Ligand Substitution Reactions of Cationic σ-Vinylplatinum(II) Triflate Species. Single-Crystal Molecular Structure of *trans*-$(CH_3)_2C{=}CHPt(PPh_3)_2I$

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A wide variety of nucleophiles readily react with the cationic $(\sigma\text{-}R_2C{=}CR')(Ph_3P)_3PtOTf$ complex, under mild conditions, resulting in ligand substitution. Neutral nucleophiles such as pyridine, CH_3CN, and CO give the corresponding trans cationic complexes via net replacement of the trans-Ph_3P ligand. Reactions with an excess of more basic phosphines such as Ph_2MeP and triphos yield the respective cationic complexes with replacement of all three Ph_3P ligands. Interaction with charged nucleophiles such as I^-, Br^-, Cl^- and PhS^- results in the neutral trans complexes $(\sigma\text{-}R_2C{=}CR)(Ph_3P)_2PtX$. From a series of equilibrium measurements it was established that the relative ligand binding strengths in trans $(CH_2{=}C(CH_3))\text{-}Pt^+(PPh_2)^2L(OTf)^-$ are py > Ph_3P > CH_3CN. An X-ray structure determination of *trans*-$(CH_3)_2C{=}CHPt(PPh_3)_2I$ is reported.

We recently reported[1] the formation, in high isolated yields, of a variety of novel, stable, four-coordinated, cationic σ-vinyl platinum(II) complexes **3**, via the interaction of vinyl triflates **1** with $(Ph_3P)_4Pt$ (eq 1). We have

$$(R)_2C{=}CR'OTf \;+\; (Ph_3P)_4Pt \xrightarrow{\text{toluene, room temp}} \underset{\mathbf{3}}{Ph_3P(OTf)Pt(PPh_3)C(R')=C(R)_2} \qquad (1)$$

1 **2**

also demonstrated[2] the role of these complexes as models in metal-mediated vinylic cross-coupling reactions.[3-6] In this paper we wish to report on the ready formation of diverse new σ-vinyl platinum(II) complexes, via the ligand substitution reactions of complex **3** with a variety of nucleophiles, along with a single-crystal molecular structure determination and equilibration studies.

Results and Discussion

The reaction of **3** with three distinct classes of nucleophiles was examined: (a) weakly nucleophilic neutral species such as CO, CH_3CN, and pyridine, (b) more basic phosphines typified by Ph_2MeP and bis(2-(diphenylphosphino)ethyl)phenylphosphine (triphos), and (c) charged nucleophiles exemplified by the halogens (I^-, Br^-, Cl^-) and PhS^-.

Interaction of 3 with CO, CH_3CN, and C_5H_5N. Reaction of **3a** with CO in CH_2Cl_2 at room temperature gave the cationic trans complex **4** (eq 2) in 67% isolated yield.

Likewise, reaction of **3a** with excess CH_3CN at 65 °C resulted in the cationic trans complex **5** in 80% yield (eq 3).

$$H_2C{=}C(CH_3)Pt(PPh_3)_3OTf \;+\; CO \xrightarrow[\text{room temp, 4 h}]{CH_2Cl_2} \underset{\mathbf{4}}{OC(OTf)Pt(PPh_3)_2C(CH_3){=}CH_2} \qquad (2)$$

3a

$$H_2C{=}C(CH_3)Pt(PPh_3)_3OTf \;+\; CH_3CN\ (\text{excess}) \xrightarrow{65\ ^\circ C,\ 4\ h} \underset{\mathbf{5}}{CH_3CN(OTf)Pt(PPh_3)_2C(CH_3){=}CH_2} \qquad (3)$$

Similarly, reaction of **3a** with excess pyridine in CH_2Cl_2 at room temperature gave the cationic trans complex **6** in 88% yield (eq 4).

$$H_2C{=}C(CH_3)Pt(PPh_3)_3OTf \;+\; C_5H_5N\ (\text{excess}) \xrightarrow[\text{room temp, 3 h}]{CH_2Cl_2} \underset{\mathbf{6}}{C_5H_5N(OTf)Pt(PPh_3)_2C(CH_3){=}CH_2} \qquad (4)$$

All three cationic complexes **4–6** were isolated as stable, colorless, microcrystalline solids and characterized by spectral means as detailed in the Experimental Section. Specifically, in addition to the ^1H and ^{13}C NMR spectra, all data are consistent with the proposed structures for the individual adducts **4–6**; particularly characteristic are the infrared absorptions at 1270 ± 5 and ~630 cm^{-1} indicative of the noncoordinating, anionic triflate group[7] and the ^{31}P NMR spectra showing a *singlet* between 15 and 21 ppm, along with the expected ^{195}Pt satellites, clearly indicative of the trans geometry for these square-planar complexes.

Reaction of 3 with Ph_2MeP and triphos. Interaction of **3** with Ph_2MeP and triphos, respectively, resulted in the

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(2) Stang, P. J.; Kowalski, M. H.; Schiavelli, M. D.; Longford, D. *J. Am. Chem. Soc.* **1989**, *111*, 3347. Stang, P. J.; Kowalski, M. H. *J. Am. Chem. Soc.* **1989**, *111*, 3356.
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(4) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508. Stille, J. K. *Pure Appl. Chem.* **1985**, *57*, 1771.
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(6) Negishi, E. *Acc. Chem. Res.* **1982**, *15*, 340.
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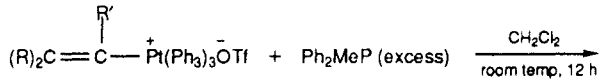
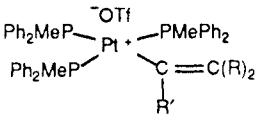
new cationic complexes **7** and **8** (eq 5 and 6), where the more basic phosphines displaced all three Ph_3P ligands in the starting material without affecting the σ-coordinated vinylic ligand.

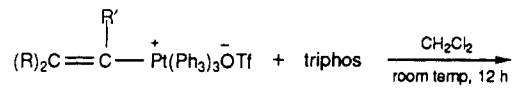


3a: R = H, R′ = CH_3
b: R = CH_3, R′ = H

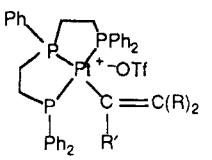


(5)

7a: R = H, R′ = CH_3
b: R = CH_3, R′ = H



3a: R = H, R′ = CH_3
b: R = CH_3, R′ = H

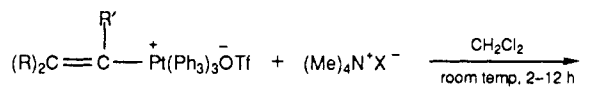


(6)

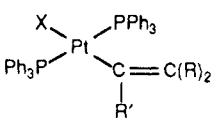
8a: R = H, R′ = CH_3
b: R = CH_3, R′ = H

Complexes **7** and **8** were isolated in 60–90% yields as stable, colorless, microcrystalline solids and characterized by spectral means as described in the Experimental Section.

Interaction of 3 with Charged Nucleophiles. Reaction of **3** with $(CH_3)_4N^+X^-$ (X = I, Br, Cl) in CH_2Cl_2 resulted in the *neutral*, square-planar, trans complexes **9–11** (eq 7) in 54–77% isolated yields.



