the reaction of 1 with PhC_2Ph at 125 °C. Because of their close structural similarity, we expected that 4 might be derived from 3 by elimination of H_2, but our efforts to achieve this transformation independently have not been successful. Likewise, it appears that 5 could be derived from its isomer 4 by a cleavage of a C–N bond and a hydrogen shift. Our efforts to obtain 5 from 4 by thermal treatment at 125 °C have not been successful, but significant amounts of 8 which can also be obtained from 5 under these conditions were obtained. This suggests that a 4–5 transformation may be involved. It does appear that 2 is a precursor to its isomer 6, but the yield of 6 from 2 is not high. When 5 is heated to 125 °C, it is decarbonylated and converted to 8 by a transformation of the propylidyne ligand to a methyl-substituted σ–π coordinated vinyl ligand. This type of transformation is rare but has been observed in other polynuclear metal complexes.[19]

The formation of compound 7 is simply the result of addition of another 1 equiv of PhC_2Ph to 3 combined with insertion into a metal–hydrogen bond and decarbonylation. Conceivably, PhC_2Ph could have abstracted H_2 from 3 and thus provide a route to 4, but since no 4 was observed in this reaction, we believe that this possible reaction is not important in this case.

Acknowledgment. These studies were supported by the U.S. Department of Energy under Grant No. DE-FG09-84ER13296.

Registry No. 1, 136131-85-6; 2, 136154-80-8; 3, 136131-88-9; 4, 137823-90-6; 5, 137823-91-7; 6, 137823-92-8; 7, 137823-93-9; 8, 137823-94-0; PhC≡CPh, 501-65-5.

Supplementary Material Available: Tables of hydrogen atom parameters and anisotropic thermal parameters (27 pages); listings of observed and calculated structure factor amplitudes (87 pages). Ordering information is given on any current masthead page.

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Synthesis, Characterization, and Reaction Chemistry of the Novel Heterobimetallic Iridium–Platinum Complexes $[(PR_3)_2(CO)Ir(\mu\text{-}H)(\mu\text{-}\eta^2{:}\eta^1\text{-}CH{=}CH_2)Pt(PR'_3)_2]^+[OTf]^-$

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Reactions of Ir(I)–triflate complexes *trans*-$Ir(OTf)(CO)(PR_3)_2$ ($PR_3 = PPh_3$, 1; $PR_3 = PMePh_2$, 2) with Pt^0–π-ethylene complexes $Pt(H_2C{=}CH_2)(PR'_3)_2$ ($PR'_3 = PPh_3$, 3; $(PR'_3)_2 = Ph_2P(CH_2)_3PPh_2$, 4) in CH_3NO_2 result in C–H bond activation and the ready formation of the novel heterobimetallic Ir–Pt complexes $[(PR_3)_2(CO)Ir(\mu\text{-}H)(\mu\text{-}\eta^2{:}\eta^1\text{-}CH{=}CH_2)Pt(PR'_3)_2]^+[OTf]^-$ ($PR_3 = PR'_3 = PPh_3$, 5; $PR_3 = PMePh_2$, $PR'_3 = PPh_3$, 6; $PR_3 = PPh_3$, $(PR'_3)_2 = Ph_2P(CH_2)_3PPh_2$, 7; $PR_3 = PMePh_2$, $(PR'_3)_2 = Ph_2P(CH_2)_3PPh_2$, 8). A definitive structural determination for these heterobimetallic Ir–Pt complexes has been established by an X-ray diffraction study on complex 5 (triclinic, $P\bar{1}$ (No. 2), $a = 13.321$ (1) Å, $b = 15.461$ (2) Å, $c = 17.753$ (2) Å, $\alpha = 90.37$ (1)°, $\beta = 95.47$ (1)°, $\gamma = 100.92$ (1)°, $Z = 2$). Reactivity tests with one of the heterobimetallic complexes 7, using $Ph_2P(CH_2)_3PPh_2$ and acids, have also been conducted.

Introduction

Heterobimetallic complexes containing asymmetric metal–metal bonds[1] have received considerable attention and are of current research interest largely because of their relevance to catalysis.[2] Although a wide variety of heterobimetallic compounds have been prepared and characterized, it is difficult to systematically devise a strategy for the synthesis of particularly desired products. Compared to the well-established organic chemistry, the synthetic chemistry of heterobimetallic complexes is still in its infancy. Therefore, it is not surprising to see in the literature that a large number of reactions leading to the formation of metal–metal-bonded compounds are seren-

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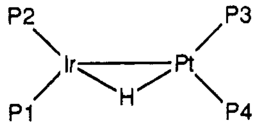
dipitous discoveries. Since the triflate anion is known to be an excellent leaving group in nucleophilic substitution reactions in organic chemistry, it seemed likely that transition-metal triflate complexes might serve as valuable and important precursors to heterobimetallic complexes generated by substitution of the relatively labile triflate ligand by an incoming transition-metal nucleophile. In order to develop the synthetic potential of the newly prepared, stable iridium triflate complexes *trans*-Ir(OTf)(CO)$(PR_3)_2$, we sought to react these compounds with transition-metal complexes in hopes of discovering a rational route to the synthesis of new heterobimetallic compounds.

In this paper, we wish to report (a) the reaction of *trans*-Ir(OTf)(CO)$(PR_3)_2$ with $Pt(H_2C{=}CH_2)(PR'_3)_2$ to give novel heterobimetallic Ir–Pt complexes, which demonstrates the first intermolecular example of olefin C–H activation by a second, different metal system of a precomplexed π-ethylene transition-metal complex,[3] (b) the X-ray crystal structure of a novel heterobimetallic Ir–Pt complex, and (c) the reactivity of the heterobimetallic Ir–Pt complex $[(PPh_3)_2(CO)Ir(\mu\text{-}H)(\mu\text{-}\eta^2{:}\eta^1\text{-}CH{=}CH_2)Pt(Ph_2P(CH_2)_3PPh_2)]^+[OTf]^-$ (**7**).

Results and Discussion

Synthesis and Characterization of Heterobimetallic Ir–Pt Complexes. It is well-known that the platinum ethylene complex $Pt(H_2C{=}CH_2)(PPh_3)_2$ (**3**)[4] is stable in the solid state. However, evolution of ethylene takes place when it is reacted with a large number of reagents.[1j,5] Oxidative addition of the M–X bond of a metal complex to a zerovalent complex of platinum has been shown to be a general and facile method for the synthesis of a wide variety of compounds containing platinum–metal bonds.[5b,e,h,i] For example, Akhtar and Clark[5i] have reported that reaction of **3** with $(\eta^5\text{-}C_5H_5)Fe(CO)_2(Cl)$ leads to the formation of the heterobimetallic Fe–Pt complex $(\eta^5\text{-}C_5H_5)(CO)_2FePt(Cl)(PPh_3)_2$ accompanied by the liberation of ethylene. More recently, Rossell et al.[5e] have reported the synthesis of heterotrimetallic Pt–Hg–Pt complexes $Hg[Pt(R)(PPh_3)_2]_2$ by reaction of **3** with $RHgPt(R)(PPh_3)_2$. They envision the formation of heterotrimetallic products as a result of insertion of the carbene-like, 14-electron $Pt(PPh_3)_2$ fragment into the Hg–R bond. With this idea in mind and in view of the rather small number of Ir–Pt complexes compared with that of other heterobimetallic systems, we sought first to utilize this strategy with iridium triflate complex *trans*-Ir(OTf)(CO)$(PPh_3)_2$ (**1**).[6] We thought that the Ir–OTf bond of **1** might oxidatively add to **3** with evolution of ethylene gas to give the anticipated heterobimetallic Ir–Pt product of the formula $(PPh_3)_2(CO)Ir{-}Pt(OTf)(PPh_3)_2$ (**9**) containing an asymmetric metal–metal bond.

Table I. $^{31}P\{^1H\}$ **NMR** (CD_3NO_2) **Monitoring Data for Heterobimetallic Ir–Pt Products**



I

		chem shift, ppm[a] (J_{P-Pt}, Hz)		
entry no.	starting material	Ir–P1 and Ir–P2	Pt–P3 and Pt–P4	product[b]
1	**1** + **3**	11.74 (<90), 6.62 (154)	22.31 (2401), 14.90 (4644)	**5**
2	**2** + **3**	−8.54 (96), −23.95 (147)	21.33 (2400), 16.26 (4688)	**6**
3	**1** + **4**	11.68 (<100), 7.19 (155)	1.69 (4286), 0.83 (2115)	**7**
4	**2** + **4**	−9.42 (<100), −23.52 (155)	1.84 (4337), −0.09 (2119)	**8**

[a] At 121 MHz and ambient temperature, referenced to external 85% H_3PO_4. [b] Isolated products from the preparative experiments.

