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En route to diplatinum polyynediyl complexes *trans,trans*-(Ar)$(R_3P)_2Pt(C{\equiv}C)_nPt(PR_3)_2$(Ar): Untold tales, including end-group strategies*

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Abstract: Reactions of $\{(C_6F_5)Pt[S(CH_2CH_2–)_2](\mu\text{-}Cl)\}_2$ and R_3P yield the bis(phosphine) species *trans*-$(C_6F_5)(R_3P)_2PtCl$ [R = Et (**Pt'Cl**), Ph, (*p*-$CF_3C_6H_4)_3P$; 88–81 %]. Additions of **Pt'Cl** and $H(C{\equiv}C)_nH$ (n = 1, 2; $HNEt_2$, 20 mol % CuI) give **Pt'C_2H** (37 %, plus **Pt'I**, 16 %) and **Pt'C_4H** (88 %). Homocoupling of **Pt'C_4H** under Hay conditions (O_2, CuCl, TMEDA, acetone) gives **Pt'C_8Pt'** (85 %), but **Pt'C_2H** affords only traces of **Pt'C_4Pt'**. However, condensation of **Pt'C_4H** and **Pt'Cl** ($HNEt_2$, 20 mol % CuI) yields **Pt'C_4Pt'** (97 %). Hay heterocouplings of **Pt'C_4H** or *trans*-(*p*-tol)$(Ph_3P)_2Pt(C{\equiv}C)_2H$ (**Pt*C_4H**) and excess $HC{\equiv}CSiEt_3$ give **Pt'C_6SiEt$_3$** (76 %) or **Pt*C_6SiEt$_3$** (89 %). The latter and wet *n*-Bu_4N^+ $F^–$ react to yield labile **Pt*C_6H** (60 %). Hay homocouplings of **Pt*C_4H** and **Pt*C_6H** give **Pt*C_8Pt*** (64 %) and **Pt*C_{12}Pt*** (64 %). Reaction of *trans*-(C_6F_5)(*p*-tol$_3P)_2PtCl$ (**PtCl**) and $HC{\equiv}CH$ ($HNEt_2$, 20 mol % CuI) yields only traces of **PtC_2H**. However, an analogous reaction with $HC{\equiv}CSiMe_3$ gives **PtC_2SiMe$_3$** (75 %), which upon treatment with silica yields **PtC_2H** (77 %). An analogous coupling of *trans*-$(C_6F_5)(Ph_3P)_2PtCl$ with $H(C{\equiv}C)_2H$ gives *trans*-$(C_6F_5)(Ph_3P)_2Pt(C{\equiv}C)_2H$ (34 %). Advantages and disadvantages of the various *trans*-(Ar)$(R_3P)_2$Pt end-groups are analyzed.

Keywords: platinum; polyynes; phosphines; oxidative coupling; Sonogashira coupling.

INTRODUCTION

Our research group has had an ongoing interest in assemblies based on diplatinum polyynediyl or $Pt(C{\equiv}C)_nPt$ complexes (n = 2, 3, 4, 5, 6, 8, 10, 12, 14), as exemplified by the isolable adducts **I** and **II** in Fig. 1, which contain extremely long sp carbon chains [1–9]. Complementary efforts involving other types of polyynediyl complexes have been reported by a number of groups [10–12]. As described in an oral presentation at the 12th International Symposium on Novel Aromatic Compounds (ISNA-12), these have been covalently linked in longitudinal arrays ($[Pt(C{\equiv}C)_4]_n$, oligomers such as **III**) [7] and lateral arrays ("bundles" such as **IV**) [6]. We have also developed two routes to complexes of the formula *trans,trans*-$(C_6F_5)(Ar_2P(CH_2)_mPAr_2)Pt(C{\equiv}C)_nPt(Ar_2P(CH_2)_mPAr_2)(C_6F_5)$ (**V**) [3–5]. These feature

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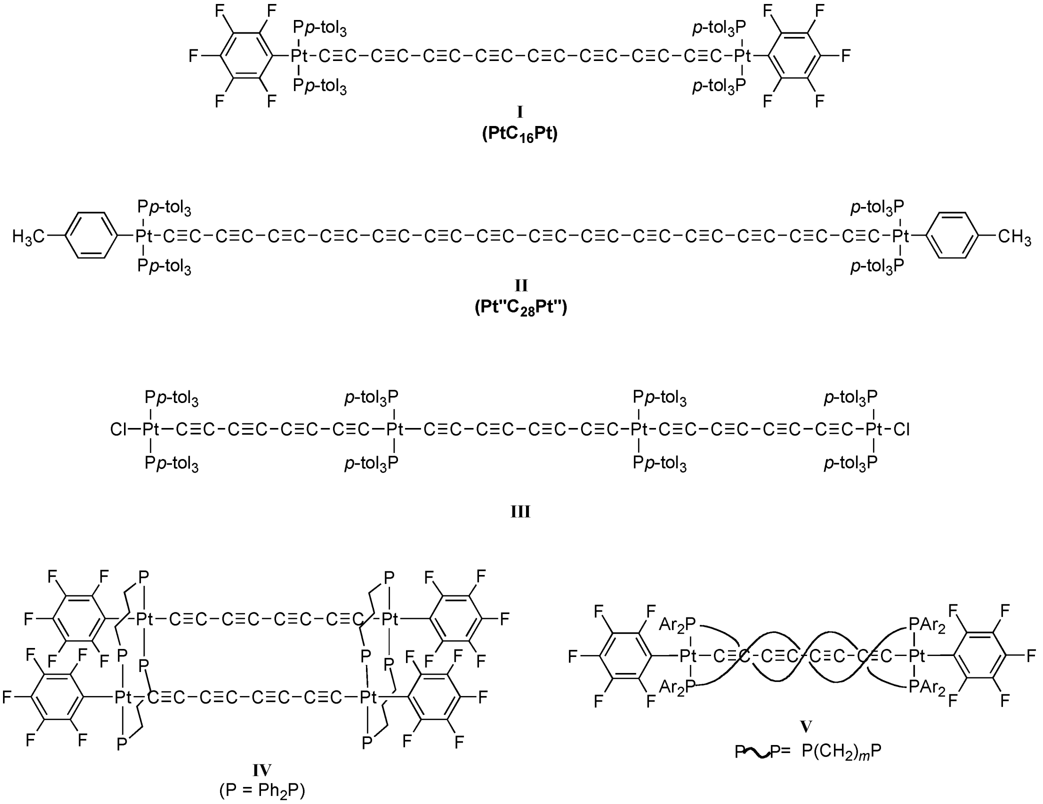


Fig. 1 Representative assemblies based on $Pt(C{\equiv}C)_nPt$ building blocks prepared in the Gladysz group.

end-group-spanning α,ω-diphosphines that sterically shield the sp carbon chains, which when sufficiently long adopt double-helical conformations.

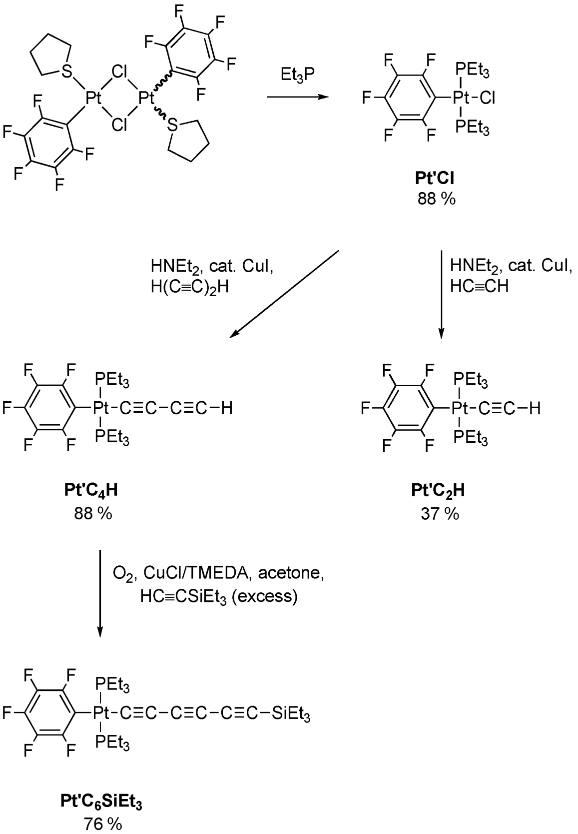
Much of this work has recently appeared in comprehensive full papers [1–4,5b,6b,9], and we prefer not to revisit these themes without new data, insight, or analyses. Thus, unpublished results relating to several classes of $Pt(C{\equiv}C)_nPt$ complexes, or potential precursors thereof, will be presented in this paper. Note that various types of end-groups are represented in Fig. 1, including *trans*-$(C_6F_5)(p\text{-}tol_3P)_2Pt$ (**Pt**), *trans*-$(p\text{-}tol)(p\text{-}tol_3P)_2Pt$ (**Pt''**), and *trans*-$(Cl)(p\text{-}tol_3P)_2Pt$. We seek to bring into sharper focus the factors that led to emphasizing these species, and/or deemphasizing others. Additional details have been archived elsewhere [13,14].

RESULTS

trans-$(C_6F_5)(Et_3P)_2Pt$ (Pt') End-groups

In previous studies, complexes of the formula *trans,trans*-$(C_6F_5)(Et_3P)_2Pt(C{\equiv}C)_nPt(PEt_3)_2(C_6F_5)$ (**Pt'C$_{2n}$Pt'** or **Pt'C$_x$Pt'**; n/x = 3/6, 4/8, 6/12) were prepared by four-fold substitutions of the triarylphosphine complexes *trans,trans*-$(C_6F_5)(p\text{-}tol_3P)_2Pt(C{\equiv}C)_nPt(Pp\text{-}tol_3)_2(C_6F_5)$ (**PtC$_x$Pt**) with excesses of the more basic phosphine Et_3P [1,6b]. Substitutions of Ph_3P ligands by Bu_3P ligands have been reported with related $PtC{\equiv}CPt$ species [16]. However, the question remained as to the most efficient way to access such systems. Might they be easier to synthesize in a manner analogous to the p-tol_3P homologs **PtC$_x$Pt**? Hence, parallel routes were investigated.

