Organometallics **1998,** *17,* 2953−2957

Synthesis of Metallacyclobutenes of Late Transition Metals via Nucleophilic Addition of Allenyl or Propargyl Complexes

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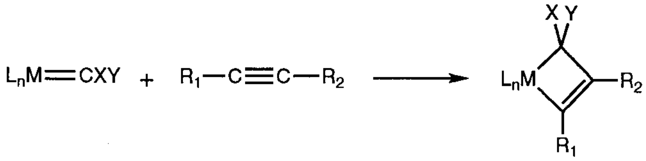
Received October 6, 1997

The regioselective addition of NEt_3, PPh_3, or pyridine to the central carbon of a cationic η^3-allenyl/propargyl complex of platinum, $\{Pt(PPh_3)_2(\eta^3\text{-}C_3H_3)\}(BF_4)$ (**1**), leads to the formation of the new cationic platinacyclobutenes $\{(PPh_3)_2Pt[CH_2C(Nu)CH]\}(BF_4)$ (Nu = NEt_3 (**2a**), PPh_3 (**2b**), C_5H_5N (**2c**)) via formation of a C−N or C−P bond, respectively. Complex **2c** can transform into $\{cis\text{-}Pt(PPh_3)_2(Py)(\eta^1\text{-}CHCCH_2)\}(BF_4)$ (**3**). The reverse reaction has not been observed. It is suggested that nucleophilic addition of **1** likely involves external attack at the central carbon of the η^3-allenyl/propargyl ligand. Protonation of **2b** yields $\{Pt(PPh_3)_2[\eta^3\text{-}CH_2C(PPh_3)CH_2]\}(BF_4)_2$ (**7**). Addition of PPh_3 to a labile η^1-allenyliridium complex, (*OC*-6-42)-$Ir(Cl)(PPh_3)_2(OTf)(CO)(\eta^1\text{-}CHCCH_2)$ (**4**), results in the iridacyclobutene $\{(Cl)(PPh_3)_2(CO)Ir[CH_2C(PPh_3)CH]\}(OTf)$ (**5**). The single-crystal X-ray structure of **5** has been determined.

Introduction

Metallacyclobutenes are important organometallic species that are involved in processes of metathesis[1] and polymer synthesis.[2] Tebbe, Parshall, and their coworkers led this field with studies of titanacyclobutenes.[3] Other workers have developed coupling reactions between metal carbene complexes and acetylenes as a useful route to such compounds (Scheme 1).[4,5] Metallacyclobutenes of late transition metals were unknown until Semmelhack et al. prepared ferracyclobutenes using the same approach.[6] These studies were extended later to the preparation of metallacyclobutenes of cobalt, rhodium, iridium, and platinum.[7]

Scheme 1



A new synthetic route, the addition of soft nucleophiles to a cationic η^3-allenyl/propargyl rhenium complex to give a rhenacyclobutene complex, was reported by Casey and co-workers.[8] We and others have independently developed the addition reactions of cationic η^3-allenyl/propargyl complexes of the late transition metals as a route to central-carbon-substituted η^3-allyl complexes, η^3-trimethylenemethane complexes, and η^3-oxa- and η^3-azatrimethylenemethane complexes.[9] Den-

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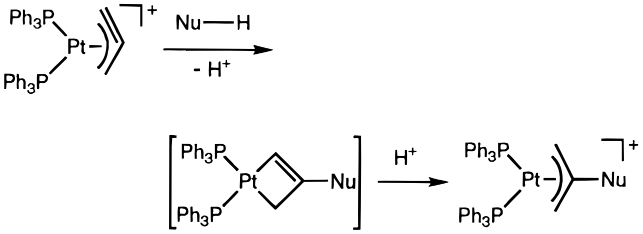
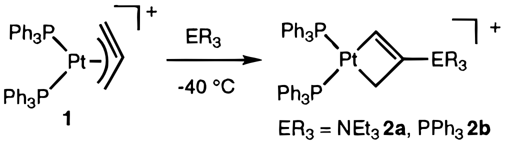
S0276-7333(97)00864-9 CCC: $15.00
Publication on Web 06/18/1998

Scheme 2



Scheme 3



sity functional caculations indicate that metallacyclobutenes are likely the kinetic intermediates in such addition reactions (Scheme 2).[10] We report here the first examples of the synthesis of platina- and iridacyclobutene complexes via addition of nitrogen- and phosphorus-centered nucleophiles to either (η^1-allenyl)- or (η^3-allenyl/propargyl)metal complexes.

