Migratory Insertion Reactions of Indenyliridium Dialkyls and Alkyl and Aryl Hydrides

Thomas Foo and Robert G. Bergman*

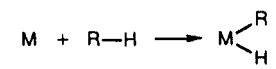
Chemical Sciences Division, Lawrence Berkeley Laboratory, and the Department of Chemistry, University of California, Berkeley, California 94720

Received October 10, 1991

This paper reports the migratory insertion chemistry of indenyliridium complexes described in the companion paper. Complexes of general formula (η^5-Ind)(PMe_3)Ir(R)(R′), where R = alkyl or aryl and R′ = alkyl, aryl, or hydride (**4–6**) react with dative ligands L such as *tert*-butylisocyanide and CO. These transformations lead to η^5 to η^1 isomerization of the indenyl ligand, giving octahedral iridium complexes of general formula (η^1–Ind)(PMe_3)$(L)_2$Ir(R)(R′) (**8**, **9**, **11**). Treatment of the methyl aryl and dimethyl η^1-indenyl complexes **9a**, **9d**, and **9e** with trimethylamine oxide removes CO, allowing the indenyl ligand to reestablish η^5-coordination by inducing CO migratory insertion to give acyl complexes **10**. Reaction of η^1-indenyl aryl and methyl hydrides **6** (as well as the dihydride (η^5-Ind)(PMe_3)IrH_2 (**7**)) with CO leads to reductive elimination of arene, methane, or H_2 rather than migratory insertion, forming (η^1-Ind)-$(CO)_3$(PMe_3)Ir (**12**) as the organometallic product. In contrast, treatment of methyl and aryl hydrides **6** with alkynes leads to the methyl vinyl complexes (η^5-Ind)(PMe_3)Ir(Me)(CR=C(R′)(H)) (**13**) and reaction of **6a** with ethylene gives the methyl ethyl complex (η^5-Ind)(PMe_3)Ir(Me)(Et) (**14**). Isotope labeling, stereochemical, and kinetic studies have been carried out on the insertion reaction of **6a** with 3,3-dimethyl-1-butyne. The results of these experiments are most consistent with a mechanism involving initial reversible coordination of alkyne to the metal center (probably with concurrent η^5–η^3 isomerization of the indenyl ligand) followed by irreversible migration of the metal-bound hydrogen to the *tert*-butyl-substituted carbon of the alkyne and then rapid recoordination of the indenyl group.

Introduction

As little as 10 years ago, the chemistry of transition-metal *cis*-alkyl hydride complexes was almost unknown. In fact, very few examples of such compounds had been isolated, much less derived from the oxidative addition of an alkane to a metal center (eq 1).[1] Although there had



(1)

been many examples of oxidative addition to arene C–H bonds and intramolecular oxidative addition of ligand sp^2- and sp^3-hybridized C–H bonds,[2] the lack of intermolecular examples with alkanes raised questions about the thermodynamic feasibility of alkane activation.[3] The observation that the complex *cis*-Pt(PPh_3)$_2$(CH_3)H undergoes irreversible loss of methane at −25 °C with a low kinetic barrier suggested that oxidative addition (at least with such mononuclear complexes) might not be a promising approach to the problem of catalytic activation of saturated hydrocarbons.[4]

The subsequent detection and isolation of *cis*-alkyl hydride compounds[5a,b] resulting from alkane oxidative addition has demonstrated the thermodynamic favorability of that process for several systems.[5] However, these discoveries were not sufficient to establish alkane oxidative addition as a useful approach to the functionalization of alkanes[6] because the predominant kinetic pathway by which these complexes react is still the reductive elimination of alkane.

The preceding paper[7] demonstrates that when the pentamethylcyclopentadienyl ligand is replaced by the indenyl ligand to give 18-electron (η^5-Ind)(PMe_3)Ir(R)(R′), (η^5-Ind)(PMe_3)Ir(R)(H), and (η^5-Ind)(PMe_3)IrH_2 systems, the ability of the iridium center to oxidatively add hydrocarbon C–H bonds remains intact. We show here that the indenyl group's ability to facilitate the opening of additional coordination sites allows insertion reactions to occur in these systems. We first discuss reactions of the dialkyl complexes with dative ligands such as CO and isonitriles. We then report the first example of a system in which insertion of unsaturated hydrocarbons into the M–H bond of a *cis*-hydridoalkyl complex occurs more rapidly than reductive elimination of alkane from that complex. A brief kinetic and mechanistic investigation of the alkyne insertion reaction reveals the role of the indenyl ligand in providing a low-barrier pathway for the rate-determining coordination of alkyne followed by facile M-H addition. In order to facilitate reading, the compound numbering established in the companion paper[7] is used in this paper as well.

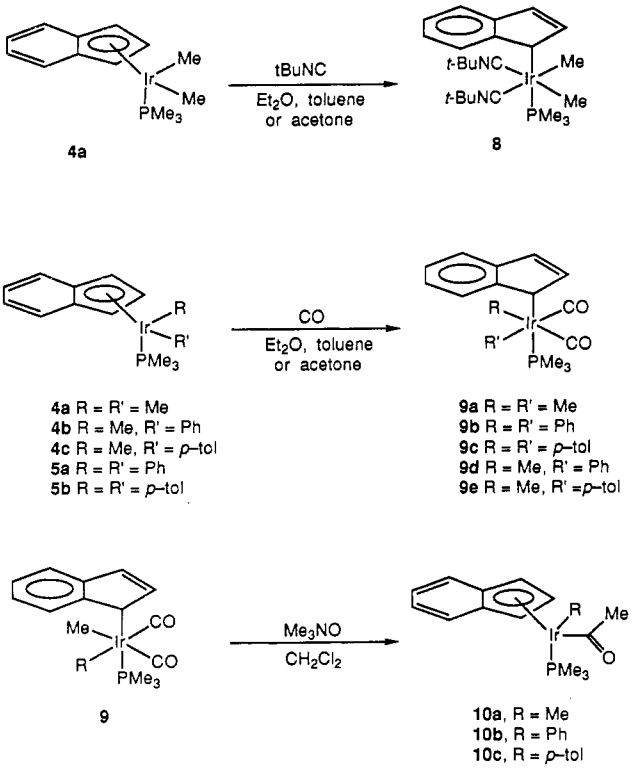
Results

Reactions of Indenyl(dialkyl)iridium Complexes with Dative Ligands: Induced η^5 to η^1 Isomerizations. Addition of excess *t*-BuNC to the dimethyl compound **4a** resulted in the immediate and quantitative formation of the η^1-indenyl bis(isocyanide) adduct **8** (Scheme I). The spectral data for **8** support the presence of an η^1 coordination mode for the indenyl ligand. The ^{1}H NMR spectrum in acetone-d_6 shows six aromatic and vinyl resonances for the indenyl ligand between δ 7.6 and 6.3 ppm and one resonance for the α-proton at δ 3.86 ppm. The ^{13}C NMR

(1) For a bibliography of *cis*-alkyl hydride complexes, see: Bullock, R. M.; Headford, C. E. L.; Kegley, S. E.; Norton, J. R. *J. Am. Chem. Soc.* **1985**, *107*, 727.
(2) (a) Chatt, J.; Davidson, J. M. *J. Chem. Soc.* **1965**, 843. (b) Parshall, G. W. *Acc. Chem. Res.* **1970**, *3*, 139. (c) Dehand, J.; Pfeffer, M. *Coord. Chem. Rev.* **1976**, *18*, 327. (d) Bruice, M. I. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 73.
(3) Norton, J. R. *Acc. Chem. Res.* **1979**, *12*, 139.
(4) Abis, L.; Sen, A.; Halpern, J. *J. Am. Chem. Soc.* **1978**, *100*, 2915.
(5) (a) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 352. (b) Hoyano, J. K.; Graham, W. A. G. *J. Am. Chem.* Soc. **1982**, *104*, 3723. For reviews of hydrocarbon C–H oxidative addition by soluble transition-metal complexes, see: (c) Shilov, A. E. *Activation of Saturated Hydrocarbons by Transition Metal Complexes*; D. Riedel Publishing Co.: Dordrecht, The Netherlands, 1984. (d) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245. (e) Green, M. L. H.; O'Hare, D. *Pure Appl. Chem.* **1985**, *57*, 1897.
(6) Halpern, J. *Acc. Chem. Res.* **1982**, *15*, 332.
(7) Foo, T.; Bergman, R. G. Preceding paper in this issue.

