# Naphthyl-Based PCP Platinum Complexes. Nucleophilic Activation of Coordinated CO and Synthesis of a Pt(II) Formyl Complex

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*Received January 23, 2007*

A series of naphthyl-based PCP Pt(II) complexes was synthesized and characterized. A single-crystal X-ray study of (PCP)PtCl (**2**) reveals stacking of the aromatic units between each pair of molecules of **2**. Chloride abstraction from **2** under nitrogen atmosphere leads to formation of the unsaturated cationic complex $[(PCP)Pt]^+BF_4^-$ (**3**), with the metal center being stabilized by the counteranion (**3a**) or by the solvent (**3b**). Abstraction of the chloride ligand from **2** under CO atmosphere leads to formation of the cationic carbonyl complex $[(PCP)Pt(CO)]^+BF_4^-$ (**4**), containing an electrophilic carbonyl ligand. The latter is attacked by nucleophiles ($MeO^-$ and $H^-$) to give the platinum carbomethoxy complex **5** and a rare platinum formyl complex, **6**. Stabilized by the bulky bis-chelating tridentate pincer-type system, the formyl complex **6** was isolated and characterized. Complex **6** is more stable than the previously reported platinum formyls. At room temperature complex **6** is slowly converted (during days) into a hydride complex, **7**.

## Introduction

Nucleophilic attack on coordinated carbon monoxide is well known for various nucleophiles.[1] Of particular interest is hydride nucleophilic addition, since it can lead to transition-metal formyl complexes,[1] which have been proposed as intermediates in the Fischer−Tropsch reaction.[2] While stable formyl complexes have been described for several group VIII and group IX late transition metals,[3] only two reports of platinum formyl complexes appeared recently.[4] In the first example, the anionic Pt(II) formyl complex $[Na][(\eta^2\text{-Tp}')Pt(Me)(C(=O)H)]$ (Tp′ = hydridotris(3,5-dimethylpyrazolyl)borate) was formed by hydride attack on the carbonyl ligand of Tp′Pt(Me)(CO). Protonation of the metal center at 193 K resulted in the Pt(IV) formyl hydride complex Tp′Pt(Me)[(C(O)H)]H.[4a] The second example describes a dinuclear platinum formyl complex, formed upon treatment of a dinuclear platinum carbonyl complex with a borohydride reagent.[4b]

Pincer-type complexes constitute a family of compounds that have attracted much recent interest. They play important roles in organometallic reactions and mechanisms, in catalysis, and in the design of new materials.[5] The high thermal stability of such complexes, particularly those based on an aromatic backbone, permits their use as catalysts at elevated temperatures in various catalytic applications.[5] Bulky bis-chelating pincer-type ligands are effective in the stabilization of highly unsaturated cationic complexes and in the stabilization of reactive species.[5,6a]

We have recently prepared naphthyl-based PCP-type rhodium complexes and have shown that they can exhibit unusual reactivity modes.[7a] With an interest in the generation of stable and isolable neutral Pt(II) formyl complexes, we have decided

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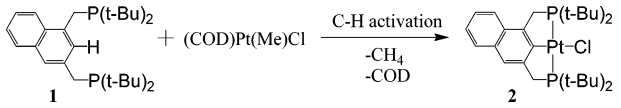
10.1021/om0700720 CCC: $37.00 
Publication on Web 04/27/2007

**Scheme 1**




to utilize the bulky naphthyl-based pincer-type ligand **1** (Scheme 1). It is expected that the electron affinity of a pincer-type naphthyl ligand, $\sigma$-bound to the metal center, might reduce the back-bonding effect to a coordinated CO ligand, enhancing its susceptibility toward nucleophilic addition. In addition, the steric bulk of the phosphine ligand might kinetically stabilize the formyl.

In this paper we report the synthesis and characterization of novel naphthyl-based PCP Pt(II) complexes. The nucleophilic reactivity of a cationic carbonyl complex is described, including the synthesis and reactivity of the PCP Pt(II) formyl complex. A platinum carbomethoxy complex is also described.

## Results and Discussion

**Synthesis and Characterization of a Naphthyl-Based PCP Pt(II) Complex.** The PCP naphthyl-based ligand **1** was synthesized by treatment of 1,3-di(bromomethyl)naphthalene with di-*tert*-butylphosphine in the presence of triethylamine.[7] The new complex **2** was obtained as a result of C−H activation and methane elimination in the reaction of ligand **1** with 1 equiv of (COD)Pt(Me)Cl at room temperature for 1 h (Scheme 1).

Interestingly, the cyclometalation to form the naphthyl-based complex **2** occurs at substantially less vigorous conditions than those used in the preparation of its phenyl-based analogue $[(C_6H_3(CH_2{}^tBu_2)_2)Pt(Cl)]$.[8] Both these complexes were prepared in our hands by the reaction of the corresponding PCP ligand with 1 equiv of (COD)Pt(Me)Cl, but the phenyl-based analogue was obtained only upon heating at 100 °C for 12 h. Since the methane reductive elimination is expected to be facile and the C−H activation is expected to be similar in both cases, it may be that the barrier for COD displacement is lower for the naphthyl-based ligand, although the reasons for that are not clear.[9]

The purified complex **2** was characterized by $^{31}P$, $^{1}H$, and $^{13}C$ NMR spectroscopy. The $^{31}P\{^{1}H\}$ NMR spectrum of **2** exhibits an AB system with a "roof" effect, due to the asymmetry of the phosphines in the complex. The AB system doublet of doublets is centered at 64.7 ppm ($J_{P-P}$ = 374 Hz) with Pt satellites ($J_{Pt-P}$ = 2858 Hz). In the $^{13}C\{^{1}H\}$ NMR spectrum the *ipso* carbon appears as a virtual triplet at 148.46 ppm ($J_{P-C}$ = 7 Hz). X-ray quality colorless crystals of complex **2** were obtained by recrystallization from pentane at room temperature. The single-crystal X-ray study reveals a slightly distorted square-planar structure (Figure 1). The P−Pt−Cl angles are about 96°, while the P−Pt−C angles are approximately 84°. The aryl C−C bond lengths and angles are quite similar to those of naphthalene. Selected bond angles and bond lengths are given in Table 1. A comparison of the naphthyl-based bisphosphine ligand structure in **2** and the structure of naphthalene[10a] shows that both C−C bonds near the *ipso* carbon are slightly elongated (1.389(7) and 1.436(7) Å) relative to the corresponding bonds in naphthalene (1.378 and 1.415 Å); this reflects the strain imposed by the metal center on the *ipso* carbon.