Results and Discussion

The reactions of the (η^3-allenyl/propargyl)platinum complex $\{Pt(PPh_3)_2(\eta^3\text{-}C_3H_3)\}(BF_4)$ (**1**) with an equimolar amount of Et_3N or Ph_3P in chloroform or methylene dichloride at −40 °C readily gave the cationic platinacyclobutene complexes $\{(PPh_3)_2\overline{Pt[CH_2C(Nu)CH]}\}(BF_4)$ (Nu = NEt_3 (**2a**), PPh_3 (**2b**)) (Scheme 3). Complex **2a** decomposes on drying in vacuo, presumably due to evaporation of Et_3N. We have characterized **2a** by NMR spectroscopy. Complex **2b** is more stable and has been isolated by crystallization below 0 °C.

The two magnetically nonequivalent phosphine ligands of **2a** or **2b** suggest that these complexes have a cis square-planar configuration. The carbon-bound phosphorus in **2b** shows smaller values of J_{P-Pt} (703.8 Hz) compared to those of the Pt-bound Ph_3P ligands (J_{P-Pt} = 2115, 2226 Hz). In the ^{1}H NMR spectra, the methylene protons, unlike the diastereotopic protons in rhenacyclobutenes,[8] give rise to one characteristic resonance at high field, δ 0.03 (J_{H-P} = 81.9 Hz, J_{H-Pt} = 81.9 Hz) for **2a** and δ 0.18 (J_{H-H} = 4.7 Hz, J_{H-P} = 81.9 Hz, J_{H-Pt} = 85.8 Hz) for **2b**. The equivalency of the hydrogens of the Pt-bound CH_2 suggest that the metallacycle overlaps with the molecular plane and bisects ∠H−C−H. Similar NMR features have been found previously for other metallacyclobutenes.[3−8] The methine resonance of **2a** is found at δ 6.01 (J_{H-Pt} = 25.9 Hz). For **2b**, this resonance is in the region of the phenyl signals and was detected by 2D H−H and C−H COSY. The ^{13}C NMR resonances for the Pt−CH$_2$ carbons are also at high field, δ −6.07 (J_{C-Pt} = 79.4 Hz) for **2a** and δ −12.6 (J_{C-Pt} = 83.5 Hz) for **2b**. The olefinic carbons appear at δ 123.1 and 142.2 for **2a** and at δ 136.3 and 161.1 for **2b**.

The reaction of **1** and pyridine at −40 °C immediately resulted in the formation of metastable $\{(PPh_3)_2\overline{Pt[CH_2C(Py)CH]}\}(BF_4)$ (**2c**) in 91% yield based on NMR integration. When the solution of **2c** was brought to −20 °C, another platinum complex that exhibits a characteristic η^1-allenyl signature was formed. The two ^{31}P doublets at δ 8.36 and 24.86 with J_{P-P} = 16.4 Hz and J_{P-Pt} = 3662 and 2113 Hz, respectively, suggest that it is a cis square-planar complex. The pyridine signals were found to indicate coordination. We assign this product as *cis*-$[Pt(PPh_3)_2(Py)(\eta^1\text{-}CHCCH_2)](BF_4)$ (**3**) accordingly. The relative abundance of **2c**:**3**:**1** changed from 0.64:0.23:0.13 after 30 min to 0.57:0.30:0.14 after 8 h. When the temperature of the solution was raised to 0 °C for 20 min, the amount of complex **3** accounted for 85% of the starting amount of **1**. Complexes **1** and **2c** were not observed after that point, no matter how much the temperature was changed. Leaving **3** in solution at 25 °C caused the formation of a mixture of platinum complexes of η^3-2-hydroxyallyl and η^3-oxatrimethylenemethane and diplatina-η^6-diallyl ether.[11] One may infer that **1** can undergo nucleophilic attack either at the central carbon to give **2c** or at the metal center to give **3**. Complex **2c** is the kinetic product, and **3** is the thermodynamic product. Both products can revert to **1** by losing pyridine. The moisture that penetrated into the reaction vessel is blamed for hydrolyzing **1** to the hydroxyallyl complex and its ensuing byproducts of η^3-O-TMM and η^6-diallyl ether complexes (Scheme 4).

