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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 $\{(C_6F_5)Pt[S(CH_2CH_2-)_2](\mu-Cl)\}_2$ and R_3P yield the bis(phosphine) species trans- $(C_6F_5)(R_3P)_2PtCl$ [R = Et (Pt'Cl), Ph, (p-CF₃C₆H₄)₃P; 88–81 %]. Additions of Pt'Cl and H(C=C)_nH (n = 1, 2; HNEt₂, 20 mol % CuI) give Pt'C₂H (37 %, plus Pt'I, 16 %) and Pt'C₄H (88 %). Homocoupling of Pt'C₄H under Hay conditions (O₂, CuCl, TMEDA, acetone) gives Pt'C₈Pt' (85 %), but Pt'C₂H affords only traces of Pt'C₄Pt'. However, condensation of Pt'C₄H and Pt'Cl (HNEt₂, 20 mol % CuI) yields Pt'C₄Pt' (97 %). Hay heterocouplings of Pt'C₄H or trans-(p-tol)(Ph₃P)₂Pt(C=C)₂H (Pt*C₄H) and excess HC=CSiEt₃ give Pt'C₆SiEt₃ (76 %) or Pt*C₆SiEt₃ (89 %). The latter and wet n-Bu₄N⁺ F⁻ react to yield labile Pt*C₆H (60 %). Hay homocouplings of Pt*C₄H and Pt*C₆H give Pt*C₈Pt* (64 %) and Pt*C₁₂Pt* (64 %). Reaction of trans-(C_6F_5)(p-tol₃P)₂PtCl (PtCl) and HC=CH (HNEt₂, 20 mol % CuI) yields only traces of PtC₂H. However, an analogous reaction with HC=CSiMe₃ gives PtC₂SiMe₃ (75 %), which upon treatment with silica yields PtC₂H (77 %). An analogous coupling of trans-(C_6F_5)(Ph₃P)₂PtCl with H(C=C)₂H gives trans-(C_6F_5)(Ph₃P)₂Pt(C=C)₂H (34 %). Advantages and disadvantages of the various trans-(Ar)(R₃P)₂Pt 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 $Pt(C\equiv C)_n Pt$ 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=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-(C₆F₅)(Ar₂P(CH₂)_mPAr₂)Pt(C=C)_nPt(Ar₂P(CH₂)_mPAr₂)(C₆F₅) (V) [3–5]. These feature

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Fig. 1 Representative assemblies based on Pt(C=C), Pt 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*-(C₆F₅)(*p*tol₃P)₂Pt (**Pt**), *trans*-(*p*-tol)(*p*-tol₃P)₂Pt (**Pt''**), and *trans*-(Cl)(*p*-tol₃P)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-(C₆F₅)(Et₃P)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_xPt'**; n/x = 3/6, 4/8, 6/12) were prepared by four-fold substitutions of the triarylphosphine complexes *trans,trans*- $(C_6F_5)(p-tol_3P)_2Pt(C\equiv C)_nPt(Pp-tol_3)_2(C_6F_5)$ (**PtC_xPt**) with excesses of the more basic phosphine Et₃P [1,6b]. Substitutions of Ph₃P ligands by Bu₃P ligands have been reported with related PtC=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*-tol₃P homologs **PtC_xPt**? 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=C)₂H and 20 mol % CuI in the basic solvent HNEt₂. The former reaction was slower, and required heating under reflux. As shown in Scheme 1, workups gave the ethynyl and butadiynyl complexes **Pt'C₂H** and **Pt'C₄H** 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=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 $Pt'C_2H$ and $Pt'C_4H$, and most other isolable species below, were characterized by NMR (¹H, ¹³C, ³¹P) and IR spectroscopy, mass spectrometry, and microanalysis, as summarized in the experimental section. All ³¹P NMR spectra exhibited ³¹P-¹⁹⁵Pt couplings, the magnitudes of which (2953–2388 Hz) require *trans* P-Pt-P linkages [21]. The spectroscopic properties of $Pt'C_2H$ and $Pt'C_4H$ were similar to the *p*-tol₃P analogs PtC_2H (below) and PtC_4H [1].

The feasibility of extending of the sp carbon chain was investigated. In accord with a protocol used for PtC_4H [1], an acetone solution of $Pt'C_4H$ and a 15-fold excess of HC=CSiEt₃ was treated with

 O_2 , CuCl, and TMEDA (Hay conditions; Scheme 1) [22]. Workup gave the desired cross-coupling product, the silylated hexatriynyl complex $Pt'C_6SiEt_3$, in 76 % yield.