0276-7333/92/2311-1811$03.00/0

Scheme I

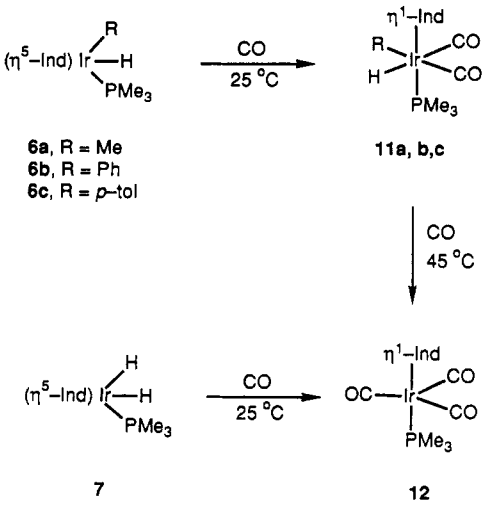


spectrum in C_6D_6 showed eight resonances in the aromatic/vinyl region between δ 160 and 116 ppm and one resonance for the α-carbon at δ 34.2 ppm. Similarly, exposure of complexes (η^5-Ind)(PMe_3)Ir(R)(R′) (**4**, **5**) to excess CO resulted in the clean and quantitative incorporation of 2 equiv of CO at the metal center to yield complexes **9** (Scheme I). Addition of less than 2 equiv of isonitrile or CO resulted in the partial conversion of the η^5-indenyl complexes to the η^1-indenyl adducts, with no intermediates (e.g. η^3-indenyl isomers) detectable.

The assignment of stereochemistry for the octahedral complex **8** is based on the following spectroscopic data. A cis disposition of the isocyanide ligands is consistent with the observation of two strong C–N stretches in the IR spectrum at 2163 and 2127 cm^{-1}. Assignment of the trans disposition of the indenyl and phosphine ligands is based upon the large coupling of the phosphorus nucleus to the α-proton (J = 14.3 Hz) and α-carbon (J = 69.3 Hz) of the η^1-indenyl ligand. In comparison, the corresponding coupling constants to the protons (J = 7.1 and 6.6 Hz) and to the carbons (J = 7.0 and 6.9 Hz) of the methyl ligands are small. No appreciable coupling to the ipso carbons of the coordinated isocyanides is evident. The inequivalence of the methyl groups and that of the isocyanides are consequences of the creation of a stereocenter at the α-carbon of the η^1-indenyl ligand.

The stereochemistry of complexes **9a–c** (R = R′ = Me, Ph, *p*-tol) is analogous to that of the products formed with *t*-BuNC. For example, two strong stretching absorptions consistent with *cis*-CO groups are observed in the IR spectrum of the dimethyl derivative **9a** at 2064 and 2021 cm^{-1}. Once again, the largest NMR couplings to the phosphine ligand in **9a** are those for the α-proton (δ 3.64 ppm (br d, J = 14.4 Hz) and the α-carbon (δ 32.9 ppm (d, J = 64.3 Hz)) of the η^1-indenyl ligand. As in the bis(isocyanide) adduct **8**, the methyl groups and the coordinated CO's of **9a** are diastereotopic. Furthermore, when R ≠ R′, exposure of complex **4b** or **4c** to CO results in the formation of the corresponding dicarbonyl adducts as a mixture of two diastereomers in an approximate 3:2 ratio (the absolute stereochemistry of the diastereomers has not been determined) because of the stereocenters at Ir and the α-carbon of the η^1-indenyl ligand. The characteristic ^{31}P NMR resonances of the octahedral, η^1-indenyl complexes **8** and **9** near δ −50 ppm contrast with those of the three-legged piano-stool, η^5-indenyl complexes **4** and **5** at δ −40 ppm.

Scheme II

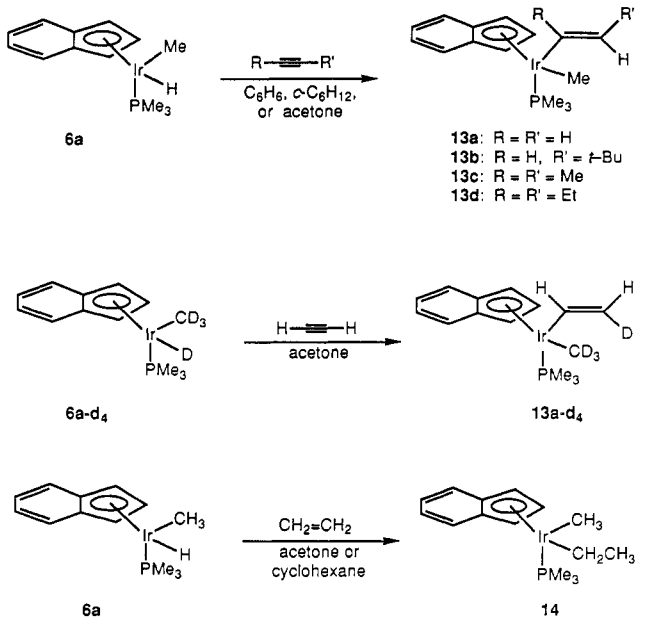


Migratory Insertion in η^1-Indenyl Complexes Induced by Trimethylamine *N*-Oxide (Me_3NO). Activation of CO is required to induce migratory insertion in the η^1-indenyl adducts. This is most efficiently carried out with amine oxides. For example, reaction of (η^1-Ind)(PMe_3)$(CO)_2$Ir$(Me)_2$ (**9a**) with Me_3NO at ambient temperature was complete after 20 h, affording a 60–75% isolated yield of the CO insertion product **10a** after chromatography on alumina III (Scheme I). The overall transformation involves removal of one of the coordinated CO's by Me_3NO, followed by insertion of the other bound CO into the Ir–Me bond in conjunction with a η^1 to η^5 hapticity change of the indenyl ligand. The use of Me_3NO was necessary to cleanly remove one CO ligand; thermolysis of the dimethyl, dicarbonyl compound **9a** in benzene at temperatures up to 140 °C resulted in decomposition of **9a** into unidentifiable products. Treatment of the aryl derivatives (η^1-Ind)(PMe_3)$(CO)_2$Ir(R)(Me) (R = Ph, *p*-tol) with Me_3NO also resulted in their immediate conversion to Ir–Me bond insertion products **10b** and **10c**.

Reaction of the Hydridoiridium Complexes 6 and 7 with CO. As shown in Scheme II, exposure of the methyl hydride **6a**, the aryl hydrides **6b** and **6c**, and the dihydride **7** to CO at room temperature led ultimately to a single product, which we believe to be (η^1-indenyl)$(CO)_3$(PMe_3)Ir (**12**). Initially, the methyl and aryl hydrides **6** reacted analogously to the dialkyl and diaryl complexes, leading to diastereomeric pairs of the corresponding octahedral dicarbonyl adducts **11a**, **11b**, and **11c**. For example, in the case of phenyl hydride **6b**, treatment with 2 atm of CO produced an immediate reaction leading to a mixture exhibiting two doublet hydride resonances having similar intensities at δ −7.98 (J_{PH} = 20 Hz) and −8.38 ppm (J_{PH} = 20 Hz), two PMe_3 doublets at δ 0.70 and 0.67 ppm and two η^1-indenyl α-hydrogen doublets at δ 4.99 (J = 12 Hz) and 4.88 ppm (J = 12 Hz).

In contrast to the behavior of the dialkyl complexes, treatment of the dicarbonyl adducts with Me_3NO did not lead to migratory insertion, but instead resulted in both reductive elimination of arene and partial regeneration of the aryl hydrides **6b**. Heating **11b** at 45 °C produced a

Scheme III



slow ($t_{1/2}$ = 70 h) reductive elimination of benzene and formation of **12**, which displayed a PMe_3 doublet in the ^1H NMR spectrum (δ 0.79, J = 10.6 Hz) along with a new resonance at δ 4.94 ppm (J = 10.8 Hz) due to the α-proton in its retained η^1-indenyl ligand. The apparent lability of the bound CO's and thermal instability of complex **12** precluded the recording of an informative ^{13}C NMR spectrum. Removal of the volatile materials in an attempt to isolate **12** resulted in its decomposition to a brown oil. In addition, complex **12** also decomposed in solution under CO upon standing to give what seemed to be ligand disproportionation products, as evidenced by the appearance of complex multiplets in the PMe_3 region of the ^1H NMR spectrum. The thermal loss of H_2 in solution from the dihydride **7** itself was not observed up to 150 °C, whereupon the dihydride decomposed to unidentifiable products.

These results demonstrate that coordination of CO to give η^1-indenyl complexes increases the propensity for reductive elimination of R–H and H–H at the iridium center. Others have previously demonstrated that prior coordination of a ligand can accelerate reductive elimination.[8]

Insertion Reactions of Indenyl Complexes with Alkynes. Reaction of (η^5-Ind)(PMe_3)Ir(CH_3)(H) (6a) with Acetylene. More promising hydride insertion results were obtained with alkynes in place of CO. Treatment of (η^5-Ind)(PMe_3)Ir(CH_3)(H) (**6a**) with excess acetylene at ambient temperature in acetone solution resulted in complete reaction of the hydridomethyl complex after 12 h (Scheme III). The major organometallic product observed by $^{31}P\{^1H\}$ NMR spectroscopy was the monoacetylene insertion product **13a**, (η^5-Ind)(PMe_3)Ir(CH_3)(CH=CH_2). A red flocculent solid, presumably polyacetylene, was produced concurrently with this product. However, isolation of the methylvinyl complex **13a** after 12 h by removal of volatile materials and subsequent distillation onto a sublimation coldfinger typically afforded 80% yields of the organometallic product as a yellow oil. The ^1H and ^{31}P NMR spectra obtained for this oil indicated the presence of two components, with the major one comprising 90% of the mixture. Resonances in the ^1H NMR spectrum corresponding to a bound PMe_3 ligand and an Ir–Me moiety for the minor component (and the successful isolation of only one product for the bulkier alkenyl complex described below) suggest that the minor component may be a rotamer of the major one.[9] Prolonged reaction times led to increased formation of the red solid and to a concomitant decrease in the yield of the organometallic product.