The reactions of other (η^1-allenyl)platinum complexes such as *trans*-$Pt(PPh_3)_2(Br)(\eta^1\text{-}CHCCH_2)$ and PPh_3 do not result in metallacyclobutene. The addition reaction of an octahedral (η^1-allenyl)iridium complex, however, was observed. Stirring a mixture of (*OC*-6-42)-$Ir(Cl)(PPh_3)_2(OTf)(CO)(\eta^1\text{-}CHCCH_2)$ (**4**)[12] and PPh_3 at −15 °C for 30 min caused a color change from reddish brown to yellow. The iridacyclobutene complex $\{(Cl)(PPh_3)_2(CO)\overline{Ir[CH_2C(PPh_3)CH]}\}(OTf)$ (**5**) was isolated in 78% yield (Scheme 5). The ^{31}P NMR data indicate that two phosphine ligands in **5** are in a trans arrangement. The ^{1}H and ^{13}C NMR data of the metallacyclobutene moiety of **5** are consistent with those of **2a**−**c** and the documented iridacyclobutenes.[7i,j] The carbonyl ligand of **5** is evidenced by an IR band at 2035 cm^{-1} and a ^{13}C NMR resonance at δ 171.5.

Single crystals of **5** were grown from a CH_2Cl_2/Et_2O solution, and an X-ray diffraction study was carried out. An ORTEP drawing showing the molecular structure of **5** is depicted in Figure 1. The metallacycle moiety, Pt−C2−C3−C4−P1, is quite coplanar, with the largest out-of-plane deviation at C3 being 0.04(2) Å and the mean deviation being 0.02 Å; X^2 is 8.25. The length of C2−C3 is consistent with a double bond, and Ir−C2(sp^2) and Ir−C4(sp^3) are in the single-bond region. Comparisons of important structural data between **5** and the closely related complex $(Br)(PMe_3)_3\overline{Ir[CH_2C(p\text{-}Tol)C(p\text{-}Tol)]}$ (**5′**)[7i] are listed in Table 1, which show excellent consistency with each other and with other titana-,[4,5] platina-,[7m,n] and rhenacyclobutenes.[8b] Two valence tautomers of metallacyclobutene, carbene

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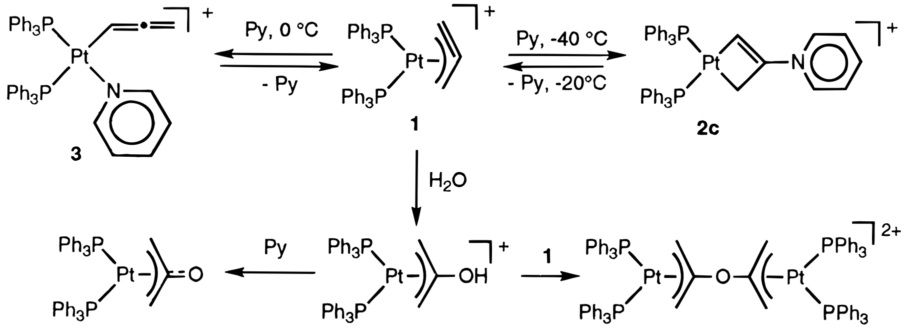
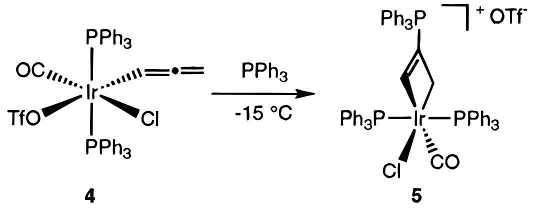
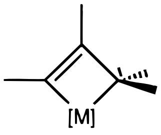
Scheme 4



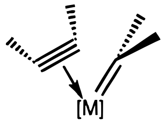
Scheme 5



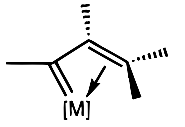
acetylene complexes (**5b**) and η^3-vinylcarbene complexes (**5c**), have been structurally characterized.[13,14] By judging the X-ray data for **5** and for species **5b** and **5c**, we unequivocally classify complex **5** to be the extreme form of metallacyclobutene, **5a**.