Accordingly, the diplatinum bis(tetrahydrothiophene) complex shown in Scheme 1 [16] was treated with a slight excess of Et_3P (1.0:4.4 mol ratio). In accord with much precedent [1,17], workup gave the monoplatinum bis(phosphine) chloride complex **Pt'Cl** [18,19] in 88 % yield. Next, **Pt'Cl** was treated with HC≡CH or $H(C{\equiv}C)_2H$ and 20 mol % CuI in the basic solvent $HNEt_2$. The former reaction was slower, and required heating under reflux. As shown in Scheme 1, workups gave the ethynyl and butadiynyl complexes **Pt'C$_2$H** and **Pt'C$_4$H** in 37 and 81 % yields, respectively. The former reaction also afforded the iodide complex **Pt'I** [18,19], which must be derived from the CuI catalyst, in 16 % yield.



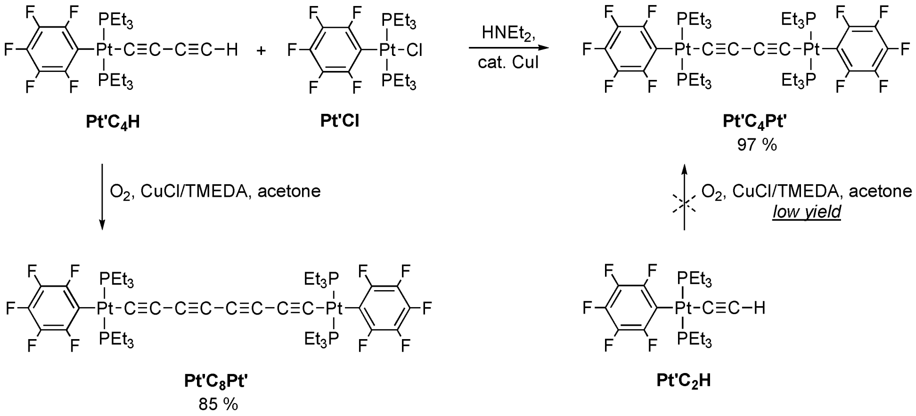
Scheme 1 Syntheses of monoplatinum complexes with *trans*-$(C_6F_5)(Et_3P)_2Pt$ (**Pt'**) end-groups.

The rate trend ($H(C{\equiv}C)_2H$ > HC≡CH) follows the order of Brønsted acidities [20], an empirical correlation that holds for all of the types of homocoupling and heterocoupling reactions described in this as well as earlier papers [1,2,4]. The complexes **Pt'C$_2$H** and **Pt'C$_4$H**, and most other isolable species below, were characterized by NMR (^1H, ^{13}C, ^{31}P) and IR spectroscopy, mass spectrometry, and microanalysis, as summarized in the experimental section. All ^{31}P NMR spectra exhibited ^{31}P-^{195}Pt couplings, the magnitudes of which (2953–2388 Hz) require *trans* P-Pt-P linkages [21]. The spectroscopic properties of **Pt'C$_2$H** and **Pt'C$_4$H** were similar to the *p*-tol$_3$P analogs **PtC$_2$H** (below) and **PtC$_4$H** [1].

The feasibility of extending of the sp carbon chain was investigated. In accord with a protocol used for **PtC$_4$H** [1], an acetone solution of **Pt'C$_4$H** and a 15-fold excess of $HC{\equiv}CSiEt_3$ was treated with

O_2, CuCl, and TMEDA (Hay conditions; Scheme 1) [22]. Workup gave the desired cross-coupling product, the silylated hexatriynyl complex **Pt'C$_6$SiEt$_3$**, in 76 % yield.

Diplatinum complexes **Pt'C$_x$Pt'** were sought. As shown in Scheme 2, an acetone solution of **Pt'C$_2$H** was subjected to Hay homocoupling conditions (O_2, CuCl/TMEDA). However, only traces of the target complex **Pt'C$_4$Pt'** were obtained. In contrast, an analogous reaction of **Pt'C$_4$H** (presumably a stronger Brønsted acid) gave the octatetraynediyl complex **Pt'C$_8$Pt'** as a yellow powder in 85 % yield. An alternative approach to **Pt'C$_4$Pt'** was investigated. As also shown in Scheme 2, **Pt'Cl** and **Pt'C$_4$H** were combined under conditions similar to those used for the heterocoupling of **Pt'Cl** and alkynes in Scheme 1. Workup gave **Pt'C$_4$Pt'** as a pale yellow powder in 97 % yield.

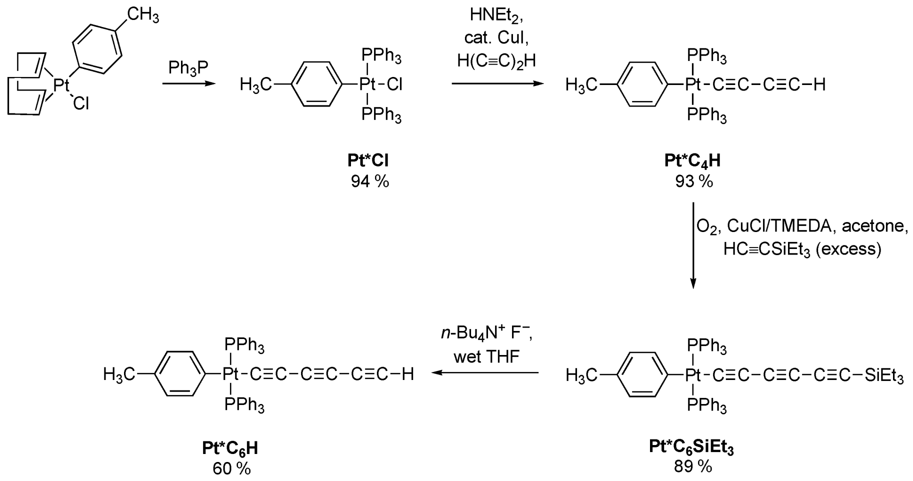


Scheme 2 Syntheses of diplatinum complexes with *trans*-$(C_6F_5)(Et_3P)_2Pt$ (**Pt'**) end-groups.

Since some of the preceding complexes were prepared in quantity, additional spectroscopic properties were probed. For example, the $^{195}Pt\{^1H\}$ NMR spectrum of **Pt'C$_4$Pt'** showed a triplet of triplet of triplets, arising from couplings to two phosphorus atoms, two *ortho* fluorine atoms, and two *meta* fluorine atoms (J = 2450, 328, and 108 Hz). The $^{19}F\{^1H\}$ spectra of the Pt' species showed a well-separated signal for the *ortho* fluorine atoms (m, ca. –117 ppm), and closely spaced *para* and *meta* signals (tm and m, ca. –161 to –165 ppm) [19]. The ^{13}C NMR chemical shifts and coupling constants associated with the sp carbon atoms followed established trends [1–6].

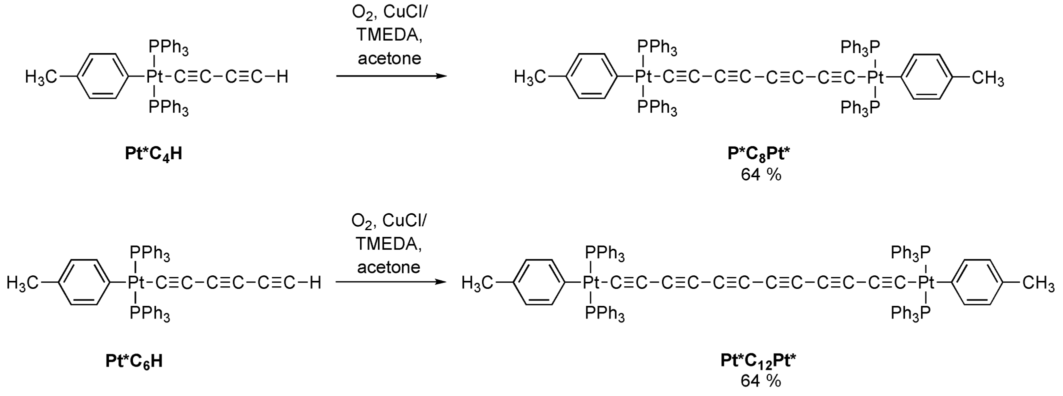
trans-(*p*-tol)(Ph$_3$P)$_2$Pt (Pt*) End-groups

Full details for the first two reactions in Scheme 3 have been disclosed previously [2,23]. The platinum COD complex readily reacts with a variety of phosphines. The bis(phosphine) chloride complex **Pt*Cl** undergoes facile heterocoupling with H(C≡C)$_2$H to give **Pt*C$_4$H** [23]. A subsequent reaction with HC≡CSiEt$_3$ under the conditions used for **Pt'C$_4$H** in Scheme 1 afforded the silylated hexatriynyl complex **Pt*C$_6$SiEt$_3$** in 89 % yield after workup. When **Pt*C$_6$SiEt$_3$** was treated with wet fluoride ion, protodesilylation occurred to give the hexatriynyl complex **Pt*C$_6$H**, which could be isolated in 60 % yield. Like all platinum hexatriynyl complexes [1,2], **Pt*C$_6$H** was quite labile. When overall yields are a concern, such species are commonly generated and used in situ [1,2,24].