The methylvinyl complex **13a** has been characterized by ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR and IR spectroscopy and high-resolution mass spectrometry. All spectral data are consistent with a pseudooctahedral, three-legged pianostool formulation for **13a**. The $^{31}P\{^1H\}$ NMR resonance at δ −38.1 ppm is diagnostic of the (η^5-Ind) ligand in this family of compounds. The ^1H NMR spectrum of **13a** exhibits the expected signature of a metal–vinyl moiety, three sets of doublets of doublets of doublets, the third splitting due to coupling to the phosphorus nucleus.

To investigate the stereochemistry of the insertion reaction, the deuterated iodomethyl complex (η^5-Ind)(PMe_3)Ir(CD_3)(I) was synthesized by treatment of (η^5-Ind)(PMe_3)IrI_2 with CD_3MgI, in analogy to the synthesis of its protiated counterpart.[7] The iodomethyl complex was subsequently converted to the partially deuterated hydridomethyl complex (η^5-Ind)(PMe_3)Ir(CD_3)(D) (**6a**-d_4) by reaction with 2.5 equiv of NaO(i-Pr)-d_7 in 2-propanol-d_8. The extent of methyl and hydride deuteration was 85 ± 5% with most of the undesired protons in the Ir–H position, as determined by mass spectrometry and ^1H NMR spectroscopy. The reaction of the deuterated methyl hydride **6a**-d_4 with acetylene, HC≡CH, afforded the partially deuterated methylvinyl complex (η^5-Ind)(PMe_3)Ir(CD_3)(*syn*-CH=CHD) (**13a**-d_4) (Scheme III). The extent of deuteration in **13a**-d_4 was also 85 ± 5%, as determined by mass spectrometry. The extent of protiation at the β-vinyl position syn (δ 4.84) to the metal center was determined to be approximately 15 ± 2% by ^1H NMR spectroscopy. We conclude that to within the limits of detection of our experiment, the insertion reaction of acetylene with the hydridomethyl complex **6a** is a stereospecific cis addition.

Reaction of (η^5-Ind)(PMe_3)Ir(CH_3)(H) (6a) with Terminal and Internal Alkyl-Substituted Alkynes. The reaction of hydridomethyl complex **6a** with 10 equiv of t-BuCCH at 65 °C in acetone resulted in complete reaction of the hydridomethyl complex after 24 h (Scheme III). The reaction also proceeded in benzene and cyclohexane. The yield of alkyne insertion product **13b** [(*E*)-(η^5-Ind)Ir(PMe_3)(CH_3)(CH=C(t-Bu)H), as determined by ^1H NMR integration in cyclohexane-d_{12} with tetramethylsilane as internal standard, was 94%. Complex **13b** was isolated as a pure, golden yellow oil in 80% yield by both column chromatography on alumina III and distillation at 50 °C (10^{-2} Torr). Heating hydridomethyl complex **6a** with 2 equiv or less of t-BuCCH resulted in a substantial increase in the amount of unidentified decomposition products. The stereochemistry about the C—C double bond in the alkenyl ligand places the two vinyl protons anti to one another, as determined by the large coupling between the two, J_{tr} = 15.6 Hz (cf. J_{tr} = 17.2

(8) See, for example: (a) Tatsumi, K.; Nakamura, A.; Komiya, S.; Yamamoto, A.; Yamamoto, T. *J. Am. Chem. Soc.* **1984**, *106*, 8181. (b) Komiya, S.; Abe, Y.; Yamamoto, A.; Yamamoto, T. *Organometallics* **1983**, *2*, 1466. (c) Braterman, P. S.; Cross, R. J.; Young, G. B.; *J. Chem. Soc., Dalton Trans.* **1977**, 1892. (d) Bayer, U.; Brune, H. A. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1983**, *38*, 226. (e) McKinney, R. J.; Roe, D. C. *J. Am. Chem. Soc.* **1985**, *107*, 261. (f) Gell, K. I.; Schwartz, J. *J. Am. Chem. Soc.* **1981**, *103*, 2687.

(9) This type of isomerism has been observed earlier; see, for example: (a) Miki, K.; Tanaka, M.; Kasai, N.; Wada, M. *J. Organomet. Chem.* **1988**, *352*, 385. (b) Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 4581. (c) Stoutland, P. O. Ph.D. Thesis, University of California, Berkeley, 1987.

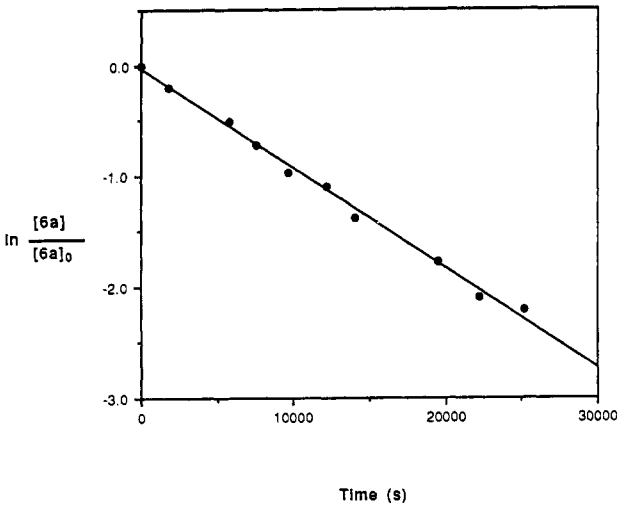


Figure 1. First-order plot for the conversion of **6a** with *t*-BuCCH to **13b**: [**6a**] = 0.017 M; [*t*-BuCCH] = 0.27 M; 50 °C.

Hz, J_{cis} = 9.7 Hz in the methylvinyl complex **13a**). This insertion therefore also proceeds with cis stereochemistry.

The thermal reaction of the hydridomethyl complex **6a** with 10 equiv of 2-butyne at 85 °C in acetone was complete after 24 h. The corresponding monoalkyne insertion product **13c**, (*E*)-(η^5-Ind)Ir(PMe_3)(CH_3)[(CH_3)C=C-(CH_3)H], was typically isolated as a pure yellow oil in 80% yield by distillation at 50 °C (10^{-2} Torr). Unlike compound **13b**, complex **13c** did not survive chromatography on alumina III. Similarly, complex **6a** was converted in high yield to the 3-hexyne insertion product **13d** (*E*)-(η^5-Ind)-Ir(PMe_3)(CH_3)[(C_2H_5)C=C(C_2H_5)H], after 48 h at 85 °C in acetone in the presence of 10 equiv of 3-hexyne (also isolated in 80% yield). Reactions of **6a** with both 2-butyne and 3-hexyne also proceeded in benzene and cyclohexane. Once again, unproductive decomposition pathways for the hydridomethyl complex **6a** during thermolysis were minimized by employing high alkyne concentrations.

The insertion stereochemistry in the case of **13c** was determined to be syn by a 2-D NOESY experiment. This experiment revealed NOE interaction between the vinyl proton and only the β-methyl group, as well as between the β-methyl group and both the vinyl proton and the α-methyl group.

Reaction of (η^5-Ind)(PMe_3)Ir(CH_3)(H) (6a) with Ethylene. When methyl hydride **6a** was heated to 45 °C in the presence of excess ethylene in either acetone or cyclohexane, the major product formed was the (methyl)(ethyl)iridium complex (η^5-Ind)(PMe_3)Ir(CH_3)(CH_2CH_3) (**14**), the result of insertion of ethylene into the Ir–H bond (Scheme III). Unfortunately, complex **14** was not isolable in pure form. Distillation of the product onto a sublimation finger gave a material containing an impurity that was not readily apparent in the ^{1}H NMR spectrum but was observable by $^{13}C\{^1H\}$ NMR spectroscopy. Consequently, **14** was characterized only by ^{1}H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy and high-resolution mass spectrometry as the major component of a mixture.

Kinetics of the Alkyne Insertion Reaction. The reactions discussed above show the following qualitative trend in the facility of insertion: acetylene > 3,3-dimethyl-1-butyne > 2-butyne > 3-hexyne. This suggested the reactions proceed via a bimolecular mechanism involving alkyne in the rate-determining step. We undertook a kinetic examination of the insertion reaction to test this hypothesis.