5a



5b



5c

The reaction of **4** with pyridine, which is less bulky than PPh_3, does not give a metallacyclobutene product. The replacement of pyridine for the triflate of **4**, instead of addition of pyridine to the allenyl ligand, takes place and gives (*OC*-6-42)-Ir(Cl)$(PPh_3)_2$(Py)(CO)(η^1-$CHCCH_2$) (**6**).[12b] Such a reactivity again supports the notion that the formation of metallacyclobutenes likely is due to external nucleophilic attack at the central carbon of an η^3-allenyl/propargyl ligand (Scheme 6). Metallacyclobutenes have been invoked as the kinetic intermediates of the formation of central-carbon-substituted η^3-allyl complexes from nucleophilic addition of η^1-allenyl and η^3-allenyl/propargyl complexes.[8−11,15] A reaction resulting in the formation of $\{Pt(PPh_3)_2[\eta^3\text{-}CH_2C(PPh_3)\text{-}CH_2]\}(BF_4)_2$ (**7**) from protonation of **2b** affords sound evidence for the former pathway (Scheme 7). On the other hand, insertion of coordinated allene into an M−L bond also was considered to be a possibility.[16]

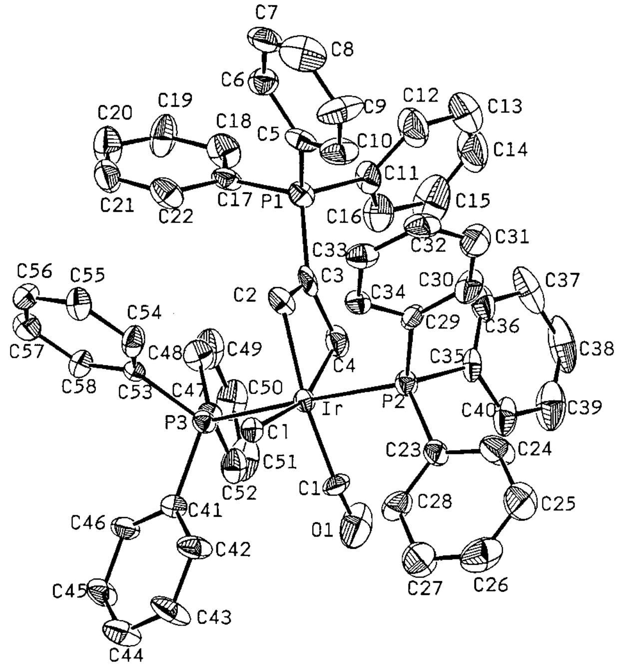


Figure 1. ORTEP drawing of $\{(Cl)(PPh_3)_2(CO)\overline{Ir[CH_2C(PPh_3)CH]}\}(OTf)$ (**5**) with 50% probability ellipsoids. The hydrogen atoms and the anion are omitted for clarity.

Table 1. Bond Comparison of 5 and 5′

5		5′	
Ir−C2	2.08(2)	Ir−C1	2.134(5)
Ir−C4	2.23(2)	Ir−C3	2.166(6)
C2−C3	1.39(2)	C1−C2	1.344(8)
C3−C4	1.53(3)	C2−C3	1.525(7)
C2−Ir−C4	66.9(7)	C1−Ir−C3	64.5(2)
C2−C3−C4	109(2)	C1−C2−C3	106.1(5)
Ir−C2−C3	97(1)	Ir−C1−C2	98.0(3)
Ir−C4−C3	87(1)	Ir−C3−C2	91.2(3)

In conclusion, regioselective addition to the η^3-allenyl/propargyl or η^1-allenyl complexes provides an alternative methodology for the synthesis of metallacyclobutenes.