Diplatinum complexes $Pt'C_xPt'$ were sought. As shown in Scheme 2, an acetone solution of $Pt'C_2H$ was subjected to Hay homocoupling conditions (O₂, CuCl/TMEDA). However, only traces of the target complex $Pt'C_4Pt'$ were obtained. In contrast, an analogous reaction of $Pt'C_4H$ (presumably a stronger Brønsted acid) gave the octatetraynediyl complex $Pt'C_8Pt'$ as a yellow powder in 85 % yield. An alternative approach to $Pt'C_4Pt'$ was investigated. As also shown in Scheme 2, Pt'Cl and $Pt'C_4H$ were combined under conditions similar to those used for the heterocoupling of Pt'Cl and alkynes in Scheme 1. Workup gave $Pt'C_4Pt'$ 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 ¹⁹⁵Pt{¹H} NMR spectrum of **Pt'C₄Pt'** 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 ¹⁹F{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 ¹³C NMR chemical shifts and coupling constants associated with the sp carbon atoms followed established trends [1–6].

trans-(p-tol)(Ph₃P)₂Pt (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 $H(C\equiv C)_2H$ to give Pt^*C_4H [23]. A subsequent reaction with $HC\equiv CSiEt_3$ under the conditions used for $Pt'C_4H$ in Scheme 1 afforded the silylated hexatriynyl complex $Pt^*C_6SiEt_3$ in 89 % yield after workup. When $Pt^*C_6SiEt_3$ was treated with wet fluoride ion, protodesilylation occurred to give the hexatriynyl complex Pt^*C_6H , which could be isolated in 60 % yield. Like all platinum hexatriynyl complexes [1,2], Pt^*C_6H 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)*(Ph₃P)₂Pt (Pt*) end-groups.

As shown in Scheme 4, oxidative homocouplings of Pt^*C_4H and Pt^*C_6H were attempted under conditions analogous to those used for $Pt'C_4H$ in Scheme 2. The latter reaction could be conducted at a slightly lower temperature (45 vs. 60 °C). Workups gave $Pt^*C_8Pt^*$ and $Pt^*C_{12}Pt^*$ in 64 % yields. However, these complexes showed much poorer solubilities. With effort, the ¹³C NMR signals of the C=C carbon atoms of $Pt^*C_8Pt^*$ could be detected, but the ¹⁹⁵Pt couplings that are usually observed were not resolved. The solubility of $Pt^*C_{12}Pt^*$ was distinctly lower, and no C=C ¹³C signals were detected with saturated samples.



Scheme 4 Syntheses of diplatinum complexes with *trans-(p-tol)*(Ph₃P)₂Pt (Pt*) end-groups.

In view of this trend, the analogous p-tol₃P 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''C₂₈Pt''** (**II**, Fig. 1). However, crystals of **Pt*C₈Pt*** could be obtained, and the crystal structure was reported with those of the p-tol₃P 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 **PtC₂H** 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=CSiMe₃ gave **PtC₂SiMe₃** in 75 % yield after workup. This complex could not be protodesilylated using common fluoride ion sources, such as that employed for **Pt*C₆SiEt₃** 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=CSiR₃ species has also been found to be problematic [25]. However, when solutions of **PtC₂SiMe₃** were stirred over silica gel for 24 h, **PtC₂H** could be isolated in 77 % yield.

The second sequence in Scheme 5 was undertaken to assay other C_6F_5 /phosphine ligand endgroup combinations. Thus, the diplatinum bis(tetrahydrothiophene) complex was treated with Ph₃P and the less basic triarylphosphine (*p*-CF₃C₆H₄)₃P. Workups gave the corresponding bis(phosphine) chloride complexes *trans*-(C_6F_5)(Ar₃P)₂PtCl in 85–81 % yields. Reactions with H(C=C)₂H were then investigated under conditions analogous to those used for **Pt'Cl** in Scheme 1. In the case of the Ph₃P complex, conversions were usually incomplete. However, chromatography gave the butadiynyl complex *trans*-(C_6F_5)(Ph₃P)₂Pt(C=C)₂H in 34 % yield. In the case of the (*p*-CF₃C₆H₄)₃P complex, only the free phosphine and the corresponding oxide were isolated. Hence, when the triarylphosphine ligands become too electron-deficient, heterocouplings with $H(C=C)_2H$ 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 $Pt'C_4H$ 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 $Pt'C_4H$, *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)*(Et₃P)₂PtCl, was obtained in 92 % yield. Thus, endgroups featuring all possible combinations of four aryl and phosphine ligands, $C_6F_5/p-tol_3P$ (**Pt**), C_6F_5/Et_3P (**Pt'**), *p-tol/p-tol*₃P (**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 $(p-\text{tol}_3P)_2\text{PtCl}_2$ [heterocoupling with Me₃Sn(C=C)₂SiMe₃], 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 penta-fluorophenyl 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)(Ph₃P)₂Pt(C=C)₃Pt(PPh₃)₂(Ph), which has been structurally characterized and features an endgroup 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)(R₃P)₂Pt-C=CPt(PR₃)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-Bu₄N⁺ F⁻ (trihydrate, Lancaster), dissolved in THF containing 5 wt % H₂O to give a 1.0 M solution; CuCl and CuI (2 × Aldrich, 99.99 %), HC=CSiEt₃ (Aldrich), HC=CSiMe₃ (Acros), Et₃P (Strem, 10 wt % in hexane), and HC=CH, used as received.