When heated at 50 °C in the presence of at least 16 equiv of 3,3-dimethyl-1-butyne, a 0.017 M solution of the hydridomethyl complex **6a** in cyclohexane-d_{12} was cleanly converted to the alkyne insertion product **13b** (≥94%) at a rate which was conveniently monitored by ^{1}H NMR spectroscopy. The rate of disappearance of **6a**, as well as the rate of appearance of **13b**, were followed by integration of the Ir–Me resonance versus an internal tetramethylsilane standard. At an alkyne concentration of 0.27 M, the reaction was cleanly first order in **6a** for 3 half-lives (Figure 1) with a pseudo-first-order rate constant $k_{obs} = 9.0 \times 10^{-5}$ s^{-1} (eq 2). The rate of reaction was also monitored at

$$-\frac{d}{dt}[\mathbf{6a}] = k_{obs}[\mathbf{6a}] \quad (2)$$

several different alkyne concentrations (Table I). The observed rate constant k_{obs} follows a linear dependence on alkyne concentration up to 1.08 M (Figure 2; eq 3). The

$$k_{obs} = k_r[\text{alkyne}] \quad (3)$$

apparent second-order rate constant, k_r, at 50 °C is 3.3 × 10^{-4} M^{-1} s^{-1}. Measurement of the reaction rate at 20, 35, 50, and 65 °C yielded the following activation parameters: $\Delta H^{\ddagger} = 13.7 \pm 1.0$ kcal/mol^{-1}, $\Delta S^{\ddagger} = -32 \pm 3$ cal mol^{-1} K^{-1} (Figure 3).

The isotope effect characteristic of this reaction was determined by measuring the rate of reaction of 3,3-dimethyl-1-butyne with **6a** and **6a**-d_4 at 35 °C with [alkyne] = 0.81 M and [**6a**] = 0.040 M. The reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy for 3 half-lives using P(*o*-tol)$_3$ as an internal integration standard. The second-order rate constant, k_H, measured for **6a**-d_0 at 35 °C was 1.1 (±0.1) × 10^{-4} M^{-1} s^{-1}, while the second-order rate constant, k_D, measured for **6a**-d_4 at 35 °C was 1.2 (±0.1) × 10^{-4} M^{-1} s^{-1} (Table II). Note that the measurement of k_H at 35 °C by $^{31}P\{^1H\}$ NMR spectroscopy is in good agreement with

Table I. Pseudo-First-Order Rate Constants for the Disappearance of (η^5-Ind)Ir(PMe_3)(CX_3)X, X = H or D (6a)

X	[*t*-BuCCH], M	[**6a**], M	temp, °C	method[a]	k_{obs}, s^{-1} [b]
H	0.27	0.017	50	^{1}H	9.0×10^{-5}
H	0.54	0.017	50	^{1}H	1.8×10^{-4}
H	0.81	0.017	50	^{1}H	2.8×10^{-4}
H	1.08	0.017	50	^{1}H	3.7×10^{-4}
H	0.27	0.017	20	^{1}H	9.2×10^{-6}
H	0.27	0.017	35	^{1}H	3.2×10^{-5}
H	0.27	0.017	65	^{1}H	2.4×10^{-4}
D	0.81	0.040	35	$^{31}P\{^1H\}$	1.0×10^{-4}
H	0.81	0.040	35	$^{31}P\{^1H\}$	8.8×10^{-5}

[a] Internal integration standard for ^{1}H NMR spectroscopy is $(CH_3)_4Si$, for $^{31}P\{^1H\}$ NMR, P(*o*-tol)$_3$. [b] All values ±10%.

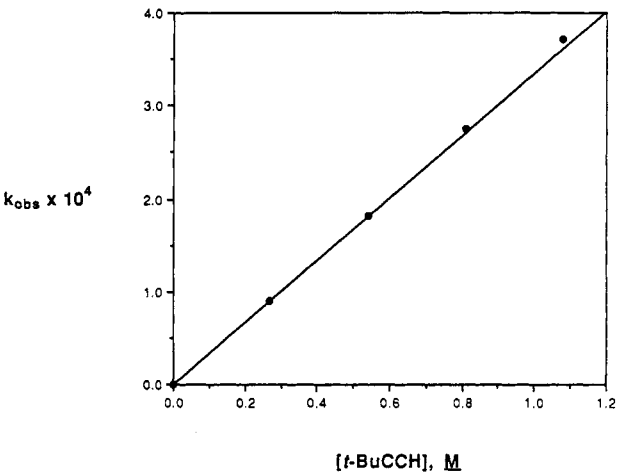


Figure 2. Linear dependence of k_{obs} on alkyne concentration at 50 °C.

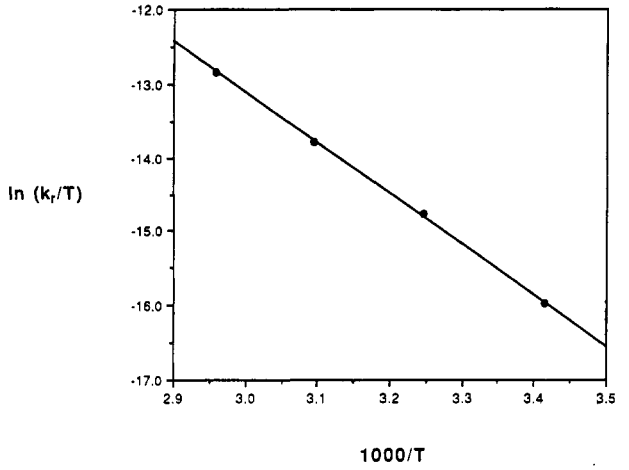


Figure 3. Eyring plot for the alkyne insertion reaction over the temperature range from 20 to 65 °C.

Table II. Determination of Kinetic Deuterium Isotope Effect (k_H/k_D) at 35 °C

X	[*t*-BuCCH], M	[**6a**], M	method[a]	k_{obs}, s^{-1} [b]	k_X, M^{-1} s^{-1} [b]
D	0.81	0.040	$^{31}P\{^1H\}$	1.0×10^{-4}	1.2×10^{-4}
H	0.81	0.040	$^{31}P\{^1H\}$	8.8×10^{-5}	1.1×10^{-4}
H	0.27	0.017	^1H	3.2×10^{-5}	1.2×10^{-4}
H			^1H	Eyring plot	1.1×10^{-4}

[a] Internal integration standard for ^1H NMR spectroscopy is $(CH_3)_4Si$; for $^{31}P\{^1H\}$ NMR, P(*o*-tol)$_3$. [b] All values ±10%.

the measurement of $k_H = 1.2\ (\pm 0.1) \times 10^{-4}\ M^{-1}\ s^{-1}$ at 35 °C by ^1H NMR spectroscopy. The two second-order rate constants, k_H and k_D, are the same within experimental error.

Discussion

The results presented in this and the companion paper[7] demonstrate that the substitution of an Ind ligand for a Cp* ligand in the Cp*(PMe$_3$)Ir(R)(R′) system opens up new avenues of reactivity at the iridium center due to the ability of the indenyl ligand to undergo hapticity changes and incorporate substrates as additional ligands. The Ind ligand undergoes a facile η^5 to η^1 ring slip at ambient temperatures to incorporate two molecules of CO or *t*-BuNC into the 18-electron complexes (η^5-Ind)(PMe$_3$)Ir(R)(R′) to give (η^1-Ind)(PMe$_3$)(L)$_2$Ir(R)(R′). In contrast, Cp*(PMe$_3$)Ir(Me)$_2$ does not react with *t*-BuNC at 110 °C for days.

Green and co-workers have reported a similar η^5- to η^1-Ind conversion induced by the addition of excess *t*-BuNC to (η^5-Ind)Rh(C$_2$H$_4$)$_2$ to yield what they formulated as (σ-Ind)Rh(*t*-BuNC)$_4$, based upon its IR spectrum.[10] Casey and co-workers have reported the η^5 to η^1 ring slip of both the Ind and the Cp ligands.[11] In the former case, the reaction of the bulky P(*n*-Bu)$_3$ ligand or the less nucleophilic 2,2′-bipyridyl ligand with (η^5-Ind)Re(CO)$_3$ afforded isolable η^1-Ind complexes, (η^1-Ind)Re(CO)$_3$L$_2$. There have also been several other examples in which complexes with η^5-Cp ligands have been converted to isolable complexes containing η^1-Cp ligands.[12]

In some cases, η^3-Ind or η^3-Cp intermediates have been proposed, but not detected. Similarly, no η^3-Ind intermediates have been spectroscopically observed in the incorporation of CO or *t*-BuNC into the (η^5-Ind)(PMe$_3$)Ir(R)(R′) complexes in the present study. These observations suggest that the η^3 binding mode of the indenyl ligand is energetically disfavored relative to the η^5 and η^1 modes for d^6 Ir(III) complexes. In a similar vein, alkylation of the stable d^8 Fe(0) anion (η^3-Ind)Fe(CO)$_3^-$ (a structurally characterized η^3-Ind complex) with methyl iodide led to two η^5-Ind complexes, (η^5-Ind)Fe(CO)$_2$CH$_3$ and (η^5-Ind)Fe(CO)$_2$COCH$_3$, with no direct observation of the presumed d^6 Fe(II) intermediate, (η^3-Ind)Fe(CO)$_3$CH$_3$.[13]

This pointed to the possibility of using recoordination of the indenyl ligand to induce the insertion of CO into an Ir–C bond following the selective cleavage of one of the bound CO's. Casey and co-workers noted that, upon thermolysis, (η^1-Cp)(CH$_3$)(NO)Re(CO)(PMe$_3$)$_2$ lost one of its coordinated phosphines[11c] to give both the CO insertion product, (η^5-Cp)(NO)Re(PMe$_3$)COCH$_3$, and the CO loss product, (η^5-Cp)(NO)Re(PMe$_3$)CH$_3$. In emphasis of the exceptionally high ligand affinity of iridium for CO, thermolysis of the dicarbonyl compound **9a** up to 140 °C resulted only in decomposition.