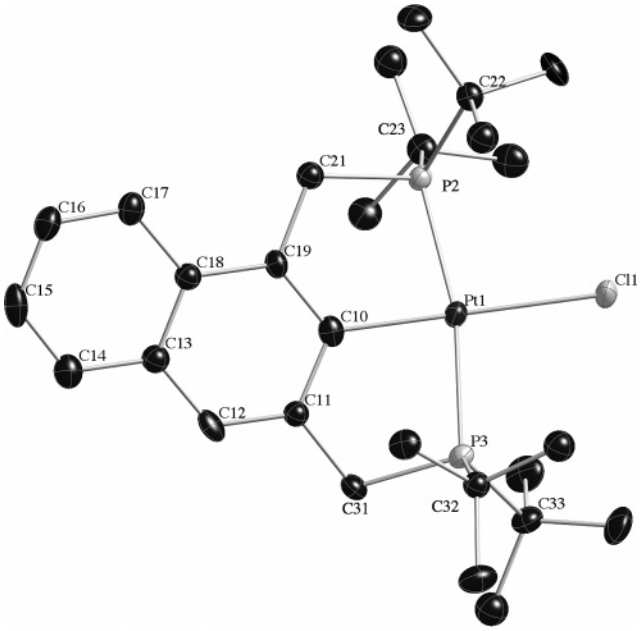



**Figure 1.** View of a molecule of complex **2** at the 50% probability level. Hydrogen atoms are omitted for clarity.

**Table 1. Selected Bond Lengths and Angles of Complex 2**

| bond length | Å | angle | deg |
|---|---|---|---|
| | | Metal Center Part | |
| Pt(1)−C(10) | 2.016(5) | C(10)−Pt(1)−P(2) | 83.5(2) |
| Pt(1)−P(2) | 2.282(2) | P(2)−Pt(1)−Cl(1) | 96.7(1) |
| Pt(1)−P(3) | 2.293(2) | C(10)−Pt(1)−P(3) | 84.3(2) |
| Pt(1)−Cl(1) | 2.431(2) | P(3)−Pt(1)−Cl(1) | 95.5(5) |
| | | Ligand Phosphine Part | |
| P(2)−C(21) | 1.832(5) | C(19)−C(21)−P(2) | 109.3(3) |
| P(2)−C(22) | 1.872(5) | C(22)−P(2)−C(23) | 112.6(2) |
| P(3)−C(31) | 1.834(5) | C(11)−C(31)−P(3) | 110.0(3) |
| P(3)−C(32) | 1.873(5) | C(32)−P(3)−C(33) | 113.0(2) |
| C(19)−C(21) | 1.516(6) | C(21)−P(2)−Pt(1) | 102.5(2) |
| C(11)−C(31) | 1.503(7) | C(31)−P(3)−Pt(1) | 101.5(2) |
| | | Ligand Aryl Part | |
| C(10)−C(11) | 1.436(7) | C(19)−C(10)−C(11) | 117.6(4) |
| C(10)−C(19) | 1.389(7) | C(18)−C(19)−C(10) | 121.4(4) |
| C(11)−C(12) | 1.373(7) | C(12)−C(11)−C(10) | 121.0(5) |
| C(12)−C(13) | 1.396(7) | C(11)−C(12)−C(13) | 122.1(5) |
| C(18)−C(19) | 1.435(7) | C(13)−C(18)−C(17) | 118.4(5) |
| C(13)−C(18) | 1.415(7) | C(13)−C(18)−C(19) | 119.5(4) |
| C(13)−C(14) | 1.421(7) | C(12)−C(13)−C(14) | 122.0(5) |
| C(17)−C(18) | 1.426(7) | C(15)−C(16)−C(17) | 120.9(5) |
| C(16)−C(17) | 1.372(7) | C(18)−C(17)−C(16) | 120.2(5) |
| C(14)−C(15) | 1.357(8) | C(13)−C(14)−C(15) | 120.5(5) |
| C(15)−C(16) | 1.400(8) | C(14)−C(15)−C(16) | 120.5(5) |

Interestingly, the crystal packing of complex **2** consists of alternating two-molecule stacks (Figure 2), which are held together by face-to-face $\pi-\pi$ interactions between each pair of molecules. The distance between two aryl planes in the stack is 3.54 Å, which is consistent with aromatic stacking.[10b]

**Cationic PCP Pt(II) Complexes.** Upon reaction of compound **2** with $AgBF_4$ in THF at room temperature for 2 days (protected from light), the $^{31}P\{^{1}H\}$ NMR spectrum revealed formation of complexes **3a** and **3b** in a 1:2 ratio, respectively (Scheme 2).

The $^{31}P\{^{1}H\}$ NMR spectrum at room temperature exhibits two doublets of doublets AB systems, which are assigned to two complexes: a minor complex (**3a**) at 75.4 ppm ($J_{P-P}$ = 332 Hz, $J_{Pt-P}$ = 2945 Hz) and a major complex (**3b**) at 71.7 ppm ($J_{P-P}$ = 337 Hz, $J_{Pt-P}$ = 2850 Hz). In the $^{13}C\{^{1}H\}$ NMR

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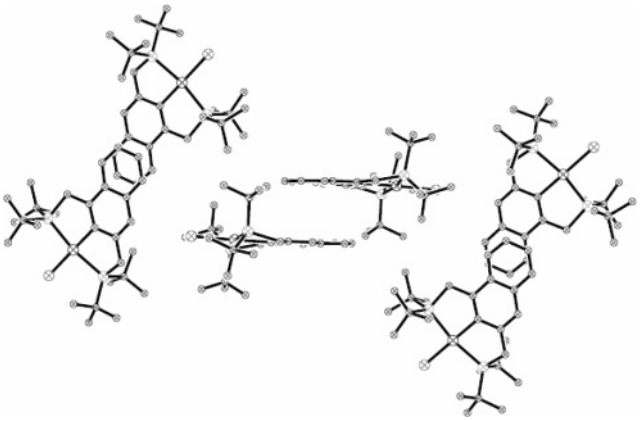

**Figure 2.** Aromatic stacking interactions between pairs of molecules of **2**.

spectrum, the *ipso* carbon of **3a** appears as a doublet of doublets at 147.21 ppm ($J_{P-C} = 6$ Hz) and the *ipso* carbon of **3b** appears as doublet of doublets at 144.55 ppm ($J_{P-C} = 6$ Hz). The $^{19}F$ NMR spectrum in THF exhibits two signals, a broad peak at −169.15 ppm, attributed to a coordinated $BF_4^-$ anion, and a sharp singlet at −151.00 ppm of free $BF_4^-$. The free $BF_4^-$ ion appears at −151.00 ppm in the $^{19}F$ NMR spectrum in THF.[6a] Coordinated $BF_4^-$ was reported to appear in the range −162 to −164 ppm. Reports of coordinated $BF_4^-$ include cationic rhodium complexes[6] and a PCN-type cationic platinum complex.[11] On the basis of the reported data, we can conclude that this anion is coordinated to the metal center in **3a**, while it is not coordinated in **3b**.