First, iridium triflate complex **1** was combined with 1.0 equiv of platinum ethylene complex **3** in CD_3NO_2 in a 5-mm NMR tube. After it was shaken, the mixture became homogeneous. The occurrence of a reaction is evidenced by the dissolution of platinum ethylene complex **3**, since complex **3** is nearly insoluble in nitromethane. $^{31}P\{^1H\}$ NMR (CD_3NO_2) monitoring shows the rapid consumption of starting materials and the appearance of four major multiplet resonances at 22.31 (J_{P-Pt} = 2401 Hz), 14.90 (J_{P-Pt} = 4644 Hz), 11.74 (J_{P-Pt} < 90 Hz), and 6.62 (J_{P-Pt} = 154 Hz) ppm with corresponding ^{195}Pt satellites (entry 1, Table I). These data imply the presence of a metal–metal bond in a product which contains four inequivalent triphenylphosphine ligands. It should be noted that the first two resonances show much larger ^{195}Pt couplings as compared to those of the last two resonances. Thus, the chemical shifts at 22.31 and 14.90 ppm are assigned to the two triphenylphosphine ligands bonded directly to the Pt metal center, while the resonances at 11.74 and 6.62 ppm are attributed to the remaining two triphenylphosphine groups attached to the Ir atom. Surprisingly, in the ^1H NMR (CD_3NO_2) spectrum a complex multiplet centered at δ −11.37 (m, J_{H-Pt} = 510 Hz) is observed accompanied by ^{195}Pt satellites. We tentatively consider this upfield chemical shift and coupling constant to be diagnostic of a bimetallic bridging hydride ligand.[7] This result also rules out the formation of the anticipated product **9**, since **9** does not contain a bridging hydride ligand. Although several low-intensity signals are also observed at δ 5.68–1.03 in the ^1H NMR spectrum, it is somewhat difficult to unambiguously rationalize these results without further purification of the product. The same heterobimetallic Ir–Pt product is also obtained by conducting the reaction of **1** and **3** in benzene-d_6. However, the reaction takes 2–3 days to go to completion as assayed by $^{31}P\{^1H\}$ NMR monitoring.

In order to probe the generality of this type of reaction between iridium triflate and platinum ethylene complexes, similar NMR tube scale reactions were subsequently

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conducted in CD_3NO_2 with *trans*-$Ir(OTf)(CO)(PMePh_2)_2$ (**2**) and **3** (entry 2, Table I), **1** and $Pt(H_2C{=}CH_2)(Ph_2P(CH_2)_3PPh_2)$ (**4**)[8] (entry 3, Table I), and **2** and **4** (entry 4, Table I). In all cases, the formation of a heterobimetallic bridging hydride complex is observed, as evidenced by four multiplet $^{31}P\{^1H\}$ NMR resonances as listed in Table I and the diagnostic ^1H NMR upfield complex multiplets centered at δ −11.49 to −11.71 (J_{H-Pt} = 472–512 Hz) accompanied by the corresponding ^{195}Pt satellites. The heterobimetallic products for entries 1 and 2 in Table I show slight differences in the chemical shifts for Pt-bonded triphenylphosphine ligands (namely 22.31 and 14.90 ppm in entry 1 vs 21.33 and 16.26 ppm in entry 2) and large differences in the chemical shifts for the different Ir-bonded phosphine groups (namely 11.74 and 6.62 ppm in entry 1 vs −8.54 and −23.95 ppm in entry 2). A similar situation is also observed for entries 3 and 4. Likewise, similar comparisons can be made for the heterobimetallic products for entries 1 and 3, which show slight differences in the chemical shifts for the Ir-bonded triphenylphosphine ligands (namely 11.74 and 6.62 ppm in entry 1 vs 11.68 and 7.19 ppm in entry 3) and large differences in the chemical shifts for the different Pt-bonded phosphine groups (namely 22.31 and 14.90 ppm in entry 1 vs 1.69 and 0.83 ppm in entry 3). A similar pattern is also observed for the heterobimetallic products for entries 2 and 4. On the basis of the similarities discussed above, we tentatively suggest that the heterobimetallic products in entries 1–4 have a common skeleton which can be represented schematically as I.

Efforts were next concentrated on the isolation and complete characterization of these heterobimetallic products. In a preparative-scale experiment, reaction of **1** with 1.0 equiv of **3** in CH_3NO_2 at room temperature for 2 h gives $[(PPh_3)_2(CO)Ir(\mu\text{-}H)(\mu\text{-}\eta^2{:}\eta^1\text{-}CH{=}CH_2)Pt(PPh_3)_2]^+[OTf]^-$ (**5**) in 58% isolated yield (Scheme I) as air-stable, bright-yellow crystals. Complex **5** has been characterized by IR and NMR (^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, ^{19}F) spectroscopy and by microanalysis. The IR spectrum of **5** displays ν_{CO} at 1981 (s) cm^{-1} due to the terminal carbonyl stretch, indicating that the heterobimetallic Ir–Pt bond is not supported by a CO bridge. The observation of stretching frequencies at 1272 (s), 1223 (m), 1148 (s), and 1031 (s) cm^{-1} is indicative of the presence of an ionic triflate group.[9] In addition, the detection of a bridging vinyl ligand is evidenced by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. The ^1H NMR spectrum ($CDCl_3$) of **5** shows resonances as assigned to the $\eta^2{:}\eta^1\text{-}CH{=}CH_2$ ligand at δ 5.60 (m, μ-CH), 2.32 (m, μ-C*H*H′), and δ 1.35 (m, μ-CH*H′*). The $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$) exhibits the μ-CH carbon resonance downfield at 141.80 ppm (dd, J_{C-P} = 85.1, 13.1 Hz), while the μ-CH_2 carbon appears upfield at 37.56 ppm (br s). These spectroscopic data are consistent with those reported for the $\eta^2{:}\eta^1\text{-}CH{=}CH_2$ coordination mode.[10]

In analogy to the above reaction of complex **3**, the interaction of cyclic analogue **4** with **1** results in a 79% isolated yield of the adduct $[(PPh_3)_2(CO)Ir(\mu\text{-}H)(\mu\text{-}\eta^2{:}\eta^1\text{-}CH{=}CH_2)Pt(Ph_2P(CH_2)_3PPh_2)]^+[OTf]^-$ (**7**) as bright yellow crystals (Scheme I). Likewise, reaction of **2** with **4** affords $[(PMePh_2)_2(CO)Ir(\mu\text{-}H)(\mu\text{-}\eta^2{:}\eta^1\text{-}CH{=}CH_2)Pt(Ph_2P(CH_2)_3PPh_2)]^+[OTf]^-$ (**8**) as bright yellow crystals with 0.1 Et_2O solvate in 73% isolated yield (Scheme I). New complexes **7** and **8** have been characterized by IR and NMR (^1H, $^{13}C\{^1H\}$, ^{19}F, $^{31}P\{^1H\}$) spectroscopy and by microanalysis. Reaction of **2** with **3** gives $[(PMePh_2)_2(CO)Ir(\mu\text{-}H)(\mu\text{-}\eta^2{:}\eta^1\text{-}CH{=}CH_2)Pt(PPh_3)_2]^+[OTf]^-$ (**6**; Scheme I). Numerous attempts to purify **6** (via benzene washing, recrystallization from CH_2Cl_2/Et_2O, CH_2Cl_2/hexane, CH_3NO_2/Et_2O) resulted in only moderately pure product. We attribute this difficulty of purification to the higher solubility of **6** compared to that of **5**, **7**, and **8** in organic solvents. Thus, complex **6** is isolated as a slightly impure, brown-yellow powder in ca. 75% yield and is characterized by IR and NMR (^1H, ^{19}F, $^{31}P\{^1H\}$) spectroscopy.

Table II. Summary of Crystallographic Data for $[(PPh_3)_2(CO)Ir(\mu\text{-}H)(\mu\text{-}\eta^2{:}\eta^1\text{-}CH{=}CH_2)Pt(PPh_3)_2]^+[OTf]^-$ (5)

mol formula	$C_{76}H_{64}F_3IrO_4P_4PtS$
mol wt	1641.60
cryst syst	triclinic
space group	$P\bar{1}$ (No. 2)
temp of collecn, °C	16 (1)
cell constants	
a, Å	13.321 (1)
b, Å	15.461 (2)
c, Å	17.753 (2)
α, deg	90.37 (1)
β, deg	95.47 (1)
γ, deg	100.92 (1)
V, Å^3	3572.70
Z	2
d_{obsd}, g/cm^3	1.470
d_{calcd}, g/cm^3	1.526
cryst dimens, mm	0.18 × 0.15 × 0.08
radiation λ, Å	1.540 56 (Cu)
data collecn method	$\theta/2\theta$
scan speed, deg/min	variable
range of indices (hkl)	0–15, ±18, ±20
no. of rflns between stds	1 X-ray h
total no. of unique data	11 738
no. of obsd data $I > 3\sigma(I)$	10 436
abs coeff (μ), cm^{-1}	87.05
min transmissn factor	0.53
max transmissn factor	0.99
no. of variables	796
$R = \sum(\lVert F_o\rvert - \lvert F_c\rVert)/\sum(F_o)$	0.0434
$R_w = \sum(\lvert F_o\rvert - \lvert F_c\rvert)w^{1/2}/\sum(F_o)w^{1/2}$	0.0499
goodness of fit	3.49
$\Delta\rho$(max), e/Å^3	2.017 about 0.95 Å from Pt

Table III. Selected Bond Lengths (Å) for 5

Pt–Ir	2.7484 (2)	Ir–C1	1.865 (5)
Pt–P3	2.244 (1)	Ir–C2	2.197 (4)
Pt–P4	2.321 (1)	Ir–C3	2.168 (4)
Pt–C3	2.014 (4)	Ir–H1	1.64
Pt–H1	1.43	C1–O1	1.159 (5)
Ir–P1	2.362 (1)	C2–C3	1.415 (6)
Ir–P2	2.337 (1)		

The exact reaction pathway for the formation of heterobimetallic Ir–Pt complexes **5**–**8** is not known. However, several aspects of the above results are noteworthy: (1) unlike the other reaction products derived from platinum ethylene complexes reported in the literature,[1j,5] complexes **3** and **4** do not lose the ethylene ligand, (2) the first intermolecular example of olefin C–H activation by a second, different metal system of a precomplexed π-ethylene transition-metal complex is observed, and (3) these reactions provide a related yet previously unexplored method for the synthesis of a new class of heterobimetallic Ir–Pt complexes with remarkable stability.