3a: R = H, R′ = CH_3
b: R = CH_3, R′ = H

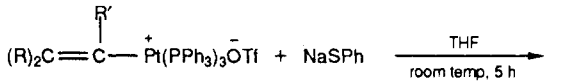


(7)

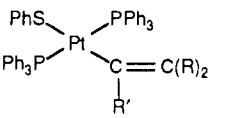
9a: R = H, R′ = CH_3, X = I
10a: R = H, R′ = CH_3, X = Br
11a: R = H, R′ = CH_3, X = Cl
9b: R = CH_3, R′ = H, X = I
10b: R = CH_3, R′ = H, X = Br

Likewise reaction of **3** with NaSPh in THF afforded the *neutral*, trans-thiophenoxide complexes **12** (eq 8) in 35% and 45% isolated yields, respectively. Complexes **9–11** are colorless, whereas **12a** and **12b** are yellow, stable microcrystalline solids. The trans geometry of complexes **9–12** is evident from the singlet (with associated Pt satellites) in the ^{31}P NMR spectra and the neutral, tetracoordinate nature from the lack of signals in both the infrared and ^{19}F NMR spectra normally associated with the triflate.

Equilibrium Determinations. In order to get some insight into the binding strength of the various ligands in these novel cationic σ-vinyl Pt complexes, we examined a series of equilibria. Equilibrium constants were determined in $CDCl_3$ at room temperature by integration of the



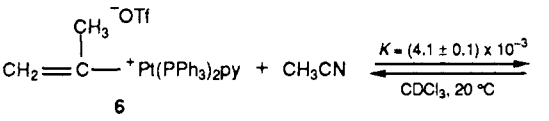
3a: R = H, R′ = CH_3
b: R = CH_3, R′ = H



(8)

12a: R = H, R′ = CH_3
b: R = CH_3, R′ = H

respective ^{31}P NMR signals in sealed NMR tubes containing known amounts of the starting complex and the two ligands. The following values (eq 9–12) represent the *average* equilibrium constant as measured from the forward and reverse directions.



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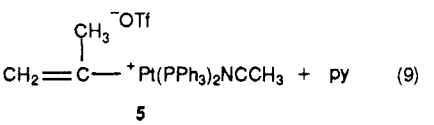
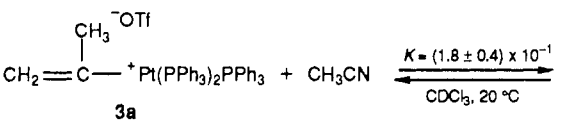
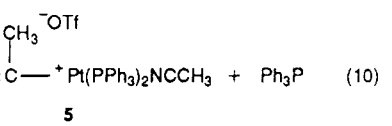


(9)

5

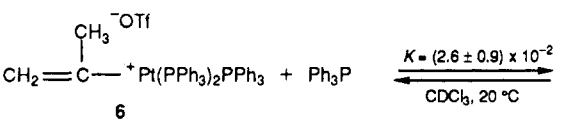


3a



(10)

5



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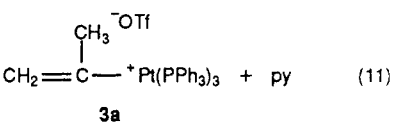
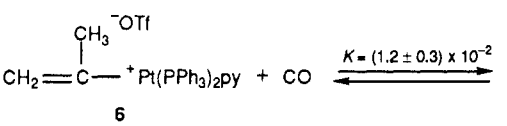


(11)

3a



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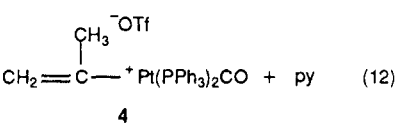

(12)

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Single-Crystal Molecular Structure Determination. Suitable single crystals of **9b** were grown from $CDCl_3$/pentane solution. An ORTEP diagram is given in Figure 1. Crystal data and selected bond lengths and bond angles are summarized in Tables I–III, respectively. Complex **9b** is square planar with all four bond angles around the Pt very nearly 90°. The Pt–C(1) bond length of 2.032 (7) Å is normal for platinum–vinyl carbon bonds,[8] as is the

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Table I. Summary of Crystallographic Data for 9b

mol formula	$C_{40}H_{37}P_2IPt$
mol wt	901.683
cryst syst	monoclinic
space group	$P2_1/n$
space group no.	14
cell dimens	
a, Å	11.918 (5)
b, Å	19.738 (9)
c, Å	15.796 (5)
α, deg	90.00 (0)
β, deg	105.84 (3)
γ, deg	90.00 (0)
V, Å^3	3575 (3)
Z	4.0
d_{calcd}, g/cm^3	1.675
cryst dimens, mm	0.28 × 0.20 × 0.14
abs coeff, cm^{-1}	49.338
radiation; γ, Å (monochromatized)	Mo; 0.710 73
no. of rflns measd	6140
no. of unique rflns	5833
scan technique	θ–2θ
2θ range, deg	3.00–48.00
scan speed, deg/min	3.0–8.0
scan range	Kα − 1.0 to Kα + 1.0
total bkgd time/scan time	0.5
no. of rflns between std	98
ignorance factor, P	0.06
no. of observns, $I > 3.0\ \sigma(I)$	3951
no. of variables	397
data to param ratio	9.952
shift to error ratio	0.002
R factor	0.0349
weighted R factor	0.0375

Table II. Selected Bond Distances (Å) for 9b[a]

Pt–I	2.709 (4)	Pt–C(1)	2.032 (7)
Pt–P(1)	2.309 (1)	C(1)–C(2)	1.288 (9)
Pt–P(2)	2.304 (1)	C(2)–C(3)	1.50 (1)
P(1)–C(5)	1.821 (5)	C(2)–C(4)	1.46 (1)
P(1)–C(11)	1.814 (6)	P(2)–C(23)	1.828 (5)
P(1)–C(17)	1.831 (6)	P(2)–C(29)	1.820 (6)
		P(2)–C(35)	1.829 (5)

[a] Numbers in parentheses are estimated deviations in the least significant digit.

Table III. Selected Bond Angles (deg) for 9b[a]

I–Pt–P(1)	90.79 (4)	Pt–C(1)–C(2)	133.3 (7)
I–Pt–P(2)	91.15 (4)	C(1)–C(2)–C(3)	119.7 (8)
P(1)–Pt–C(1)	90.1 (1)	C(1)–C(2)–C(4)	128.0 (1)
P(2)–Pt–C(1)	89.6 (2)	C(3)–C(2)–C(4)	112.7 (9)
I–Pt–C(1)	169.2 (2)		
P(1)–Pt–P(2)	171.35 (5)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digit.

C(1)–C(2) double bond of 1.288 (9) Å. Two of the bond angles around C(2) are distorted from the usual 120° around trigonal carbons, presumably due to the effect of the bulky Pt moiety.

Conclusion. The above data clearly indicate that cationic σ-vinyl Pt(II) complexes readily undergo ligand substitutions. Neutral nucleophiles, represented by CO, CH_3CN, and pyridine, displace exclusively a trans phosphine, resulting in new, unique cationic trans σ-vinyl Pt(II) complexes with CO, CH_3CN, and pyridine as ligands trans to the σ-alkenyl group. Net substitution at the trans position is no doubt due to the trans influence of the σ-vinyl group.[9] Equilibration studies indicate that the relative binding strengths of these ligands are py > Ph_3P > CH_3CN, in accord with thermodynamic data for related tungsten complexes.[10]

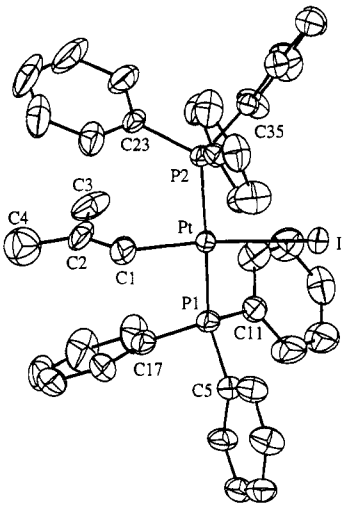

Figure 1. ORTEP diagram of **9b**.