Scheme 3 Syntheses of monoplatinum complexes with *trans*-(*p*-tol)(Ph$_3$P)$_2$Pt (**Pt***) end-groups.

As shown in Scheme 4, oxidative homocouplings of **Pt*C$_4$H** and **Pt*C$_6$H** were attempted under conditions analogous to those used for **Pt'C$_4$H** in Scheme 2. The latter reaction could be conducted at a slightly lower temperature (45 vs. 60 °C). Workups gave **Pt*C$_8$Pt*** and **Pt*C$_{12}$Pt*** in 64 % yields. However, these complexes showed much poorer solubilities. With effort, the ^{13}C NMR signals of the C≡C carbon atoms of **Pt*C$_8$Pt*** could be detected, but the ^{195}Pt couplings that are usually observed were not resolved. The solubility of **Pt*C$_{12}$Pt*** was distinctly lower, and no C≡C ^{13}C signals were detected with saturated samples.

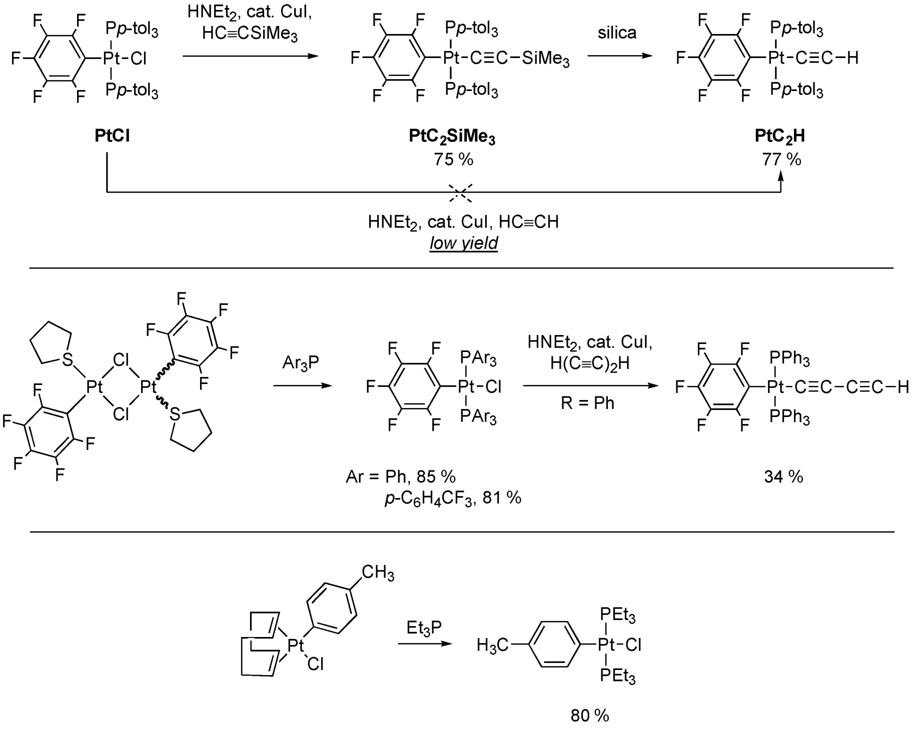


Scheme 4 Syntheses of diplatinum complexes with *trans*-(*p*-tol)(Ph$_3$P)$_2$Pt (**Pt***) end-groups.

In view of this trend, the analogous *p*-tol$_3$P complexes (**Pt"X**) were prepared as described elsewhere [2], and exhibited notably higher solubilities. This series was then elaborated to longer sp chain lengths, culminating in the current record-holding complex **Pt"C$_{28}$Pt"** (**II**, Fig. 1). However, crystals of **Pt*C$_8$Pt*** could be obtained, and the crystal structure was reported with those of the *p*-tol$_3$P analogs [2].

Other end-groups

In the course of the preceding investigations, other reactions were attempted to probe or define limits associated with other end-groups, or provide starting materials for future publications. Successful results are summarized in Scheme 5.



Scheme 5 Syntheses of monoplatinum complexes with other end-groups.

As illustrated in the first sequence, **PtCl** and HC≡CH did not efficiently condense under the conditions used for **Pt'Cl** in Scheme 1. Only modest yields of **PtC$_2$H** could be realized. Thus, trialkylphosphine-substituted end-groups appear to undergo heterocoupling more readily than triarylphosphine analogs, at least with respect to the less Brønsted acidic reaction partner HC≡CH. Interestingly, an analogous reaction with excess HC≡CSiMe$_3$ gave **PtC$_2$SiMe$_3$** in 75 % yield after workup. This complex could not be protodesilylated using common fluoride ion sources, such as that employed for **Pt*C$_6$SiEt$_3$** in Scheme 3. As established elsewhere, PtC$_x$ fragments become increasingly better leaving groups as the C$_x$ chain is lengthened [2], and the deprotection of other PtC≡CSiR$_3$ species has also been found to be problematic [25]. However, when solutions of **PtC$_2$SiMe$_3$** were stirred over silica gel for 24 h, **PtC$_2$H** could be isolated in 77 % yield.

The second sequence in Scheme 5 was undertaken to assay other C$_6$F$_5$/phosphine ligand end-group combinations. Thus, the diplatinum bis(tetrahydrothiophene) complex was treated with Ph$_3$P and the less basic triarylphosphine (p-CF$_3$C$_6$H$_4$)$_3$P. Workups gave the corresponding bis(phosphine) chloride complexes *trans*-(C$_6$F$_5$)(Ar$_3$P)$_2$PtCl in 85–81 % yields. Reactions with H(C≡C)$_2$H were then investigated under conditions analogous to those used for **Pt'Cl** in Scheme 1. In the case of the Ph$_3$P complex, conversions were usually incomplete. However, chromatography gave the butadiynyl complex *trans*-(C$_6$F$_5$)(Ph$_3$P)$_2$Pt(C≡C)$_2$H in 34 % yield. In the case of the (p-CF$_3$C$_6$H$_4$)$_3$P complex, only the free phosphine and the corresponding oxide were isolated. Hence, when the triarylphosphine ligands become too electron-deficient, heterocouplings with $H(C{\equiv}C)_2H$ can be problematic.

The homocoupling of *trans*-$(C_6F_5)(Ph_3P)_2Pt(C{\equiv}C)_2H$ was attempted using the Hay conditions employed for **Pt'C$_4$H** in Scheme 2. Some of the corresponding $Pt(C{\equiv}C)_4Pt$ species formed, but conversions were incomplete and it could not be purified under the chromatographic conditions investigated. Thus, more electron-rich triarylphosphine appears to promote this oxidation. Also, in contrast to **Pt'C$_4$H**, *trans*-$(C_6F_5)(Ph_3P)_2Pt(C{\equiv}C)_2H$ is only partially soluble under the Hay conditions.

The final reaction in Scheme 5 is a simple extension of the first transformation in Scheme 3. The *p*-tolyl-substituted chloride complex, *trans*-(*p*-tol)$(Et_3P)_2PtCl$, was obtained in 92 % yield. Thus, end-groups featuring all possible combinations of four aryl and phosphine ligands, C_6F_5/*p*-tol$_3$P (**Pt**), C_6F_5/Et_3P (**Pt'**), *p*-tol/*p*-tol$_3$P (**Pt"**), and *p*-tol/Et_3P, are now available. The last one will be a key building block in an upcoming paper [26].

DISCUSSION

Schemes 1–5, and the other reactions presented, illustrate a variety of logical end-group effects on rates, yields, and solubilities. Although with continued experimentation it would likely be possible to find solutions for certain problems—such as the low yield of *trans*-$(C_6F_5)(Ph_3P)_2Pt(C{\equiv}C)_2H$ in Scheme 5—the results are helpful from the standpoint of synthetic planning. The means by which the phosphine ligands are introduced in Schemes 1, 3, and 5 appear quite versatile, and should allow virtually any end-group of the formulae *trans*-$(C_6F_5)(R_3P)_2Pt$ or *trans*-(*p*-tol)$(R_3P)_2Pt$ to be obtained.

A variety of platinum pentafluorophenyl complexes have been synthesized by other researchers, especially in Spain [27]. In our experience, they are particularly crystalline, and stacking interactions with other aryl groups are often found in the solid state [1,3–7]. The physical basis for these attractive forces has been extensively studied, and elegantly exploited in crystal engineering [28]. However, crystals of *trans*-(*p*-tol)$(R_3P)_2Pt$ derivatives are also easily obtained [2].

One theme not addressed above involves end-groups that can be functionalized, as exemplified in the dichloride complex **III** (Fig. 1). This series of compounds was accessed by the desymmetrization of the building block (*p*-tol$_3$P)$_2$PtCl$_2$ [heterocoupling with $Me_3Sn(C{\equiv}C)_2SiMe_3$], a type of reaction that in our experience cannot be taken for granted. We had hoped that the end-groups **Pt** and **Pt'** would prove functionalizable, as it is often possible to selectively replace the *para* fluorine atom of a pentafluorophenyl group via nucleophilic addition [29,30]. However, we have not been able to realize such reactions to date.

Other researchers have synthesized diplatinum polyynediyl complexes with as many as four carbon–carbon triple bonds [10,15]. Of these, the most relevant is the hexatriynediyl complex *trans,trans*-$(Ph)(Ph_3P)_2Pt(C{\equiv}C)_3Pt(PPh_3)_2(Ph)$, which has been structurally characterized and features an end-group very similar to **Pt*** [10c]. This adduct was obtained in low yield by a serendipitous route. Additional related species, but with shorter sp chains, include *trans,trans*-$(Cl)(R_3P)_2Pt$-$C{\equiv}CPt(PR_3)_2(Cl)$ (R = Ph, Bu) [15]. The other diplatinum polyynediyl complexes contain distinctly different types of end-group ligands, such as COD or chelating nitrogen donors.