trans-(C₆F₅)(Et₃P)₂PtCI (Pt'CI) [18,19]

A Schlenk flask was charged with { $(C_6F_5)Pt[S(CH_2CH_2-)_2](\mu-Cl)$ } (0.972 g, 1.00 mmol) [16], Et₃P (0.65 mL, 4.4 mmol), and CH₂Cl₂ (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 CH₂Cl₂/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 C₁₈H₃₀ClF₅P₂Pt: C, 34.11; H, 4.77. Found: C, 34.27; H, 4.68.

NMR (δ, CDCl₃) [32]: ¹H 1.63 (m, 12H, CH₂), 1.04 (m, 18H, CH₃); ¹³C{¹H} 146.2 (dd, ¹ J_{CF} = 225 Hz, ² J_{CF} = 23 Hz, *o* to Pt), 136.7 (dm, ¹ J_{CF} = 240 Hz, *m/p* to Pt), 106.1 (br m, *i* to Pt), 13.7 (virtual t, J_{CP} = 17.0 Hz, ² J_{CPt} = 33 Hz [33], CH₂), 7.7 (s, ³ J_{CPt} = 24 Hz [33], CH₃); ¹⁹F{¹H} –117.3 (m, ³ J_{FPt} = 465 Hz [33], 2F, *o* to Pt), -161.5 (tm, ³ J_{FF} = 20 Hz, 1F, *p* to Pt), -162.9 (m, ⁴ J_{FPt} = 103 Hz [33], 2F, *m* to Pt); ³¹P{¹H} 15.5 (s, ¹ J_{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-(C₆F₅)(Et₃P)₂PtC=CH (Pt'C₂H)

A Schlenk flask was charged with **Pt'Cl** (0.317 g, 0.500 mmol), CuI (0.020 g, 0.106 mmol), and HNEt₂ (40 mL), and fitted with a condenser. The mixture was refluxed and aspirated with a stream of HC=CH. After 22 h, the solvent was removed by oil pump vacuum. The residue was chromatographed (silica, $20 \times 2 \text{ cm}$ column, $30:70 \text{ v/v} \text{ CH}_2\text{Cl}_2$ /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).

 $\begin{array}{l} Data \, for \, \mathbf{\dot{Pt}'C_2H}: \, \mathrm{NMR}\;(\delta, \mathrm{CDCl_3})\; [32]: \, ^{1}\mathrm{H}\; 2.20\;(\mathrm{t}, \, ^{4}J_{\mathrm{HP}}=2.1\;\mathrm{Hz}, \, ^{3}J_{\mathrm{HPt}}=46\;\mathrm{Hz}\; [33], \,\mathrm{1H}, \equiv \mathrm{CH}),\\ 1.73\;(\mathrm{m},\; 12\;\mathrm{H},\,\mathrm{CH}_2),\; 1.03\;(\mathrm{m},\; 18\mathrm{H},\,\mathrm{CH}_3); \, ^{13}\mathrm{C}\{^{1}\mathrm{H}\}\; 146.9\;(\mathrm{dd},\, ^{1}J_{\mathrm{CF}}=224\;\mathrm{Hz},\, ^{2}J_{\mathrm{CF}}=21\;\mathrm{Hz},\, o\;\mathrm{to}\;\mathrm{Pt}),\\ 136.8\;(\mathrm{dm},\, ^{1}J_{\mathrm{CF}}=245\;\mathrm{Hz},\, p\;\mathrm{to}\;\mathrm{Pt}),\; 120.6\;(\mathrm{t},\, ^{2}J_{\mathrm{CF}}=53\;\mathrm{Hz},\, i\;\mathrm{to}\;\mathrm{Pt}),\; 99.1\;(\mathrm{s},\, ^{1}J_{\mathrm{CPt}}=962\;\mathrm{Hz}\; [33],\,\mathrm{PtC}\equiv),\\ 92.8\;(\mathrm{s},\, ^{2}J_{\mathrm{CPt}}=271\;\mathrm{Hz}\; [33],\,\mathrm{PtC}\equiv C),\; 15.4\;(\mathrm{virtual}\;\mathrm{t},\, J_{\mathrm{CP}}=17.7\;\mathrm{Hz},\,\mathrm{CH}_2),\; 7.8\;(\mathrm{s},\, ^{3}J_{\mathrm{CPt}}=25\;\mathrm{Hz}\; [33],\\ \mathrm{CH}_3);\; ^{19}\mathrm{F}\{^{1}\mathrm{H}\}\; -117.3\;(\mathrm{m},\, ^{3}J_{\mathrm{FPt}}=294\;\mathrm{Hz}\; [33],\; 4\mathrm{F},\, o\;\mathrm{to}\;\mathrm{Pt}),\; -165.3\;(\mathrm{m},\, ^{4}J_{\mathrm{FPt}}=110\;\mathrm{Hz}\; [33],\; 4\mathrm{F},\, m\;\mathrm{to}\;\mathrm{Pt}),\\ \mathrm{Pt},\; -166.2\;(\mathrm{t},\, ^{3}J_{\mathrm{FF}}=20\;\mathrm{Hz},\; 2\mathrm{F},\, p\;\mathrm{to}\;\mathrm{Pt});\; ^{31}\mathrm{P}\{^{1}\mathrm{H}\}\; 12.4\;(\mathrm{s},\, ^{1}J_{\mathrm{PPt}}=2441\;\mathrm{Hz}\; [33]).\\ \end{array}$