A definitive structural assignment for the heterobimetallic Ir–Pt complexes is established by an X-ray diffraction study on complex **5**. The numbering diagram and

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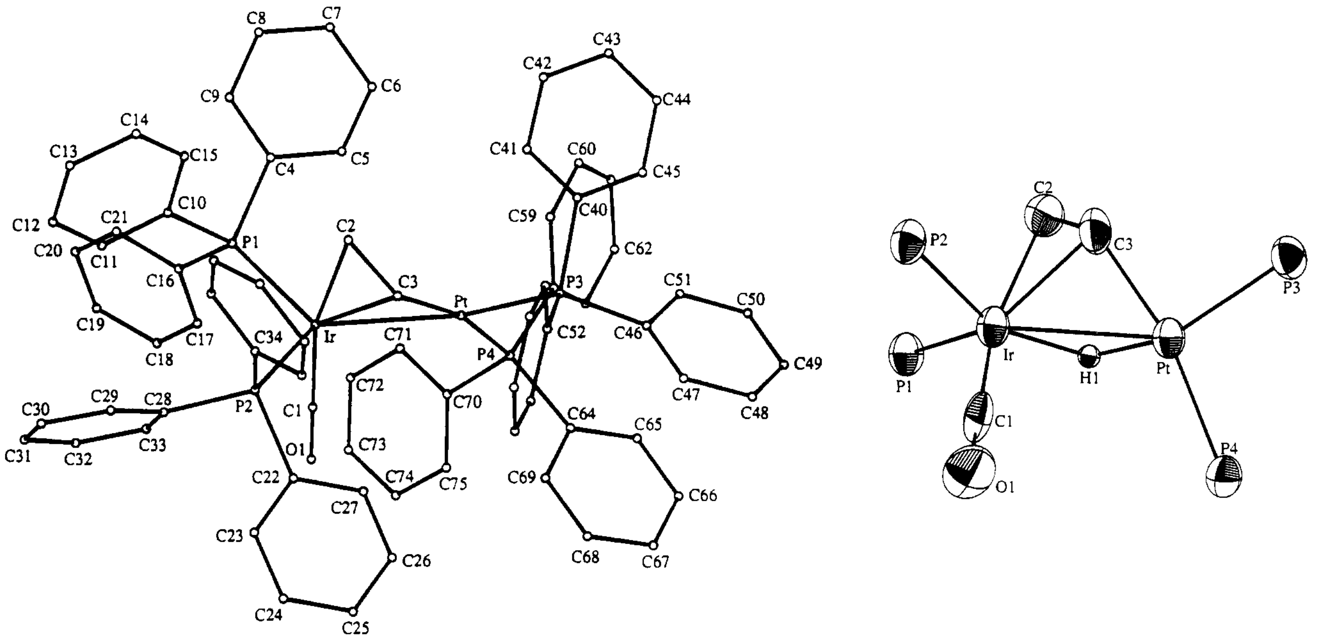

Figure 1. Two views of the structure of the cation of **5**: (a, left) numbering diagram (hydrogen atoms are omitted for clarity); (b, right) simplified ORTEP representation (phenyl rings of the PPh_3 groups and hydrogen atoms other than the μ-hydride ligand are omitted for clarity).

Scheme I

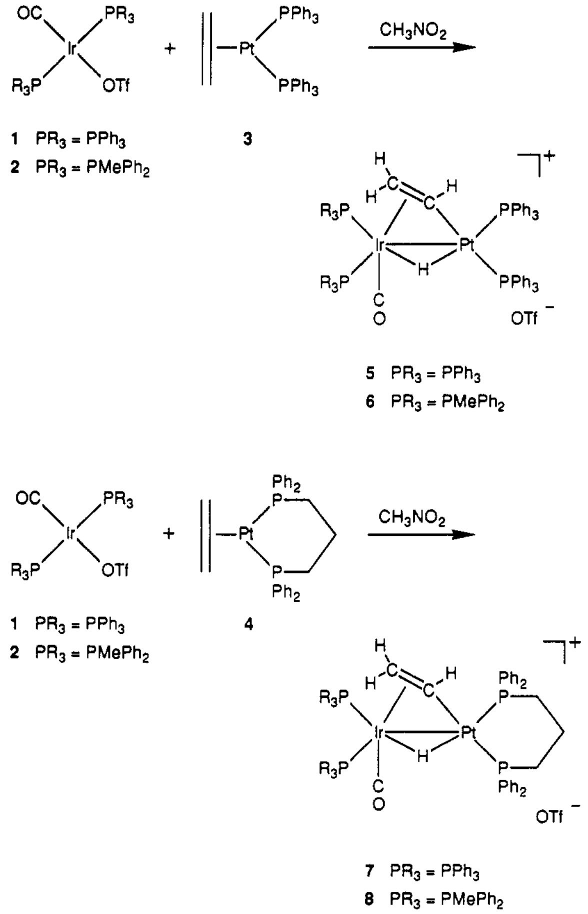

Table IV. Selected Bond Angles (deg) for 5

Ir–Pt–P3	142.74 (3)	P1–Ir–C3	123.5 (1)
Ir–Pt–P4	115.70 (3)	P1–Ir–H1	103.59 (3)
Ir–Pt–C3	51.4 (1)	P2–Ir–C1	87.2 (1)
Ir–Pt–H1	28.34 (1)	P2–Ir–C2	94.3 (1)
P3–Pt–P4	101.06 (4)	P2–Ir–C3	91.3 (1)
P3–Pt–C3	91.4 (1)	P2–Ir–H1	148.28 (3)
P3–Pt–H1	149.21 (3)	C1–Ir–C2	163.5 (2)
P4–Pt–C3	166.0 (1)	C1–Ir–C3	125.8 (2)
P4–Pt–H1	102.25 (3)	C1–Ir–H1	95.8 (1)
C3–Pt–H1	68.6 (1)	C2–Ir–C3	37.8 (2)
Pt–Ir–P1	127.25 (3)	C2–Ir–H1	74.5 (1)
Pt–Ir–P2	124.17 (3)	C3–Ir–H1	61.5 (1)
Pt–Ir–H1	24.43 (0)	Pt–H1–Ir	127.23 (1)
Pt–Ir–C1	92.0 (1)	Ir–C1–O1	178.6 (4)
Pt–Ir–C2	73.6 (1)	Ir–C2–C3	70.0 (2)
Pt–Ir–C3	46.5 (1)	Pt–C3–Ir	82.1 (2)
P1–Ir–P2	105.26 (4)	Pt–C3–C2	120.7 (3)
P1–Ir–C1	108.9 (1)	Ir–C3–C2	72.2 (2)
P1–Ir–C2	86.6 (1)		

simplified ORTEP representation of the cation are shown in Figure 1. X-ray data are summarized in Table II. The bridging hydride ligand is located by difference Fourier methods. Key bond lengths, important bond angles, and atomic coordinates are summarized in Tables III–V. The bridging hydride ligand is asymmetrically bound to the heterobimetallic Ir–Pt center with an Ir–H1 distance of 1.64 Å, a Pt–H1 distance of 1.43 Å, and an Ir–H1–Pt angle of approximately 127°. The existence of a heterobimetallic Ir–Pt bond is indicated by the distance of 2.7484 (2) Å, which is shorter than the value of 2.8393 (12) Å found for the unbridged Ir–Ir distance in $[(\eta^5\text{-}C_5Me_5)(CO)_2Ir\text{–}Ir(CO)_2(\eta^5\text{-}C_5Me_5)]^{2+}[BF_4]^-_2$.[11] The vinyl ligand is coordinated to the Ir center by η^2 binding and is attached to the Pt atom by a σ bond through C3. The Ir–C2, Ir–C3, and Pt–C3 distances are 2.197 (4), 2.168 (4), and 2.014 (4) Å, respectively. The C2–C3 distance of 1.415 (6) Å lies between the bond distances of a C—C single and C═C double bond. The dihedral angle between the P1–Ir–P2 plane and P3–Pt–P4 plane is about 67°.