In summary, we have been able to significantly extend the repertoire of end-groups in Fig. 1. In this process, a variety of attributes have been defined that will aid future synthetic planning. Applications of some of these complexes will be reported in future publications [26].

EXPERIMENTAL

General

Instrumentation, and procedures for recording DSC/TGA [31] data, were identical to those in previous papers [1–4,5b,6b]. Reactions were conducted under N_2 atmospheres, and workups in air. Chemicals were treated as follows: hexanes and THF, distilled from Na/benzophenone; methanol, ethanol, and TMEDA (Aldrich), distilled; CH_2Cl_2, distilled from CaH_2, $HNEt_2$, distilled from KOH; $CDCl_3$, stored over molecular sieves; n-Bu_4N^+ F^- (trihydrate, Lancaster), dissolved in THF containing 5 wt % H_2O to give a 1.0 M solution; CuCl and CuI (2 × Aldrich, 99.99 %), $HC{\equiv}CSiEt_3$ (Aldrich), $HC{\equiv}CSiMe_3$ (Acros), Et_3P (Strem, 10 wt % in hexane), and $HC{\equiv}CH$, used as received.

trans-$(C_6F_5)(Et_3P)_2PtCl$ (Pt'Cl) [18,19]

A Schlenk flask was charged with $\{(C_6F_5)Pt[S(CH_2CH_2{-})_2](\mu\text{-}Cl)\}_2$ (0.972 g, 1.00 mmol) [16], Et_3P (0.65 mL, 4.4 mmol), and CH_2Cl_2 (80 mL). The solution was stirred for 20 h and filtered through a Celite®/decolorizing carbon/glass frit assembly. The solvent was removed by rotary evaporation. The residue was chromatographed (silica, 25 × 2 cm column, 30:70 v/v CH_2Cl_2/hexanes). The solvent was removed from the product containing fractions by oil pump vacuum to give **Pt'Cl** as a white powder (1.120 g, 1.77 mmol, 88 %), mp 118–119 °C (lit.: 119–120 °C) [18]. DSC: endotherm with T_i, 101.7 °C; T_e, 119.8 °C; T_p, 120.5 °C; T_c, 123.4 °C; T_f, 136.6 °C. TGA: 170.9 °C (mass loss, onset). Calcd for $C_{18}H_{30}ClF_5P_2Pt$: C, 34.11; H, 4.77. Found: C, 34.27; H, 4.68.

NMR (δ, $CDCl_3$) [32]: ^{1}H 1.63 (m, 12H, CH_2), 1.04 (m, 18H, CH_3); $^{13}C\{^1H\}$ 146.2 (dd, $^1J_{CF}$ = 225 Hz, $^2J_{CF}$ = 23 Hz, *o* to Pt), 136.7 (dm, $^1J_{CF}$ = 240 Hz, *m/p* to Pt), 106.1 (br m, *i* to Pt), 13.7 (virtual t, J_{CP} = 17.0 Hz, $^2J_{CPt}$ = 33 Hz [33], CH_2), 7.7 (s, $^3J_{CPt}$ = 24 Hz [33], CH_3); $^{19}F\{^1H\}$ –117.3 (m, $^3J_{FPt}$ = 465 Hz [33], 2F, *o* to Pt), –161.5 (tm, $^3J_{FF}$ = 20 Hz, 1F, *p* to Pt), –162.9 (m, $^4J_{FPt}$ = 103 Hz [33], 2F, *m* to Pt); $^{31}P\{^1H\}$ 15.5 (s, $^1J_{PPt}$ = 2485 Hz [33]).

IR (cm^{-1}, powder film), 2968 m, 2937 w, 2880 w, 1498 s, 1455 vs, 1440 vs, 1417 m, 1382 w, 1254 m, 1058 s, 1034 vs, 1007 m, 953 vs, 803 s, 760 vs, 733 vs, 714 s. MS [34], 633 ($[M - H]^+$, 72 %), 598 ($[(C_6F_5)Pt(PEt_3)_2]^+$, 100 %), 429 ($[Pt(PEt_3)_2 - 2H]^+$, 45 %), and fragments with lower mass due to the loss of C_2H_5.

trans-$(C_6F_5)(Et_3P)_2PtC{\equiv}CH$ (Pt'C$_2$H)

A Schlenk flask was charged with **Pt'Cl** (0.317 g, 0.500 mmol), CuI (0.020 g, 0.106 mmol), and $HNEt_2$ (40 mL), and fitted with a condenser. The mixture was refluxed and aspirated with a stream of $HC{\equiv}CH$. After 22 h, the solvent was removed by oil pump vacuum. The residue was chromatographed (silica, 20 × 2 cm column, 30:70 v/v CH_2Cl_2/hexanes). The solvent was removed from the product containing fractions by oil pump vacuum to give **Pt'C$_2$H** as a white powder (0.115 g, 0.184 mmol, 37 %), mp >194 °C (dec.), and **Pt'I** [18,19] (0.059 g, 0.081 mmol, 16 %) as a white powder, mp 155–158 °C (lit. [18]: 163–164 °C), dec pt 258 °C. DSC (**Pt'I**): endotherm with T_i, 151.7 °C; T_e, 158.4 °C; T_p, 161.5 °C; T_c, 163.5 °C; T_f, 165.1 °C. TGA: 181.0 °C (mass loss, onset).

Data for **Pt'C$_2$H**: NMR (δ, $CDCl_3$) [32]: ^{1}H 2.20 (t, $^4J_{HP}$ = 2.1 Hz, $^3J_{HPt}$ = 46 Hz [33], 1H, ≡CH), 1.73 (m, 12 H, CH_2), 1.03 (m, 18H, CH_3); $^{13}C\{^1H\}$ 146.9 (dd, $^1J_{CF}$ = 224 Hz, $^2J_{CF}$ = 21 Hz, *o* to Pt), 136.8 (dm, $^1J_{CF}$ = 245 Hz, *p* to Pt), 120.6 (t, $^2J_{CF}$ = 53 Hz, *i* to Pt), 99.1 (s, $^1J_{CPt}$ = 962 Hz [33], PtC≡), 92.8 (s, $^2J_{CPt}$ = 271 Hz [33], PtC≡*C*), 15.4 (virtual t, J_{CP} = 17.7 Hz, CH_2), 7.8 (s, $^3J_{CPt}$ = 25 Hz [33], CH_3); $^{19}F\{^1H\}$ –117.3 (m, $^3J_{FPt}$ = 294 Hz [33], 4F, *o* to Pt), –165.3 (m, $^4J_{FPt}$ = 110 Hz [33], 4F, *m* to Pt), –166.2 (t, $^3J_{FF}$ = 20 Hz, 2F, *p* to Pt); $^{31}P\{^1H\}$ 12.4 (s, $^1J_{PPt}$ = 2441 Hz [33]).

IR (cm^{-1}, powder film), 3293 w, 2968 w, 2937 w, 2880 w, $\nu_{C\equiv C}$ 1976 w, 1613 m, 1489 s, 1447 s, 1382 w, 1254 w, 1058 m, 1034 vs, 950 vs, 787 m, 764 vs, 733 vs, 710 s.

Data for **Pt'I**: NMR (δ, $CDCl_3$) [32]: ^{1}H 1.80 (m, 12H, CH_2), 1.02 (m, 18H, CH_3); $^{13}C\{^1H\}$ 145.6 (dd, $^1J_{CF}$ = 224 Hz, $^2J_{CF}$ = 23 Hz, *o* to Pt), 137.0 (dm, $^1J_{CF}$ = 250 Hz, *m/p* to Pt), 111.3 (t, $^1J_{CF}$ = 45 Hz, *i* to Pt), 15.4 (virtual t, J_{CP} = 17.6 Hz, $^2J_{CPt}$ = 17 Hz [33], CH_2), 7.6 (s, $^3J_{CPt}$ = 24 Hz [33], CH_3); $^{19}F\{^1H\}$ –117.9 (m, $^3J_{FPt}$ = 443 Hz [33], 2F, *o* to Pt), –160.9 (t, $^3J_{FF}$ = 20 Hz, 1F, *p* to Pt), –162.5 (m, 2F, *m* to Pt); $^{31}P\{^1H\}$ 9.9 (s, $^1J_{PPt}$ = 2428 Hz [33]).

IR (cm^{-1}, powder film), 2964 m, 2930 m, 2876 w, 2856 w, 1502 s, 1451 s, 1417 m, 1363 w, 1258 m, 1100 m, 1061 s, 1031 vs, 953 vs, 795 vs, 760 vs, 730 vs. MS [34], 725 (M$^+$, 55 %), 598 ([(C_6F_5)Pt(PEt_3)$_2$]$^+$, 100 %), 558 ([Pt(PEt_3)$_2$I]$^+$, 46 %), 429 ([Pt(PEt_3)$_2$ – 2H]$^+$, 54 %).

trans-(C_6F_5)(Et_3P)$_2$Pt(C≡C)$_2$H (Pt'C_4H)

A Schlenk flask was charged with **Pt'Cl** (0.158 g, 0.250 mmol), CuI (0.010 g, 0.053 mmol), and $HNEt_2$ (25 mL), and cooled to –45 °C. Then H(C≡C)$_2$H (8.6 mL, 24.1 mmol, 2.8 M in THF [35]) was added with stirring. The cold bath was allowed to warm to room temperature (ca. 3 h). After an additional 16 h, the solvent was removed by oil pump vacuum. The residue was extracted with toluene (3 × 25 mL). The combined extracts were filtered through a neutral alumina (7 cm column, packed in toluene). The solvent was removed by oil pump vacuum. The residue was chromatographed (silica, 20 × 2 cm column, 30:70 v/v CH_2Cl_2/hexanes). The solvent was removed from the product containing fractions by oil pump vacuum to give **Pt'C_4H** as an off-white solid (0.143 g, 0.221 mmol, 88 %), mp 147 °C (capillary, onset), dec pt 152 °C (turning black) and 266 °C (bubbling). DSC: endotherm with T_i, 145.6 °C; T_e, 151.1 °C; T_p, 152.3 °C; T_c, 153.4 °C; T_f, 153.4 °C; exotherm with T_i, 153.5 °C; T_e, 153.4 °C; T_p, 155.4 °C; T_c, 175.2 °C; T_f, 191.4 °C. TGA: 259.2 °C (mass loss, onset). Calcd for $C_{22}H_{31}F_5P_2Pt$: C, 40.81; H, 4.83. Found: C, 40.75; H, 5.00.