However, selective removal of one bound CO can be accomplished with Me$_3$NO in CH$_2$Cl$_2$.[14] The overall reaction involves one of the few examples of CO insertion into an Ir–C bond,[15] and appears to be driven by the η^1 to η^5 hapticity change of the indenyl ligand. Examples of chemically induced η^1 to η^5 ring slips are rare, but precedented. O'Hare has demonstrated that chloride abstraction from (η^1-Ind)Pt(COD)Cl or protonation of (η^1-Ind)$_2$Pt(COD) leads to the η^5-Ind cation, (η^5-Ind)Pt(COD)$^+$.[16] Belmont and Wrighton have observed the photoinduced loss of both CO's from (η^5-Ind)Fe(CO)$_2$(η^1-Ind), (η^5-Cp)Fe(CO)$_2$(η^1-Ind), and (η^5-Cp)Fe(CO)$_2$(η^1-Cp) to form the corresponding sandwich compounds.[17]

The lack of reactions other than reductive elimination in *cis*-alkyl hydride complexes has been well documented. Graham and co-workers have not reported any insertion chemistry of either the Cp*(CO)Ir(R)(H) system[5b] or the (HBPz*$_3$)(CO)Rh(R)(H) system,[18a] although they have reported the overall addition of ethylene and CO to benzene to give propiophenone in the (HBPz*$_3$)Rh(CO) system.[18b] It seems clear that insertion of CO into M(CO)(H)(R) complexes must occur in recently discovered photocatalytic arene and alkane carbonylation reactions.[19] The Cp*(PMe$_3$)Ir(R)(H) system, studied in our own laboratories, has not shown any tendency toward CO or ethylene insertion.[9b,c,20] Preliminary results did indicate

(10) (a) Caddy, P.; Green, M.; O'Brien, E.; Smart, L. E.; Woodward, P. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 648. (b) Caddy, P.; Green, M.; O'Brien, E.; Smart, L. E.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1980**, 962.

(11) (a) Casey, C. P.; O'Connor, J. M. *Organometallics* **1985**, *4*, 384. (b) Casey, C. P.; O'Connor, J. M.; Jones, W. D.; Haller, K. J. *Organometallics* **1983**, *2*, 535. (c) Casey, C. P.; Jones, W. D. *J. Am. Chem. Soc.* **1980**, *102*, 6154.

(12) (a) Hames, B. W.; Legzdins, P.; Martin, D. T. *Inorg. Chem.* **1978**, *17*, 3644. (b) Werner, H.; Kuhn, A. *Angew. Chem.* **1979**, *91*, 447. (c) Goel, A. B.; Goel, S.; VanDerVeer, D.; Clark, H. C. *Inorg. Chim. Acta* **1981**, *53*, L117.

(13) Forschner, T. C.; Cutler, A. R.; Kullnig, R. K. *Organometallics* **1987**, *6*, 889.

(14) Albers, M. O.; Coville, N. J. *Coord. Chem. Rev.* **1984**, *53*, 227.

(15) For other examples of CO insertion into Ir–C bonds, see: (a) Shaw, B. L.; Singleton, E. *J. Chem. Soc. A* **1967**, 1683. (b) von Deuten, K.; Dahlenburg, L. *Transition Met. Chem.* **1980**, *5*, 222. (c) Rees, W. M.; Churchill, M. R.; Li, Y.-J.; Atwood, J. D. *Organometallics* **1985**, *4*, 1162. (d) Kubota, M.; McClesky, T. M.; Hayashi, R. K.; Webb, C. G. *J. Am. Chem. Soc.* **1987**, *109*, 7569.

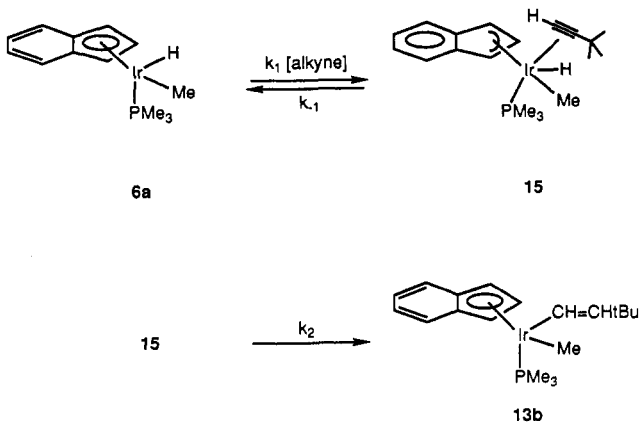
(16) O'Hare, D. *Organometallics* **1987**, *6*, 1766.

(17) Belmont, J. A.; Wrighton, M. S. *Organometallics* **1986**, *5*, 1421.

(18) Pz* = 3,5-dimethylpyrazolyl. (a) Ghosh, C. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1987**, *109*, 4726. (b) Ghosh, C. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1989**, *111*, 375.

(19) See, for example: (a) Kunin, A. J.; Eisenberg, R. *Organometallics* **1988**, *7*, 2124. (b) Sakakura, T.; Sasaki, K.; Tokunaga, Y.; Wada, K.; Tanaka, M. *Chem. Lett.* **1988**, 155. (c) Maguire, J. A.; Boese, W. T.; Goldman, A. S. *J. Am. Chem. Soc.* **1989**, *111*, 7088. However, see also: (d) Boese, W. T.; Goldman, A. S. *J. Am. Chem. Soc.* **1992**, *114*, 350.

Scheme IV



insertion of acetylene in this system, but the process is stereorandom, erratic in rate, and substrate-specific for acetylene.[9c] We believe it proceeds by a radical chain mechanism. The reaction of the *16-electron* complex $(Cy_2PCH_2CH_2PCy_2)$Pt(neopentyl)H with 3,3-dimethyl-1-butyne or diphenylacetylene provides perhaps the most striking example of the kinetic preference of *cis*-alkyl hydride complexes for the loss of alkane over other pathways.[21] Alkyne insertion was subsequently demonstrated for the more stable $(Cy_2PCH_2CH_2PCy_2)$Pt(acetylide)(H) complex (which was obtained by the activation of a terminal alkyne after alkane loss), but the rate of this reaction was substantially slower than the rate of alkane loss from the alkyl hydride.

When the thermolysis of **6a** was carried out in the presence of alkynes or ethylene, the major reaction pathway for **6a** involved insertion of the unsaturated substrate into the Ir–H bond. The reaction is a stereospecific syn addition with acetylene, 3,3-dimethyl-1-butyne, and 2-butyne. A qualitative dependence of the alkyne insertion reaction rate on the identity of the alkyne suggested a bimolecular mechanism involving alkyne in the rate-determining step. This was confirmed by a study of the rate dependence on alkyne concentration for *t*-BuCCH, which showed a linear correlation between reaction rate and alkyne concentration. Furthermore, a study of the temperature dependence of the reaction rate afforded a highly negative value, -32 ± 3 eu for the entropy of activation, $\Delta S^{\ddagger}$. A low enthalpy of activation for the reaction, 13.7 $\pm$ 1.0 kcal mol^{-1}, should also be noted. These data are consistent with a bimolecular mechanism involving coordination of alkyne to the iridium center concomitant with an η^5 to η^3 ring slip of the ligand, followed by insertion of the alkyne into the Ir–H bond along with the restoration of the η^5 binding mode for the indenyl ligand (Scheme IV).

A remaining question concerns whether the highest-energy transition state involves coordination of alkyne ($k_2 \gg k_{-1}$) or insertion ($k_{-1} \gg k_2$). Application of the steady-state approximation to the mechanism summarized in Scheme IV leads to the rate law given in eq 4.

$$-\frac{d}{dt}[\mathbf{6a}] = \frac{k_1k_2}{k_{-1} + k_2}[\text{alkyne}][\mathbf{6a}] \quad (4)$$

If the former inequality holds, the rate law will be given by eq 5; the latter inequality gives eq 6. In either case, one would expect to see a linear dependence of k_{obs} on alkyne concentration and a highly negative overall entropy of

$$-\frac{d}{dt}[\mathbf{6a}] = k_1[\text{alkyne}][\mathbf{6a}] \quad (5)$$

$$-\frac{d}{dt}[\mathbf{6a}] = \frac{k_1k_2}{k_{-1}}[\text{alkyne}][\mathbf{6a}] \quad (6)$$

activation. Labeling the Ir–H position of the methyl hydride compound **6a** with deuterium revealed that there is no appreciable kinetic deuterium isotope effect on the insertion reaction. Because it seems that there should be a significant isotope effect on k_2, we believe that coordination of alkyne (k_1) is rate-limiting ($k_2 \gg k_{-1}$). That is, once coordinated to the Ir center, the alkyne prefers to undergo insertion rather than dissociation back to free alkyne and **6a**. This result also provides evidence against a concerted reaction involving a direct bimolecular attack of the alkyne on the Ir–H bond.

