. (b) Dunitz, J. D. *ChemBioChem* **2004**, *5*, 614-621. (c) Albinsson, B.; Michl, J. *J. Phys. Chem.* **1996**, *100*, 3418-3429. (d) Watkins, E. K.; Jorgensen, W. L. *J. Phys. Chem. A* **2001**, *105*, 4118-4125. (e) Jang, S. S.; Blanco, M.; Goddard, W. A. III; Caldwell, G.; Ross, R. B. *Macromolecules* **2003**, *36*, 5331-5341.

(21) Mohr, W.; Stahl, J.; Hampel, F.; Gladysz, J. A. *Chem. Eur. J.* **2003**, *9*, 3324-3340.

(22) Gladysz, J. A.; Emnet, C. In *Handbook of Fluorous Chemistry*; Gladysz, J. A., Curran, D. P., Horvath, I. T., Eds.; Wiley/VCH: Weinheim, 2004, pp 11-23.

(23) Matsubara, H.; Ryu, I. *Topics in Current Chemistry* **2012**, *308*, 135-152.

(24) Gladysz, J. A. in *Handbook of Green Chemistry*, Anastas, P., Ed.; Volume 1: *Homogeneous Catalysis*; Crabtree, R. H. Volume Ed.; Wiley/VCH, Weinheim, **2009**, 17-38.

(25) Gladysz, J. A.; Emnet, C.; Rabai, J. In *Handbook of Fluorous Chemistry*; Gladysz, J. A., Curran, D. P., Horvath, I. T., Eds.; Wiley/VCH: Weinheim, 2004, p 56-100.

(26) Stahl, J. Doctoral Thesis, Friedrich-Alexander-Universität Erlangen-Nürnberg, Erlangen, Germany, 2003.

(27) (a) Matsubara, H.; Maeda, L.; Sugiyama, H.; Ryu, I. *Synthesis* **2007**, 2901-2902. (b) Tucker, W. B.; Mecozzi, S. J. *Fluorine Chem.* **2013**, 156, 26-29. (c) Gladysz, J. A.; Jurisch, M. In *Fluorous Chemistry*; Horvath, I. T., Ed.; Springer-Verlag Berlin: Berlin, 2012; Vol. 308, pp 1-23 (see Figure 7).

(28) (a) Bresciani-Pahor, N.; Plazzotta, M.; Randaccio, L.; Bruno, G.; Ricevuto, V.; Romeo, R.; Belluco, U. *Inorg. Chim. Acta* **1978**, 31, 171-175. (b) Hughes, R. P.; Ward, A. J.; Golden, J. A.; Incarvito, C. D.; Rheingold, A. L.; Zakharov, L. N. *Dalton Trans.* **2004**, 2720-2727.

(29) The *ipso* C₆F₅ signal was not observed.

(30) The most upfield CF₂ signal is assigned to the CF₂CH₂ carbon. See reference [27a](#), Figure 6.

(31) The most upfield CH₂ signal is assigned to the PCH₂ carbon and the most downfield CH₂ signal is assigned to the CH₂CF₂ carbon. [15b](#)

(32) This coupling represents a satellite (d, ¹⁹⁵Pt = 33.8%), and is not reflected in the peak multiplicity given.

(33) Verkruijsse, H. D.; Brandsma, L. *Synth. Commun.* **1991**, 21, 657-659.

(34) Since the microanalytical data are in poor agreement, the ¹H, ¹³C{¹H}, and ³¹P{¹H} spectra are provided in Supporting Information. These show minor impurities.

(35) APEX2, "Program for Data Collection on Area Detectors" BRUKER AXS Inc., 5465 East Cheryl Parkway, Madison, WI 53711-5373 USA.;

(36) Sheldrick, G. M. *SADABS, Program for Absorption Correction of Area Detector Frames*, BRUKER AXS Inc., 5465 East Cheryl Parkway, Madison, WI 53711-5373, USA.

(37) Sheldrick, G. *Acta Crystallogr.* **2008**, A64, 112-122.

Table 1. $^{31}\text{P}\{^1\text{H}\}$ signals of the fluorous platinum complexes (recorded in C_6F_6 unless noted).

	δ , ppm ($^1J_{\text{PPt}}$, Hz)
8a	11.2 (2628)
8b	9.6 (2550)
8c	10.1 (2324) ^a
9a	9.2 (2535)
9b	8.0 (2470)
9c	9.7 (2520)
10a	9.1 (2304)
10b	7.6 (2458)
10c	9.7 (2600)

^a $\text{C}_6\text{F}_6/\text{CDCl}_3$.