IR (cm⁻¹, powder film), 3293 w, 2968 w, 2937 w, 2880 w, $v_{C=C}$ 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, CDCl₃) [32]: ¹H 1.80 (m, 12H, CH₂), 1.02 (m, 18H, CH₃); ¹³C{¹H} 145.6 (dd, ¹ $J_{CF} = 224$ Hz, ² $J_{CF} = 23$ Hz, *o* to Pt), 137.0 (dm, ¹ $J_{CF} = 250$ Hz, *m/p* to Pt), 111.3 (t, ¹ $J_{CF} = 45$ Hz, *i* to Pt), 15.4 (virtual t, $J_{CP} = 17.6$ Hz, ² $J_{CPt} = 17$ Hz [33], CH₂), 7.6 (s, ³ $J_{CPt} = 24$ Hz [33], CH₃); ¹⁹F{¹H} -117.9 (m, ³ $J_{FPt} = 443$ Hz [33], 2F, *o* to Pt), -160.9 (t, ³ $J_{FF} = 20$ Hz, 1F, *p* to Pt), -162.5 (m, 2F, *m* to Pt); ³¹P{¹H} 9.9 (s, ¹ $J_{PPt} = 2428$ 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 ($[Pt(PEt_3)_2I]^+$, 46 %), 429 ($[Pt(PEt_3)_2 - 2H]^+$, 54 %).

$trans-(C_6F_5)(Et_3P)_2Pt(C=C)_2H(Pt'C_4H)$

A Schlenk flask was charged with **Pt'Cl** (0.158 g, 0.250 mmol), CuI (0.010 g, 0.053 mmol), and HNEt₂ (25 mL), and cooled to -45 °C. Then H(C=C)₂H (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, $30:70 \text{ v/v } \text{CH}_2\text{Cl}_2/\text{hexanes}$). The solvent was removed from the product containing fractions by oil pump vacuum to give **Pt'C₄H** 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 C₂₂H₃₁F₅P₂Pt: C, 40.81; H, 4.83. Found: C, 40.75; H, 5.00.

NMR (δ , CDCl₃) [32]: ¹H 1.83 (t, ⁶J_{HP} = 1.0 Hz, ⁵J_{HPt} = 9.9 Hz [33], 1H, =CH), 1.73 (m, 12H, CH₂), 1.05 (m, 18H, CH₃); ¹³C{¹H} 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), 59.3 (s, PtC=CC=C), 15.5 (virtual t, J_{CP} = 17.6 Hz, CH₂), 7.8 (s, ³J_{CPt} = 25 Hz [33], CH₃); ¹⁹F{¹H} -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); ³¹P{¹H} 13.1 (s, ¹J_{PPt} = 2400 Hz [33]).