Reactivity of Heterobimetallic Ir–Pt Complex 7. It is known that the metal–metal bond in bimetallic systems is usually weaker than the metal–ligand bonds and is often the center of reactivity.[1] In order to explore the chemistry of these newly prepared heterobimetallic Ir–Pt complexes **5**–**8**, we investigated the reactions of **7** with $Ph_2P(CH_2)_3PPh_2$ and acids.

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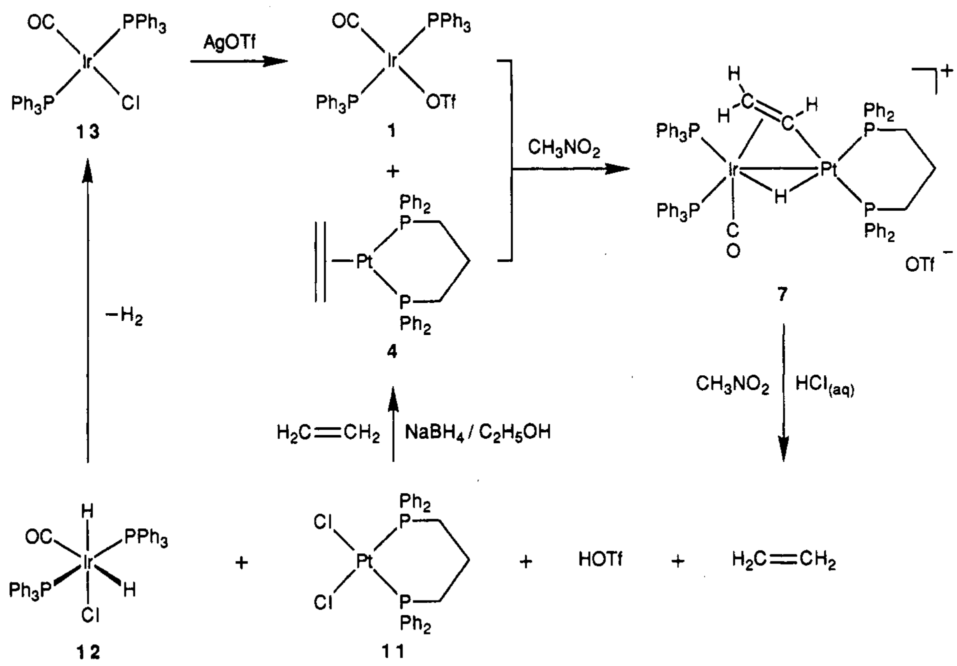
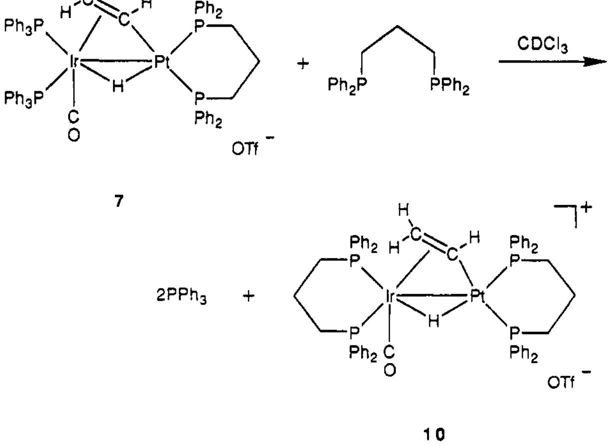
(11) Einstein, F. W. B.; Jones, R. H.; Zhang, X.; Yan, X.; Nagelkerke, R.; Sutton, D. *J. Chem. Soc., Chem. Commun.* **1989**, 1424.

Scheme II



A. Reaction with Ph$_2$P(CH$_2$)$_3$PPh$_2$. Reaction of heterobimetallic complex 7 with 2.0 equiv of Ph$_2$P(CH$_2$)$_3$PPh$_2$ (eq 1) in CDCl$_3$ in a 5-mm NMR tube at 50 °C was monitored by ^{31}P{^{1}H} NMR spectroscopy. The ^{31}P{^{1}H} NMR spectrum shows two singlet resonances in a 1:1 ratio at −5.14 and −17.20 ppm for PPh$_3$ and unreacted Ph$_2$P(CH$_2$)$_3$PPh$_2$, respectively, and four new multiplet resonances at −0.97 ($J_{\text{P-Pt}}$ = 4237 Hz), −2.93 ($J_{\text{P-Pt}}$ = 2048 Hz), −11.39 ($J_{\text{P-Pt}}$ = 142 Hz), and −25.93 ($J_{\text{P-Pt}}$ = 81 Hz) ppm with corresponding ^{195}Pt satellites appear over the course of 24 h as four multiplet resonances for 7 diminish. The above data clearly indicate the two triphenylphosphine ligands originally attached to the Ir metal center have been displaced by the more electron-donating ligand Ph$_2$P(CH$_2$)$_3$PPh$_2$ to give a new heterobimetallic complex, whose structure is proposed as [(Ph$_2$P(CH$_2$)$_3$PPh$_2$)(CO)Ir(μ-H)(μ-η^2:η^1-CH=CH$_2$)Pt(Ph$_2$P(CH$_2$)$_3$PPh$_2$)]$^+$[OTf]$^-$ (10; eq 1). The structure of 10 is assigned by analogy to the other heterobimetallic complexes 5–8. In the ^{1}H NMR spectrum, a complex multiplet resonance for the bimetallic bridging hydride ligand is centered at δ −11.82 ($J_{\text{H-Pt}}$ = 531 Hz) and is accompanied by ^{195}Pt satellites. In addition, the bridging vinyl ligand η^2:η^1-CH=CH$_2$ gives rise to a μ-CH resonance at δ 4.74 as a broad multiplet, while the μ-CH$_2$ proton signals are obscured by the unresolved complex resonances at δ 3.32–1.45 which arise from the protons of the two inequivalent cyclic P(CH$_2$)$_3$P moieties. In the IR spectrum, ν_{CO} is observed at 1970 cm^{-1} for the terminal carbonyl group. In addition, the decrease of CO stretching frequency from 1980 cm^{-1} for the reactant (7) to 1970 cm^{-1} for the product (10) is consistent with an increase in electron density at the iridium metal center, as expected when PPh$_3$ is replaced with the more electron-donating Ph$_2$P(CH$_2$)$_3$PPh$_2$ ligand, which enhances the back-bonding from the metal.



(1)

B. Reaction with Acids. Reaction of heterobimetallic complex 7 with excess HCl (37% aqueous) in CD$_3$NO$_2$ in a 5-mm NMR tube was monitored by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy at room temperature. The results are summarized in Scheme II. After having been shaken vigorously, the yellow solution immediately turned colorless, and a white precipitate formed. The ^{1}H NMR spectrum of the supernatant shows the clean formation of ethylene (s, δ 5.39) and *cis*-Pt(Cl)$_2$(Ph$_2$P(CH$_2$)$_3$PPh$_2$) (11).[8] This result indicates that cleavage of the Ir–Pt bond has occurred. The identities of ethylene and 11 are confirmed by NMR comparisons with an ethylene-saturated CD$_3$NO$_2$ solution and an independently prepared authentic sample of 11, respectively. The corresponding ^{31}P{^{1}H} NMR spectrum of the supernatant shows a singlet at −3.64 ppm ($J_{\text{P-Pt}}$ = 3407 Hz) accompanied by ^{195}Pt satellites for complex 11. These results suggest the white precipitate must be the Ir-containing product. Thus, the supernatant was removed by syringe, and the white residue was dried under vacuum for ca. 5 min. The white precipitate was then dissolved in CDCl$_3$, and the NMR spectra were immediately recorded. The ^{31}P{^{1}H} NMR spectrum shows (relative peak intensity) a singlet resonance at 10.18 ppm (100%) and a singlet resonance of very low intensity at 24.28 ppm (ca. 5.0%). The corresponding ^{1}H NMR spectrum shows the clean formation of known dihydrido complex Ir(H)$_2$(Cl)(CO)(PPh$_3$)$_2$ (12),[12] as evidenced by the

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[12] (a) Deutsch, P. P.; Eisenberg, R. *Chem. Rev.* **1988**, *88*, 1147. (b) Vaska, L. *J. Am. Chem. Soc.* **1966**, *88*, 4100. (c) Taylor, R. C.; Young, J. F.; Wilkinson, G. *Inorg. Chem.* **1966**, *5*, 20. (d) Chock, P. B.; Halpern, J. *J. Am. Chem. Soc.* **1966**, *88*, 3511. (e) Vaska, L.; Rhodes, R. E. *J. Am. Chem. Soc.* **1965**, *87*, 4970. (f) Vaska, L.; Diluzio, J. W. *J. Am. Chem. Soc.* **1962**, *84*, 679.