NMR (δ, $CDCl_3$) [32]: ^{1}H 1.83 (t, $^6J_{HP}$ = 1.0 Hz, $^5J_{HPt}$ = 9.9 Hz [33], 1H, ≡CH), 1.73 (m, 12H, CH_2), 1.05 (m, 18H, CH_3); ^{13}C{^{1}H} 146.8 (dd, $^1J_{CF}$ = 220 Hz, $^2J_{CF}$ = 23 Hz, *o* to Pt), 136.9 (dm, $^1J_{CF}$ = 235 Hz, *m/p* to Pt), 119.5 (t, $^2J_{CF}$ = 53 Hz, *i* to Pt), 99.9 (s, $^1J_{CPt}$ = 1007 Hz [33], PtC≡), 89.1 (s, $^2J_{CPt}$ = 286 Hz [33], PtC≡*C*), 72.4 (s, $^3J_{CPt}$ = 37 Hz [33], PtC≡C*C*), 59.3 (s, PtC≡CC≡*C*), 15.5 (virtual t, J_{CP} = 17.6 Hz, CH_2), 7.8 (s, $^3J_{CPt}$ = 25 Hz [33], CH_3); ^{19}F{^{1}H} –116.4 (m, $^3J_{FPt}$ = 330 Hz [33], 2F, *o* to Pt), –161.1 (t, $^3J_{FF}$ = 20 Hz, 1F, *p* to Pt), –162.9 (m, $^4J_{FPt}$ = 110 Hz [33], 2F, *m* to Pt); ^{31}P{^{1}H} 13.1 (s, $^1J_{PPt}$ = 2400 Hz [33]).

IR (cm^{-1}, powder film), 3312 w, 2968 w, 2937 w, 2914 w, 2880 w, $\nu_{C≡C}$ 2146 m, 1502 m, 1447 s, 1417 m, 1258 m, 1100 m, 1034 vs, 950 vs, 803 s, 762 vs, 733 vs. UV–vis [nm (ε, M^{-1} cm^{-1}), CH_2Cl_2, 1.25 × 10^{-4} M], 261 (7500), 275 (4800), 299 (6200). MS [34], 647 (M$^+$, 42 %), 598 ([(C_6F_5)Pt(PEt_3)$_2$]$^+$, 40 %), 480 ([(C_6F_5)Pt(PEt_3)]$^+$ and [Pt(PEt_3)$_2C_4$H]$^+$, 35 %), 429 ([Pt(PEt_3)$_2$ – 2H]$^+$, 100 %), and fragments with lower mass due to the loss of C_2H_5.

trans-(C_6F_5)(Et_3P)$_2$Pt(C≡C)$_3$SiEt_3 (Pt'C_6SiEt_3)

A three-necked flask was charged with **Pt'C_4H** (0.174 g, 0.269 mmol), acetone (15 mL), and HC≡CSiEt_3 (0.72 mL, 4.0 mmol), and fitted with a gas dispersion tube and a condenser with circulating –18 °C ethanol. A Schlenk flask was charged with CuCl (0.100 g, 1.01 mmol) and acetone (15 mL), and TMEDA (0.200 mL, 1.20 mmol) was added with stirring. After 0.5 h, stirring was halted (blue supernatant/yellow–green solid). Then O_2 was bubbled through the three-necked flask with stirring and the solution was heated to 65 °C. The blue supernatant was added in portions over 4 h. The solvent was removed by rotary evaporation and oil pump vacuum. The residue was extracted with hexanes (2 × 5 mL) and then toluene (3 × 5 mL). The extracts were filtered in sequence through alumina (4 × 2 cm column), which was rinsed with toluene. The solvent was removed from the toluene fractions by rotary evaporation. The residue was chromatographed (silica, 15 × 1.5 cm column, 90:10 v/v hexanes/CH_2Cl_2). The solvent was removed from the product containing fractions by oil pump vacuum to give **Pt'C_6SiEt_3** as a pale yellow solid (0.161 g, 0.204 mmol, 76 %).

NMR (δ, $CDCl_3$): ^{1}H 1.74–1.69 (m, 12H, PCH_2), 1.07–0.98 (m, 18H, PCH_2CH_3), 0.95 (t, 9H, $^3J_{HH}$ = 7.9 Hz, SiCH_2CH_3), 0.57 (q, 6H, $^3J_{HH}$ = 7.9 Hz, SiCH_2); ^{31}P{^{1}H} 13.1 (s, $^1J_{PPt}$ = 2388 Hz [33]).

IR (cm^{-1}, powder film), $\nu_{C\equiv C}$ 2150 m and 2011 m. MS [34], 785 (M$^+$, 70 %), 598 ([M – C_6SiEt_3]$^+$, 80 %), 429 ([M – C_6SiEt_3 – C_6F_5]$^+$, 100 %).

***trans,trans*-$(C_6F_5)(Et_3P)_2Pt(C{\equiv}C)_4Pt(PEt_3)_2(C_6F_5)$ (Pt'C$_8$Pt')**

A three-necked flask was charged with **Pt'C$_4$H** (0.098 g, 0.150 mmol) and acetone (10 mL), and fitted with a gas dispersion tube and a condenser. A Schlenk flask was charged with CuCl (0.100 g, 1.01 mmol) and acetone (30 mL), and TMEDA (0.10 mL, 0.60 mmol) was added with stirring. After 30 min, stirring was halted, and a green solid separated from a blue supernatant. Then O_2 was bubbled through the three-necked flask with stirring, and the solution was heated to 65 °C. After 10 min, the blue supernatant was added in portions. After 8 h, the solvent was removed by rotary evaporation. The residue was extracted with toluene (2 × 10 mL). The combined extracts were filtered through neutral alumina (7 cm column, packed in toluene). The solvent was removed by rotary evaporation. Ethanol (10 mL) was added, and the yellow powder was collected by filtration and dried by oil pump vacuum to give **Pt'C$_8$Pt'** (0.083 g, 0.064 mmol, 85 %), dec pt 189–192 °C.

NMR (δ, $CDCl_3$) [32]: ^{1}H 1.72 (m, 24H, CH_2), 1.04 (m, 36H, CH_3); $^{13}C\{^1H\}$ 146.9 (dd, $^1J_{CF}$ = 226 Hz, $^2J_{CF}$ = 22 Hz, *o* to Pt), 137.1 (dm, $^1J_{CF}$ = 245 Hz, *m/p* to Pt), 103.4 (s, PtC≡ [36]), 91.1 (s, $^2J_{CPt}$ = 285 Hz [33], PtC≡*C*), 63.9 (s, PtC≡C*C*), 57.6 (s, PtC≡CC≡*C*), 15.5 (virtual t, J_{CP} = 17.5 Hz, CH_2), 7.7 (s, $^3J_{CPt}$ = 24 Hz [33], CH_3); $^{19}F\{^1H\}$ –116.4 (m, $^3J_{FPt}$ = 328 Hz, 4F, *o* to Pt), –161.0 (t, $^3J_{FF}$ = 20 Hz, 2F, *p* to Pt), –162.8 (m, $^4J_{FPt}$ = 107 Hz [33], 4F, *m* to Pt); $^{31}P\{^1H\}$ 13.2 (s, $^1J_{PPt}$ = 2393 Hz [33]).

IR (cm^{-1}, powder film), 2970 w, 2937 w, 2879 w, $\nu_{C\equiv C}$ 2140 s and 1997 m, 1499 s, 1449 s, 1436 m, 1258 w, 1034 s, 953 vs, 785 s, 768 s, 735 s. UV–vis (nm (ε, M^{-1} cm^{-1}), CH_2Cl_2, 1.25 × 10^{-4} M), 271 (62 000), 288 (118 000), 314 (131 000), 350 (4000), 378 (4000), 410 (2000). MS [34], 1292 (M$^+$, 26 %), 598 ([$(C_6F_5)Pt(PEt_3)_2$]$^+$, 28 %).

***trans,trans*-$(C_6F_5)(Et_3P)_2Pt(C{\equiv}C)_2Pt(PEt_3)_2(C_6F_5)$ (Pt'C$_4$Pt')**

A Schlenk flask was charged with **Pt'Cl** (0.128 g, 0.202 mmol), **Pt'C$_4$H** (0.131 g, 0.202 mmol), CuI (0.010 g, 0.053 mmol), and $HNEt_2$ (10 mL). The mixture was stirred for 100 h. The solvent was removed by oil pump vacuum. The residue was extracted with toluene (3 × 10 mL). The combined extracts were filtered through neutral alumina (4 cm column, packed in toluene). The solvent was removed by oil pump vacuum to give **Pt'C$_4$Pt'** as a pale yellow powder (0.243 g, 0.195 mmol, 97 %), mp 180 °C (capillary), dec pt 261 (capillary, onset). DSC: endotherm with T_i, 178.1 °C; T_e, 193.7 °C; T_p, 196.7 °C; T_c, 198.0 °C; T_f, 203.0 °C. TGA: 251.8 °C (mass loss, onset). Calcd for $C_{40}H_{60}F_{10}P_4Pt_2$: C, 38.59; H, 4.86. Found: C, 38.39; H, 5.09.