IR (cm⁻¹, powder film), 3312 w, 2968 w, 2937 w, 2914 w, 2880 w, $v_{C=C}$ 2146 m, 1502 m, 1447 s, 1417 m, 1258 m, 1100 m, 1034 vs, 950 vs, 803 s, 762 vs, 733 vs. UV-vis [mm (ϵ , M⁻¹ cm⁻¹), CH₂Cl₂, 1.25 × 10⁻⁴ M], 261 (7500), 275 (4800), 299 (6200). MS [34], 647 (M⁺, 42 %), 598 ([(C₆F₅)Pt(PEt₃)₂]⁺, 40 %), 480 ([(C₆F₅)Pt(PEt₃)]⁺ and [Pt(PEt₃)₂C₄H]⁺, 35 %), 429 ([Pt(PEt₃)₂ - 2H]⁺, 100 %), and fragments with lower mass due to the loss of C₂H₅.

trans- $(C_6F_5)(Et_3P)_2Pt(C=C)_3SiEt_3$ (Pt'C₆SiEt₃)

A three-necked flask was charged with $Pt'C_4H$ (0.174 g, 0.269 mmol), acetone (15 mL), and $HC\equiv CSiEt_3$ (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 O₂ 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/CH₂Cl₂). The solvent was removed from the product containing fractions by oil pump vacuum to give Pt'C₆SiEt₃ as a pale yellow solid (0.161 g, 0.204 mmol, 76 %).

NMR (δ , CDCl₃): ¹H 1.74–1.69 (m, 12H, PCH₂), 1.07–0.98 (m, 18H, PCH₂CH₃), 0.95 (t, 9H, ³J_{HH} = 7.9 Hz, SiCH₂CH₃), 0.57 (q, 6H, ³J_{HH} = 7.9 Hz, SiCH₂); ³¹P{¹H} 13.1 (s, ¹J_{PPt} = 2388 Hz [33]).

IR (cm⁻¹, powder film), $v_{C=C}$ 2150 m and 2011 m. MS [34], 785 (M⁺, 70 %), 598 ([M - C₆SiEt₃]⁺, 80 %), 429 ([M - C₆SiEt₃ - C₆F₅]⁺, 100 %).

trans, trans- $(C_6F_5)(Et_3P)_2Pt(C=C)_4Pt(PEt_3)_2(C_6F_5)$ (Pt'C₈Pt')

A three-necked flask was charged with $Pt'C_4H$ (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 O₂ 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'C₈Pt' (0.083 g, 0.064 mmol, 85 %), dec pt 189–192 °C.

NMR (δ , CDCl₃) [32]: ¹H 1.72 (m, 24H, CH₂), 1.04 (m, 36H, CH₃); ¹³C{¹H} 146.9 (dd, ¹*J*_{CF} = 226 Hz, ²*J*_{CF} = 22 Hz, *o* to Pt), 137.1 (dm, ¹*J*_{CF} = 245 Hz, *m/p* to Pt), 103.4 (s, PtC≡ [36]), 91.1 (s, ²*J*_{CPt} = 285 Hz [33], PtC≡C), 63.9 (s, PtC≡CC), 57.6 (s, PtC≡CC=C), 15.5 (virtual t, *J*_{CP} = 17.5 Hz, CH₂), 7.7 (s, ³*J*_{CPt} = 24 Hz [33], CH₃); ¹⁹F{¹H} -116.4 (m, ³*J*_{FPt} = 328 Hz, 4F, *o* to Pt), -161.0 (t, ³*J*_{FF} = 20 Hz, 2F, *p* to Pt), -162.8 (m, ⁴*J*_{FPt} = 107 Hz [33], 4F, *m* to Pt); ³¹P{¹H} 13.2 (s, ¹*J*_{PPt} = 2393 Hz [33]).

IR (cm⁻¹, powder film), 2970 w, 2937 w, 2879 w, $\nu_{C=C}$ 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), CH₂Cl₂, 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 ([(C₆F₅)Pt(PEt₃)₂]⁺, 28 %).

trans,trans-(C_6F_5)(Et₃P)₂Pt(C=C)₂Pt(PEt₃)₂(C_6F_5) (Pt'C₄Pt')

A Schlenk flask was charged with **Pt'Cl** (0.128 g, 0.202 mmol), **Pt'C₄H** (0.131 g, 0.202 mmol), CuI (0.010 g, 0.053 mmol), and HNEt₂ (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'C₄Pt'** 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 C₄₀H₆₀F₁₀P₄Pt₂: C, 38.59; H, 4.86. Found: C, 38.39; H, 5.09.