Table V. Atomic Coordinates and Equivalent Isotropic Thermal Parameters of Non-Hydrogen Atoms in 5[a]

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
Pt	0.11247 (2)	0.31278 (2)	0.2590 (2)	2.6801 (6)	C32	0.5158 (8)	0.0593 (7)	0.1396 (6)	5.6 (2)
Ir	0.23032 (2)	0.18768 (2)	0.24051 (2)	2.714 (6)	C33	0.4622 (7)	0.1154 (6)	0.1752 (6)	4.9 (2)
S	−0.4084 (2)	−0.2680 (2)	0.2418 (2)	6.22 (7)	C34	0.4133 (7)	0.1794 (6)	0.3964 (5)	4.1 (2)
P1	0.1718 (2)	0.0368 (1)	0.2086 (1)	2.95 (4)	C35	0.443 (1)	0.2343 (9)	0.5256 (6)	7.6 (3)
P2	0.3989 (2)	0.1981 (1)	0.2953 (1)	3.20 (4)	C36	0.4391 (8)	0.2494 (7)	0.4479 (6)	5.4 (2)
P3	0.0606 (2)	0.3946 (1)	0.3471 (1)	3.25 (4)	C37	0.3913 (8)	0.0928 (6)	0.4224 (5)	5.0 (2)
P4	0.0543 (2)	0.3753 (1)	0.1487 (1)	3.04 (4)	C38	0.395 (1)	0.0777 (8)	0.4993 (6)	7.0 (3)
F1	−0.3941 (9)	−0.2179 (7)	0.1051 (6)	12.9 (3)	C39	0.421 (1)	0.147 (1)	0.5505 (6)	7.8 (4)
F2	−0.475 (1)	−0.3466 (9)	0.1156 (8)	15.9 (4)	C40	−0.0506 (6)	0.3334 (5)	0.3892 (4)	3.5 (2)
F3	−0.5456 (9)	−0.2339 (8)	0.1375 (6)	13.3 (3)	C41	−0.0839 (7)	0.2443 (6)	0.3722 (5)	4.5 (2)
O1	0.3219 (5)	0.2813 (5)	0.1068 (4)	5.6 (2)	C42	−0.1751 (9)	0.1996 (7)	0.3966 (6)	5.8 (2)
O2	−0.3945 (7)	−0.1774 (4)	0.2640 (5)	7.9 (2)	C43	−0.2327 (8)	0.2431 (7)	0.4386 (6)	5.6 (2)
O3	0.4883 (6)	0.3244 (5)	0.7233 (5)	7.7 (2)	C44	−0.1992 (7)	0.3299 (7)	0.4573 (6)	5.5 (2)
O4	−0.3150 (6)	−0.3016 (5)	0.2378 (7)	9.2 (3)	C45	−0.1094 (7)	0.3762 (6)	0.4329 (5)	4.8 (2)
C1	0.2859 (5)	0.2447 (5)	0.1574 (5)	3.6 (2)	C46	0.0174 (6)	0.4973 (5)	0.3253 (5)	3.5 (2)
C2	0.1616 (6)	0.1593 (5)	0.3475 (4)	3.5 (2)	C47	0.0723 (8)	0.5794 (6)	0.3512 (6)	5.6 (2)
C3	0.1888 (6)	0.2514 (5)	0.3390 (5)	3.5 (2)	C48	0.031 (1)	0.6547 (6)	0.3376 (8)	7.1 (3)
C4	0.0326 (6)	−0.0022 (5)	0.2139 (5)	3.4 (2)	C49	−0.062 (1)	0.6491 (6)	0.2969 (7)	6.8 (3)
C5	−0.0332 (7)	0.0567 (5)	0.2140 (5)	4.1 (2)	C50	−0.1169 (7)	0.5682 (6)	0.2697 (6)	5.3 (2)
C6	−0.1368 (7)	0.0291 (6)	0.2218 (6)	4.9 (2)	C51	−0.0776 (7)	0.4926 (5)	0.2829 (5)	4.2 (2)
C7	−0.1748 (7)	−0.0597 (6)	0.2298 (6)	4.9 (2)	C52	0.1649 (7)	0.4255 (6)	0.4221 (5)	4.3 (2)
C8	−0.1118 (7)	−0.1196 (6)	0.2274 (6)	4.6 (2)	C53	0.1579 (8)	0.3970 (7)	0.4963 (6)	5.8 (2)
C9	−0.0079 (7)	−0.0909 (5)	0.2197 (5)	4.3 (2)	C54	0.244 (1)	0.418 (1)	0.5487 (6)	7.9 (3)
C10	0.2257 (6)	−0.0387 (5)	0.2717 (5)	3.4 (2)	C55	0.3351 (9)	0.462 (1)	0.5281 (7)	8.7 (3)
C11	0.3128 (7)	−0.0719 (5)	0.2567 (5)	4.0 (2)	C56	0.3440 (8)	0.4900 (8)	0.4549 (7)	7.3 (3)
C12	0.3540 (7)	−0.1288 (6)	0.3058 (6)	5.1 (2)	C57	0.2588 (8)	0.4704 (7)	0.4019 (6)	5.4 (2)
C13	0.3088 (8)	−0.1533 (6)	0.3715 (6)	5.5 (2)	C58	−0.0840 (6)	0.3518 (5)	0.1238 (4)	3.2 (2)
C14	0.2243 (8)	−0.1189 (6)	0.3889 (6)	5.4 (2)	C59	−0.1450 (7)	0.2936 (6)	0.1684 (5)	4.2 (2)
C15	0.1822 (7)	−0.0630 (5)	0.3397 (5)	4.3 (2)	C60	−0.2506 (8)	0.2693 (7)	0.1484 (6)	5.5 (2)
C16	0.1887 (6)	−0.0032 (5)	0.1142 (5)	3.6 (2)	C61	−0.2954 (8)	0.3032 (7)	0.0860 (7)	6.1 (3)
C17	0.2075 (9)	0.0527 (6)	0.0566 (5)	5.8 (3)	C62	−0.2365 (8)	0.3604 (7)	0.0414 (6)	5.7 (2)
C18	0.221 (1)	0.0232 (7)	−0.0152 (6)	8.2 (4)	C63	−0.1306 (7)	0.3844 (6)	0.0593 (5)	4.3 (2)
C19	0.216 (1)	−0.0637 (7)	−0.0288 (6)	7.0 (3)	C64	0.1033 (6)	0.4929 (5)	0.1539 (5)	3.4 (2)
C20	0.1966 (9)	−0.1236 (6)	0.0281 (6)	5.8 (2)	C65	0.0484 (7)	0.5583 (5)	0.1331 (5)	3.9 (2)
C21	0.1822 (8)	−0.0938 (6)	0.0992 (5)	4.8 (2)	C66	0.0953 (8)	0.6464 (6)	0.1418 (6)	5.1 (2)
C22	0.4758 (6)	0.3080 (5)	0.2861 (5)	3.6 (2)	C67	0.1973 (9)	0.6709 (6)	0.1700 (6)	5.8 (3)
C23	0.5818 (7)	0.3208 (6)	0.2920 (6)	5.2 (2)	C68	0.2529 (8)	0.6072 (6)	0.1912 (6)	5.3 (2)
C24	0.6395 (8)	0.4035 (7)	0.2863 (8)	6.8 (3)	C69	0.2068 (7)	0.5183 (6)	0.1831 (5)	4.5 (2)
C25	0.5926 (8)	0.4763 (6)	0.2754 (7)	5.5 (2)	C70	0.0991 (6)	0.3400 (5)	0.0609 (4)	3.6 (2)
C26	0.4885 (8)	0.4641 (6)	0.2709 (6)	5.2 (2)	C71	0.0606 (7)	0.2546 (6)	0.0347 (5)	4.5 (2)
C27	0.4305 (7)	0.3814 (5)	0.2777 (6)	4.9 (2)	C72	0.0956 (9)	0.2255 (7)	−0.0323 (6)	6.1 (3)
C28	0.4753 (6)	0.1280 (5)	0.2523 (5)	3.5 (2)	C73	0.1661 (9)	0.2809 (8)	−0.0707 (6)	6.5 (3)
C29	0.5439 (7)	0.0851 (6)	0.2947 (6)	4.6 (2)	C74	0.2033 (9)	0.3669 (8)	−0.0446 (6)	6.2 (3)
C30	0.5955 (7)	0.0291 (6)	0.2596 (6)	5.5 (2)	C75	0.1698 (7)	0.3974 (6)	0.0219 (5)	4.9 (2)
C31	0.5813 (7)	0.0166 (6)	0.1827 (6)	5.6 (2)	C76	−0.474 (2)	−0.275 (1)	0.139 (1)	18.3 (6)