Table 2. Crystallographic data for **8b**.

Empirical formula	C ₇₂ H ₃₆ ClF ₁₀₇ P ₂ Pt
Formula weight	3226.49
Temperature	110(2) K
Diffractometer	BRUKER GADDS
Wavelength	1.54178 Å
Crystal system	Triclinic
Space group	<i>P</i> -1
Unit cell dimensions	
<i>a</i>	11.4468(16) Å
<i>b</i>	15.504(2) Å
<i>c</i>	30.558(5) Å
α	103.379(16)°
β	95.714(16)°
γ	103.257(11)°
<i>V</i>	5068.2(14) Å ³
<i>Z</i>	2
Density (calculated)	2.114 Mg/m ³
Absorption coefficient	5.413 mm ⁻¹
<i>F</i> (000)	3112
Crystal size	0.09 x 0.05 x 0.01 mm ³
Theta range for data collection	1.51 to 50.00°
Index ranges	-11 ≤ <i>h</i> ≤ 11, -14 ≤ <i>k</i> ≤ 15, -30 ≤ <i>l</i> ≤ 30
Reflections collected	44792
Independent reflections	10107 [<i>R</i> (int) = 0.0830]
Completeness to theta = 50.00°	96.9 %
Max. and min. transmission	0.9479 and 0.6415
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	10107 / 178 / 1413
Goodness-of-fit on <i>F</i> ²	1.045
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0865, <i>wR</i> 2 = 0.2236
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1016, <i>wR</i> 2 = 0.2411
Extinction coefficient	0.00025(6)
Largest diff. peak and hole	2.642 and -1.702 eÅ ⁻³

Table 3. Key crystallographic distances [Å] and angles [°] for **8b**.^a

Pt–C1P ^b	1.987(13)	P1–Pt–Cl	89.97(14)
Pt–Cl	2.355(4)	P2–Pt–Cl	87.37(13)
Pt–P1	2.312(4)	P2–Pt–P1	174.88(13)
Pt–P2	2.302(4)	C1P ^b –Pt–P1	91.2(4)
		C1P ^b –Pt–P2	91.6(4)
		C1P ^b –Pt–Cl	178.2(4)
Chain 1		Chain 2	
C1–P1	1.772(18)	C1E–P1	1.865(17)
C1–C2	1.57(2)	C1E–C2E	1.51(2)
C2–C3	1.52(2)	C2E–C3E	1.50(3)
C3–C4	1.51(2)	C3E–C4E	1.45(3)
C4–C5	1.47(3)	C4E–C5E	1.50(3)
C5–C6	1.50(2)	C5E–C6E	1.50(3)
C6–C7	1.54(3)	C6E–C7E	1.50(2)
C7–C8	1.54(3)	C7E–C8E	1.49(2)
C8–C9	1.55(3)	C8E–C15	1.42(2)
C9–C10	1.49(3)	C15–C16	1.31(2)
C10–C11	1.54(3)	C16–C17	1.30(2)
C2–C1–P1	112.7(13)	C2E–C1E–P1	114.3(12)
C3–C2–C1	113.9(15)	C3E–C2E–C1E	124.4(18)
C4–C3–C2	117.0(15)	C4E–C3E–C2E	115(2)
C5–C4–C3	116.6(15)	C3E–C4E–C5E	119(2)
C4–C5–C6	117.6(15)	C4E–C5E–C6E	123.8(19)
C5–C6–C7	116.9(14)	C7E–C6E–C5E	120.7(17)
C6–C7–C8	115.4(14)	C8E–C7E–C6E	120.2(16)
C7–C8–C9	116.2(15)	C15–C8E–C7E	129.4(15)
C10–C9–C8	116.5(16)	C16–C15–C8E	145.2(13)
C9–C10–C11	123(2)	C17–C16–C15	159.7(13)
Chain 3		Chain 4	
C1G–P1	1.805(17)	C1A–P2	1.833(14)
C1G–C2G	1.54(2)	C1A–C2A	1.54(2)
C2G–C3G	1.52(2)	C2A–C3A	1.50(2)
C3G–C4G	1.48(3)	C3A–C4A	1.50(2)
C4G–C5G	1.39(3)	C4A–C5A	1.57(2)
C5G–C6G	1.44(3)	C5A–C6A	1.50(2)
C6G–C7G	1.46(3)	C6A–C7A	1.56(2)
C7G–C8G	1.44(3)	C7A–C8A	1.53(2)