Phosphines more basic than Ph_3P, such as $(Ph_3P)_2MeP$ and triphos, displace all three Ph_3P groups in complex **3**, yielding the new cationic σ-vinyl Pt(II) phosphine complexes **7** and **8**.

Finally, charged nucleophiles, represented by the halogens and PhS^-, also displace exclusively the trans phosphine in **3**, resulting in the neutral, square-planar σ-vinyl Pt(II) complexes **9–12**. These complexes may be looked upon as the formal "insertion" of the $(Ph_3P)_2Pt$ fragment into the carbon–halogen bond of vinyl halides or the carbon–sulfur bond of vinyl sulfides. By using simple alkyl-substituted vinyl triflates as cationic equivalents instead of vinyl substrates "activated" by aromatic or halo groups,[11] it is possible to prepare a wide variety of Pt(II) vinyl complexes. In turn these metal centers may be fine-tuned by addition of nucleophiles with Lewis basicity higher than that of triphenylphosphine, including other phosphines, neutral pyridine and CO, halides, and pseudohalides.

Experimental Section

General Data. All melting points are uncorrected and were measured on a Mel-Temp capillary apparatus. Infrared spectra were obtained as KBr pellets on a Perkin-Elmer 298 spectrometer and are reported in wavenumbers (cm^{-1}). ^1H NMR spectra were recorded on a Varian XL-300 spectrometer, and all chemical shifts are reported in ppm relative to internal tetramethylsilane (Me_4Si) or the proton resonance resulting from incomplete deuteriation of the NMR solvents: $CDCl_3$ (7.24 ppm), CD_2Cl_2 (5.32 ppm), CD_3NO_2 (4.33 ppm). ^{13}C NMR spectra were obtained on a Varian XL-300 instrument at 75 MHz, and the chemical shifts are reported in ppm relative to the carbon resonance of the deuteriated NMR solvents: $CDCl_3$ (77.0 ppm), CD_2Cl_2 (53.8 ppm), CD_3NO_2 (62.8 ppm). ^{31}P NMR spectra were recorded on a Varian XL-300 instrument at 121 MHz with the magnet locked on the deuteriated solvent, and chemical shifts are reported relative to external 85% H_3PO_4 at 0.0 ppm. Fast atom bombardment mass spectra were obtained with a VG Analytical 7050-E mass spectrometer. The X-ray crystal structure was obtained with a Syntex P$\bar{1}$ diffractometer at ambient temperature (16 ± 1 °C).

Materials. In general, solvents either were reagent grade or were purified according to known procedures. Specifically, acetonitrile and pyridine were freshly distilled from CaH_2. Deu-

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teriated NMR solvents were purified by drying over CaH_2 and then vacuum-transferred.

The cationic tris(phosphine) vinylic platinum(II) complexes **3** were prepared according to known procedures.[1,2] Tetramethylammonium halides and triphos (bis(2-(diphenylphosphino)ethyl)phenylphosphine) were purchased from Aldrich. Methyldiphenylphosphine was purchased from Strem and used without further purification.

Reaction of 3a with CO To Form 4. Carbon monoxide was bubbled through a solution of 101 mg (0.0862 mmol) of (2-propenyl)$(PPh_3)_3$Pt(OTf) (**3a**) in 20 mL of methylene chloride for 4 h, during which time the solution changed to light yellow. The solution was reduced to 2 mL by concentration on a rotavaporator. After filtration to remove minor amounts of impurities, toluene was added until colorless crystals precipitated. The solution was then kept in the refrigerator for 1 h. The crystals were recovered by filtration, washed with toluene, and dried under high vacuum, to yield 54 mg (67%) of **4**, mp 173–174 °C dec. IR: 3050 (m), 2932 (w), 2092 (s), 1598 (w), 1586 (w), 1480 (m), 1433 (s), 1275 (s), 1219 (m), 1135 (s), 1095 (s), 1028 (s), 995 (m), 883 (w), 870 (w), 750 (s), 749 (m), 708 (m), 690 (s), 631 (s). ^{1}H NMR (CD_2Cl_2): δ 0.78 (br s, $^3J_{PtH}$ = 29.2 Hz, 3 H, CH_3), 4.56 (br s, $^3J_{PtH}$ = 43.2 Hz, 1 H, (*Z*)-CH=), 5.46 (q, $^4J_{HH}$ = 1.7 Hz, $^3J_{PtH}$ = 76.6 Hz, 1 H, (*E*)-CH=), 7.5–7.7 (aromatics, 30 H). ^{31}P NMR (CD_2Cl_2): δ 15.8 (s, $^1J_{PtP}$ = 2784 Hz). ^{13}C NMR (CD_2Cl_2): δ 27.3 (br s, $^2J_{PtC}$ = 26.4 Hz, CH_3), 121.1 (br s, CH_2=), 121.4 (q, $^1J_{FC}$ = 321.0 Hz, CF_3), 127.5 (t, $^1J_{PC}$ = 30.0 Hz, $^2J_{PtC}$ = 30.7 Hz, ipso-C), 129.7 (t, $^3J_{PC}$ = 5.5 Hz, *m*-C), 133.0 (s, *p*-C), 134.7 (t, $^2J_{PC}$ = 6.0 Hz, *o*-C), 153.8 (t, $^2J_{PC}$ = 10.1 Hz, PtC=), 178.2 (t, $^2J_{PC}$ = 8.5 Hz). FAB MS: 788 (M^+, 3.7%), 761 (88%), 760 (100%), 759 (69%), 720 (20%), 719 (62%), 718 (52%), 457 (19%), 456 (47%), 455 (44%), 154 (70%). Anal. Calcd for $C_{41}H_{35}O_4F_3P_2SPt$: C, 52.51; H, 3.76. Found: C, 52.87; H, 3.83.

Reaction of 3a with CH_3CN To Form 5. To 10 mL of acetonitrile was added 119 mg (0.102 mmol) of **3a**. The mixture was degassed through three freeze–pump–thaw cycles and then heated in a 65 °C oil bath under N_2 for 4 h, during which time it changed to light yellow. Acetonitrile was quickly reduced to about 1 mL, and 2 mL of methylene chloride was added. After filtration to remove minor solid impurities, 20 mL of toluene was added. The solution remained clear. Hexane was then slowly added while the solution was vigorously shaken until white crystals precipitated. The crystals were recovered by filtration, washed with hexane, and dried under high vacuum to give 78 mg (80%) of **5**, mp 163–164 °C dec. IR: 3055 (w), 2925 (w), 2285 (w), 1587 (m), 1479 (m), 1432 (s), 1364 (w), 1265 (s), 1220 (m), 1149 (s), 1095 (s), 1027 (s), 995 (w), 852 (w), 749 (m), 707 (m), 690 (s), 633 (s). ^{1}H NMR ($CDCl_3$): δ 0.83 (br s, $^3J_{PtH}$ = 40.5 Hz, 3 H, CH_3), 1.32 (t, $^5J_{PH}$ = 0.8 Hz, 3 H, CH_3CN), 4.53 (s, $^3J_{PtH}$ = 59.6 Hz, 1 H, (*Z*)-CH=), 5.15 (q, $^4J_{HH}$ = 1.0 Hz, $^3J_{PtH}$ = 108.4 Hz, 1 H, (*E*)-CH=), 7.4–7.7 (aromatics, 30 H). ^{31}P NMR ($CDCl_3$): δ 20.6 (s, $^1J_{PtP}$ = 3171 Hz). ^{13}C NMR ($CDCl_3$): δ 1.9 (s, CH_3(CN)), 28.9 (br s, CH_3), 116.9 (t, $^3J_{PC}$ = 4.6 Hz, CH_2=), 120.9 (q, $^1J_{FC}$ = 320.5 Hz, CF_3), 122.9 (s, C≡N), 127.7 (t, $^1J_{PC}$ = 28.4 Hz, $^2J_{PtC}$ = 30.2 Hz, ipso-C), 128.8 (t, $^3J_{PC}$ = 5.3 Hz, *m*-C), 131.6 (s, *p*-C), 134.4 (t, $^2J_{PC}$ = 6.3 Hz, *o*-C), 137.5 (t, $^2J_{PC}$ = 9.3 Hz, PtC=). FAB MS: 761 (73%), 760 (82%), 759 (57%), 720 (33%), 719 (54%), 718 (46%), 717 (32%), 457 (32%), 456 (38%), 455 (33%), 154 (100%). Anal. Calcd for $C_{42}H_{38}O_3NP_2F_3SPt$: C, 53.05; H, 4.03. Found: C, 53.17; H, 3.94.