[a] Atoms refined anisotropically are given in the form of the isotropic equivalent displacement parameters, defined as $^4/_3[a^2B_{1,1} + b^2B_{2,2} + c^2B_{3,3} + ab(\cos\gamma)B_{1,2} + ac(\cos\beta)B_{1,3} + bc(\cos\alpha)B_{2,3}]$.

observation of two upfield multiplet resonances centered at δ −7.31 ($J_{\text{H-H}}$ = 4.7 Hz, $J_{\text{H-P}}$ = 17.5 Hz) and −18.49 ($J_{\text{H-H}}$ = 4.7 Hz, $J_{\text{H-P}}$ = 14.0 Hz). After sitting at room temperature for 1–2 days, the solution turns yellow with the resonance at 24.28 ppm in the $^{31}P\{^1H\}$ NMR spectrum having increased in intensity. The product corresponding to the resonance at 24.28 ppm is then identified as Vaska's complex, *trans*-Ir(Cl)(CO)(PPh$_3$)$_2$ (**13**),[13] by NMR and IR comparisons with an independently prepared authentic sample. This observation of decomposition of **12** to **13** is consistent with results reported by others;[12a,d,e] complex **13** reacts rapidly and reversibly with H$_2$ to give the dihydrido compound **12**. At low hydrogen pressure, complex **12** is converted to Vaska's complex **13** via evolution of H$_2$. Since the reaction was carried out in the presence of excess aqueous HCl, the triflate anion of **7** is likely converted to CF$_3$SO$_3$H. Next, heterobimetallic complex **7** and excess HCl (37% aqueous) were reacted on a preparative scale. After workup, **11** and **12** are obtained in 89% and 62% isolated yield, respectively. As shown in Scheme II, **11** and **12** can be recycled to give **4** and **13**, respectively. Complex **13** in turn can be converted by reaction with AgOTf to iridium triflate complex **1**, which can then be reacted with **4** to give heterobimetallic Ir–Pt complex **7**. It is interesting to note that heterobimetallic complex **7** can be cleaved into mononuclear iridium and platinum complexes, which can then be assembled to regenerate heterobimetallic complex **7** in the reaction cycle.

Next, **7** was treated with CF$_3$SO$_3$H and then CF$_3$CO$_2$H in CD$_3$NO$_2$. However, only unidentifiable complex mixtures of products were formed from both reactions, as indicated by $^{31}P\{^1H\}$ NMR spectroscopy.

Conclusion

In an effort to discover a rational method for the synthesis of new heterobimetallic compounds, we have examined and described the utility of iridium triflate complexes *trans*-Ir(OTf)(CO)(PR$_3$)$_2$ in the reactions with platinum ethylene complexes. The interaction of Ir(I)–triflate complexes **1** and **2** with Pt^0–π-ethylene complexes **3** and **4** results in C–H bond activation and the ready formation of novel heterobimetallic Ir–Pt complexes **5**–**8**. A definitive structural determination for these heterobimetallic Ir–Pt complexes is established by an X-ray diffraction study on complex **5**. These results not only demonstrate a unique

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(13) Vrieze, K.; Collman, J. P.; Sears, C. T. Jr.; Kubota, M. *Inorg. Synth.* **1968**, *11*, 101.

synthetic method for the preparation of new heterobimetallic Ir–Pt complexes but also uncover a remarkable vinylic C–H bond activation process. Furthermore, our system represents the first example of an intermolecular, homogeneous transition-metal olefin C–H activation of a prior π-complexed alkene and the isolation of unique ethylene-bridged Ir–Pt complexes. In order to gain some insight into the chemical properties of these newly prepared products, we have also conducted reactivity tests with one of the heterobimetallic complexes, 7, using $Ph_2P(CH_2)_3PPh_2$ and acids.

Experimental Section

Materials and Measurements. All reactions were conducted under a dry nitrogen atmosphere using Schlenk techniques, unless otherwise noted. IR spectra were recorded on a Mattson Polaris FT-IR spectrometer. All NMR spectra were recorded on a Varian XL-300 spectrometer. ^1H NMR spectra were recorded at 300 MHz, and all chemical shifts are reported in ppm relative to internal tetramethylsilane (Me_4Si) or the proton resonance resulting from incomplete deuteration of the NMR solvent: $CDCl_3$ (7.24 ppm) or CD_3NO_2 (4.33 ppm). ^{13}C NMR spectra were recorded at 75 MHz, and all chemical shifts are reported in ppm relative to the carbon of the deuterated NMR solvent: $CDCl_3$ (77.0 ppm) or CD_3NO_2 (62.8 ppm). ^{31}P NMR spectra were recorded at 121 MHz, and all chemical shifts are reported in ppm relative to external 85% H_3PO_4 at 0.0 ppm. ^{19}F NMR spectra were recorded at 282 MHz, and all chemical shifts are reported upfield relative to external $CFCl_3$ at 0.0 ppm. Elemental analyses were conducted by Atlantic Microlab, Inc., of Norcross, GA. Melting points were determined in evacuated capillaries and were not corrected.

Solvents were purified as follows: CH_3NO_2, CH_2Cl_2, benzene, hexane, and toluene were purified by literature procedures[14] and were distilled from CaH_2; ether was purified by literature procedures[14] and was distilled from Na–benzophenone; CD_3NO_2 was distilled from CaH_2; $CDCl_3$ and C_6D_6 were vacuum-transferred from CaH_2. All solvents were freeze–thaw–pump-degassed three times before use.

Reagents were obtained as follows: Silver triflate (Aldrich) was recrystallized from diethyl ether and vacuum-dried; 1,3-bis(diphenylphosphino)propane (Aldrich), 37% HCl (J. T. Baker), CF_3SO_3H (3M), and CF_3COOH (Fisher Scientific) were used as received; *trans*-Ir(Cl)(CO)(PPh_3)$_2$ (**13**),[13] *trans*-Ir(Cl)(CO)($PMePh_2$)$_2$,[15] *trans*-Ir(OTf)(CO)(PPh_3)$_2$ (**1**),[6] Pt($H_2C{=}CH_2$)(PPh_3)$_2$ (**3**),[4] *cis*-Pt(Cl)$_2$($Ph_2P(CH_2)_3PPh_2$) (**11**),[8] and Pt($H_2C{=}CH_2$)($Ph_2P(CH_2)_3PPh_2$) (**4**)[8] were prepared by literature procedures.

Preparation of *trans*-Ir(OTf)(CO)(PMePh$_2$)$_2$ (2). A Schlenk flask was charged with *trans*-Ir(Cl)(CO)($PMePh_2$)$_2$ (0.400 g, 0.610 mmol), AgOTf (0.160 g, 0.623 mmol), and a magnetic stirring bar and was capped with a rubber septum. Freshly distilled, degassed benzene (ca. 80 mL) was added via cannula. The reaction mixture was stirred at room temperature for 2 h and then was filtered under nitrogen. The solvent was reduced to ca. 8 mL. Hexane (ca. 80 mL) was added to precipitate a brown solid which contained many minor impurities as assayed by $^{31}P\{^1H\}$ NMR spectroscopy. The mixture was filtered, and the filtrate was concentrated under vacuum to give **2** (0.274 g, 0.356 mmol, 58%) as a yellow, microcrystalline solid: mp 161–163 °C dec; IR (cm^{-1}, KBr) ν_{CO} 1975 s, $\nu_{asym,SO}$ 1326 s; ^1H NMR (δ, $CDCl_3$) 7.76–7.65, 7.50–7.41 (m, 4 C_6H_5), 2.25 (t, J_{H-P} = 3.5 Hz, 2 CH_3); $^{13}C\{^1H\}$ NMR (ppm, $CDCl_3$) 167.27 (t, J_{C-P} = 12.2 Hz, CO), aryl carbons at 133.52 (t, J_{C-P} = 27.6 Hz), 132.78 (t, J_{C-P} = 6.3 Hz), 130.66 (s), 128.57 (t, J_{C-P} = 5.2 Hz), triflate carbon not observed, 13.38 (t, J_{C-P} = 17.3 Hz, CH_3); $^{31}P\{^1H\}$ NMR (ppm, $CDCl_3$) 15.91 (s); ^{19}F NMR (ppm, $CDCl_3$) −77.63 (s). Anal. Calcd for $C_{28}H_{26}F_3IrO_4P_2S$: C, 43.69; H, 3.40. Found: C, 43.75; H, 3.40.

Reaction of *trans*-Ir(OTf)(CO)(PPh$_3$)$_2$ (PR$_3$ = PPh$_3$, 1; PR$_3$ = PMePh$_2$, 2) with Pt(H$_2$C=CH$_2$)(PR′$_3$)$_2$ (PR′$_3$ = PPh$_3$, 3; (PR′$_3$)$_2$ = Ph$_2$P(CH$_2$)$_3$PPh$_2$, 4). The following experiment is representative. A 5-mm NMR tube was charged with **1** (0.012 g, 0.013 mmol) and **3** (0.010 g, 0.013 mmol) and was capped with a rubber septum. A needle, connected to a vacuum line, was inserted through the rubber septum. The NMR tube was degassed under vacuum and then was saturated with nitrogen. CD_3NO_2 (0.7 mL) was injected by syringe. The NMR tube was removed from the vacuum line and was shaken vigorously to effect dissolution. The mixture was kept at room temperature, and the reaction was periodically monitored by $^{31}P\{^1H\}$ NMR spectroscopy. Spectroscopic data: see Table I.