Experimental Section

General Considerations. Solvents were dried by standard procedures. IR spectra were recorded on a Bio-Rad FTS-

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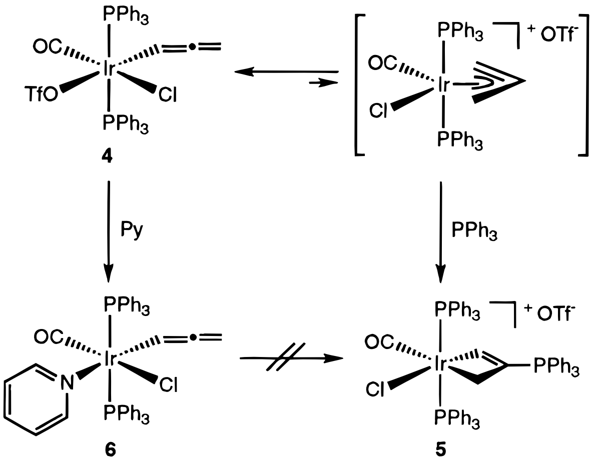
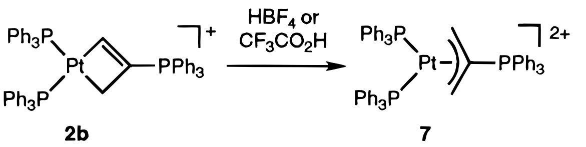
Scheme 6



Scheme 7



40 spectrophotometer. The NMR spectra were recorded on a Bruker AC-200 or a ACE-300 spectrometer. Spectrometer frequencies of 81.015 or 121.496 MHz for ^{31}P NMR, 200.133 or 300.135 MHz for ^{1}H NMR, and 50.323 or 75.469 MHz for ^{13}C NMR spectra were employed. Mass spectrometric analyses were collected on a JEOL SX-102A spectrometer. Elemental analyses were done on a Perkin-Elmer 2400 CHN analyzer.

Synthesis and Characterization. *cis*-{$(PPh_3)_2Pt[CH_2C(NEt_3)CH]$}$(BF_4)$ (2a). A two-necked round-bottomed flask was charged with **1** (45 mg, 0.05 mmol)[11] and dry $CDCl_3$ (0.7 mL). Triethylamine (21 μL, 0.05 mmol) was injected into the solution at −40 °C. The conversion to **2a** was quantitative on the basis of the NMR data. Attempted isolation of **2a** by crystallization resulted in its decomposition even at −20 °C. ^{31}P NMR ($CDCl_3$, 233 K, 81.015 MHz): δ 20.9 (d with ^{195}Pt satellites, $J_{P-P} = 10.2$ Hz, $J_{P-Pt} = 2470$ Hz), 21.1 (d with ^{195}Pt satellites, $J_{P-P} = 10.2$ Hz, $J_{P-Pt} = 2335$ Hz). ^{1}H NMR ($CDCl_3$, 233 K, 200 MHz): δ 0.03 (2H, m with ^{195}Pt coupling, $J_{H-Pt} = 81.9$ Hz, $PtCH_2$), 1.12 (9H, t, $J_{H-H} = 6.77$ Hz, CH_2CH_3), 2.99 (6H, q, $J_{H-H} = 6.77$ Hz, NCH_2), 6.01 (1H, s with ^{195}Pt coupling, $J_{H-Pt} = 25.9$ Hz, PtC*H*), 7.1−7.3 (30H, m, phenyl H). ^{13}C NMR ($CDCl_3$, 263 K, 50.323 MHz): δ −6.07 (d, $J_{C-P} = 79.4$, $PtCH_2$), 7.36 (s, CH_2CH_3), 47.0 (s, NCH_2), 123.1 (dd, $J_{C-P} = 6.3$, 106.8 Hz, Pt*C*H), 127−134 (phenyl carbons), 142.2 (d with ^{195}Pt satellites, $J_{C-P} = 7.02$ Hz, $J_{C-Pt} = 96.5$ Hz, *C*N).