In conclusion, the ability of the indenyl ligand to provide a low-kinetic-barrier, bimolecular pathway for the insertion of alkynes into the Ir–H bond of the *cis*-hydridomethyl complex **6a** has enabled us to demonstrate that with an appropriate ligand environment, the kinetic preference of *cis*-alkyl hydrides for reductive elimination of alkane can be defeated in favor of productive chemistry. This result emphasizes the utility of the low barrier to associative ring slip pathways made available by the indenyl ligand. The next important goal in this system is to find a means to cleanly induce reductive elimination in the alkyl hydride/alkyne insertion products, so that overall conversion of an alkane to a functionalized organic compound (in this case, a chain-extended alkene) can be achieved.

Experimental Section

General Information. General experimental details are summarized in the accompanying paper. Acetylene was used as a 1.24 M solution in acetone (99+%), purchased from Alfa. The acetylene solution was carefully stored at −40 °C in the drybox freezer. 3,3-Dimethyl-1-butyne was stored over P_2O_5 under vacuum and was used by vacuum transfer. 2-Butyne and 3-hexyne were distilled under vacuum from Na and stored under vacuum. *tert*-Butylisocyanide was purchased from Aldrich, transferred to a glass bomb under nitrogen, degassed, and used by vacuum transfer. Trimethylamine *N*-oxide was purified by literature methods.[22] The synthesis of complexes **4a–c**, **5a,b**, **6a–c**, and **7** are described in the companion paper.[7]

(η^1-C_9H_7)(PMe_3)(CN-*t*-Bu)$_2$Ir(CH_3)$_2$ (8). In the drybox, 41 mg (0.10 mmol) of the dimethyl complex **4a** was dissolved in 5 mL of Et_2O. The solution was placed in a 30-mL glass bomb and degassed with one freeze–pump–thaw cycle, and 2.2 equiv of *t*-BuNC was condensed into the solution from a known-volume bulb (28 Torr, 141.23 mL, 293 K, 0.22 mmol) at 77 K. The solution was allowed to warm to ambient temperature, at which point the yellow color of the solution began to disappear. After standing for 2 h, the solution had become completely colorless. After the color had disappeared, the volatile materials were removed under vacuum, leaving 56 mg (0.097 mmol, 97% yield) of the bis(isocyanide) adduct **8** as an analytically pure white solid. ^{1}H NMR (acetone-d_6): δ 7.57 (m, 1 H), 7.25 (m, 1 H), 6.96 (m, 1 H), 6.86 (m, 2 H), 6.32 (br, 1 H), 3.86 (br d, J = 14.3 Hz, 1 H), 1.43 (d, J = 9.7 Hz, 9 H), 1.39 (br s, 9 H), 1.13 (br s, 9 H), 0.23 (d, J = 7.1 Hz, 3 H), 0.00 (d, J = 6.6 Hz, 3 H) ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ −50.2 ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 159.9 (s), 152.5 (d, J = 4.6 Hz), 143.1 (s), 131.7 (br), 131.1 (br), 122.8 (s), 121.4 (s), 121.2 (s), 120.0 (s), 116.3 (d, J = 3.9 Hz), 55.5 (s), 55.4 (s), 34.2 (d, J = 69.3 Hz), 30.5 (s), 30.2 (s), 14.6 (d, J = 31.5 Hz), −15.5 (d, J = 7.0 Hz), −16.2 (d, J = 6.9 Hz), ppm. IR (KBr pellet): ν_{CN} 2163, 2127 cm^{-1}. MS (FAB): m/e 580 (M^+). Anal. Calcd for $C_{24}H_{40}N_2PIr$: C, 49.72;

(20) Janowitz, A. J. Ph.D. Thesis, University of California, Berkeley, 1982.

(21) (a) Hackett, M.; Ibers, J. A.; Jernakoff, P.; Whitesides, G. M. *J. Am. Chem. Soc.* **1986**, *108*, 8094. (b) Hackett, M.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 1449.

(22) Soderquist, J. A.; Anderson, C. L. *Tetrahedron Lett.*, **1986**, *27*, 3961.

H, 6.95; N, 4.83. Found: C, 49.8; H, 6.54; N, 4.73. The product may be crystallized from toluene by diffusion of hexane into the solution at −40 °C.

(η^1-C_9H_7)(PMe_3)(CO)$_2$Ir(CH_3)$_2$ (9a). In the drybox, 41 mg (0.10 mmol) of dimethyl complex **4a** was dissolved in 5 mL of Et_2O, and the resulting solution was placed in a 30-mL glass bomb. The solution was degassed with two freeze–pump–thaw cycles and allowed to warm to ambient temperature. The bomb was then pressurized with 700 Torr of CO. As CO diffused into the solution, its color began to disappear. After standing for 12 h, the solution had become completely colorless. After complete conversion was assured by the loss of color, the volatile materials were removed under the vacuum, leaving 45 mg (0.096 mmol, 96% yield) of the dicarbonyl adduct **9a** as an analytically pure off-white solid. ^{1}H NMR (acetone-d_6): δ 7.56 (m, 1 H), 7.34 (m, 1 H), 7.03 (m, 1 H), 6.98 (m, 2 H), 6.44 (m, 1 H), 3.64 (br d, J = 14.4 Hz, 1 H), 1.67 (d, J = 10.4 Hz, 9 H), 0.61 (d, J = 8.1 Hz, 3 H), 0.41 (d, J = 7.7 Hz, 3 H) ppm. ^{31}P{^{1}H} NMR (acetone-d_6): δ −49.3 ppm. ^{13}C{^{1}H} NMR (acetone-d_6): δ 169.94 (d, J = 5 Hz), 169.89 (d, J = 5 Hz), 158.3 (d, J = 3.3 Hz), 149.6 (d, J = 5.2 Hz), 142.1 (s), 123.6 (s), 122.7 (s), 122.2 (s), 121.1 (s), 119.7 (d, J = 4.4 Hz), 32.9 (d, J = 64.3 Hz), 14.6 (d, J = 35.1 Hz), −12.6 (d, J = 6.6 Hz), −12.8 (d, J = 6.6 Hz) ppm. IR (KBr pellet): ν_{CO} 2064, 2021, 1984 (sh) cm^{-1}. MS (EI): m/e 470, 115 (M$^+$, base). Anal. Calcd for $C_{16}H_{22}O_2PIr$: C, 40.93; H, 4.72. Found: C, 41.11; H, 4.77. The product may be crystallized from toluene by diffusion of hexane into the solution at −40 °C.

(η^1-C_9H_7)(PMe_3)(CO)$_2$Ir(C_6H_5)$_2$ (9b). The dicarbonyl adduct of the diphenyl complex, **9b**, was prepared by a procedure similar to the one described for compound **9a**, starting with 27 mg (0.05 mmol) of the diphenyl complex **5a**. The yield of the dicarbonyl adduct **9b** was 28 mg (0.047 mmol, 94% yield) of a tan solid. The crude reaction residue appeared pure by NMR analysis, despite its color. The product was precipitated from toluene/hexane at −40 °C to give **9b** as a white solid suitable for elemental analysis. ^{1}H NMR (acetone-d_6): δ 7.78 (m, 4 H), 7.31 (m, 1 H), 7.13 (m, 7 H), 6.92 (m, 1 H), 6.71 (m, 1 H), 6.49 (m, 1 H), 6.38 (m, 1 H), 4.30 (br d, J = 14.5 Hz, 1 H), 1.55 (d, J = 10.6 Hz, 9 H) ppm. ^{31}P{^{1}H} NMR (acetone-d_6): δ −45.9 ppm. ^{13}C{^{1}H} NMR (acetone-d_6): δ 170.5 (d, J = 4.6 Hz), 170.2 (d, J = 3.9 Hz), 158.0 (s), 149.4 (d, J = 4.9 Hz), 143.3 (d, J = 3.9 Hz), 142.2 (d, J = 3.4 Hz), 142.0 (d, J = 10.4 Hz), 140.3 (d, J = 9.6 Hz), 128.7 (s), 128.5 (s), 127.3 (s), 124.4 (s), 124.3 (s), 124.1 (s), 123.3 (s), 122.9 (s), 121.0 (s), 120.9 (d, J = 4.7 Hz), 33.9 (d, J = 59.3 Hz), 15.7 (d, J = 35.8 Hz) ppm. IR (KBr pellet): ν_{CO} 2078, 2032 cm^{-1}. MS (FAB): m/e 595 (MH$^+$). Anal. Calcd for $C_{26}H_{26}O_2PIr$: C, 52.60; H, 4.41. Found: C, 52.88; H, 4.46.