Preparation of [(PPh$_3$)$_2$(CO)Ir(μ-H)(μ-η^2:η^1-CH=CH$_2$)Pt(PPh$_3$)$_2$]$^+$[OTf]$^-$ (5). A Schlenk flask was charged with **1** (0.110 g, 0.123 mmol), **3** (0.092 mg, 0.123 mmol), and a magnetic stirring bar and was capped with a rubber septum. CH_3NO_2 (10 mL) was added via cannula. The reaction mixture was stirred at room temperature for 2 h and then was filtered under nitrogen. The solvent was removed from the filtrate under vacuum. The residue was recrystallized by layering a CH_2Cl_2 solution with benzene to give **5** (0.117 g, 0.071 mmol, 58%) as yellow crystals: mp (gradual darkening) 179–182 °C dec; IR (cm^{-1}, KBr) ν_{CO} 1981 s, ν_{OTf} 1272 s, 1223 m, 1148 s, 1031 s; ^1H NMR (δ, $CDCl_3$) 7.45–7.10 (m, 12 C_6H_5), 5.60 (m, μ-CH), 2.32 (m, μ-C*H*H′), 1.35 (m, μ-CH*H*′), −11.54 (m, J_{H-Pt} = 515 Hz, Ir–H–Pt); $^{13}C\{^1H\}$ NMR (ppm, $CDCl_3$) 176.26 (d, J_{C-P} = 12.0 Hz, CO), 141.80 (dd, J_{C-P} = 85.1, 13.1 Hz, μ-CH), 135.58–127.80 (m, 12 C_6H_5), 120.96 (q, J_{C-F} = 320.6 Hz, CF_3SO_3), 37.56 (br s, μ-CH_2); $^{31}P\{^1H\}$ NMR (ppm, $CDCl_3$) 21.30 (m, J_{P-Pt} = 2383 Hz, Pt–P), 13.61 (m, J_{P-Pt} = 4633 Hz, Pt–P′), 9.40 (m, J_{P-Pt} < 90 Hz, Ir–P), 5.15 (m, J_{P-Pt} = 160 Hz, Ir–P′); ^{19}F NMR (ppm, $CDCl_3$) −77.92 (s). Anal. Calcd for $C_{76}H_{64}F_3IrO_4P_4PtS$: C, 55.61; H, 3.93. Found: C, 55.35; H, 3.95.

Preparation of [(PMePh$_2$)$_2$(CO)Ir(μ-H)(μ-η^2:η^1-CH=CH$_2$)Pt(PPh$_3$)$_2$]$^+$[OTf]$^-$ (6). A Schlenk flask was charged with **2** (0.293 g, 0.381 mmol), **3** (0.285 mg, 0.381 mmol), and a magnetic stirring bar and was capped with a rubber septum. CH_3NO_2 (10 mL) was added via cannula. The reaction mixture was stirred at room temperature for 2 h and then was filtered under nitrogen. All attempts at isolating the desired product from the crude reaction mixture (via benzene washing, recrystallization from CH_3NO_2/Et_2O, CH_2Cl_2/benzene, and CH_2Cl_2/hexane) led only to a moderately clean, brown-yellow solid (0.434 g, 0.286 mmol, 75%). Data for **6**: IR (cm^{-1}, KBr) ν_{CO} 1980 s, ν_{OTf} 1269 s, 1223 m, 1148 s, 1031 s; ^1H NMR (δ, CD_3NO_2) 7.55–7.00 (m, 10 C_6H_5), 6.14 (m, μ-CH), 2.75 (m, μ-C*H*H′), 2.12 (d, J_{H-P} = 8.3 Hz, PMe), 1.83 (m, μ-CH*H*′), 1.72 (d, J_{H-P} = 9.3 Hz, PMe′), −11.49 (m, J_{H-Pt} = 512 Hz, Ir–H–Pt); $^{31}P\{^1H\}$ NMR (ppm, CD_3NO_2) 21.33 (m, J_{P-Pt} = 2400 Hz, Pt–P), 16.26 (m, J_{P-Pt} = 4688 Hz, Pt–P′), −8.54 (m, J_{P-Pt} = 96 Hz, Ir–P), −23.95 (m, J_{P-Pt} = 147 Hz, Ir–P′); ^{19}F NMR (ppm, CD_3NO_2) −78.81 (s).

Preparation of [(PPh$_3$)$_2$(CO)Ir(μ-H)(μ-η^2:η^1-CH=CH$_2$)Pt(Ph$_2$P(CH$_2$)$_3$PPh$_2$)]$^+$[OTf]$^-$ (7). A Schlenk flask was charged with **1** (0.183 g, 0.205 mmol), **4** (0.130 g, 0.205 mmol), and a magnetic stirring bar and was capped with a rubber septum. CH_3NO_2 (15 mL) was added via cannula. The reaction mixture was stirred at room temperature for 2 h and then was filtered under nitrogen. The solvent was removed under vacuum to give a bright yellow residue. Benzene (ca. 50 mL) was added with stirring. The volume of the solution was then reduced to ca. 10 mL. During the course of concentration, a yellow solid formed. The solvent was decanted, and the solid was washed with benzene (ca. 15 mL each portion) in air until the washings were no longer colored. The solid was collected and dried under vacuum to give **7** (0.246 g, 0.161 mmol, 79%) as a yellow, microcrystalline solid: mp 142–146 °C dec; IR (cm^{-1}, KBr) ν_{CO} 1980 s, ν_{OTf} 1273 s, 1223 m, 1149 s, 1031 s; ^1H NMR (δ, $CDCl_3$) 7.61–6.65 (m, 10 C_6H_5), 5.74 (m, μ-CH), 3.17–1.92 (m, $P(CH_2)_3P$ and μ-C*H*H′), 1.39 (m, μ-CH*H*′), −11.77 (m, J_{H-Pt} = 480 Hz, Ir–H–Pt); $^{13}C\{^1H\}$ NMR (ppm, $CDCl_3$) 175.77 (dd, J_{C-P} = 10.7, 2.8 Hz, CO), 136.90 (dd, J_{C-P} = 85.0, 11.2 Hz, μ-CH), 136.12–127.81 (m, 10 C_6H_5), 120.98 (q, J_{C-F} = 320.5 Hz, CF_3SO_3), 34.37 (d, J_{C-P} = 3.7 Hz, μ-CH_2), 26.36–25.69 (m, $PCH_2CH_2CH_2$), 19.51 (br s, $PCH_2CH_2CH_2P$); $^{31}P\{^1H\}$ NMR (ppm, $CDCl_3$) 8.80 (m, J_{P-Pt} < 100 Hz, Ir–P), 5.03 (m, J_{P-Pt} = 156 Hz, Ir–P′), 0.71 (m, J_{P-Pt} = 4268 Hz, Pt–P), −0.50 (m, J_{P-Pt} = 2106 Hz, Pt–P′); ^{19}F NMR (ppm, $CDCl_3$) −77.93 (s). Anal. Calcd for $C_{67}H_{60}F_3IrO_4P_4PtS$: C, 52.62; H, 3.95. Found: C, 52.87; H, 4.05.

Preparation of [(PMePh$_2$)$_2$(CO)Ir(μ-H)(μ-η^2:η^1-CH=CH$_2$)Pt(Ph$_2$P(CH$_2$)$_3$PPh$_2$)]$^+$[OTf]$^-$ (8). A Schlenk flask was