***cis*-{$(PPh_3)_2Pt[CH_2C(PPh_3)CH]$}$(BF_4)$ (2b).** A two-necked round-bottomed flask was charged with $[Pt(PPh_3)_2(\eta^3\text{-}C_3H_3)](BF_4)$ (**1**;[11] 45 mg, 0.05 mmol) and dry $CDCl_3$ (1 mL). Addition of triphenylphosphine (13 mg, 0.05 mmol) to the solution at −40 °C immediately resulted in the formation of **2b**. The solid product was isolated by crystallization at 0 °C from C_6H_6/Et_2O in 83% yield (48 mg). ^{31}P NMR ($CDCl_3$, 273 K, 121.496 MHz): δ 8.2 (dd with ^{195}Pt coupling, $J_{P-P} = 38.6$ Hz, 21.7 Hz, $J_{P-Pt} = 703.8$ Hz), 19.2 (dd with ^{195}Pt coupling, $J_{P-P} = 10.4$ Hz, 38.6 Hz, $J_{P-Pt} = 2226$ Hz), 22.4 (dd with ^{195}Pt coupling, $J_{P-P} = 10.4$ Hz, 21.7 Hz, $J_{P-Pt} = 2115$ Hz). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 0.18 (dd with ^{195}Pt coupling, $J_{H-H} = 4.7$ Hz, $J_{H-P} = 4.4$ Hz, $J_{H-Pt} = 85.8$ Hz, 2H, $PtCH_2$), 7.35 (PtC*H*), 6.8−7.8 (m, phenyl H). ^{13}C NMR ($CDCl_3$, 263 K, 50.323 MHz): δ −12.6 (d, $J_{C-P} = 83.5$, $PtCH_2$), 127−134 (phenyl carbons), 136.3 (d, $J_{C-P} = 38.6$ Hz, *C*P), 161.1 (d, $J_{C-P} = 107.0$ Hz, Pt*C*H). MS (FAB, *m/z*): 1020.5 ($M^+ - BF_4$). Anal. Calcd for $PtC_{57}H_{48}P_3BF_4$: C, 61.77; H, 4.37. Found: C, 60.85; H, 4.42.

Table 2. X-ray Crystal Parameters and Data Collection Details for 5

formula	$C_{59}H_{48}O_4P_3ClSF_3Ir\cdot 2.5H_2O$
fw	1267.64
cryst dimns, mm	0.10 × 0.15 × 0.40
space group	$P\bar{1}$
a, Å	10.063(5)
b, Å	12.821(1)
c, Å	22.353(3)
α, deg	102.57(1)
β, deg	99.93(3)
γ, deg	97.12(3)
V, Å^3	2733(1)
Z	2
ρ(calcd), Mg m^{-3}	1.540
F(000)	1264
radiation; *λ*, Å	Mo Kα; 0.7107
T, K	298
μ, mm^{-1}	2.57
transmission	0.83−1.0
max 2*θ*, deg	45
h, *k*, *l*	±10, 13, ±24
no. of rflns measd	7145
no. of rflns obsd	4551 (>2.0*σ*)
no. of variables	587
R(*F*)	0.059
$R_w(F)$	0.059
S	1.88
$(\Delta/\sigma)_{max}$	0.0138

Table 3. Selected Bond Distances (Å) and Angles (deg) for 5

Ir−Cl	2.502(4)	Ir−P2	2.383(4)	Ir−P3	2.377(4)
Ir−C1	1.91(2)	Ir−C2	2.08(2)	Ir−C4	2.23(2)
C1−O1	1.00(2)	C2−C3	1.39(2)	C3−C4	1.53(3)
C3−P1	1.83(2)				
Cl−Ir−P2	90.(1)	Cl−Ir−P3	89.8(1)	Cl−Ir−C1	100.9(7)
Cl−Ir−C2	93.7(5)	Cl−Ir−C4	160.6(5)	P2−Ir−P3	177.9(2)
P2−Ir−C1	88.6(5)	P2−Ir−C2	90.7(4)	P2−Ir−C4	91.5(4)
P3−Ir−C1	89.5(5)	P3−Ir−C2	91.3(4)	P3−Ir−C4	89.4(4)
C1−Ir−C2	165.4(8)	C1−Ir−C4	98.5(8)	C2−Ir−C4	66.9(7)
C3−P1−C5	110.8(8)	C3−P1−C11	107.8(8)	C3−P1−C17	112.0(7)
Ir−C1−O1	172(2)	Ir−C2−C3	97(1)	P1−C3−C2	120(1)
P1−C3−C4	131(1)	C2−C3−C4	109(2)	Ir−C4−C3	87(1)