Reaction of 3a with Pyridine To Form 6. Complex **3a** (196 mg, 0.167 mmol) was dissolved in 20 mL of methylene chloride; then 40 mg (0.51 mmol) of dry pyridine was added. The solution was stirred at room temperature for 3 h and remained colorless throughout the reaction course. The solution was reduced to 2 mL, and then toluene was added, giving a microcrystalline product. The product was recovered by filtration, washed with toluene, and finally dried under high vacuum to yield 146 mg (88%) of **6**, mp 195–196 °C dec. IR: 3055 (m), 2935 (w), 1605 (m), 1586 (m), 1480 (m), 1432 (s), 1358 (w), 1265 (s), 1220 (s), 1144 (s), 1095 (s), 1064 (m), 1027 (s), 995 (m), 863 (m), 750 (s), 693 (s), 633 (s). ^{1}H NMR ($CDCl_3$): δ 1.04 (s, $^3J_{PtH}$ = 34.9 Hz, 3 H, CH_3), 4.59 (br s, $^3J_{PtH}$ = 52.3 Hz, 1 H, (*Z*)-CH=), 5.09 (br s, $^3J_{PtH}$ = 98.6 Hz, 1 H, (*E*)-CH=), 6.69 (m, 2 H, py H), 7.93 (m, 2 H, py H), 7.1–7.7 (aromatics, 31 H). ^{31}P NMR ($CDCl_3$): δ 21.0 (s, $^1J_{PtP}$ = 3182 Hz). ^{13}C NMR ($CDCl_3$): δ 30.1 (s, $^2J_{PtC}$ = 34.5 Hz, CH_3), 119.2 (t, $^3J_{PC}$ = 4.5 Hz, CH_2=), 121.2 (q, $^1J_{FC}$ = 320.9 Hz, CF_3), 126.0 (br s, py C), 127.6 (t, $^1J_{PC}$ = 28.1 Hz, $^2J_{PtC}$ = 26.4 Hz, ipso-C), 128.7 (t, $^3J_{PC}$ = 5.2 Hz, *m*-C), 131.2 (s, *p*-C), 134.2 (t, $^2J_{PC}$ = 5.9 Hz, *o*-C), 135.6 (t, $^2J_{PC}$ = 9.6 Hz, PtC=), 137.5 (s, py C), 151.5 (s, py C). FAB MS: 839 (M^+, 1.1%), 761 (80%), 760 (100%), 759 (33%), 720 (24%), 719 (73%), 718 (29%), 457 (24%), 456 (23%), 455 (25%). Anal. Calcd for $C_{45.25}H_{40.5}O_3NF_3Cl_{0.5}P_2SPt$ ($^1/_4$ CH_2Cl_2 solvate): C, 53.80; H, 4.04. Found: C, 53.82; H, 4.16.

Reaction of 3a with Ph_2MeP To Form 7a. Methylene chloride (25 mL) was degassed through three freeze–pump–thaw cycles and then added to 265 mg (1.32 mmol) of methyldiphenylphosphine. The addition of 455 mg (0.375 mmol) of **3a** immediately caused the solution to change to light yellow. The solution was stirred overnight under N_2, during which time it changed to colorless. The solution was concentrated to about 2 mL, and toluene was added until a small amount of microcrystals were observed; then hexane was slowly added. The mixture was kept in the refrigerator for 1 h. The white microcrystals were recovered by filtration, washed with hexane, and dried under vacuum, giving 337 mg (90%) of **7a**, mp 205–207 °C dec. IR: 3050 (m), 2923 (m), 1587 (w), 1478 (m), 1434 (m), 1265 (ms), 1219 (m), 1137 (s), 1097 (m), 1026 (s), 995 (w), 887 (s), 740 (m), 691 (s), 631 (s). ^{1}H NMR (CD_2Cl_2): δ 1.40 (d, $^4J_{PH}$ = 5.3 Hz, $^3J_{PtH}$ = 29.1 Hz, 3 H, CH_3C=), 1.47 (d, $^2J_{PH}$ = 7.9 Hz, $^3J_{PtH}$ = 25.3 Hz, 3 H, CH_3P), 1.83 (t, $^2J_{PH}$ = 3.6 Hz, $^3J_{PtH}$ = 33.4 Hz, 6 H, CH_3P), 4.69 (dt, $^4J_{PH}$ = 8.5 Hz, $^4J_{PH}$ = 1.1 Hz, $^3J_{PtH}$ = 42.8 Hz, 1 H, (*Z*)-CH=), 5.64 (dt, $^4J_{PH}$ = 19.0 Hz, $^4J_{PH}$ = 1.4 Hz, $^3J_{PtH}$ = 89.1 Hz, 1 H, (*E*)-CH=), 7.1–7.5 (aromatics, 30 H). ^{31}P NMR (CD_2Cl_2): δ −3.1 (t, $^2J_{PP}$ = 20.8 Hz, $^1J_{PtP}$ = 1693 Hz, 1 P), 3.4 (d, $^2J_{PP}$ = 20.8 Hz, $^1J_{PtP}$ = 2910 Hz, 2 P). ^{13}C NMR (CD_2Cl_2): δ 15.5 (m, CH_3P), 29.8 (t, $^3J_{PC}$ = 2.4 Hz, $^2J_{PtC}$ = 29.2 Hz, CH_3), 122.0 (br d, $^3J_{PC}$ = 3.4 Hz, CH_2=), 121.5 (q, $^1J_{FC}$ = 321.7 Hz, CF_3), 128.0–134.0 (aromatics), 155.4 (dt, $^2J_{PC}$ = 84.4 Hz, $^2J_{PC}$ = 11.7 Hz, $^1J_{PtC}$ = 584.7 Hz, PtC=). FAB MS: 837 (13%), 836 (M^+, 14%), 835 (10%), 637 (83%), 636 (100%), 635 (75%), 596 (17%), 595 (59%), 594 (52%). Anal. Calcd for $C_{43}H_{44}O_3F_3P_3SPt$: C, 52.39; H, 4.50. Found: C, 52.31; H, 4.54.