NMR (δ, $CDCl_3$) [32]: ^{1}H 1.75 (m, 24H, CH_2), 1.04 (m, 36H, CH_3); $^{13}C\{^1H\}$ 147.4 (dd, $^1J_{CF}$ = 223 Hz, $^2J_{CF}$ = 22 Hz, *o* to Pt), 137.1 (dm, $^1J_{CF}$ = 250 Hz, *m/p* to Pt), 121.4 (s, $^2J_{CF}$ = 54.1 Hz, $^1J_{CPt}$ = 670 Hz [33], *i* to Pt), 95.6 (s, $^2J_{CPt}$ = 280 Hz [33], $^3J_{CP}$ = 32 Hz [33], PtC≡*C*), 90.3 (s, $^1J_{CPt}$ = 989 Hz [33], Pt*C*≡), 16.0 (virtual t, J_{CP} = 17.3 Hz, $^2J_{CPt}$ = 36 Hz [33], CH_2), 8.2 (s, $^3J_{CPt}$ = 24 Hz [33], CH_3); $^{19}F\{^1H\}$ –116.1 (m, $^3J_{FPt}$ = 328 Hz [33], 4F, *o* to Pt), –162.1 (t, $^3J_{FF}$ = 20 Hz, 2F, *p* to Pt), –163.5 (m, $^4J_{FPt}$ = 108 Hz [33], 4F *m* to Pt); $^{31}P\{^1H\}$ 12.5 (s, $^1J_{PPt}$ = 2447 Hz [33]); $^{195}Pt\{^1H\}$ –3058 (ttt, $^1J_{PPt}$ = 2450 Hz, $^3J_{FPt}$ = 328 Hz, $^4J_{FPt}$ = 108 Hz).

IR (cm^{-1}, powder film), 2968 m, 1498 m, 1447 m, 1262 m, 1092 m, 1031 vs, 950 vs, 799 vs, 780 vs, 764 vs, 733 vs, 714 s. UV-vis (nm (ε, M^{-1} cm^{-1}), CH_2Cl_2, 1.25 × 10^{-4} M), 276 (18 000), 312 (16 600), 333 (15 600). MS [34], 1244 (M$^+$, 46 %), 764 ([$(C_6F_5)Pt(PEt_3)_3C_4$]$^+$, 100 %), 598 ([$(C_6F_5)Pt(PEt_3)_2$]$^+$, 12 %), 429 ([$Pt(PEt_3)_2$ – 2H]$^+$, 26 %), and fragments with lower mass due to the loss of C_2H_5.

trans-(*p*-tol)$(Ph_3P)_2Pt(C{\equiv}C)_3SiEt_3$ ($Pt^*C_6SiEt_3$)

A three-necked flask was charged with **Pt^*C_4H** (0.120 g, 0.139 mmol) [23], acetone (25 mL), and $HC{\equiv}CSiEt_3$ (0.123 g, 0.877 mmol), and fitted with a gas dispersion tube and a condenser. A Schlenk flask was charged with CuCl (0.050 g, 0.51 mmol) and acetone (20 mL), and TMEDA (0.030 mL, 0.20 mmol) was added with stirring. After 0.5 h, stirring was halted, and a grayish solid separated from a blue supernatant. The three-necked flask was placed in a 45 °C oil bath, and O_2 was bubbled through the solution. After ca. 5 min, the blue supernatant was added in portions. After 1 h, the solvent was removed by rotary evaporation. The residue extracted with hexane (3 × 5 mL) and then benzene (3 × 5 mL). The extracts were filtered in sequence through alumina (7 cm column). The solvent was removed from the benzene extract by rotary evaporation. The pale yellow solid was dried by oil pump vacuum to give **$Pt^*C_6SiEt_3$** (0.124 g, 0.125 mmol, 89 %), dec pt 170 °C. Calcd for $C_{55}H_{52}P_2SiPt$: C, 66.18; H, 5.25. Found: C, 65.99; H, 5.39.

NMR (δ, $CDCl_3$) [32]: ^1H 7.46–7.21 (m, 30H, C_6H_5), 6.34 (d, $^3J_{HH}$ = 7.5 Hz [36], 2H, *o* to Pt), 6.08 (d, $^3J_{HH}$ = 7.5 Hz, 2H, *m* to Pt), 1.93 (s, 3H, $C_6H_4CH_3$), 0.91 (t, $^3J_{HH}$ = 7.8 Hz, 9H, CH_2CH_3), 0.52 (q, $^3J_{HH}$ = 7.8 Hz, 6H, $SiCH_2$); $^{13}C\{^1H\}$ 150.0 (s, *i* to Pt), 139.3 (s, *o* to Pt), 135.3 (virtual t, J_{CP} = 6.0 Hz, *o* to P), 131.4 (virtual t, J_{CP} = 28.7 Hz, *i* to P), 130.8 (s, *p* to Pt), 130.4 (s, *p* to P), 128.8 (s, *m* to Pt), 128.3 (virtual t, J_{CP} = 5.0 Hz, *m* to P), 116.4 (s [36], PtC≡), 97.0 (s, PtC≡*C*), 92.3 (s, ≡CSi), 80.0 (s, *C*≡CSi), 66.9 (s, PtC≡C*C*), 55.7 (s, PtC≡CC≡*C*), 21.1 (s, CH_3/*p* to Pt), 8.1 (s, CH_2CH_3), 5.1 (s, CH_2CH_3); $^{31}P\{^1H\}$ 21.2 (s, $^1J_{PPt}$ = 2953 Hz [33]).

IR (cm^{-1}, CH_2Cl_2), $\nu_{C\equiv C}$ 2145 s and 2009 m.

trans-(*p*-tol)$(Ph_3P)_2Pt(C{\equiv}C)_3H$ (Pt^*C_6H)

A Schlenk flask was charged with **$Pt^*C_6SiEt_3$** (0.125 g, 0.125 mmol) and THF (60 mL), and $n\text{-}Bu_4N^+$ F^- (1.0 M in THF/5 wt % H_2O; 0.125 mL, 0.125 mmol) was added with stirring. After 30 min, the solution was poured into water (40 mL). The mixture was extracted with CH_2Cl_2 (3 × 30 mL). The combined extracts were dried ($MgSO_4$). The solvent was removed by rotary evaporation. Ethanol (15 mL) was added, and the tan powder was collected by filtration and dried by oil pump vacuum to give **Pt^*C_6H** (0.066 g, 0.075 mmol, 60 %), dec pt 170 °C.

NMR (δ, $CDCl_3$) [32]: ^1H 7.48–7.23 (m, 30H, C_6H_5), 6.33 (d, $^3J_{HH}$ = 7.8 Hz [36], 2H, *o* to Pt), 6.10 (d, $^3J_{HH}$ = 7.8 Hz, 2H, *m* to Pt), 1.94 (s, 3H, CH_3), 1.81 (s, 1H, ≡CH); $^{31}P\{^1H\}$ 21.1 (s, $^1J_{PPt}$ = 2941 Hz [33]).

trans,trans-(*p*-tol)$(Ph_3P)_2Pt(C{\equiv}C)_4Pt(PPh_3)_2$(*p*-tol) ($Pt^*C_8Pt^*$)

A three-necked flask was charged with **Pt^*C_4H** (0.120 g, 0.139 mmol) and acetone (25 mL), and fitted with a gas dispersion tube and a condenser. A Schlenk flask was charged with CuCl (0.050 g, 0.51 mmol) and acetone (20 mL), and TMEDA (0.030 mL, 0.20 mmol) was added with stirring. After 0.5 h, stirring was halted, and a grayish solid separated from a blue supernatant. The three-necked flask was placed in a 60 °C oil bath, and O_2 was bubbled through the solution. After ca. 5 min, the blue supernatant was added in portions. After 1.5 h, the solvent was removed by rotary evaporation. The residue was extracted with benzene (3 × 10 mL). The extract was filtered through alumina (7 cm column). The solvent was removed by rotary evaporation. Ethanol (15 mL) was added and the yellow powder collected by filtration and dried by oil pump vacuum to give **$Pt^*C_8Pt^*$** (0.077 g, 0.045 mmol, 64 %), dec pt 170 °C. Calcd for $C_{94}H_{74}P_4Pt_2$: C, 65.94; H, 4.44. Found: C, 65.73; H, 4.34.

NMR (δ, $CDCl_3$) [32]: ^1H 7.46–7.18 (m, 60H, C_6H_5), 6.32 (d, $^3J_{HH}$ = 7.5 Hz [36], 4H, *o* to Pt), 6.07 (d, $^3J_{HH}$ = 7.5 Hz, 4H, *m* to Pt), 1.92 (s, 6H, CH_3); $^{13}C\{^1H\}$ 150.0 (s, *i* to Pt), 139.5 (s, *o* to Pt), 135.4 (virtual t, J_{CP} = 6.1 Hz, *o* to P), 131.5 (virtual t, J_{CP} = 28.7 Hz, *i* to P), 130.5 (s, *p* to P), 130.3

(s, *p* to Pt), 128.7 (s, *m* to Pt), 128.3 (virtual t, J_{CP} = 5.0 Hz, *m* to P), 112.9 (s [36], PtC≡), 98.6 (s, PtC≡*C*), 64.3 (s, PtC≡C*C*), 58.4 (s, PtC≡CC≡*C*), 21.5 (s, CH_3); $^{31}P\{^1H\}$ 21.0 (s, $^1J_{PPt}$ = 2953 Hz [33]).