NMR (δ , CDCl₃) [32]: ¹H 1.75 (m, 24H, CH₂), 1.04 (m, 36H, CH₃); ¹³C{¹H} 147.4 (dd, ¹*J*_{CF} = 223 Hz, ²*J*_{CF} = 22 Hz, *o* to Pt), 137.1 (dm, ¹*J*_{CF} = 250 Hz, *m/p* to Pt), 121.4 (s, ²*J*_{CF} = 54.1 Hz, ¹*J*_{CPt} = 670 Hz [33], *i* to Pt), 95.6 (s, ²*J*_{CPt} = 280 Hz [33], ³*J*_{CP} = 32 Hz [33], PtC=C), 90.3 (s, ¹*J*_{CPt} = 989 Hz [33], PtC=), 16.0 (virtual t, *J*_{CP} = 17.3 Hz, ²*J*_{CPt} = 36 Hz [33], CH₂), 8.2 (s, ³*J*_{CPt} = 24 Hz [33], CH₃); ¹⁹F{¹H} -116.1 (m, ³*J*_{FPt} = 328 Hz [33], 4F, *o* to Pt), -162.1 (t, ³*J*_{FF} = 20 Hz, 2F, *p* to Pt), -163.5 (m, ⁴*J*_{FPt} = 108 Hz [33], 4F *m* to Pt); ³¹P{¹H} 12.5 (s, ¹*J*_{PPt} = 2447 Hz [33]); ¹⁹⁵Pt{¹H} -3058 (ttt, ¹*J*_{PPt} = 2450 Hz, ³*J*_{FPt} = 328 Hz, ⁴*J*_{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), CH₂Cl₂, 1.25 × 10⁻⁴ M), 276 (18000), 312 (16 600), 333 (15 600). MS [34], 1244 (M⁺, 46 %), 764 ([(C₆F₅)Pt(PEt₃)₃C₄]⁺, 100 %), 598 ([(C₆F₅)Pt(PEt₃)₂]⁺, 12 %), 429 ([Pt(PEt₃)₂ – 2H]⁺, 26 %), and fragments with lower mass due to the loss of C₂H₅.

trans-(p-tol)(Ph3P)2Pt(C=C)3SiEt3 (Pt*C6SiEt3)

A three-necked flask was charged with $Pt*C_4H$ (0.120 g, 0.139 mmol) [23], acetone (25 mL), and HC=CSiEt₃ (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 O₂ 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 , CDCl₃) [32]: ¹H 7.46–7.21 (m, 30H, C₆H₅), 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, C₆H₄CH₃), 0.91 (t, ³J_{HH} = 7.8 Hz, 9H, CH₂CH₃), 0.52 (q, ³J_{HH} = 7.8 Hz, 6H, SiCH₂); ¹³C{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=CC), 55.7 (s, PtC=CC=C), 21.1 (s, CH₃/*p* to Pt), 8.1 (s, CH₂CH₃), 5.1 (s, CH₂CH₃); ³¹P{¹H} 21.2 (s, ¹J_{PPt} = 2953 Hz [33]).

IR (cm⁻¹, CH₂Cl₂), $v_{C=C}$ 2145 s and 2009 m.

trans-(p-tol)(Ph₃P)₂Pt(C=C)₃H (Pt*C₆H)

A Schlenk flask was charged with $Pt^*C_6SiEt_3$ (0.125 g, 0.125 mmol) and THF (60 mL), and *n*-Bu₄N⁺ F⁻ (1.0 M in THF/5 wt % H₂O; 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 CH₂Cl₂ (3 × 30 mL). The combined extracts were dried (MgSO₄). 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 , CDCl₃) [32]: ¹H 7.48–7.23 (m, 30H, C₆H₅), 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, CH₃), 1.81 (s, 1H, =CH); ³¹P{¹H} 21.1 (s, ¹J_{PPt} = 2941 Hz [33]).

trans,trans-(p-tol)(Ph₃P)₂Pt(C=C)₄Pt(PPh₃)₂(p-tol) (Pt*C₈Pt*)

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 O₂ 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 $C_{94}H_{74}P_4Pt_5$: C, 65.94; H, 4.44. Found: C, 65.73; H, 4.34.

NMR (δ , CDCl₃) [32]: ¹H 7.46–7.18 (m, 60H, C₆H₅), 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, CH₃); ¹³C{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=CC), 58.4 (s, PtC=CC=C), 21.5 (s, CH₃); ³¹P{¹H} 21.0 (s, ¹ $J_{PPt} = 2953$ Hz [33]). IR (cm⁻¹, CH₂Cl₂) $v_{C=C}$ 2139 s and 1984 m. MS [34], 1717 (M⁺, 30 %), 810 ([(tol)(Ph₃P)₂Pt]⁺, 80 %), 719 ([(Ph₃P)₂Pt]⁺, 100 %); no other peaks above 400 of >3 %.

trans,trans-(p-tol)(Ph₃P)₂Pt(C=C)₆Pt(PPh₃)₂(p-tol) (Pt*C₁₂Pt*)

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 O₂ 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 , CDCl₃) [32,37]: ¹H 7.44–7.21 (m, 60H, C₆H₅), 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, CH₃); ³¹P{¹H} 21.0 (s, ¹J_{PPt} = 2730 Hz [33]).