Reaction of 3b with Ph_2MeP To Form 7b. The reaction was performed as for **3a** above, with use of 125 mg (0.105 mmol) of **3b** and 74 mg (0.37 mmol) of methyldiphenylphosphine in 10 mL of methylene chloride, yielding 71 mg (67%) of **7b** as a white powder, mp 168–170 °C dec. IR: 3050 (w), 2918 (w), 1584 (w), 1570 (w), 1478 (m), 1431 (s), 1265 (s), 1140 (s), 1025 (s), 884 (s), 737 (s), 691 (s), 631 (s). ^{1}H NMR (CD_3NO_2): δ 1.11 (br s, 3 H, CH_3), 1.43 (br s, 3 H, CH_3), 1.70 (br d, $^2J_{PH}$ = 8.2 Hz, $^3J_{PtH}$ = 9.1 Hz, 3 H, CH_3P), 1.98 (t, $^2J_{PH}$ = 3.5 Hz, $^3J_{PtH}$ = 32 Hz, 6 H, CH_3P), 5.16 (m, 1 H, CH=), 7.2–7.6 (aromatics, 30 H). ^{31}P NMR (CD_3NO_2): δ 2.4 (t, $^1J_{PtP}$ = 1918 Hz), 6.3 (d, $^2J_{PP}$ = 19.5 Hz, $^1J_{PtP}$ = 2790 Hz). ^{13}C NMR (CD_3NO_2): δ 12.5 (t, $^1J_{PC}$ = 20 Hz, CH_3P), 14.0 (d, $^1J_{PC}$ = 32 Hz, CH_3P), 26.2 (d, $^4J_{PC}$ = 4.5 Hz, $^3J_{PtC}$ = 43 Hz, (*Z*)-CH_3), 29.5 (d, $^4J_{PC}$ = 11 Hz, $^3J_{PtC}$ = 58 Hz, (*E*)-CH_3), 129.7 (dt, J_{PC} = 21 Hz, J_{PC} = 5 Hz), 130.2 (d, J_{PC} = 11 Hz), 131.7 (s), 132.0 (s), 137.5 (t, $^3J_{PC}$ = 5 Hz).

Reaction of 3a with triphos To Form 8a. Methylene chloride (25 mL) was degassed through three freeze–pump–thaw cycles and then added to 159 mg (0.297 mmol) of triphos and 238 mg (0.196 mmol) of **3a**. The solution was stirred overnight under N_2. The methylene chloride was removed, giving a yellow oil, which was dissolved in a small amount of methylene chloride followed by addition of toluene and hexane to give a crystalline solid. The white crystals were recovered by filtration, washed with hexane, and dried under high vacuum to yield 118 mg (65%) of **8a**, mp 170–171 °C dec. IR: 3055 (m), 2913 (m), 1625 (w), 1581 (w), 1480 (w), 1431 (m), 1410 (m), 1265 (s), 1221 (m), 1150 (m), 1105 (m), 1025 (s), 995 (s), 889 (w), 867 (m), 820 (m), 800 (m), 751 (m), 717 (m), 703 (s), 695 (s), 632 (s). ^{1}H NMR ($CDCl_3$): δ 1.43 (br d, $^4J_{PH}$ = 5.2 Hz, $^3J_{PtH}$ = 30.0 Hz, 3 H, CH_3), 2.2–2.5 (m, 4 H, CH_2P), 2.9–3.5 (m, 4 H, CH_2P), 4.41 (br d, $^4J_{PH}$ = 7.9 Hz, $^3J_{PtH}$ = 46.2 Hz, 1 H, (*Z*)-CH=), 5.91 (br d, $^4J_{PH}$ = 17.5 Hz, $^3J_{PtH}$ = 89.1 Hz, 1 H, (*E*)-CH=), 7.3–8.0 (aromatics, 25 H). ^{31}P NMR ($CDCl_3$): δ 37.5 (d, J_{PP} = 3.7 Hz, $^1J_{PtP}$ = 2825 Hz, 2 P), 91.8 (t, J_{PP} = 3.7 Hz, $^1J_{PtP}$ = 1409 Hz, 1 P). ^{13}C NMR ($CDCl_3$): δ 26.0 (dt, $^1J_{PC}$ = 33.1 Hz, $^2J_{PC}$ = 5.1 Hz, $^2J_{PtC}$ = 82.4 Hz, CH_2P), 30.5 (d, $^3J_{PC}$ = 3.0 Hz, $^2J_{PtC}$ = 34.8 Hz, CH_3), 34.4 (m, CH_2P), 118.6 (d, $^3J_{PC}$ = 3.4 Hz, $^2J_{PtC}$ = 37.0 Hz, CH_2=), 120.8 (q, $^1J_{FC}$ = 321.0 Hz, CF_3), 127.0–134.0 (aromatics), 160.8 (dt, $^2J_{PC}$ = 87.3 Hz, $^2J_{PC}$ = 8.9 Hz,

PtC=). FAB MS: 771 (87%), 770 (M^+, 100%), 769 (71%), 730 (6%), 729 (6%), 154 (12%). Anal. Calcd for $C_{38}H_{38}O_3P_3F_3SPt$: C, 49.62; H, 4.16. Found: C, 49.47; H, 4.37.

Reaction of 3b with triphos To Form 8b. The reaction was performed as above with use of 80 mg of (0.067 mmol) of **3b** and 72 mg (0.14 mmol) of triphos in 5 mL of methylene chloride, yielding 37 mg (59%) of **8b** as a white solid, mp 238–240 °C dec. IR: 3057 (w), 2903 (w), 1587 (w), 1573 (w), 1481 (m), 1433 (s), 1265 (s), 1145 (s), 1103 (s), 1026 (s), 748 (s), 695 (s), 633 (s). ^1H NMR (CD_3NO_2): δ 0.74 (br s, 3 H, CH_3), 1.52 (br s, 3 H, CH_3), 2.46 (m, 4 H, CH_2P), 3.03 (m, 2 H, CH_2P), 3.57 (m, 2 H, CH_2P), 6.64 (br d, $^3J_{PH}$ = 7 Hz, 1 H, CH=), 7.3–8.0 (aromatics, 25 H). ^{31}P NMR (CD_3NO_2): δ 38.7 (s, $^1J_{PtP}$ = 2731 Hz, 2 P), 94.6 (s, $^1J_{PtP}$ = 1496 Hz, 1 P). ^{13}C NMR (CD_3NO_2): δ 26.2 (d, $^4J_{PC}$ = 4.0 Hz, $^3J_{PtC}$ = 48 Hz, CH_3), 27.4 (dt, $^1J_{PC}$ = 33 Hz, $^2J_{PC}$ = 6.0 Hz, CH_2P), 30.6 (d, $^4J_{PC}$ = 11 Hz, $^3J_{PtC}$ = 66 Hz, CH_2P), 34.7 (m), 139.4 (s).