The cationic carbonyl complex **4** was prepared directly from complex **2** by abstraction of the chloride ligand with silver tetrafluoroborate in THF at room temperature under carbon monoxide (Scheme 3).[12] This reaction goes to completion faster and in higher yield than chloride abstraction under an inert atmosphere followed by reaction with CO.

The $^{31}P\{^1H\}$ NMR spectrum of **4** shows a doublet of doublets AB system centered at 84.9 ppm ($J_{P-P} = 247$ Hz) with Pt satellites ($J_{Pt-P} = 2334$ Hz). In the $^{13}C\{^1H\}$ NMR spectrum the *ipso* carbon exhibits a virtual triplet at 160.51 ppm ($J_{P-C} = 7$ Hz) with Pt satellites ($J_{Pt-C} = 260$ Hz), and a peak of the carbonyl ligand appears at 183.87 ppm as a singlet with Pt satellites ($J_{Pt-C} = 980$ Hz). In the IR spectrum, the carbonyl stretch was observed at 2080 $cm^{-1}$, indicating little back-bonding and a relatively low electron density at the metal center. The noncoordinated $BF_4^-$ anion appears in the $^{19}F$ NMR spectrum as a singlet at −150.87 ppm. Complex **4** was crystallized by slow evaporation of a $CH_2Cl_2$/THF solution at room temperature, to give orange crystals. A single-crystal X-ray analysis of **4** exhibits a square-planar structure, with the carbonyl ligand being coordinated *trans* to the aromatic ring (Figure 3) and $BF_4^-$ located out of the coordination sphere.[13] Selected bond lengths and bond angles of complex **4** are given in Table 2. The C−O bond length in complex **4** (1.131(15) Å) is comparable to the bond length of a free CO molecule (1.128 Å).[14] In view of these data, the carbonyl ligand is expected to be electrophilic.

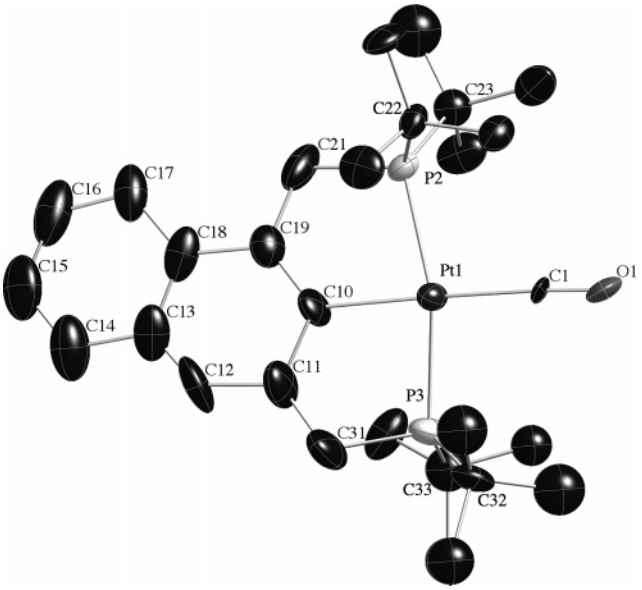


**Figure 3.** View of a molecule of complex **4** at the 30% probability level. Hydrogen atoms and $BF_4^-$ anion are omitted for clarity.

**Table 2. Selected Bond Lengths and Angles of Complex 4**

| bond length | Å | angle | deg |
|---|---|---|---|
| | Metal Center Part | | |
| Pt(1)−C(10) | 2.052(16) | C(10)−Pt(1)−C(1) | 177.0(7) |
| Pt(1)−P(2) | 2.298(5) | P(2)−Pt(1)−C(1) | 98.4(6) |
| Pt(1)−P(3) | 2.332(6) | C(1)−Pt(1)−P(3) | 95.4(6) |
| Pt(1)−C(1) | 1.886(13) | C(10)−Pt(1)−P(2) | 82.7(7) |
| C(1)−O(1) | 1.131(15) | O(1)−C(1)− Pt(1) | 175.8(2) |
| | Ligand Phosphine Part | | |
| P(2)−C(21) | 1.83(2) | C(19)−C(21)−P(2) | 111.1(2) |
| P(2)−C(22) | 1.88(2) | C(22)−P(2)−C(23) | 111.3(9) |
| P(2)−C(23) | 1.89(2) | C(23)−P(2)−C(21) | 106.5(2) |
| P(3)−C(31) | 1.81(2) | C(11)−C(31)−P(3) | 111.5(2) |
| P(3)−C(32) | 1.82(2) | C(32)−P(3)−C(33) | 120.1(9) |
| P(3)−C(33) | 1.84(3) | C(31)−P(3)−C(33) | 102.9(9) |
| C(19)−C(21) | 1.48(3) | C(21)−P(2)−Pt(1) | 101.6(8) |
| C(11)−C(31) | 1.40(4) | C(31)−P(3)−Pt(1) | 101.4(9) |

**Nucleophilic Activation of Coordinated Carbon Monoxide. Formation of a Carbomethoxy Complex by Methoxide Attack.** The chemistry of alkoxycarbonyl complexes of transition metals is of significant interest due to their recognition as intermediates in several important catalytic processes, such as carbonylation of alcohols, hydrocarboxylation of olefins to saturated and unsaturated esters, carbonylation of alkyl halides, and synthesis of alkyl carbonates and oxalates from alcohols.[15] Alkoxycarbonyl complexes of platinum, their reactivity, and their role in carbonylation reactions are well known.[16]

The facility of nucleophilic attack on coordinated CO ligands has been shown to be directly related to $\nu_{CO}$ of the CO ligand.[17] As expected from the relatively high frequency, $\nu_{CO}$ (2080 $cm^{-1}$), of **4**, it reacts with NaOMe in THF at room temperature to form the carbomethoxy complex **5** (Scheme 4).

Complex **5** exhibits in the $^{31}P\{^1H\}$ NMR spectrum a doublet of doublets AB system centered at 70.8 ppm ($J_{P-P} = 338$ Hz)

(11) Poverenov, E.; Gandelman, M.; Shimon, L. J. W.; Rozenberg, H.; Ben-David, Y.; Milstein, D. *Organometallics* **2005**, *24*, 1082.

(12) Cherwinski, W. J.; Clark, H. C. *Inorg. Chem.* **1971**, *10*, 2263.