IR (cm^{-1}, CH_2Cl_2) $\nu_{C\equiv C}$ 2139 s and 1984 m. MS [34], 1717 (M^+, 30 %), 810 ($[(tol)(Ph_3P)_2Pt]^+$, 80 %), 719 ($[(Ph_3P)_2Pt]^+$, 100 %); no other peaks above 400 of >3 %.

trans,trans-(*p*-tol)$(Ph_3P)_2Pt(C\equiv C)_6Pt(PPh_3)_2$(*p*-tol) ($Pt^*C_{12}Pt^*$)

Complex **Pt^*C_6H** (0.060 g, 0.068 mmol), CH_2Cl_2 (15 mL), acetone (5 mL), CuCl (0.050 g, 0.51 mmol), acetone (20 mL), TMEDA (0.030 mL, 0.20 mmol) and O_2 were combined in a procedure analogous to that for **$Pt^*C_8Pt^*$** (45 °C oil bath). A similar workup (3 × 5 mL benzene extraction) gave **$Pt^*C_{12}Pt^*$** (0.038 g, 0.022 mmol, 64 %) as an orange powder, dec pt 177 °C.

NMR (δ, $CDCl_3$) [32,37]: ^1H 7.44–7.21 (m, 60H, C_6H_5), 6.31 (d, $^3J_{HH}$ = 8.0 Hz [36], 4H, *o* to Pt), 6.10 (d, $^3J_{HH}$ = 8.0 Hz, 4H, *m* to Pt), 1.94 (s, 6H, CH_3); $^{31}P\{^1H\}$ 21.0 (s, $^1J_{PPt}$ = 2730 Hz [33]).

MS [34], 1767 (M^+, 30 %), 810 ($[(tol)(Ph_3P)_2Pt]^+$, 80 %), 719 ($[(Ph_3P)_2Pt]^+$, 100 %); no other peaks above 400 of >3 %.

trans-(C_6F_5)(*p*-$tol_3P)_2PtC\equiv CSiMe_3$ (PtC_2SiMe_3)

A Schlenk flask was charged with **PtCl** (0.338 g, 0.336 mmol) [1], CuI (0.032 g, 0.17 mmol), and $HNEt_2$ (34 mL). Then $HC\equiv CSiMe_3$ (2.5 mL, 18 mmol) was added in portions (5 × 0.5 mL) every 12 h with stirring. The solvent was removed by oil pump vacuum. The residue was extracted with toluene (3 × 10 mL). The combined extracts were filtered through neutral alumina (5 cm column, packed in toluene). The solvent was removed by oil pump vacuum. The white solid was washed with ethanol (2 × 10 mL) and dried by oil pump vacuum to give **PtC_2SiMe_3** (0.262 g, 0.252 mmol, 75 %), mp 188 °C (capillary, with darkening). DSC: endotherm with T_i, 180.5 °C; T_e, 213.3 °C; T_p, 215.4 °C; T_c, 216.9 °C; T_f, 224.4 °C. TGA: 198.3–244.8 °C (first mass loss regime; 2.4 %), 264.4 °C (second mass loss regime, onset). Calcd for $C_{53}H_{51}F_5P_2PtSi$: C, 59.60; H, 4.81. Found: C, 59.51; H, 4.89.

NMR (δ, $CDCl_3$) [32]: ^1H 7.53 (m, 12H, *o* to P), 7.08 (d, $^3J_{HH}$ = 7.8 Hz, 12H, *m* to P), 2.35 (s, 18H, $C_6H_4CH_3$), –0.53 (s, 9H, $SiCH_3$); $^{13}C\{^1H\}$ 145.8 (dd, $^1J_{CF}$ = 225 Hz, $^2J_{CF}$ = 22 Hz, *o* to Pt), 140.3 (s, *p* to P), 138.2 (non-obscured portion of dm, *m/p* to Pt), 134.5 (virtual t, J_{CP} = 6.3 Hz, *o* to P), 128.2 (virtual t, J_{CP} = 5.5 Hz, *m* to P), 127.8 (virtual t, J_{CP} = 29.9 Hz, *i* to P), 123.8 (br m [36], PtC≡), 118.3 (s, $^2J_{CPt}$ = 225 Hz [33], PtC≡*C*), 21.3 (s, $C_6H_4CH_3$), 0.5 (s, $SiCH_3$); $^{19}F\{^1H\}$ –117.1 (m, $^3J_{FPt}$ = 287 Hz [33], 4F, *o* to Pt), –165.4 (m, $^4J_{FPt}$ = 108 Hz [33], 4F, *m* to Pt), –166.1 (t, $^3J_{FF}$ = 20 Hz, 2F, *p* to Pt); $^{31}P\{^1H\}$ 18.0 (s, $^1J_{PPt}$ = 2716 Hz [33]).

IR (cm^{-1}, powder film), 2964 w, $\nu_{C\equiv C}$ 2046 w, 1602 w, 1498 m, 1455 m, 1262 w, 1189 w, 1100 m, 1050 m, 1019 m, 950 m, 861 m, 834 m, 803 vs, 756 m, 737 m, 710 m. MS [34], 1068 ($[M + H]^+$, 22 %), 970 ($[(C_6F_5)Pt(Ptol_3)_2]^+$, 100 %), 827 ($[Pt(Ptol_3)_2C_2]^+$, 67 %), 803 ($[Pt(Ptol_3)_2]^+$, 97 %), 498 ($[Pt(Ptol_3) - H]^+$, 40 %), and fragments with lower mass due to the loss of C_7H_7.

trans-(C_6F_5)(*p*-$tol_3P)_2PtC\equiv CH$ (PtC_2H)

A Schlenk flask was charged with **PtC_2SiMe_3** (0.050 g, 0.047 mmol), hexanes (14.0 mL), CH_2Cl_2 (6.0 mL), and silica (5.0 g). The mixture was stirred for 24 h. The silica was collected on a glass frit, and washed with CH_2Cl_2 until no more complex eluted (TLC). The solvent was removed from the washings by oil pump vacuum. The residue was chromatographed (silica, 10 × 2 cm column, 30:70 v/v CH_2Cl_2/hexanes). The solvent was removed from the product containing fractions by oil pump vacuum to give **PtC_2H** as white powder (0.036 g, 0.036 mmol, 77 %), dec pt 194 °C (capillary, onset).

NMR (δ, $CDCl_3$) [32]: ^1H 7.57 (m, 12H, *o* to P), 7.10 (d $^3J_{HH}$ = 7.8 Hz, 12H, *m* to P), 2.35 (s, 18H, CH_3), 1.91 (t, $^4J_{HP}$ = 2.1 Hz, $^3J_{HPt}$ = 44 Hz [33], 1H, ≡CH); $^{13}C\{^1H\}$ 145.9 (dd, $^1J_{CF}$ = 220 Hz,

${}^2J_{CF}$ = 20 Hz, *o* to Pt), 140.5 (s, *p* to P), 137.9 (non-obscured portion of dm, *p* to Pt), 134.5 (virtual t, J_{CP} = 6.4 Hz, *o* to P), 128.4 (virtual t, J_{CP} = 5.5 Hz, *m* to P), 127.6 (virtual t, J_{CP} = 29.6 Hz, *i* to P), 99.8 (s, ${}^2J_{CPt}$ = 254 Hz [33], PtC≡*C*), 97.0 (br s [36], PtC≡), 21.3 (s, CH_3); ${}^{19}F\{{}^1H\}$ –117.3 (m, ${}^3J_{FPt}$ = 294 Hz [33], 4F, *o* to Pt), –165.3 (m, ${}^4J_{FPt}$ = 110 Hz [33], 4F, *m* to Pt), –166.2 (t, ${}^3J_{FF}$ = 20 Hz, 2F, *p* to Pt); ${}^{31}P\{{}^1H\}$ 18.4 (s, ${}^1J_{PPt}$ = 2710 Hz [33]).

IR (cm^{-1}, powder film), 3289 w, 3022 w, 2953 w, 2922 w, 2868 w, $\nu_{C\equiv C}$ 1984 w, 1598 m, 1489 vs, 1451 vs, 1397 m, 1355 w, 1312 w, 1274 w, 1189 m, 1100 vs, 1046 s, 1023 m, 950 vs, 803 vs, 797 s, 710 s. MS [34], 995 (M^+, 28 %), 970 ($[(C_6F_5)Pt(Ptol_3)_2]^+$, 83 %), 827 ($[Pt(Ptol_3)_2C_2]^+$, 23 %), 802 ($[Pt(Ptol_3)_2 - H]^+$, 72 %), 497 ($[Pt(Ptol_3) - 2H]^+$, 40 %), and fragments with lower mass due to the loss of C_7H_7.

trans-$(C_6F_5)(Ph_3P)_2PtCl$

A Schlenk flask was charged with $\{(C_6F_5)Pt[S(CH_2CH_2-)_2](\mu\text{-}Cl)\}_2$ (0.340 g, 0.350 mmol) [16], Ph_3P (0.370 g, 1.41 mmol), and CH_2Cl_2 (40 mL). The solution was stirred for 16 h and filtered through a Celite®/decolorizing carbon/glass frit assembly. The solvent was removed by rotary evaporation. The residue was washed with methanol (2 × 10 mL) and dried by oil pump vacuum to give *trans*-$(C_6F_5)(Ph_3P)_2PtCl$ as a white powder (0.550 g, 0.596 mmol, 85 %), dec pt 308–310 °C (capillary, onset). TGA: 294.3 °C (mass loss, onset). Calcd for $C_{42}H_{30}ClF_5P_2Pt$: C, 54.70; H, 3.28. Found: C, 54.23; H, 3.38.