Reaction of 3b with Me_4NI To Form 9b. To a solution of 280 mg (0.236 mol) of **3b** in 20 mL of methylene chloride was added 142 mg (0.706 mmol) of tetramethylammonium iodide. The iodide salt was only partly soluble. The mixture was stirred overnight, during which time the solution changed to light yellow. Column chromatography on silica gel, with CH_2Cl_2/hexane (4:1) as eluent, followed by recrystallization in CH_2Cl_2/hexane, gave 114 mg (54%) of **9b** as a light yellow crystalline product, mp 223–224 °C dec. IR: 3050 (m), 2890 (m), 2840 (w), 1586 (w), 1571 (w), 1480 (m), 1431 (s), 1271 (m), 1182 (m), 1126 (m), 1092 (s), 1025 (w), 995 (m), 740 (s), 690 (s). ^1H NMR ($CDCl_3$): δ 0.70 (dt, $^4J_{HH}$ = 1.2 Hz, $^5J_{PH}$ = 2.4 Hz, 3 H, (*Z*)-CH_3), 1.07 (s, $^4J_{PtH}$ = 11.5 Hz, 3 H, (*E*)-CH_3), 5.46 (br t, $^3J_{PH}$ = 4.9 Hz, 1 H, CH=), 7.4 (m, 18 H, ArH), 7.7 (m, 12 H, ArH). ^{31}P NMR ($CDCl_3$): δ 23.1 (s, $^1J_{PtP}$ = 3106 Hz). ^{13}C NMR ($CDCl_3$): δ 25.9 (s, $^3J_{PtC}$ = 72.8 Hz, (*Z*)-CH_3), 27.1 (s, $^3J_{PtC}$ = 89.3 Hz, (*E*)-CH_3), 127.5 (t, $^3J_{PC}$ = 5.3 Hz, *m*-C), 128.3 (t, $^3J_{PC}$ = 4.3 Hz, $(CH_3)_2C$=), 130.0 (s, *p*-C), 131.4 (t, $^2J_{PC}$ = 9.6 Hz, PtC=), 131.7 (t, $^1J_{PC}$ = 28.3 Hz, $^2J_{PtC}$ = 31.1 Hz, ipso-C), 135.3 (t, $^2J_{PC}$ = 5.9 Hz, *o*-C). FAB MS: 901 (M^+, 2%), 776 (79%), 775 (80%), 774 (60%), 721 (66%), 720 (100%), 719 (81%), 458 (47%), 457 (53%), 456 (55%). Anal. Calcd for $C_{40}H_{37}P_2IPt$: C, 53.28; H, 4.14. Found: C, 53.25; H, 4.06.

Reaction of 3a with Me_4NI To Form 9a. A solution of 289 mg (0.247 mmol) of **3a** and 143 mg (0.711 mmol) of Me_4NI in 20 mL of methylene chloride was stirred for 2 h and worked up as above to give 163 mg (77%) of **9a**, mp 203–204 °C dec. IR: 3042 (m), 2921 (w), 2888 (w), 1955 (br, w), 1885 (br, w), 1810 (br, w), 1577 (m), 1477 (m), 1429 (s), 1303 (w), 1180 (m), 1161 (m), 1090 (s), 1022 (m), 993 (m), 855 (s), 740 (s), 698 (s), 688 (s), 611 (w). ^1H NMR ($CDCl_3$): δ 0.88 (s, $^3J_{PtH}$ = 48.0 Hz, 3 H, CH_3), 4.68 (s, $^3J_{PtH}$ = 67.6 Hz, 1 H, (*Z*)-CH=), 5.03 (t, $^4J_{PH}$ = 1.2 Hz, $^3J_{PtH}$ = 135.6 Hz, 1 H, (*E*)-CH=), 7.4 (m, 18 H, ArH), 7.8 (m, 12 H, ArH). ^{31}P NMR ($CDCl_3$): δ 21.5 (s, $^1J_{PtP}$ = 3221 Hz). ^{13}C NMR ($CDCl_3$): δ 29.0 (s, $^2J_{PtC}$ = 47.9 Hz, CH_3), 114.3 (t, $^3J_{PC}$ = 4.3 Hz, CH_2=), 127.6 (t, $^3J_{PC}$ = 5.2 Hz, *m*-C), 130.1 (s, *p*-C), 131.5 (t, $^1J_{PC}$ = 28.1 Hz, $^2J_{PtC}$ = 32.7 Hz, ipso-C), 135.5 (t, $^2J_{PC}$ = 5.9 Hz, *o*-C), 151.8 (t, $^2J_{PC}$ = 8.4 Hz, PtC=). FAB MS: 761 (32%), 760 (36%), 759 (20%), 720 (34%), 719 (40%), 717 (35%), 457 (19%), 456 (26%), 455 (21%), 279 (100%). Anal. Calcd for $C_{39}H_{35}P_2IPt$: C, 52.77; H, 3.97. Found: C, 52.08; H, 4.11.

Reaction of 3a with Me_4NBr To Form 10a. A solution of 143 mg (0.122 mmol) of **3a** and 56 mg (0.36 mmol) of Me_4NBr in 20 mL of methylene chloride was stirred for 2 h. Column chromatography on silica gel, with CH_2Cl_2/hexane (6:1) as eluent, followed by recrystallization from CH_2Cl_2/hexane, yielded 75 mg (74%) of colorless crystalline product **10a** as a $^1/_4$-mol CH_2Cl_2 solvate according to ^1H NMR spectroscopy; mp 196–197 °C dec. IR: 3048 (m), 2928 (w), 1572 (m), 1479 (m), 1430 (s), 1306 (w), 1170 (w), 1092 (s), 1025 (w), 995 (w), 857 (w), 742 (s), 690 (s). ^1H NMR ($CDCl_3$): δ 0.87 (t, $^4J_{PH}$ = 1.2 Hz, $^3J_{PtH}$ = 46.7 Hz, 3 H, CH_3), 4.64 (s, $^3J_{PtH}$ = 63.7 Hz, 1 H, (*Z*)-CH=), 5.04 (t, $^4J_{PH}$ = 1.4 Hz, $^3J_{PtH}$ = 128.4 Hz, 1 H, (*E*)-CH=), 7.3 (m, 18 H, ArH), 7.8 (m, 12 H, ArH). ^{31}P NMR ($CDCl_3$): 23.7 (s, $^1J_{PtP}$ = 3262 Hz). ^{13}C NMR ($CDCl_3$): δ 29.6 (br s, CH_3), 114.5 (t, $^3J_{PC}$ = 4.7 Hz, CH_2=), 127.6 (t, $^3J_{PC}$ = 5.7 Hz, *m*-C), 130.1 (s, *p*-C), 130.7 (t, $^1J_{PC}$ = 28.0 Hz, ipso-C), 135.2 (t, $^2J_{PC}$ = 6.0 Hz, *o*-C), 147.3 (t, $^2J_{PC}$ = 8.0 Hz, PtC=). FAB MS: 842 (M^+, 0.2%), 840 (M^+, 0.3%), 761 (8%), 760 (9%), 720 (49%), 719 (60%), 718 (50%), 154 (100%). Anal. Calcd for $C_{39.25}H_{35.5}P_2BrCl_{0.5}Pt$: C, 54.70; H, 4.15. Found: C, 54.27; H, 4.07.