MS [34], 1767 (M⁺, 30 %), 810 ([(tol)(Ph₃P)₂Pt]⁺, 80 %), 719 ([(Ph₃P)₂Pt]⁺, 100 %); no other peaks above 400 of >3 %.

trans-(C₆F₅)(p-tol₃P)₂PtC=CSiMe₃ (PtC₂SiMe₃)

A Schlenk flask was charged with **PtCl** (0.338 g, 0.336 mmol) [1], CuI (0.032 g, 0.17 mmol), and HNEt₂ (34 mL). Then HC=CSiMe₃ (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 **PtC₂SiMe₃** (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 C₅₃H₅₁F₅P₂PtSi: C, 59.60; H, 4.81. Found: C, 59.51; H, 4.89.

NMR (δ , CDCl₃) [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, C₆H₄CH₃), -0.53 (s, 9H, SiCH₃); ¹³C{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, C₆H₄CH₃), 0.5 (s, SiCH₃); ¹⁹F{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); ³¹P{¹H} 18.0 (s, ¹J_{PPt} = 2716 Hz [33]).

IR (cm⁻¹, powder film), 2964 w, $v_{C=C}$ 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 ([(C₆F₅)Pt(Ptol₃)₂]⁺, 100 %), 827 ([Pt(Ptol₃)₂C₂]⁺, 67 %), 803 ([Pt(Ptol₃)₂]⁺, 97 %), 498 ([Pt(Ptol₃) – H]⁺, 40 %), and fragments with lower mass due to the loss of C₇H₇.

trans-(C₆F₅)(p-tol₃P)₂PtC=CH (PtC₂H)

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 , CDCl₃) [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, CH₃), 1.91 (t, ⁴J_{HP} = 2.1 Hz, ³J_{HPt} = 44 Hz [33], 1H, =CH); ¹³C{¹H} 145.9 (dd, ¹J_{CF} = 220 Hz,

 ${}^{2}J_{CF}$ = 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, ${}^{2}J_{CPt}$ = 254 Hz [33], PtC≡C), 97.0 (br s [36], PtC≡), 21.3 (s, CH₃); ${}^{19}F{}^{1}H{}^{1}$ -117.3 (m, ${}^{3}J_{FPt}$ = 294 Hz [33], 4F, *o* to Pt), -165.3 (m, ${}^{4}J_{FPt}$ = 110 Hz [33], 4F, *m* to Pt), -166.2 (t, ${}^{3}J_{FF}$ = 20 Hz, 2F, *p* to Pt); ${}^{31}P{}^{1}H{}^{1}$ 18.4 (s, ${}^{1}J_{PPt}$ = 2710 Hz [33]).

IR (cm⁻¹, powder film), 3289 w, 3022 w, 2953 w, 2922 w, 2868 w, $v_{C=C}$ 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 ([(C₆F₅)Pt(Ptol₃)₂]⁺, 83 %), 827 ([Pt(Ptol₃)₂C₂]⁺, 23 %), 802 ([Pt(Ptol₃)₂ - H]⁺, 72 %), 497 ([Pt(Ptol₃) - 2H]⁺, 40 %), and fragments with lower mass due to the loss of C₇H₇.

trans-(C₆F₅)(Ph₃P)₂PtCl

A Schlenk flask was charged with $\{(C_6F_5)Pt[S(CH_2CH_2-)_2](\mu-Cl)\}_2$ (0.340 g, 0.350 mmol) [16], Ph₃P (0.370 g, 1.41 mmol), and CH₂Cl₂ (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, CDCl₃) [32]: ¹H 7.63 (m, 12H, *o* to P), 7.38 (m, 6H, *p* to P), 7.30 (m, 12H, *m* to P); ¹³C{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); ¹⁹F{¹H} –118.6 (m, ³ $J_{FPt} = 397$ Hz [33], 2F, *o* to Pt), –164.0 to –164.6 (m, 3F, *m/p* to Pt); ³¹P{¹H} 21.5 (s, ¹ $J_{PPt} = 2751$ 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 ([(C₆F₅)Pt(PPh₃)₂]⁺, 100 %), 719 ([Pt(PPh₃)₂]⁺, 69 %), 455 ([Pt(PPh₃) – 2H]⁺, 16 %), 377 ([Pt(PPh₂) – 3H]⁺, 22 %), 262 ([PPh₃]⁺, 85 %).