Table 3 (Continued)

C8G–C9G	1.36(3)	C8A–C9A	1.50(2)
C9G–C10G	1.41(3)	C9A–C10A	1.57(3)
C10G–C11G	1.35(3)	C10A–C11A	1.52(3)
C2G–C1G–P1	115.4(11)	C2A–C1A–P2	116.4(1)
C3G–C2G–C1G	110.7(14)	C3A–C2A–C1A	111.4(12)
C4G–C3G–C2G	113.5(17)	C4A–C3A–C2A	112.4(12)
C5G–C4G–C3G	125.8(18)	C3A–C4A–C5A	113.2(12)
C4G–C5G–C6G	128.7(19)	C6A–C5A–C4A	117.7(13)
C5G–C6G–C7G	128(2)	C5A–C6A–C7A	116.5(13)
C8G–C7G–C6G	131.3(19)	C8A–C7A–C6A	116.4(13)
C9G–C8G–C7G	136.6(19)	C9A–C8A–C7A	117.2(14)
C8G–C9G–C10G	143.4(19)	C8A–C9A–C10A	120.1(16)
C11G–C10G–C9G	148.7(17)	C11A–C10A–C9A	117.9(15)
Chain 5		Chain 6	
C1B–P2	1.840(15)	C1D–P2	1.849(15)
C1B–C2B	1.50(2)	C1D–C2D	1.50(2)
C2B–C3B	1.51(2)	C2D–C3D	1.53(2)
C3B–C4B	1.46(2)	C3D–C4D	1.49(3)
C4B–C5B	1.53(2)	C4D–C5D	1.52(3)
C5B–C6B	1.54(2)	C5D–C6D	1.54(2)
C6B–C7B	1.53(2)	C6D–C7D	1.54(3)
C7B–C8B	1.54(2)	C7D–C8D	1.54(2)
C8B–C9B	1.51(2)	C8D–C9D	1.50(3)
C9B–C10B	1.49(2)	C9D–C10D	1.39(3)
C10B–C11B	1.50(3)	C10D–C11D	1.36(3)
C2B–C1B–P2	117.4(12)	C2D–C1D–P2	112.8(1)
C1B–C2B–C3B	116.0(13)	C1D–C2D–C3D	111.61(2)
C4B–C3B–C2B	114.5(12)	C4D–C3D–C2D	113.91(3)
C3B–C4B–C5B	117.8(12)	C3D–C4D–C5D	118.91(5)
C4B–C5B–C6B	117.4(12)	C4D–C5D–C6D	118.81(4)
C7B–C6B–C5B	115.8(12)	C7D–C6D–C5D	115.31(4)
C6B–C7B–C8B	115.8(12)	C8D–C7D–C6D	116.11(4)
C9B–C8B–C7B	118.6(14)	C9D–C8D–C7D	118.91(6)
C10B–C9B–C8B	118.8(16)	C10D–C9D–C8D	127(2)
C9B–C10B–C11B	120.0(18)	C11D–C10D–C9D	138(2)

^a chains are numbered as given in Figure 1. ^b C1P = C_{ipso}.

Table 4. Cyclic voltammetry data for the fluorous and non-fluorous diplatinum octatetraynediyl complexes.

complex	E _{p,a} (V)	E _{p,c} (V)	i _{c/a}
10a ^a	1.19	-	0
10b ^a	1.02	-	0
10c ^a	1.14	-	0
11	1.25 ^a	1.18 ^{a,b}	0.27 ^a
	1.26 ^c	1.14 ^c	0.48 ^c
12 ^c	1.31	1.22	0.42
13 ^c	1.30	1.21	0.68

^a conditions: scan rate 100 mV/s in 50:50 v/v acetonitrile/CF₃C₆H₅ as described in the experimental section. ^b The shape of the trace make it difficult to precisely assign this value. ^c conditions: scan rate 100 mV/s, substrate 7-9 × 10⁻⁴ M in *n*-Bu₄N⁺ BF₄⁻/CH₂Cl₂, Ag wire pseudoreference electrode, other parameters per **a**.

TEXT for TABLE OF CONTENTS GRAPHIC

When the sp chains of polyynes are lengthened, stabilities often decrease, and the title compounds are designed to "insulate" the wire like linkages with perfluoroalkyl groups, which show a marked tendency to phase separate from non-fluorous domains in solution and the solid state.