Reaction of 3b with Me_4NBr To Form 10b. A mixture of 280 mg (0.236 mmol) of **3b** and 109 mg (0.708 mmol) of Me_4NBr in 20 mL of methylene chloride was stirred overnight and worked up as above, yielding 108 mg (54%) of **10b** as a colorless crystalline solid, mp 201–202 °C dec. IR: 3050 (m), 2890 (m), 2840 (w), 1586 (w), 1570 (w), 1479 (m), 1430 (s), 1357 (w), 1305 (w), 1275 (m), 1180 (m), 1154 (w), 1127 (m), 1090 (s), 1023 (m), 995 (m), 840 (w), 806 (w), 739 (s), 690 (s), 623 (w). ^1H NMR ($CDCl_3$): δ 0.72 (dt, $^5J_{PH}$ = 2.3 Hz, $^4J_{HH}$ = 0.6 Hz, 3 H, (*Z*)-CH_3), 1.02 (s, $^4J_{PtH}$ = 11.6 Hz, 3 H, (*E*)-CH_3), 5.46 (br t, $^3J_{PH}$ = 3.6 Hz, 1 H, CH=), 7.4 (m, 18 H, ArH), 7.7 (m, 12 H, ArH). ^{31}P NMR ($CDCl_3$): d 24.9 (s, $^1J_{PtP}$ = 3145 Hz). ^{13}C NMR ($CDCl_3$): δ 26.2 (s, $^3J_{PtC}$ = 74.1 Hz, (*Z*)-CH_3), 27.0 (s, $^3J_{PtC}$ = 89.6 Hz, (*E*)-CH_3), 126.8 (t, $^2J_{PC}$ = 10.0 Hz, PtC=), 127.6 (t, $^3J_{PC}$ = 5.2 Hz, *m*-C), 128.4 (t, $^3J_{PC}$ = 4.0 Hz, $(CH_3)_2C$=), 130.0 (s, *p*-C), 131.1 (t, $^1J_{PC}$ = 27.9 Hz, $^2J_{PtC}$ = 30.6 Hz, ispo-C), 135.1 (t, $^2J_{PC}$ = 6.1 Hz, *o*-C). FAB MS: 854 (M^+, 0.5%), 775 (10%), 774 (12%), 720 (77%), 719 (100%), 718 (86%), 457 (15%), 456 (16%), 455 (17%). Anal. Calcd for $C_{40}H_{37}P_2BrPt$: C, 56.21; H, 4.36. Found: C, 56.41; H, 4.31.

Reaction of 3a with Me_4NCl To Form 11a. A solution of 152 mg (0.130 mmol) of **3a** and 41 mg (0.37 mmol) of Me_4NCl in 10 mL of methylene chloride was stirred overnight. Workup as above gave **11a** (57 mg, 56%), a colorless crystalline product as a $^1/_8$ CH_2Cl_2 solvate according to ^1H NMR spectroscopy; mp 159–160 °C dec. IR: 3045 (w), 2920 (w), 1578 (w), 1478 (m), 1430 (s), 1091 (s), 840 (m), 742 (s), 688 (s). ^1H NMR ($CDCl_3$): δ 0.88 (s, $^3J_{PtH}$ = 44.7 Hz, 3 H, CH_3), 4.59 (s, $^3J_{PtH}$ = 62.2 Hz, 1 H, (*Z*)-CH=), 5.05 (t, $^4J_{PH}$ = 1.4 Hz, $^3J_{PtH}$ = 121.4 Hz, 1 H, (*E*)-CH=), 7.4 (m, 18 H, ArH), 7.8 (m, 12 H, ArH). ^{31}P NMR ($CDCl_3$): δ 24.4 (s, $^1J_{PtP}$ = 3285 Hz). ^{13}C NMR ($CDCl_3$): δ 29.9 (s, $^2J_{PtC}$ = 47.6 Hz, CH_3), 114.9 (br t, $^3J_{PC}$ = 5.0 Hz, $^2J_{PtC}$ = 36.3 Hz, CH_2=), 127.7 (t, $^3J_{PC}$ = 5.3 Hz, *m*-C), 130.2 (s, *p*-C), 130.5 (t, $^1J_{PC}$ = 27.3 Hz, $^2J_{PtC}$ = 29.8 Hz, ipso-C), 135.2 (t, $^2J_{PC}$ = 6.2 Hz, *o*-C), 145.0 (t, $^2J_{PC}$ = 8.8 Hz, PtC=). FAB MS: 797 (0.2%), 796 (0.4%), 761 (21%), 760 (25%), 759 (17%), 720 (60%), 719 (81%), 718 (64%), 154 (100%). Anal. Calcd for $C_{39.13}H_{35.25}Cl_{1.25}P_2Pt$: C, 58.25; H, 4.40. Found: C, 57.29; H, 4.26.

Reaction of 3b with PhSNa To Form 12b. To a solution of 140 mg (0.118 mmol) of **3b** in 5 mL of dry THF was added 47 mg (0.356 mmol) of sodium thiophenoxide. The solution immediately changed to bright yellow and was stirred for 5 h, during which time a white precipitate formed. The THF was removed by evaporation on a rotovaporator. Chromatography of the residue on silica gel, with CH_2Cl_2/hexane (9:1) as eluent, followed by recrystallization in CH_2Cl_2/hexane gave 47 mg (45%) of **12b** as yellow crystals, mp 157–158 °C dec. IR: 3050 (m), 2890 (m), 1571 (m), 1468 (m), 1430 (m), 1275 (w), 1179 (w), 1088 (m), 1020 (w), 995 (w), 814 (w), 737 (s), 688 (s). ^1H NMR ($CDCl_3$): δ 0.80 (br s, $^4J_{PtH}$ = 10.0 Hz, 3 H, (*E*)-CH_3), 0.87 (br d, $^4J_{HH}$ = 1.1 Hz, 3 H, (*Z*)-CH_3), 5.63 (br t, $^3J_{PH}$ = 4.3 Hz, 1 H, CH=), 6.60 (overlapping, 3 H, ArH), 6.96 (dd, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 2.0 Hz, 2 H, *o*-H), 7.2–7.7 (aromatics, 30 H). ^{31}P NMR 22.7 (s, $^1J_{PtP}$ = 3133 Hz). ^{13}C NMR ($CDCl_3$): δ 25.6 (s, $^3J_{PtC}$ = 53.3 Hz, (*Z*)-CH_3), 28.7 (s, $^3J_{PtC}$ = 72.2 Hz, (*E*)-CH_3), 120.4 (s), 126.1 (s), 127.3 (t, $^3J_{PC}$ = 5.0 Hz, *m*-C), 129.5 (s, *p*-C), 131.1 (t, $^1J_{PC}$ = 27.7 Hz, $^2J_{PtC}$ = 30.9 Hz, ipso-C), 132.0 (s, $^2J_{PtC}$ = 21.2 Hz, ipso-C (PhS)), 134.5 (t, $^2J_{PC}$ = 5.4 Hz, *o*-C), 148.0 (s). FAB MS: 883 (M^+, 6%), 829 (3%), 775 (64%), 774 (77%), 773 (50%), 720 (60%), 719 (97%), 718 (100%), 717 (53%), 457 (91%), 456 (93%), 455 (89%), 262 (18%).

Reaction of 3a with PhSNa To Form 12a. This reaction was carried out as above with 139 mg (0.119 mmol) of **3a** and 48 mg (0.36 mmol) of sodium thiophenoxide in 5 mL of dry THF, yielding 35 mg (34%) of **12a** as yellow crystals, mp 187–190 °C dec. IR: 3050 (m), 2920 (m), 1572 (m), 1477 (m), 1465 (m), 1429 (s), 1305 (w), 1179 (m), 1154 (m), 1090 (s), 1020 (m), 990 (w), 852 (m), 739 (s), 728 (s), 685 (s). ^1H NMR ($CDCl_3$): δ 1.03 (s, $^3J_{PtH}$ = 34.4 Hz, 3 H, CH_3), 4.62 (br s, $^3J_{PtH}$ = 49.2 Hz, 1 H, (*Z*)-CH=), 5.22 (t, $^4J_{PH}$ = 1.8 Hz, $^3J_{PtH}$ = 101.8 Hz, 1 H, (*E*)-CH=), 6.54 (overlapping, 3 H, ArH), 6.90 (dd, $^3J_{HH}$ = 7.3 Hz, $^2J_{HH}$ = 2.1 Hz, 2 H, *o*-H), 7.1–7.8 (aromatics, 30 H). ^{31}P NMR ($CDCl_3$): δ 21.8 (s, $^1J_{PtP}$ = 3217 Hz). ^{13}C NMR ($CDCl_3$): δ 30.5 (s, $^2J_{PtC}$ = 32.9 Hz, CH_3), 117.2 (t, $^3J_{PC}$ = 3.5 Hz, CH_2=), 120.1 (s), 125.9 (s), 127.3 (t, $^3J_{PC}$ = 5.1 Hz, *m*-C), 129.7 (s, *p*-C), 130.7 (t, $^1J_{PC}$ = 27.7 Hz, $^2J_{PtC}$ = 31.6 Hz, ipso-C), 131.5 (s, $^2J_{PtC}$ = 19.9 Hz, ipso-C (PhS)), 134.7 (t, $^2J_{PC}$ = 5.8 Hz, *o*-C), 147.5 (s), 154.0 (t, $^2J_{PC}$ = 9.3 Hz, PtC=). FAB MS: 869 (M^+, 3%), 762 (28%), 761 (60%), 760

(58%), 720 (65%), 719 (100%), 718 (99%), 716 (60%), 457 (70%), 456 (69%), 455 (82%), 262 (18%).