(η^1-C_9H_7)(PMe_3)(CO)$_2$Ir(p-$CH_3C_6H_4$)$_2$ (9c). The dicarbonyl adduct of the bis(p-tolyl) complex, **9c**, was prepared by a procedure similar to the one described for compound **9a**, starting with 28 mg (0.05 mmol) of the bis(p-tolyl) complex **5b**. The yield of the dicarbonyl adduct **9c** was 30 mg (0.048 mmol, 97% yield) of a tan solid. The crude reaction residue appeared pure by NMR analysis despite its color. The product was recrystallized from toluene/hexane at −40 °C to give **9c** as tan crystals suitable for elemental analysis. ^{1}H NMR (acetone-d_6): δ 7.63 (m, 4 H), 7.30 (d, J = 7.5 Hz, 1 H), 7.12 (d, J = 5.0 Hz, 1 H), 6.94 (m, 5 H), 6.73 (m, 1 H), 6.51 (d, J = 7.7 Hz, 1 H), 6.47 (m, 1 H), 4.29 (br d, J = 14.6, 1 H), 2.31 (s, 3 H), 2.26 (s, 3 H), 1.53 (d, J = 10.4 Hz, 9 H) ppm. ^{31}P{^{1}H} NMR (acetone-d_6): δ −46.2 ppm. ^{13}C{^{1}H} NMR (acetone-d_6): δ 170.6 (d, J = 4.7 Hz), 170.3 (d, J = 4.4 Hz), 158.0 (s), 149.6 (d, J = 5.3 Hz), 143.1 (d, J = 4.1 Hz), 142.2 (br), 142.1 (d, J = 3.5 Hz), 137.5 (d, J = 9.6 Hz), 136.0 (d, J = 10.4 Hz), 133.3 (s), 133.1 (s), 129.6 (s), 129.3 (s), 124.0 (s), 123.3 (s), 122.8 (s), 120.9 (s), 120.6 (d, J = 5.0 Hz), 33.8 (d, J = 59.8 Hz), 21.0 (s), 20.9 (s), 15.7 (d, J = 35.9 Hz) ppm. IR (KBr pellet): ν_{CO} 2075, 2027 cm^{-1}. MS (FAB): m/e 623 (MH$^+$). Anal. Calcd for $C_{28}H_{30}O_2PIr$: C, 54.09; H, 4.86. Found: C, 54.55; H, 5.09.

(η^5-C_9H_7)Ir(PMe_3)(CH_3)($COCH_3$) (10a). In the drybox, 28 mg (0.06 mmol) of complex **9a**, (η^1-C_9H_7)(CH_3)$_2$Ir(PMe_3)(CO)$_2$, and 6 mg (0.08 mmol, 1.3 equiv) of Me_3NO were weighed into a 50-mL round-bottom flask equipped with a stirbar and a vacuum stopcock. Methylene chloride (15 mL) was transferred into the flask under vacuum, and the reaction mixture was allowed to stir at ambient temperature for 20 h, at which time the volatile materials were removed under vacuum. The residue was extracted with two 1.5-mL portions of Et_2O, and the extracts were loaded onto an 8-mL plug of alumina III supported on a 15-mL fritted-glass filter. The yellow product was eluted with a 1:1 (v:v) mixture of Et_2O/pentane. Evaporation of the solvent and subsequent distillation of the product at 40 °C, 10^{-2} Torr, onto a sublimation coldfinger afforded a 76% yield (20 mg, 0.045 mmol) of the CO insertion product **10a** as a yellow oil, pure by NMR analysis. Note that the product **10a** solidifies on the coldfinger at −78 °C but melts upon warming to ambient temperature. However, the oil remains on the coldfinger due its high viscosity and can be washed from the coldfinger in the drybox with pentane or Et_2O. ^{1}H NMR (THF-d_8): δ 7.26 (m, 2 H), 7.10 (m, 1 H), 6.95 (m, 1 H), 5.89 (m, 1 H), 5.77 (br, 1 H), 5.62 (m, 1 H), 2.24 (s, 3 H), 1.27 (d, J = 10.8 Hz, 9 H), 0.28 (d, J = 5.5 Hz), 3 H) ppm. ^{31}P{^{1}H} NMR (THF-d_8): δ −39.4 ppm. ^{13}C{^{1}H} NMR (THF-d_8): δ 199.5 (d, J = 7.9 Hz), 126.2 (s), 123.6 (s), 123.1 (s), 122.2 (s), 120.2 (s), 114.8 (s), 98.2 (s), 71.7 (s), 68.2 (d, J = 17.5 Hz), 47.4 (d, J = 3.2 Hz), 15.5 (d, J = 38.0 Hz), −35.5 (d, J = 8.0 Hz) ppm. IR (pentane): ν_{CO} 1626 cm^{-1}. High-resolution MS (EI): m/e calcd for $C_{15}H_{22}OPIr$, 442.1039/440.1014 (M$^+$, ^{193}Ir/^{191}Ir); m/e found, 442.1035/440.1008 (M$^+$, ^{193}Ir/^{191}Ir).

(η^5-C_9H_7)Ir(PMe_3)(C_6H_5)($COCH_3$) (10b). A 30-mL glass bomb was charged with an Et_2O solution of the phenylmethyl complex **4b** (20 mg, 0.042 mmol in 5 mL) in the drybox. The solution was degassed with two freeze–pump–thaw cycles, and the bomb was pressurized at ambient temperature with 700 Torr of CO. After the solution was allowed to turn colorless under the CO atmosphere, the volatile materials were removed under vacuum, leaving a 3:2 mixture of two diastereomeric dicarbonyl adducts **9d** as a white solid. This mixture was characterized spectroscopically by NMR analysis. ^{1}H NMR (acetone-d_6): δ 7.8–6.2 (aromatic); major isomer δ 3.80 (br d, J = 14 Hz, α-Ind), 1.53 (d, J = 10.5 Hz, PMe_3), 0.68 (d, J = 8.2 Hz, Ir–Me); minor isomer δ 3.84 (br d, J = 13 Hz, α-Ind), 1.54 (d, J = 10.5 Hz, PMe_3), 0.89 (d, J = 8.6 Hz, Ir–Me) ppm. ^{31}P{^{1}H} NMR (acetone-d_6): major isomer δ −47.0; minor isomer δ −46.7 ppm. ^{13}C{^{1}H} NMR (acetone-d_6): major isomer δ 170.8 (d, J = 4 Hz), 169.6 (d, J = 4 Hz), 158.4 (d, J = 2.5 Hz), 149.5 (d, J = 5 Hz), 141.6 (s), 139.7 (d, J = 10 Hz), 139.5 (br), 128.9 (s), 124.3 (s), 123.7 (s), 123.2 (s), 122.7 (s), 120.8 (s), 120.3 (d, J = 5.0 Hz), 35.6 (d, J = 60 Hz), 14.7 (d, J = 35.6 Hz), −10.3 (d, J = 7 Hz); minor isomer δ 170.9 (d, J = 4 Hz), 169.9 (d, J = 4 Hz), 157.8 (br), 150.7 (d, J = 5 Hz), 142.1 (s), 139.4 (d, J = 10 Hz), 138.9 (br), 129.0 (s), 124.2 (s), 123.9 (s), 122.8 (s), 122.2 (s), 121.2 (s), 119.1 (d, J = 4 Hz), 35.8 (d, J = 60 Hz), 14.7 (d, J = 35.6 Hz), −10.6 (d, J = 8 Hz) ppm. (Note that the PMe_3 resonances of both isomers are coincident. In addition, the olefin indenyl carbon resonances near δ 150 cannot be assigned to the appropriate isomers because of an insufficient difference in intensities.)

The mixture of dicarbonyl adducts was removed from the NMR tube by extraction with Et_2O in the drybox. After the solvent was removed under vacuum, 3.5 mg (0.046 mmol, 1.1 equiv) of Me_3NO was added to the white residue. The resulting mixture turned pale yellow upon dissolution in 1 mL of CD_2Cl_2, and ^{1}H NMR analysis showed that the reaction was complete within a matter of seconds. The solvent was removed, and the residue was dissolved in a minimum amount of toluene. Column chromatography on alumina III, eluting with a 1:1 mixture of Et_2O/pentane, gave 17 mg (0.034 mmol, 80% yield) of the product **10b** as a pure pale yellow solid. Complex **10b** was crystallized from toluene/pentane at −40 °C for elemental analysis. ^{1}H NMR (acetone-d_6): δ 7.50 (m, 1 H), 7.41 (m, 1 H), 7.16 (m, 1 H), 7.03 (m, 1 H), 6.70 (m, 1 H), 6.63 (m, 2 H), 6.14 (m, 1 H), 6.12 (m, 1 H), 6.09 (m, 2 H), 5.83 (m, 1 H), 2.53 (s, 3 H), 1.16 (d, J = 11.1 Hz, 9 H) ppm. ^{31}P{^{1}H} NMR (acetone-d_6): δ −36.2 ppm. ^{13}C{^{1}H} NMR (acetone-d_6): δ 199.0 (d, J = 6.4 Hz), 139.1 (d, J = 2.0 Hz), 127.5 (d, J = 13.6 Hz), 127.3 (s, 2 C), 127.0 (s), 126.1 (s), 124.0 (s), 123.2 (s), 122.0 (s), 121.0 (s), 116.8 (s), 99.1 (s), 71.7 (s), 67.8 (d, J = 17.9 Hz), 47.6 (d, J = 2.6 Hz), 15.6 (d, J = 30.4 Hz) ppm. IR (KBr pellet): ν_{CO} 1615 cm^{-1}. MS (EI): m/e 504 (M$^+$). Anal. Calcd for $C_{20}H_{24}PIr$: C, 47.70; H, 4.80. Found: C, 47.61; H, 4.90.