(13) There is a difference of 0.03 Å in the Pt−P bond lengths for the slightly distorted crystal structure of compound **4**, due to $BF_4^-$ counteranion presence. A difference of only 0.01 Å was obtained for the Pt−P bond lengths in the highly ordered crystal structure of compound **2**.

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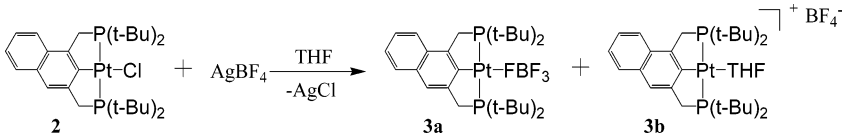
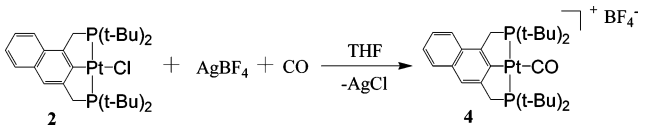
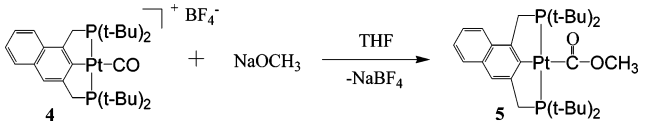
**Scheme 2**



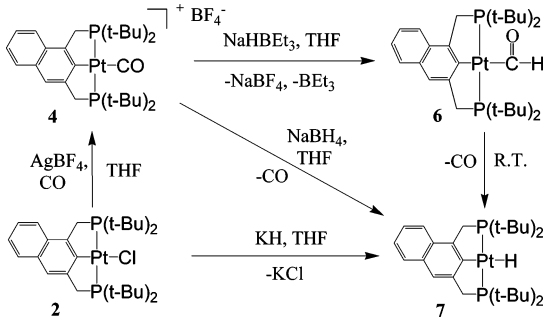

**Scheme 3**




**Scheme 4**




**Scheme 5**




with Pt satellites ($J_{Pt-P}$ = 2856 Hz). In the $^{13}C\{^1H\}$ NMR spectrum the *ipso* carbon exhibits a virtual triplet at 168.79 ppm ($J_{P-C}$ = 7 Hz) with Pt satellites ($J_{Pt-C}$ = 605 Hz), a peak of the carbonyl appears at 206.51 ppm as a singlet with Pt satellites ($J_{Pt-C}$ = 910 Hz), and a peak of methoxide appears as a singlet at 47.31 ppm. The IR spectrum of complex **5** exhibits bands at 1619 ($\nu_{C=O}$) and 1015 cm$^{-1}$ ($\nu_{C-O-C}$). The carbomethoxy complex **5** is stable for weeks both in solution and in the solid state.

**Formation of a PCP Pt(II) Formyl Complex by Hydride Nucleophilic Addition.** Reaction of the cationic carbonyl complex **4** with Na[$Et_3BH$] in THF leads to the formation of the neutral Pt(II) formyl complex **6** (Scheme 5), as assessed by NMR spectroscopy. At room temperature the $^{31}P\{^1H\}$ NMR spectrum of **6** shows a doublet of doublets AB system centered at 73.3 ppm ($J_{P-P}$ = 315 Hz) with Pt satellites ($J_{Pt-P}$ = 2850 Hz). In the $^1H$ NMR at room temperature, the formyl proton exhibits a singlet at a typically low field of 16.66 ppm with Pt satellites ($J_{Pt-H}$ = 114 Hz). In the $^{13}C\{^1H\}$ NMR spectrum measured at −70 °C, the formyl ligand gives rise to a peak at 284.75 ppm and displays one-bond coupling to platinum ($J_{Pt-C}$ = 765 Hz). A $^{13}C$ DEPT experiment and $^{13}C-^1H$ gs-HSQC correlation also confirm the presence of a metal-bound formyl moiety. The *ipso* carbon exhibits a peak at 167.43 ppm with Pt satellites ($J_{Pt-C}$ = 554 Hz). The IR spectrum of complex **6** shows absorption of the formyl at 1580 ($\nu_{C=O}$) and 2650 cm$^{-1}$ ($\nu_{C-H}$).

On warming at room temperature the formyl complex **6** slowly lost the CO ligand and was converted into the hydride complex **7** (Scheme 5). After 48 h at room temperature in toluene-$d_8$, the $^{31}P\{^1H\}$ NMR spectrum revealed a 3:1 ratio between complexes **6** and **7**, respectively. Complex **6** is more stable than the previously reported platinum formyls. [Na][($\eta^2$-Tp′)Pt(Me)(C(=O)H)] was prepared and characterized at 195 K;[4a] attempts to isolate the formyl hydride complex Tp′Pt(Me)-[(C(O)H)]H resulted in decarbonylation to the dihydride complex Tp′Pt(Me)$(H)_2$.[4a] A dinuclear platinum formyl complex[4b] was reported to lose CO to form a hydride complex, with a decomposition half-life of 5 h at room temperature.

Extensive studies of the decomposition pathway of the ruthenium formyl complex[18a] $[Ru(CHO)(CO)(dppe)_2]^+$ [dppe = 1,2-bis(diphenylphosphino)ethane] show that reversible dissociation of a Ru−P bond is followed by rate-determining hydride migration. Subsequent reactions involve loss of CO and recoordination of the free phosphine group to give the hydride complex $[RuH(CO)(dppe)_2]^+$, while the major pathway proposed for decomposition of $[Ru(CHO)(CO)(dppbz)_2]^+$ [dppbz = 1,2-bis(diphenylphosphino)benzene] to a hydride complex involves a concerted transfer of hydride to ruthenium and loss of CO via a three-centered transition state.[18b] The use of dppb in place of dppe stabilizes the formyl complex, by suppressing Ru−P bond rupture.

Since dissociation of a phosphine "arm" in a pincer-type complex at room temperature is not facile,[5] the slow conversion of the bulky pincer-type formyl complex **6** to hydride complex **7** can be attributed to the presence of a three-centered transition state, with a relatively high energy barrier, as a result of the hampered movement of the carbonyl ligand between the bulky *tert*-butyl groups.

**Independent Synthesis of the PCP Pt(II) Hydride Complex 7.** The hydride complex **7** was prepared independently upon treatment of **2** with potassium hydride in THF at room temperature (Scheme 5). The $^{31}P\{^1H\}$ NMR spectrum of **7** shows a doublet of doublets AB system centered at 87.3 ppm ($J_{P-P}$ = 367 Hz) with Pt satellites ($J_{Pt-P}$ = 2910 Hz). In the $^1H$ NMR, the hydride exhibits a triplet at −1.78 ppm ($J_{P-H}$ = 16 Hz) with Pt satellites ($J_{Pt-H}$ = 747 Hz). In the $^{13}C\{^1H\}$ NMR spectrum the *ipso* carbon exhibits a virtual triplet at 151.46 ppm ($J_{P-C}$ = 7 Hz).