Equilibration Studies. All equilibrium values were determined in $CDCl_3$ at room temperature (20 °C) in a septum-sealed NMR tube by integration of the respective ^{31}P signals in the NMR spectrum after 24 h of reaction (when no further changes were observed in the NMR spectrum). Equilibrium constants were determined for both the forward and reverse reactions and calculated from the known values of the concentrations of the starting complex and the respective ligands.

Equilibration of 6 and 5 (Eq 9). Complex **6** (17.4 mg, 1.76 × 10^{-2} mmol) was dissolved in 0.450 mL of $CDCl_3$ solution containing 0.176 mmol of CH_3CN. After equilibration and integration of the ^{31}P signals K was calculated to be 4.2 × 10^{-3}. For the reverse reaction 17.5 mg (1.84 × 10^{-2} mmol) of **5** was dissolved in a mixture of 0.250 mL of $CDCl_3$ containing 3.14 × 10^{-2} mmol of pyridine and 0.360 mL of $CDCl_3$ containing 8.10 × 10^{-2} mmol of CH_3CN. After equilibration and integration of the respective ^{31}P signals K was found to be 4.0 × 10^{-3} for an average value of K = (4.1 ± 0.1) × 10^{-3}.

Equilibration of 3a and 5 (Eq 10). The equilibrium constant for the forward reaction was found to be 0.225 by dissolving 21.9 mg (1.87 × 10^{-2} mmol) of **3a** in 0.350 mL of $CDCl_3$ containing 7.88 mmol of CH_3CN. For the reverse reaction K was found to be 0.146 by dissolving 25.6 mg (2.69 × 10^{-2} mmol) of **5** and 13.0 mg (4.96 × 10^{-2} mmol) of Ph_3P in $CDCl_3$.

Equilibration of 6 and 3a (Eq 11). The value of K was found to be 0.035 from 12.1 mg (1.22 × 10^{-2} mmol) of **6** and 6.6 mg (2.52 × 10^{-2} mmol) of Ph_3P in $CDCl_3$. For the reverse reaction K was found to be 0.0175 by dissolving 21.1 mg (1.80 × 10^{-2} mmol) of **3a** and 1.36 mmol of pyridine in $CDCl_3$ for an average value of K = (2.6 ± 0.9) × 10^{-2}.

Equilibration of 6 and 4 (Eq 12). CO was bubbled through 0.740 mL of a $CDCl_3$ solution of 18.0 mg (1.82 × 10^{-2} mmol) of **6** for 1 h in an NMR tube, which was then sealed with a septum. Integration of the ^{31}P signals gave a K value of 1.49 × 10^{-2}. For the reverse reaction 27.1 mg (2.89 × 10^{-2} mmol) of **4** and 5.64 × 10^{-2} mmol of pyridine were dissolved in 0.778 mL of $CDCl_3$ in an NMR tube, which was flushed with CO for 0.5 h and then sealed under CO with a septum. Integration of the ^{31}P signals gave a K value of 0.940 × 10^{-2} for an average K = (1.2 ± 0.3) × 10^{-2}.

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Supplementary Material Available: Tables of all bond distances and angles, positional parameters, least-squares planes, and displacement parameter for **9b** (14 page); a listing of observed and calculated structure factors for **9b** (14 pages). Ordering information is given any any current masthead page.

Nickel, Palladium, and Platinum Complexes Derived from Octafluorocyclooctatetraene. Synthesis of 1-2:5-6-η-Octafluorocyclooctatetraene Complexes of Nickel(0) and η^2-Octafluorobicyclo[3.3.0]octa-2,7-diene-4,6-diyl Complexes of Nickel(II), Palladium(II), and Platinum(II)

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The zerovalent complexes $[M(COD)_2]$ (M = Pt, Ni; COD = 1,5-cyclooctadiene) and $[Ni_2(COT)_2]$ (COT = 1,3,5,7-cyclooctatetraene) do not react with octafluorocyclooctatetraene (**1**). Addition of 2 equiv of a ligand to $[Pt(COD)_2]$, followed by **1**, affords the octafluorobicyclo[3.3.0]octa-2,7-diene-4,6-diyl complexes **7** (L = PPh_3, $AsPh_3$, *t*-BuNC). In two cases, octafluorocycloocta-2,5,7-triene-1,4-diyl intermediates **8** (L = PPh_3, $AsPh_3$) were observed by ^{19}F NMR spectroscopic monitoring of the reaction mixture. The tetrakis(phosphine) complexes $[ML_4]$ also react with **1** to afford octafluorobicyclo[3.3.0]octa-2,7-diene-4,6-diyl complexes **7** (M = Pt; L = PPh_2Me, $PPhMe_2$) and **10** (M = Pd; L = PPh_3). The palladium analogue **10** (L = *t*-BuNC) has also been prepared by addition of *t*-BuNC to tris(dibenzylideneacetone)dipalladium, followed by addition of **1**. In contrast, reaction of **1** with $[Ni(COD)L_2]$, prepared in situ from $[Ni(COD)_2]$ and 2 equiv of L, yields the four-coordinate 1-2:5-6η-OFCOT complexes **11** (L = PMe_3, $PPhMe_2$), which do not react further to give octafluorobicyclo[3.3.0]octa-2,7-diene-4,6-diyl complexes of Ni(II). Addition of other ligands (L = PCy_3, PPh_3, PPh_2Me, $P(OPh)_3$, $P(OMe)_3$) to solutions of $[Ni(COD)_2]$ and **1** result in no reaction with OFCOT. Similary the complexes $[Ni(C_2H_4)L_2]$ (L = PPh_3, PPh_2Me) do not react with **1**. In contrast, addition of 2 equiv of *t*-BuNC to $[Ni(COD)_2]$ in the presence of **1** yields the four-coordinate octafluorobicyclo[3.3.0]octa-2,7-diene-4,6-diyl complex **12**. This latter compound does not exchange the *t*-BuNC ligands with exogenous ligands, nor does it undergo any reductive elimination chemistry but instead forms the five-coordinate adducts **13** (L = PMe_3, PPh_3, *t*-BuNC). Comparisons are made of the chemistry of **1** with group 10 metals and the previously reported chemistry of cobalt and rhodium.

Introduction

Octafluorocyclooctatetraene (OFCOT, **1**)[1,2] possesses a varied transition-metal coordination chemistry, which in many respects differs significantly from that of its hydrocarbon analogue cyclooctatetraene (COT).[3] We have previously shown that photolysis of the (pentamethylcyclopentadienyl)cobalt and -rhodium complexes **2a,b**

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