NMR (δ, $CDCl_3$) [32]: ${}^1H$ 7.63 (m, 12H, *o* to P), 7.38 (m, 6H, *p* to P), 7.30 (m, 12H, *m* to P); ${}^{13}C\{{}^1H\}$ 134.5 (virtual t, J_{CP} = 6.2 Hz, *o* to P), 130.6 (s, *p* to P), 129.4 (virtual t, J_{CP} = 28.7 Hz, *i* to P), 128.0 (virtual t, J_{CP} = 5.3 Hz, *m* to P); ${}^{19}F\{{}^1H\}$ –118.6 (m, ${}^3J_{FPt}$ = 397 Hz [33], 2F, *o* to Pt), –164.0 to –164.6 (m, 3F, *m*/*p* to Pt); ${}^{31}P\{{}^1H\}$ 21.5 (s, ${}^1J_{PPt}$ = 2751 Hz [33]).

IR (cm^{-1}, powder film), 3061 w, 1502 m, 1482 w, 1459 m, 1436 s, 1096 s, 1058 m, 1027 w, 953 s, 807 m, 745 s, 706 m, 691 vs. MS [34], 922 (M^+, 4 %), 886 ($[(C_6F_5)Pt(PPh_3)_2]^+$, 100 %), 719 ($[Pt(PPh_3)_2]^+$, 69 %), 455 ($[Pt(PPh_3) - 2H]^+$, 16 %), 377 ($[Pt(PPh_2) - 3H]^+$, 22 %), 262 ($[PPh_3]^+$, 85 %).

trans-$(C_6F_5)((p\text{-}CF_3C_6H_4)_3P)_2PtCl$

A Schlenk flask was charged with $\{(C_6F_5)Pt[S(CH_2CH_2-)_2](\mu\text{-}Cl)\}_2$ (0.972 g, 1.00 mmol), $(p\text{-}CF_3C_6H_4)_3P$ (1.865 g, 4.000 mmol) [38], and CH_2Cl_2 (35 mL). The solution was stirred for 16 h and filtered through a Celite®/decolorizing carbon/glass frit assembly. The solvent was removed by rotary evaporation. The residue was washed with methanol (2 × 10 mL) and dried by oil pump vacuum to give *trans*-$(C_6F_5)((p\text{-}CF_3C_6H_4)_3P)_2PtCl$ as a white powder (2.160 g, 1.624 mmol, 81 %), dec pt 326–328 °C (capillary). Calcd for $C_{48}H_{24}ClF_{23}P_2Pt$: C, 43.34; H, 1.82. Found: C, 42.79; H, 1.78.

NMR (δ, $CDCl_3$) [32]: ${}^1H$ 7.73 (m, 12H, *o* to P), 7.65 (m, 12H, *m* to P); ${}^{13}C\{{}^1H\}$ 134.7 (virtual t, J_{CP} = 6.4 Hz, *o* to P), 133.7 (q, ${}^2J_{CF}$ = 33.4 Hz, *p* to P), 131.8 (virtual t, J_{CP} = 28.5 Hz, *i* to P), 125.4 (m, *m* to P), 123.3 (q, ${}^1J_{CF}$ = 273 Hz, CF_3); ${}^{19}F\{{}^1H\}$ –63.0 (s, 18F, CF_3), –118.3 (m, ${}^3J_{FPt}$ = 370 Hz [33], 2F, *o* to Pt), –160.8 (tm, ${}^3J_{FF}$ = 20 Hz, 1F, *p* to Pt), –162.0 (m, 2F, *m* to Pt); ${}^{31}P\{{}^1H\}$ 21.7 (s, ${}^1J_{PPt}$ = 2828 Hz [33]).

IR (cm^{-1}, powder film), 1610 w, 1502 m, 1463 m, 1401 m, 1324 vs, 1166 s, 1123 vs, 1061 vs, 1015 s, 957 s, 830 s, 807 w, 706 s. MS [34], 1329 ($[M - H]^+$, 3 %), 1294 ($[(C_6F_5)Pt(P(C_6H_4CF_3)_3)_2]^+$, 13 %), 1127 ($[Pt(P(C_6H_4CF_3)_3)_2]^+$, 20 %), 660 ($[Pt(P(C_6H_4CF_3)_3) - H]^+$, 14 %), 466 ($[P(C_6H_4CF_3)_3 - H]^+$, 47 %).

trans-$(C_6F_5)(Ph_3P)_2Pt(C{\equiv}C)_2H$

A Schlenk flask was charged with *trans*-$(C_6F_5)(Ph_3P)_2PtCl$ (0.500 g, 0.542 mmol), CuI (0.030 g, 0.16 mmol), and $HNEt_2$ (125 mL), and cooled to –45 °C. Then $H(C{\equiv}C)_2H$ (8.0 mL, 11.2 mmol, 1.4 M in THF [35]) was added with stirring. The cold bath was allowed to warm to room temperature (ca. 3 h). After an additional 3 h, the solvent was removed by oil pump vacuum. The residue was extracted with toluene (5 × 20 mL). The combined extracts were filtered through neutral alumina (7 cm column, packed in toluene). The solvent was removed by rotary evaporation. The residue was washed with ethanol (20 mL) and dried by oil pump vacuum. The crude product was chromatographed (silica, 10 × 2 cm column, 60:40 v/v CH_2Cl_2/hexanes). The solvent was removed from the product containing fractions by rotary evaporation to give *trans*-$(C_6F_5)(Ph_3P)_2Pt(C{\equiv}C)_2H$ as a white powder (0.174 g, 0.186 mmol, 34 %), dec pt 170 °C (capillary, onset).

NMR (δ, $CDCl_3$) [32]: ^1H 7.61 (m, 12H, *o* to P), 7.38 (m, 6H, *p* to P), 7.31 (m, 12H, *m* to P), 1.43 (t, $^6J_{HP}$ = 1.9 Hz, 1H, ≡CH); $^{13}C\{^1H\}$ 134.4 (virtual t, J_{CP} = 6.4 Hz, *o* to P), 130.6 (s, *p* to P), 130.2 (virtual t, J_{CP} = 29.4 Hz, *i* to P), 128.0 (virtual t, J_{CP} = 5.5 Hz, *m* to P), 97.0 (s [36], PtC≡), 95.2 (s, $^2J_{CPt}$ = 270 Hz [33], PtC≡*C*), 72.1 (s, PtC≡C*C*), 60.0 (s, PtC≡CC≡*C*); $^{31}P\{^1H\}$ 19.7 (s, $^1J_{PPt}$ = 2678 Hz [33]).

IR (cm^{-1}, powder film), 3300 m, 3063 w, 2961 w, 2926 w, 2856 w, $\nu_{C\equiv C}$ 2142 m, 1502 m, 1482 m, 1455 m, 1436 s, 1359 w, 1262 m, 1185 w, 1162 w, 1096 s, 1058 s, 950 s, 791 s, 745 s, 691 vs. MS [34], 936 (M^+, 67 %), 886 ($[(C_6F_5)Pt(PPh_3)_2]^+$, 100 %), 767 ($[Pt(PPh_3)_2C_4]^+$, 19 %), 718 ($[Pt(PPh_3)_2 - H]^+$, 87 %).

trans-(*p*-tol)$(Et_3P)_2PtCl$

A Schlenk flask was charged with (COD)Pt(*p*-tol)(Cl) (0.500 g, 1.16 mmol) [2], Et_3P (0.35 mL, 0.28 g, 2.4 mmol), and CH_2Cl_2 (15 mL) with stirring. After 16 h, the solvent was removed by oil pump vacuum. The residue was chromatographed (alumina, 15 × 1.5 cm column, 43:57 v/v hexanes/CH_2Cl_2). The solvent was removed from the product containing fractions by oil pump vacuum to give *trans*-(*p*-tol)$(Et_3P)_2PtCl$ as a white solid (0.516 g, 0.925 mmol, 80 %), dec pt > 274 °C. Calcd for $C_{19}H_{37}ClP_2Pt$: C, 40.90; H, 6.68. Found: C, 41.92; H, 6.95.

NMR (δ, $CDCl_3$) [32]: ^1H 7.14 (d, 2H, $^3J_{HH}$ = 7.9. Hz, $^3J_{HPt}$ = 34.4 Hz [33], *o* to Pt), 6.68 (d, 2H, $^3J_{HH}$ = 7.7 Hz, *m* to Pt), 2.15 (s, 3H, $C_6H_4CH_3$), 1.64–1.54 (m, 12H, PCH_2), 1.09–0.99 (m, 18H, PCH_2CH_3); $^{13}C\{^1H\}$ 136.6 (s, $^2J_{CPt}$ = 18.6 Hz [33], *o* to Pt), 132.6 (s, *i* to Pt), 130.4 (s, *p* to Pt), 128.6 (s, $^3J_{CPt}$ = 37.7 Hz [33], *m* to Pt), 20.7 (s, $C_6H_4CH_3$), 133.3 (virtual t, J_{CP} = 16.7 Hz, PCH_2), 7.6 (s, PCH_2CH_3); $^{31}P\{^1H\}$ 14.1 (s, $^1J_{PPt}$ = 2570 Hz [33]).

IR (cm^{-1}, powder film), 2966 m, 2933 w, 2912 w, 2877 w, 1484 m, 1455 m, 1412 m, 1378 w, 1256 w, 1100 w, 1034 s, 1019 m, 801 s, 764 vs, 727 vs. MS [34], 558 (M^+, 5 %), 522 ($[M - Cl]^+$, 100 %), 429 ($[(Et_3P)_2Pt]^+$, 80 %).

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