***cis*-{$(PPh_3)_2Pt[CH_2C(Py)CH]$}(BF_4) (2c).** The reaction of **1** (45 mg, 0.05 mmol) and pyridine (4.0 μL, 0.05 mmol) in $CDCl_3$ (0.7 mL) at −40 °C produced **2c** in 91% yield based on the NMR data. ^{31}P NMR ($CDCl_3$, 233 K, 121.496 MHz): δ 19.6 (d with ^{195}Pt coupling, $J_{P-P} = 12.72$ Hz, $J_{P-Pt} = 2445$ Hz), 21.6 (d with ^{195}Pt coupling, $J_{P-P} = 12.72$ Hz, $J_{P-Pt} = 2332$ Hz). ^{1}H NMR ($CDCl_3$, 233 K, 200 MHz): δ 0.47 (2H, m with ^{195}Pt coupling, $J_{H-Pt} = 80.4$ Hz, $PtCH_2$), 6.73 (1H, s with ^{195}Pt coupling, $J_{H-Pt} = 24.6$ Hz, PtC*H*), 6.8−7.3 (m, phenyl H), 8.03 (2H, m, $o\text{-}H_{Py}$), 8.40 (1H, m, $p\text{-}H_{Py}$). ^{13}C NMR ($CDCl_3$, 233 K, 50.32 MHz): δ −4.89 (d, $J_{C-P} = 78.4$, $PtCH_2$), 123.7 (d, $J_{C-P} = 8.32$, 151.7 Hz, Pt*C*H), 123.75 (s, $m\text{-}C_{Py}$), 127−134.5 (phenyl C), 136.4 (s, $p\text{-}C_{Py}$), 143.6 (d, $J_{C-P} = 7.76$ Hz, C_{Py}), 144.8 (s, $o\text{-}C_{Py}$).

***cis*-$[Pt(PPh_3)_2(\eta^1\text{-}CHCCH_2)(Py)](BF_4)$ (3).** The temperature of a solution of **2c**, first at −40 °C, was raised to 0 °C for 20 min, which gave **3** in 85% yield based on the NMR data. ^{31}P NMR ($CDCl_3$, 273 K, 121.496 MHz): δ 8.36 (d with ^{195}Pt coupling, $J_{P-P} = 16.4$ Hz, $J_{P-Pt} = 3662$ Hz), 24.86 (d with ^{195}Pt coupling, $J_{P-P} = 16.4$ Hz, $J_{P-Pt} = 2113$ Hz). ^{1}H NMR ($CDCl_3$, 273 K, 200 MHz): δ 3.48 (2H, m, CH_2), 5.02 (1H, m with ^{195}Pt coupling, $J_{H-Pt} = 47.2$ Hz, C*H*), 6.8−7.8 (33H, m, phenyl H, Py), 8.37 (2H, m, $o\text{-}H_{Py}$). ^{13}C NMR ($CDCl_3$, 273 K, 50.323 MHz): δ 67.4 (d, $J_{C-P} = 8.2$ Hz, CH_2), 88.1 (dd, $J_{C-P} = 10.24$, 93.6 Hz, *C*H), 127−135 (phenyl C), 126.0 (s, $p\text{-}C_{Py}$), 138.3 (s, $m\text{-}C_{Py}$), 151.0 (s, $o\text{-}C_{Py}$), 205.5 (s, =C=).