Interestingly, treatment of the cationic carbonyl complex **4** with $NaBH_4$ (3 equiv) in THF for 1 h at room temperature led to formation of the hydride complex **7** (Scheme 5), with only traces of the formyl complex **6** (no reaction took place at −30 °C). Formation of unidentified byproducts in the region 63−65 ppm in the $^{31}P\{^1H\}$ NMR spectrum measured in THF was observed. This may indicate that the less sterically hindered borohydride reagent (as compared with Na[$Et_3BH$]) attacks the metal center of **4** rather than the carbonyl ligand.

## Summary

A series of naphthyl-based PCP platinum(II) complexes was synthesized and fully characterized. Unexpectedly, cyclometalation to form the naphthyl-based complex **2** occurred at substantially less vigorous conditions than with its phenyl-based analogue. Abstraction of chloride from **2** by $AgBF_4$ resulted in uncommon coordination of $BF_4^-$ to the metal center of the unsaturated cationic Pt(II) complex **3**. Treatment of the chloride

(18) (a) Smith, G.; Cole-Hamilton, D. J. *J. Chem. Soc., Dalton Trans.* **1984**, 1203. (b) Barratt, D. S.; Cole-Hamilton, D. J. *J. Chem. Soc., Dalton Trans.* **1987**, 2683.

complex **2** with carbon monoxide in the presence of silver tetrafluoroborate resulted in a stable cationic carbonyl complex **4**, which underwent nucleophilic attack by a methoxide anion to form the carbomethoxy complex **5**. The same methodology, nucleophilic addition to coordinated CO, has been employed with Na[$Et_3BH$], as a hydride transfer agent, to prepare the rare PCP Pt(II) formyl complex **6**, which was isolated and fully characterized. **6** is stabilized by the bulky bis-chelating tridentate pincer-type system. Further studies on the properties and reactivity of PCP platinum formyl complexes are underway.

## Experimental Section

**General Procedures.** All experiments with metal complexes and phosphine ligands were carried out in oven-dried glassware under an atmosphere of purified nitrogen in a Vacuum Atmospheres glovebox equipped with an MO 40-2 inert gas purifier. All solvents were reagent grade or better. All nondeuterated solvents were refluxed over sodium/benzophenone ketyl and distilled under an argon atmosphere. Deuterated solvents were used as received. All the solvents were degassed with argon and kept in the glovebox over 4 Å molecular sieves. Commercially available reagents were used as received. The precursor Pt(COD)($CH_3$)Cl was prepared according to a literature procedure.[19]

**Analysis.** The NMR spectra were recorded at 250 MHz ($^1$H), 101 MHz ($^{31}$P), and 235 MHz ($^{19}$F) using a Bruker DPX 250 spectrometer, at 400 MHz ($^1$H), 100 MHz ($^{13}$C), 162 MHz ($^{31}$P), and 376 MHz ($^{19}$F) using a Bruker AMX 400 NMR spectrometer, and at 500 MHz ($^1$H), 126 MHz ($^{13}$C), and 202 MHz ($^{31}$P) using a Bruker DPX 500 spectrometer. All spectra, except $^{13}$C{$^1$H} NMR spectra of **6**, were recorded at 23 °C. $^1$H NMR and $^{13}$C{$^1$H} NMR chemical shifts are reported in parts per million downfield from tetramethylsilane. $^1$H NMR chemical shifts were referenced to the residual hydrogen signal of the deuterated solvents (7.15 ppm, benzene; 7.24 ppm, chloroform; 2.09 ppm, toluene). In $^{13}$C{$^1$H} NMR measurements the signals of $C_6D_6$ (128.0 ppm), $CDCl_3$ (77.0 ppm), and toluene-$d_8$ (137.5 ppm) were used as a reference. $^{31}$P NMR chemical shifts are reported in ppm downfield from $H_3PO_4$ and referenced to an external 85% solution of phosphoric acid in $D_2O$. $^{19}$F NMR chemical shifts were referenced to $C_6F_6$ (−163 ppm). Abbreviations used in the description of NMR data are as follows: b, broad; s, singlet; d, doublet; t, triplet; m, multiplet; v, virtual. IR spectra were measured with a Nicolet-460 FT-IR spectrometer. Elemental analyses were performed by the Unit of Chemical Research Support, Weizmann Institute of Science.

**Preparation of the Naphthyl-Based PCP Ligand $C_{10}H_6$-$(CH_2P^tBu_2)_2$ (1).** The PCP naphthyl-based ligand **1** was synthesized by treatment of 1,3-di(bromomethyl)naphthalene with di-*tert*-butylphosphine in the presence of triethylamine.[7]

**Reaction of the PCP Ligand (1) with (COD)Pt(Cl)Me. Formation of [$(C_{10}H_5(CH_2P^tBu_2)_2)$Pt(Cl)] (2).** To a THF solution (5 mL) of (COD)Pt(Cl)$CH_3$ (COD = cyclooctadiene; 21.0 mg, 0.059 mmol) was added 26.0 mg (0.059 mmol) of ligand **1** in THF (5 mL). The mixture was stirred at room temperature for 1 h, resulting in a light yellow solution. The $^{31}$P{$^1$H} NMR spectrum revealed formation of **2**. The solvent was evaporated, and the complex was washed with pentane and dissolved in benzene. Benzene evaporation yielded 33.9 mg (0.050 mmol, clean substance yield 85%) of **2**. X-ray quality, colorless crystals were obtained from pentane washes at room temperature.

$^{31}$P{$^1$H} NMR ($CDCl_3$): 64.7 (dd (AB), $J_{P-P}$ = 374 Hz, $J_{Pt-P}$ = 2858 Hz). $^1$H NMR ($CDCl_3$): 7.75 (m, 1H, Ar), 7.54 (m, 1H, Ar) 7.41 (m, 1H, Ar), 7.13 (m, 1H, Ar), 7.06 (m, 1H, Ar), 3.36 (bd, $J_{P-H}$ = 7 Hz, 2H, Ar-C$H_2$-P), 3.22 (bd, $J_{P-H}$ = 7 Hz, 2H, Ar-C$H_2$-P), 1.33 (m, 36 H, P-*t-Bu*). $^{13}$C{$^1$H} NMR ($CDCl_3$): 148.46 (vt, $J_{P-C}$ = 7 Hz, *ipso*), 143.7 (t, $J_{P-C}$ = 1 Hz, Ar), 129.03 (s, Ar), 128.68 (s, Ar), 128.22 (d, Ar), 127.72 (s, Ar), 126.50 (s, Ar), 125.29 (s, Ar), 124.73(s, Ar), 123.96 (s, Ar), 31.53 (d, $J_{P-C}$ = 9 Hz, Ar-*C*$H_2$-P), 34.49 (d, $J_{P-C}$ = 9 Hz, Ar-*C*$H_2$-P), 32.45 (s, P-*C*-($CH_3$)$_3$), 29.28 (m, P-C-(*C*$H_3$)$_3$). (Assignment of $^{13}$C{$^1$H} NMR signals was confirmed by $^{13}$C DEPT.) Anal. Found (Calcd for $C_{28}H_{45}ClP_2Pt$): C, 49.55 (49.89); H, 6.71 (6.73).