trans-(C₆F₅)((p-CF₃C₆H₄)₃P)₂PtCl

A Schlenk flask was charged with $\{(C_6F_5)Pt[S(CH_2CH_2-)_2](\mu-Cl)\}_2$ (0.972 g, 1.00 mmol), $(p-CF_3C_6H_4)_3P$ (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*-(C₆F₅)((*p*-CF₃C₆H₄)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 , CDCl₃) [32]: ¹H 7.73 (m, 12H, *o* to P), 7.65 (m, 12H, *m* to P); ¹³C{¹H} 134.7 (virtual t, $J_{CP} = 6.4$ Hz, *o* to P), 133.7 (q, ² $J_{CF} = 33.4$ 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, ¹ $J_{CF} = 273$ Hz, CF₃); ¹⁹F{¹H} -63.0 (s, 18F, CF₃), -118.3 (m, ³ $J_{FPt} = 370$ Hz [33], 2F, *o* to Pt), -160.8 (tm, ³ $J_{FF} = 20$ Hz, 1F, *p* to Pt), -162.0 (m, 2F, *m* to Pt); ³¹P{¹H} 21.7 (s, ¹ $J_{PPt} = 2828$ 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 ([(C₆F₅)Pt(P(C₆H₄CF₃)₃)₂]⁺, 13 %), 1127 ([Pt(P(C₆H₄CF₃)₃)₂]⁺, 20 %), 660 ([Pt(P(C₆H₄CF₃)₃) – H]⁺, 14 %), 466 ([P(C₆H₄CF₃)₃ – H]⁺, 47 %).

trans-(C₆F₅)(Ph₃P)₂Pt(C≡C)₂H

A Schlenk flask was charged with *trans*-(C_6F_5)(Ph₃P)₂PtCl (0.500 g, 0.542 mmol), CuI (0.030 g, 0.16 mmol), and HNEt₂ (125 mL), and cooled to -45 °C. Then H(C=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 CH₂Cl₂/hexanes). The solvent was removed from the product containing fractions by rotary evaporation to give *trans*-(C_6F_5)(Ph₃P)₂Pt(C=C)₂H as a white powder (0.174 g, 0.186 mmol, 34 %), dec pt 170 °C (capillary, onset).

NMR (δ , CDCl₃) [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); ¹³C{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=CC), 60.0 (s, PtC=CC=C); ³¹P{¹H} 19.7 (s, ¹J_{PPt} = 2678 Hz [33]).

IR (cm⁻¹, powder film), 3300 m, 3063 w, 2961 w, 2926 w, 2856 w, $v_{C=C}$ 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 ([(C₆F₅)Pt(PPh₃)₂]⁺, 100 %), 767 ([Pt(PPh₃)₂C₄]⁺, 19 %), 718 ([Pt(PPh₃)₂ - H]⁺, 87 %).

trans-(p-tol)(Et₃P)₂PtCl

A Schlenk flask was charged with (COD)Pt(*p*-tol)(Cl) (0.500 g, 1.16 mmol) [2], Et₃P (0.35 mL, 0.28 g, 2.4 mmol), and CH₂Cl₂ (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/CH₂Cl₂). The solvent was removed from the product containing fractions by oil pump vacuum to give *trans*-(*p*-tol)(Et₃P)₂PtCl as a white solid (0.516 g, 0.925 mmol, 80 %), dec pt > 274 °C. Calcd for C₁₉H₃₇ClP₂Pt: C, 40.90; H, 6.68. Found: C, 41.92; H, 6.95.

NMR (δ , CDCl₃) [32]: ¹H 7.14 (d, 2H, ³ J_{HH} = 7.9. Hz, ³ J_{HPt} = 34.4 Hz [33], *o* to Pt), 6.68 (d, 2H, ³ J_{HH} = 7.7 Hz, *m* to Pt), 2.15 (s, 3H, C₆H₄CH₃), 1.64–1.54 (m, 12H, PCH₂), 1.09–0.99 (m, 18H, PCH₂CH₃); ¹³C{¹H} 136.6 (s, ² J_{CPt} = 18.6 Hz [33], *o* to Pt), 132.6 (s, *i* to Pt), 130.4 (s, *p* to Pt), 128.6 (s, ³ J_{CPt} = 37.7 Hz [33], *m* to Pt), 20.7 (s, C₆H₄CH₃), 133.3 (virtual t, J_{CP} = 16.7 Hz, PCH₂), 7.6 (s, PCH₂CH₃); ³¹P{¹H} 14.1 (s, ¹ J_{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 ([(Et₃P)₂Pt]⁺, 80 %).

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