{$(Cl)(PPh_3)_2(CO)Ir[CH_2C(PPh_3)CH]$}(OTf) (5). To a two-necked round-bottomed flask was charged with **4** (200 mg, 0.22

mmol)[12] and PPh_3 (67 mg, 0.25 mmol), and the CH_2Cl_2 (15 mL) was vacuum-transferred. The reaction solution was stirred at −15 °C for 30 min. The resulting yellow solution was concentrated, and the product was precipitated by adding hexane to give **5** in 78% yield (215 mg). IR (KBr pellet): ν_{CO} 2035 cm^{-1}. ^{31}P NMR ($CDCl_3$, 121.496 MHz): δ −5.33, 3.23 (d, d, $J_{P-P} = 3.65$ Hz). ^1H NMR ($CDCl_3$, 200 MHz): δ 1.70 (2H, t, $J_{H-P} = 5$ Hz, PtCH_2), 6.6−7.7 (35H, m, phenyl H). ^{13}C NMR ($CDCl_3$, 75.469 MHz): δ −5.49 (t, $J_{C-P} = 6.38$ Hz, PtCH_2), 118.16 (d, $J_{C-P} = 85.1$ Hz, *ipso*-C of $CPPh_3$), 122.8 (td, $J_{C-P} =$ 8.15, 38.4 Hz, $CPPh_3$), 128−135 (phenyl C), 146.0 (t, $J_{C-P} =$ 5.93 Hz, PtCH), 171.5 (t, $J_{C-P} = 8.19$ Hz, CO). MS (FAB, *m*/*z*): 1230.30 (M^+), 1081.40 (M^+ − OTf). Anal. Calcd for $IrC_{59}H_{48}O_4F_3P_3SCl\cdot2.5H_2O$: C, 55.57; H, 4.19. Found: C, 56.42; H, 4.01.

{Pt(PPh$_3$)$_2$[η^3-CH$_2$C(PPh$_3$)CH$_2$]}(BF$_4$)$_2$ (7). To a $CDCl_3$ solution (0.5 mL) containing **2b** (30 mg, 0.059 mmol) was added an equimolar amount of HBF_4/etherate or CF_3CO_2H at 25 °C. The conversion to **7** was over 90% based on the NMR data. ^{31}P NMR ($CDCl_3$, 121.496 MHz): δ 11.1 ($J_{P-Pt} = 4027$ Hz), 17.1 ($J_{P-Pt} = 69.3$ Hz). ^1H NMR ($CDCl_3$, 300 MHz): δ 3.46 (2H, ddd, $J_{H-H} = 1.5$ Hz, $J_{H-P} = 1.5$, 12.1 Hz syn-H), 4.63 (2H, ddd, $J_{H-H} = 1.5$ Hz, $J_{H-P} = 6.1$, 29.9 Hz, $J_{H-Pt} = 47.1$ Hz, anti-H), 7.0−8.0 (35H, m, phenyl H). ^{13}C NMR ($CDCl_3$, 125.773 MHz): δ 74.8 (dd, $J_{C-P} = 5$, 14, 38 Hz, $J_{C-Pt} \approx 35$ Hz, C_t), 117.9 (d, $J_{C-P} = 87$ Hz, C_c), 128−135 (phenyl C).

X-ray Crystallographic Analysis. Diffraction data were measured at 298 K on a Nonius CAD-4 diffractometer with graphite-monochromatized Mo Kα radiation. Cell parameters were determined by a least-squares fit on 25 reflections. Intensity data were corrected for absorption on the basis of an experimental ψ rotation curve. The refinement procedure was by a full-matrix least-squares method including all the non-hydrogen atoms anisotropically. Hydrogen atoms were fixed at the ideal geometry and a C−H distance of 1.0 Å; their isotopic thermal parameters were fixed to the values of the attached carbon atoms at the convergence of the isotropic refinement. Atomic scattering factors were taken from ref 17. Computing programs are from the NRCC SDP VAX package.[18] Crystallographic data and selected bond parameters of **5** are collected in Tables 2 and 3, respectively. Other detailed data are supplied in the Supporting Information.

Acknowledgment. We thank the National Science Council, Taiwan, ROC, for financial support.

Supporting Information Available: Tables giving the complete crystal parameters and data collection details, atomic coordinates and isothermal data, and bond lengths (Å) and angles (deg) for complex **5** and figures giving the NMR spectra of **2a**−**c**, **3**, and **7** (24 pages). Ordering information is given on any current masthead page.

OM9708642

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