**X-ray Structural Analysis of 2.** Complex **2** was crystallized from pentane at room temperature to give colorless crystals. Crystal data: $C_{28}H_{45}P_2ClPt$, colorless, plate, 0.2 × 0.2 × 0.02 mm$^3$, monoclinic, *P*2(1)/*n*, $a$ = 16.195(3) Å, $b$ = 10.440(2) Å, $c$ = 17.580(4) Å, α = 90.0°, $\beta$ = 109.21(3)°, $\gamma$ = 90.0° from 20 degrees of data, $T$ = 120(2) K, $V$ = 2806.9(10) Å$^3$, $Z$ = 4, fw = 674.11, $D_c$ = 1.595 Mg/m$^3$, $\mu$ = 5.22 mm$^{-1}$. Data collection and treatment: Nonius KappaCCD diffractometer, Mo Kα ($\lambda$ = 0.71073 Å), graphite monochromator, 23 329 reflections collected, $-20 \le h \le 19$, $0 \le k \le 13$, $0 \le l \le 22$, frame scan width 2.0°, scan speed 1° per 40 s, typical peak mosaicity 0.36$^0$, 6796 independent reflections ($R_{int}$ = 0.075). The data were processed with Denzo-Scalepack. Solution and refinement: structure solved by direct methods with SHELXS-97, full-matrix least-squares refinement based on $F^2$ with SHELXL-97, 256 parameters with 0 restraints, final $R_1$ = 0.0384 (based on $F^2$) for data with $I > 2\sigma(I)$ and $R_1$ = 0.0646 on 6438 reflections, $wR_2$ = 0.0925, goodness of fit on $F^2$ = 0.990, largest electron density peak 2.841 e/Å$^3$.

**Formation of [$(C_{10}H_5(CH_2P^tBu_2)_2)Pt^+(BF_4)^-$] (3).** To a THF solution (25 mL) of (PCP)PtCl **2** (79.0 mg, 0.117mmol) was added 24.0 mg (0.123 mmol) of $AgBF_4$, resulting in immediate formation of white precipitate of AgCl. The reaction mixture was stirred vigorously at room temperature for 2 days in a vial protected from light, resulting in a suspension of precipitated AgCl. The $^{31}$P{$^1$H} NMR spectrum at room temperature revealed formation of two new complexes, **3a** (minor) and **3b** (major), in a 1:2 ratio, respectively. The suspension was filtered through a frit covered with Celite, and the solvent was evaporated. The resulting yellow solid was washed with pentane and dissolved in benzene. After evaporation of benzene, 30 mg (0.041 mmol, 35% clean product yield) of the yellow complex **3** was obtained.

**3a** (coordinated $BF_4^-$): $^{31}$P{$^1$H} NMR ($CDCl_3$): 75.4 (dd (AB), $J_{P-P}$ = 332 Hz, $J_{Pt-P}$ = 2945 Hz). $^{19}$F NMR ($CDCl_3$): −170.34 (bs, coordinated $BF_4^-$). **3b** (free $BF_4^-$): $^{31}$P{$^1$H} NMR ($CDCl_3$): 71.7 (dd (AB), $J_{P-P}$ = 337 Hz, $J_{Pt-P}$ = 2850 Hz). $^{19}$F NMR ($CDCl_3$): −150.87 (s, free $BF_4^-$). **3a** and **3b** signals overlap (except methylene group hydrogens and *ipso* carbons): $^1$H NMR ($CDCl_3$): 7.84 (d, $J_{H-H}$ = 7 Hz, 1H, Ar), 7.67 (d, $J_{H-H}$ = 7 Hz, 1H, Ar), 7.49(m, 1H, Ar), 7.24 (m, 1H, Ar), 7.17 (m, 1H, Ar), 3.47 (bd, $J_{P-H}$ = 7 Hz, 2H, **3a**, Ar-C$H_2$-P), 3.32 (bd, $J_{P-H}$ = 7 Hz, 2H, **3a**, Ar-C$H_2$-P), 3.27 (bd, $J_{P-H}$ = 8 Hz, 2H, **3b**, Ar-C$H_2$-P), additional methylene group signal overlaps with THF residue, 1.41 (m, 36H, P-*t-Bu*). $^{13}$C{$^1$H} NMR ($CDCl_3$): 147.21 (dd, $J_{P-C}$ = 6 Hz, *ipso*, **3a**, coordinated $BF_4^-$), 144.55 (dd, $J_{P-C}$ = 6 Hz, *ipso*, **3b**, free $BF_4^-$), 132.06 (s, Ar), 129.01 (s, Ar), 128.64 (s, Ar), 128.16 (s, Ar), 127.67 (s, Ar), 126.48 (s, Ar), 125.65 (s, Ar), 125.08 (s, Ar), 124.39 (s, Ar), 34.10 (s, P-*C*-($CH_3$)$_3$), 31.97 (d, $J_{P-C}$ = 6 Hz, Ar-*C*$H_2$-P), 31.79 (d, $J_{P-C}$ = 6 Hz, Ar-*C*$H_2$-P), 29.10 (s, P-C-(*C*$H_3$)$_3$). (Assignment of $^{13}$C{$^1$H} NMR signals was confirmed by $^{13}$C DEPT.) Anal. Found (Calcd for $C_{28}H_{45}P_2PtBF_4$): C, 46.78 (46.36); H, 6.99 (6.25).