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charged with **2** (0.075 g, 0.097 mmol), **4** (0.063 mg, 0.099 mmol), and a magnetic stirring bar and was capped with a rubber septum. CH_3NO_2 (10 mL) was added via cannula. The reaction mixture was stirred at room temperature for 2 h and then was filtered under nitrogen. The product was obtained by vapor diffusion of diethyl ether into a concentrated CH_3NO_2 solution to give **8**$\cdot 0.1(CH_3CH_2)_2O$ (0.101 g, 0.071 mmol, 73%) as yellow crystals: mp 187–190 °C dec; IR (cm^{-1}, KBr) ν_{CO} 1978 s, ν_{OTf} 1272 s, 1223 m, 1149 s, 1031 s; ^1H NMR (δ, CD_3NO_2) 7.73–7.18 (m, 8 C_6H_5), 6.20 (m, μ-CH), 3.43 (q, $J = 7.0$ Hz, $(CH_3(C\mathit{H}_2)_2O)$, 3.13–1.50 (m, PMe, PMe′, μ-CH_2, and $P(CH_2)_3P$), 1.12 (t, $J = 7.0$ Hz, $(C\mathit{H}_3CH_2)_2O$), −11.71 (m, $J_{H-Pt} = 474$ Hz, Ir–H–Pt); $^{13}C\{^1H\}$ NMR (ppm, CD_3NO_2) 177.84 (dd, $J_{C-P} = 5.4$, 2.7 Hz, CO), μ-CH carbon not located, 136.58–129.63 (m, 8 C_6H_5), 122.43 (q, $J_{C-F} = 320.9$ Hz, CF_3SO_3), 66.67 (s, $(CH_3\mathit{C}H_2)_2O$), 30.31 (br s, μ-CH_2), 27.49 (dd, $J_{C-P} = 38.2$, 5.3 Hz, $P\mathit{C}H_2CH_2CH_2P$), 26.62 (dd, $J_{C-P} = 30.2$, 2.6 Hz, $PCH_2CH_2\mathit{C}H_2P$), 20.71 (br s, $PCH_2\mathit{C}H_2CH_2P$), 20.40 (br d, $J_{C-P} = 33$ Hz, PMe), 15.74 (s, $(\mathit{C}H_3CH_2)_2O$), 13.73 (br d, $J_{C-P} = 37$ Hz, PMe′); $^{31}P\{^1H\}$ NMR (ppm, CD_3NO_2) 1.84 (m, $J_{P-Pt} = 4337$ Hz, Pt–P), −0.09 (m, $J_{P-Pt} = 2119$ Hz, Pt–P′), −9.42 (m, $J_{P-Pt} < 100$ Hz, Ir–P), −23.52 (m, $J_{P-Pt} = 155$ Hz, Ir–P′); ^{19}F NMR (ppm, CD_3NO_2) −78.66 (s). Anal. Calcd for $C_{57}H_{56}F_3IrO_4P_4PtS\cdot 0.1(CH_3CH_2)_2O$: C, 48.80; H, 4.07. Found: C, 48.64; H, 4.01.

Single-Crystal X-ray Diffraction Study of 5. Yellow crystals of **5** were obtained by slow crystallization from benzene/CH_2Cl_2. A suitable crystal with dimensions 0.18 × 0.15 × 0.08 mm was mounted on a glass fiber for preliminary data collection on an Enraf-Nonius CAD-4 diffractometer. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, using setting angles of 25 reflections in the range $20° < 2\theta < 30°$. The triclinic cell parameters and calculated volume are as follows: $a = 13.321$ (1) Å, $b = 15.461$ (2) Å, $c = 17.753$ (2) Å, $\alpha = 90.37$ (1)°, $\beta = 95.47$ (1)°, $\gamma = 100.92$ (1)°, and $V = 3572.70$ Å^3. The space group was determined to be $P\bar{1}$ (No. 2). The data were collected at a temperature of 16 (1) °C using a variable scan rate. A total of 12321 reflections were collected, of which 11738 were unique and not systematically absent. As a check on crystal and electronic stability, two representative reflections were measured every 200 reflections. Lorentz and polarization corrections, and an empirical absorption correction based upon a series of ψ scans, were applied to the data. The intensities of standard reflections remained constant within experimental error throughout data collection. An anisotropic decay correction was applied. The structure was solved by the Patterson heavy-atom method. The structure was refined in full-matrix least squares, where the function minimized was $\sum w(|F_o| - |F_c|)^2$, with a weight of 1.0 for all observed reflections. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atom positions, except the bridging hydride, which was located by difference Fourier methods, were calculated and were not refined. Scattering factors, and $\Delta f'$ and $\Delta f''$ values, were taken from the literature.[16] Anomalous dispersion effects were included in F_c.[17] All calculations were performed on a VAX 8300 computer with the SDP/VAX package.[18]

Reaction of 7 with $Ph_2P(CH_2)_3PPh_2$. A 5-mm NMR tube was charged with heterobimetallic complex **7** (0.025 g, 0.016 mmol) and $Ph_2P(CH_2)_3PPh_2$ (0.014 g, 0.034 mmol) and was capped with a rubber septum. A needle, connected to a vacuum line, was inserted through the rubber septum. The NMR tube was degassed under vacuum and then was saturated with nitrogen. $CDCl_3$ (0.7 mL) was injected by syringe. The NMR tube was removed from the vacuum line, was shaken vigorously to effect dissolution, and then was placed in a 50 °C oil bath. The reaction was periodically monitored by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy. Data for **10**: IR (cm^{-1}, thin film) ν_{CO} 1970 s, ν_{OTf} 1271 s, 1223 m, 1152 s, 1031 s; ^1H NMR (δ, $CDCl_3$) 7.60–6.98 (m, 8 C_6H_5), 4.74 (m, μ-CH), 3.32–1.45 (m, μ-CH_2 and 2 $P(CH_2)_3P$), −11.82 (m, $J_{H-Pt} = 531$ Hz, Ir–H–Pt); $^{31}P\{^1H\}$ NMR (ppm, $CDCl_3$) −0.97 (m, $J_{P-Pt} = 4237$ Hz, Pt–P), −2.93 (m, $J_{P-Pt} = 2048$, Pt–P′), −11.39 (m, $J_{P-Pt} = 142$ Hz, Ir–P), −25.93 (m, $J_{P-Pt} = 81$ Hz, Ir–P′).

Reaction of 7 with Acids. A. NMR-Monitored Experiment. A 5-mm NMR tube was charged with heterobimetallic complex **7** (0.012 g, 0.008 mmol) and was capped with a rubber septum. A needle, connected to a vacuum line, was inserted through the rubber septum. The mixture was degassed under vacuum and then was saturated with nitrogen. CD_3NO_2 (0.7 mL) was injected by syringe. To this resulting yellow solution was added HCl (20 μL) by syringe. The NMR tube was removed from the vacuum line and was shaken vigorously. The reaction mixture changed from yellow to white in a few seconds with the formation of a white precipitate. The sample was then analyzed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. The ^1H NMR spectrum indicated the formation of ethylene (δ 5.39 (s)) and *cis*-$Pt(Cl)_2(Ph_2P(CH_2)_3PPh_2)$ (**11**). A $^{31}P\{^1H\}$ NMR spectrum (CD_3NO_2) showed that all of the heterobimetallic complex had been consumed, and **11** (−3.62 ppm (s with ^{195}Pt satellites, $J_{P-Pt} = 3407$ Hz)) was present. The liquid phase was removed by syringe, leaving a white solid, which was then dried under vacuum for ca. 5 min. $CDCl_3$ (0.7 mL) was added by syringe under nitrogen to effect dissolution. The ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded immediately. Analysis of ^1H and $^{31}P\{^1H\}$ NMR spectra indicated $Ir(H)_2(Cl)(CO)(PPh_3)_2$ (**12**) was present accompanied by a trace amount of *trans*-$Ir(Cl)(CO)(PPh_3)_2$ (**13**; ca. 5% by $^{31}P\{^1H\}$ NMR). Data for **12**: IR (cm^{-1}, KBr) ν_{CO} 1992 s, ν_{Ir-H} 2224 m, 2091 s; ^1H NMR (δ, $CDCl_3$) 7.65–7.57, 7.41–7.32 (m, 6 C_6H_5), −7.31 (dt, $J_{H-H} = 4.7$ Hz, $J_{H-P} = 17.5$ Hz, Ir–H), −18.49 (dt, $J_{H-H} = 4.7$ Hz, $J_{H-P} = 14.0$ Hz, Ir–H′); $^{31}P\{^1H\}$ NMR (ppm, $CDCl_3$) 10.18 (s).

B. Preparative-Scale Experiment. A Schlenk flask was charged with heterobimetallic complex **7** (0.257 g, 0.168 mmol) and a magnetic stirring bar. The flask was capped with a rubber septum and was attached to a vacuum line. CH_3NO_2 (10 mL) was added by syringe. To this yellow solution was added HCl (0.31 mL, 37%) by syringe with stirring. The resulting solution became colorless in a few seconds, during which time a white precipitate formed. The reaction mixture was stirred at room temperature for ca. 20 min. The solid was collected by filtration, washed with CH_3NO_2 (2 × 15 mL), and dried under vacuum for 30 min to give **12** (0.081 g, 0.104 mmol, 62%) as a white solid, which was immediately characterized by ^1H and $^{31}P\{^1H\}$ NMR and IR spectroscopy. The CH_3NO_2 washings were then concentrated under vacuum. CH_2Cl_2 (ca. 40 mL) was added to dissolve the residue. The resulting light yellow solution was washed with water (2 × 20 mL) to remove excess acid. The organic layer was separated, dried over $MgSO_4$, and filtered. Hexane was added to the filtrate to effect precipitation. The solid was collected by filtration and recrystallized from CH_2Cl_2/toluene to give **11** (0.101 g, 0.149 mmol, 89%) as a white solid.

However, a complex mixture of unidentifiable products was obtained when **7** was treated with CF_3SO_3H and CF_3COOH in CD_3NO_2, as assayed by $^{31}P\{^1H\}$ NMR spectroscopy.

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Supplementary Material Available: A listing of anisotropic thermal parameters for **5** (4 pages); a listing of calculated and observed structure factors (37 pages). Ordering information is given on any current masthead page.

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