**Synthesis of [$(C_{10}H_5(CH_2P^tBu_2)_2)Pt(CO)^+(BF_4)^-$] (4).** To a 8 mL screw-cap vial, containing 29 mg (0.148 mmol) of $AgBF_4$, protected from light, was added a THF solution (5 mL) of (PCP)-PtCl **2** (100 mg, 0.148 mmol). The screw-cap vial was sealed with a Teflon septum cap, and 10 mL (0.400 mmol) of CO gas was injected. The reaction mixture was shaken vigorously at room temperature for 12 h using a mechanical shaker. The $^{31}$P{$^1$H} NMR spectrum revealed the formation of (PCP)Pt(CO)$^+BF_4^-$ complex **4**. The brown reaction mixture suspension was filtered through a

(19) Clark. H. C.; Manzer, L. E. *J. Organomet. Chem.* **1973**, *59*, 411.

frit covered with Celite, and the solvent was evaporated. The resulting solid was washed with pentane and dissolved in toluene. Complex **4** was precipitated from a toluene (2 mL)/pentane (10 mL) two-phase mixture at −30 °C. After removing the liquid and drying the precipitate, 43.2 mg (0.057 mmol, 39% pure product yield) of **4** was obtained as a brown solid. Small needle-like crystals of **4** were obtained from a saturated THF solution at room temperature. X-ray quality orange crystals of **4** were obtained by recrystallization of these crystals from a $CH_2Cl_2$/THF solution at room temperature.

$^{31}P\{^1H\}$ NMR ($CDCl_3$): 84.9 (dd (AB), $J_{P-P} = 247$ Hz, $J_{Pt-P} = 2334$ Hz). $^1H$ NMR ($CDCl_3$): 7.98 (d, $J_{H-H} = 8$ Hz, 1H, Ar), 7.85 (s, 1H, Ar), 7.67 (d, $J_{H-H} = 8$ Hz, 1H, Ar), 7.43 (t, $J_{H-H} = 7$ Hz, 1H, Ar), 7.39 (t, $J_{H-H} = 7.5$ Hz, 1H, Ar), 4.11 (bd, $J_{P-H} = 7.9$ Hz, 2H, Ar-C$H_2$-P), 3.89 (bd, $J_{P-H} = 7.6$ Hz, 2H, Ar-C$H_2$-P), 1.35 (m, 36H, P-*t-Bu*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 183.87 (s, $J_{Pt-C} = 980$ Hz, Pt-*CO*), 160.51 (vt, $J_{P-C} = 7$ Hz, $J_{Pt-C} = 260$ Hz, *ipso*), 150.58 (t, $J_{P-C} = 7$ Hz, Ar), 148.82 (t, $J_{P-C} = 7$ Hz, Ar), 133.42 (s, Ar), 128.21 (s, Ar), 127.60 (s, Ar), 127.18 (s, Ar), 123(s, Ar), 37.17 (s, P-*C*-$(CH_3)_3$), 34.87 (d, $J_{P-C} = 30$ Hz, Ar-*C*$H_2$-P), 33.24 (d, $J_{P-C} = 32$ Hz, Ar-*C*$H_2$-P), 29.18 (m, P-C-(*C*$H_3$)$_3$). (Assignment of $^{13}C\{^1H\}$ NMR signals was confirmed by $^{13}C$ DEPT.) $^{19}F$ NMR ($CDCl_3$): −150.87 (s, free $BF_4^-$). IR (film): (Pt-*CO*) 2080 $cm^{-1}$. ES-MS: $m/z^+$ 666.72 [calc 666.72] (M − CO), $m/z^-$ 87.11 [calc 86.80] ($BF_4^-$).

**X-ray Structural Analysis of 4.** Complex **4** was crystallized from $CH_2Cl_2$/THF solution at room temperature to give orange crystals. Crystal data: $C_{29}H_{45}P_2OPt^+BF_4^-$, orange, plate, 0.5 × 0.4 × 0.2 $mm^3$, orthorhombic, *Pna*2(1) (#33), $a = 12.097(2)$ Å, $b = 15.150(3)$ Å, $c = 38.514(8)$ Å, $\alpha = 90.0°$, $\beta = 90°$, $\gamma = 90°$ from 20 degrees of data, $T = 120(2)$ K, $V = 7058(2)$ $Å^3$, $Z = 8$, fw = 753.49, $D_c = 1.418$ $Mg/m^3$, $\mu = 4.106$ $mm^{-1}$. Data collection and treatment: Nonius KappaCCD diffractometer, Mo Kα ($\lambda = 0.71073$ Å), graphite monochromator, 47 195 reflections collected, $0 \le h \le 14$, $-18 \le k \le 0$, $-46 \le l \le 0$, frame scan width 0.4°, scan speed 1° per 120 s, typical peak mosaicity 0.46°, 7175 independent reflections ($R_{int} = 0.049$). The data were processed with Denzo-Scalepack. Solution and refinement: structure solved by direct methods with SHELXS-97, full-matrix least-squares refinement based on $F^2$ with SHELXL-97, 563 parameters with 38 restraints, final $R_1 = 0.0549$ (based on $F^2$) for data with $I > 2\sigma(I)$ and $R_1 = 0.0634$ on 6560 reflections, $wR_2 = 0.1524$, goodness of fit on $F^2 = 1.059$, largest electron density peak 1.923 e/$Å^3$.

**Synthesis of [($C_{10}H_5$(C$H_2$P$^t$B$u_2$)$_2$)Pt(COOC$H_3$)] (5).** To a THF solution (7 mL) of (PCP)Pt(CO)$^+BF_4^-$ **4** (21 mg, 0.028 mmol) was added sodium methoxide (9 mg, 0.168 mmol). The colloidal solution was stirred at room temperature for 10 min, resulting in a dark brown solution. The residue of unreacted sodium methoxide was separated from the suspension by centrifugation, and the solvent was evaporated. The resulting brown solid was extracted with pentane. After evaporation of pentane, 7.5 mg (0.011 mmol, 39% pure product yield) of (PCP)Pt(COOMe) **5** was obtained.

$^{31}P\{^1H\}$ NMR ($C_6D_6$): 70.8 (dd (AB), $J_{P-P} = 338$ Hz, $J_{Pt-P} = 2856$ Hz). $^1H$ NMR ($C_6D_6$): 7.92 (m, 1H, Ar), 7.82 (m, 1H, Ar), 7.59 (s, 1H, Ar), 7.42 (m, 1H, Ar), 7.40 (m, 1H, Ar), 3.75 (s, 3H, Pt-CO-O-C*H*$_3$), 3.69 (bd, $J_{P-H} = 7$ Hz, 2H, Ar-C$H_2$-P), 3.34 (bd, $J_{P-H} = 7$ Hz, 2H, Ar-C$H_2$-P), 1.26 (m, 36H, P-*t-Bu*). $^{13}C\{^1H\}$ NMR ($C_6D_6$): 206.51 (s, $J_{Pt-C} = 910$ Hz, Pt-*C*O−O−CH$_3$), 168.79 (vt, $J_{P-C} = 7$ Hz, $J_{Pt-C} = 605$ Hz, *ipso*), 150.22 (t, $J_{P-C} = 7$ Hz, Ar), 145.57 (t, $J_{P-C} = 7$ Hz, Ar), 132.94 (s, Ar), 130.77 (s, Ar), 125.77 (s, Ar), 125.30 (s, Ar), 119.94 (s, Ar), 47.31 (s, Pt-CO-O-*C*H$_3$), 38.59 (d, $J_{P-C} = 22$ Hz, Ar-*C*$H_2$-P), 35.98 (d, $J_{P-C} = 26$ Hz, Ar-*C*$H_2$-P), 35.67 (s, P-*C*-$(CH_3)_3$), 29.16 (s, P-C-(*C*$H_3$)$_3$). (Assignment of $^{13}C\{^1H\}$ NMR signals was confirmed by $^{13}C$ DEPT.) IR (film): 1619 $cm^{-1}$ (Pt-*CO*-O-CH$_3$), 1015 $cm^{-1}$ (−*C*-O-CH$_3$). Anal. Found (Calcd for $C_{30}H_{48}O_2P_2Pt$): C, 51.75 (51.64); H, 7.16 (6.93).

**Synthesis of [($C_{10}H_5$(C$H_2$P$^t$B$u_2$)$_2$)Pt(COH)] (6).** To a precooled to −30 °C THF solution (7 mL) of (PCP)Pt(CO)$^+BF_4^-$ **4** (37 mg, 0.049 mmol) was added sodium triethylborohydride (50 μL, 1 M in toluene, 0.050 mmol). The mixture was stirred at room temperature for 1 min and left at −30 °C for 30 min. The solvent was quickly evaporated, and the resulting brown solid was dissolved in toluene-$d_8$. The precipitate was removed from the solution by centrifugation, and after evaporation of the solvent 12.7 mg of **6** (0.019 mmol, 39% yield) was obtained.

$^{31}P\{^1H\}$ NMR ($C_7D_8$): 73.3 (dd (AB), $J_{P-P} = 315$ Hz, $J_{Pt-P} = 2850$ Hz). $^1H$ NMR ($C_7D_8$): 16.66 (s, $J_{Pt-H} = 114$ Hz, Pt-CO*H*), 7.84 (m, 1H, Ar), 7.75 (m, 1H, Ar), 7.52 (s, 1H, Ar), 7.37 (m, 2H, Ar), 3.64 (bd, $J_{P-H} = 7$ Hz, 2H, Ar-C$H_2$-P) 3.27 (bd, $J_{P-H} = 7$ Hz, 2H, Ar-C$H_2$-P), 1.14 (m, 36 H, P-*t-Bu*). $^{13}C\{^1H\}$ NMR ($C_7D_8$, −70 °C): 284.75 (s, $J_{Pt-C} = 765$ Hz, Pt-*C*O−H), 167.43 (s, $J_{Pt-C} = 554$ Hz, *ipso*), 149.32 (s, Ar), 145.46 (s, Ar), 132.82 (s, Ar), 120.28 (s, Ar), 37.49 (d, $J_{P-C} = 17$ Hz, Ar-*C*$H_2$-P), 34.72 (d, $J_{P-C} = 17$ Hz, Ar-*C*$H_2$-P), 35.31 (s, P-*C*-$(CH_3)_3$), 20.57 (s, P-C-(*C*$H_3$)$_3$). (Assignment of $^{13}C\{^1H\}$ NMR signals was confirmed by $^{13}C$ DEPT and by $^{13}C-^1H$ gs-HSQC correlation.) IR (film): 1580 $cm^{-1}$ (Pt-*CO*-H), 2650 $cm^{-1}$ (formyl *C*-H). ES-MS: *m*/*z* 667.75 [calc 667.72].

**Synthesis of [($C_{10}H_5$(C$H_2$P$^t$B$u_2$)$_2$)Pt(H)] (7).** To a THF solution (7 mL) of (PCP)Pt(Cl) **2** (32 mg, 0.048 mmol) was added potassium hydride (38.5 mg, 0.960 mmol). The colloidal mixture was stirred at room temperature for 7 days, resulting in a red solution. The byproduct solids were separated from the suspension by centrifugation, and the solvent was evaporated. The resulting red solid was extracted with pentane. After evaporation of pentane 10.3 mg (0.016 mmol, 33% pure product yield) of the brown complex **7** was obtained.

$^{31}P\{^1H\}$ NMR ($C_7D_8$): 87.3 (dd (AB), $J_{P-P} = 367$ Hz, $J_{Pt-P} = 2910$ Hz). $^1H$ NMR ($C_7D_8$): 7.93 (m, 1H, Ar), 7.74 (m, 1H, Ar), 7.36 (m, 1H, Ar), 7.29 (s, 1H, Ar), 7.13 (m, 1H, Ar), 3.76 (bd, $J_{P-H} = 7$ Hz, 2H, Ar-C$H_2$-P), 3.46 (bd, $J_{P-H} = 7$ Hz, 2H, Ar-C$H_2$-P), 1.27 (m, 36 H, P-*t-Bu*), −1.78 (t, $J_{P-H} = 16$ Hz, $J_{Pt-H} = 747$ Hz, Pt-*H*). $^{13}C\{^1H\}$ NMR ($C_6D_6$): 151.46 (vt, $J_{P-C} = 7$ Hz, *ipso*), 145.66 (s, $J_{P-C} = 6$ Hz, Ar), 137.77 (s, $J_{P-C} = 6$ Hz, Ar), 136.52 (s, Ar), 134.72 (s, Ar), 126.92 (s, Ar), 125.95 (s, Ar), 125.21 (s, Ar), 123.52 (s, Ar), 120.15 (s, Ar), 38.93 (d, $J_{P-C} = 25$ Hz, Ar-*C*$H_2$-P), 36.68 (d, $J_{P-C} = 25$ Hz, Ar-*C*$H_2$-P), 34.35 (s, P-*C*-$(CH_3)_3$), 29.41 (m, P-C-(*C*$H_3$)$_3$). (Assignment of $^{13}C\{^1H\}$ NMR signals was confirmed by $^{13}C$ DEPT.) Anal. Found (Calcd for $C_{28}H_{46}P_2Pt$): C, 52.53 (52.57); H, 7.17 (7.25).

**Acknowledgment.** This work was supported by the Israel Science Foundation, by the MINERVA foundation, and by The Helen and Martin Kimmel Center for Molecular Design. D.M. holds the Israel Matz Professorial Chair of Organic Chemistry.

**Supporting Information Available:** CIF files containing X-ray crystallographic data for complexes **2** and **4**. Copies of NMR spectra of complex **6** and data from the CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0700720