(η^5-C_9H_7)Ir(PMe_3)(p-$CH_3C_6H_4$)($COCH_3$) (10c). Compound **10c** was prepared by a procedure similar to the one described for complex **10b**, starting with the tolylmethyl complex **4c** (32 mg, 0.065 mmol in 5 mL). A 3:2 mixture of the two diastereomeric dicarbonyl adducts **9e** was characerized spectroscopically by NMR

analysis. ^{1}H NMR (acetone-d_6): δ 7.7–6.2 (aromatic); major isomer δ 3.80 (br d, J = 14 Hz, α-Ind), 2.29 (s, tol), 1.52 (d, J = 10.5 Hz, PMe_3), 0.67 (d, J = 8.2 Hz, Ir–Me); minor isomer δ 3.84 (br d, J = 13 Hz, α-Ind), 2.25 (s, tol), 1.53 (d, J = 10.5 Hz, PMe_3), 0.88 (d, J = 8.6 Hz, Ir–Me) ppm. ^{31}P{^{1}H} NMR (acetone-d_6): major isomer δ −47.1; minor isomer δ −46.9 ppm. ^{13}C{^{1}H} NMR (acetone-d_6): major isomer δ 170.9 (d, J = 4 Hz), 170.8 (d, J = 4 Hz), 158.4 (d, J = 2.5 Hz), 149.6 (d, J = 5.1 Hz), 141.6 (s), 139.4 (br s), 135.3 (d, J = 10.6 Hz), 133.1 (s), 129.9 (s), 123.6 (s), 123.3 (s), 122.7 (s), 120.8 (s), 120.2 (d, J = 4.9 Hz), 35.5 (d, J = 61.1 Hz), 21.0 (s), 14.77 (d, J = 35.6 Hz), −10.3 (d, J = 7.3 Hz); minor isomer δ 170.0 (d, J = 3.8 Hz), 169.7 (d, J = 4.5 Hz), 157.9 (d, J = 2 Hz), 150.9 (d, J = 5.0 Hz), 142.2 (s), 138.8 (br s), 135.0 (d, J = 10.2 Hz), 133.0 (s), 130.0 (s), 123.9 (s), 122.8 (s), 122.2 (s), 121.2 (s), 119.1 (d, J = 3.9 Hz), 35.7 (d, J = 61.2 Hz), 20.9 (s), 14.80 (d, J = 35.6 Hz), −10.6 (d, J = 7.6 Hz) ppm. (Note that the ipso tolyl carbon resonances near δ 135 cannot be assigned to the appropriate isomers because of an insufficient difference in intensities).

After treatment of the dicarbonyl adducts with Me_3NO, column chromatography on alumina III, eluting with a 1:1 mixture of Et_2O/pentane gave 32 mg (0.062 mmol, 95% yield) of complex **10c** as a pure pale yellow solid. Product **10c** was crystallized from toluene/pentane at −40 °C for elemental analysis. ^{1}H NMR (acetone-d_6): δ 7.49 (m, 1 H), 7.40 (m, 1 H), 7.15 (m, 1 H), 7.03 (m, 1 H), 6.49 (d, J = 7.8 Hz, 2 H), 6.06 (m, 2 H), 6.01 (d, J = 7.8 Hz, 2 H), 5.79 (m, 1 H), 2.52 (s, 3 H), 2.10 (s, 3 H), 1.16 (d, J = 11.1 Hz, 9 H) ppm. ^{31}P{^{1}H} NMR (acetone-d_6): δ −36.3 ppm. ^{13}C{^{1}H} NMR (acetone-d_6): δ 199.0 (d, J = 6.6 Hz), 138.8 (d, J = 2.0 Hz), 130.5 (s), 128.3 (s), 126.9 (s), 126.0 (s), 123.9 (s), 123.2 (s), 122.4 (d, J = 13.5 Hz), 121.0 (d, J = 11.7 Hz), 116.8 (s), 99.0 (s), 71.6 (s), 67.7 (d, J = 18.1 Hz), 47.6 (d, J = 2.1 Hz), 20.7 (s), 15.6 (d, J = 40.4 Hz) ppm. IR (KBr pellet): ν_{CO} 1613 cm^{-1}, MS (EI): m/e 518 (M^+). Anal. Calcd for $C_{21}H_{26}OPIr$: C, 48.73; H, 5.06. Found: C, 48.68; H, 5.01.

(η^5-C_9H_7)Ir(PMe_3)(CH_3)($CH{=}CH_2$) (13a). In the drybox, 20 mg (0.05 mmol) of the hydridomethyl compound **6a** was dissolved in 0.5 mL of acetone and placed in an NMR tube. To this solution was added 1.5 mL of a 1.24 M acetone solution of acetylene (Alfa). The NMR tube was capped, and the resulting mixture was allowed to stand for 15 h, after which a red precipitate was removed by filtration through a plug of glass wool. The volatile materials were removed under vacuum, distillation of the residue at 50 °C, 10^{-2} Torr, onto a sublimation coldfinger, kept at −78 °C with a dry ice/acetone mixture, gave a thin film of yellow solid on the coldfinger. The solid melted upon warming the coldfinger to ambient temperature, but the high viscosity of the oil allowed it to remain on the coldfinger. The oil was washed off the coldfinger in the drybox with pentane. Removal of the pentane solvent gave **13a** (16 mg, 0.038 mmol, 75% yield) as a bright yellow oil. In the ^{1}H and ^{31}P{^{1}H} NMR spectra, resonances are assigned to one major product, which comprises about 90% of the mixture. The minor component has a ^{31}P chemical shift at δ −38.3 ppm, only 0.2 ppm upfield of the major component, while ^{1}H NMR resonances corresponding to a PMe_3 ligand at δ 1.19 and an Ir–Me moiety at δ 0.48 are evident. The minor component appears to be a second rotamer of the major component. ^{1}H NMR (acetone-d_6): δ 7.34 (m, 2 H), 7.22 (ddd, J_{tr} = 17.2 Hz, J_{cis} = 9.7 Hz, J_{HP} = 1.7 Hz, 1 H), 7.05 (m, 2 H), 5.76 (ddd, J_{cis} = 9.7 Hz, J_{gem} = J_{HP} = 2.6 Hz), 5.53 (m, 1 H), 5.44 (m, 1 H), 5.40 (m, 1 H), 4.84 (ddd, J_{tr} = 17.2 Hz, J_{gem} = 2.6 Hz, J_{HP} = 2.1 Hz, 1 H), 1.20 (d, J = 10.6 Hz, 9 H), 0.54 (d, J = 5.5 Hz, 3 H) ppm. ^{31}P{^{1}H} NMR (acetone-d_6): δ −38.1 ppm. ^{13}C{^{1}H} NMR (acetone-d_6): δ 128.1 (d, J = 13.4 Hz), 124.3 (s), 124.1 (s), 122.4 (s), 122.0 (s), 119.0 (d, J = 4.1 Hz), 111.4 (s), 111.3 (s), 99.1 (s), 70.0 (d, J = 7.5 Hz), 68.7 (d, J = 9.6 Hz), 14.4 (d, J = 39.2 Hz), −31.1 (d, J = 8.4 Hz) ppm. IR (KBr pellet): 2952, 2915, 2880, 1552, 1322, 1282, 1264, 952, 938, 740, 732, 679, 442 cm^{-1}. High-resolution MS (oil) (EI): m/e calcd for $C_{15}H_{22}PIr$, 426.1090/424.1065 (M^+, ^{193}Ir/^{191}Ir); m/e found, 426.1078/424.1062 (M^+, ^{193}Ir/^{191}Ir).

(*E*)-(η^5-C_9H_7)Ir(PMe_3)(CH_3)[CH=C(*t*-Bu)H] (13b). In the drybox, 20 mg (0.05 mmol) of the hydridomethyl compound **6a** was dissolved in 1 mL of acetone-d_6 and placed in an 8-in. NMR tube. The NMR tube was fitted with a Cajon adaptor, and the solution was degassed with three freeze–pump–thaw cycles. From a known-volume bulb, 10 equiv of *tert*-butylacetylene (18.0 Torr, 508.5 mL at 293 K, 0.50 mmol) was condensed into the solution at 77 K. The resulting mixture was heated to 65 °C for 24 h, at which time the reaction appeared to be complete by NMR spectroscopy. Column chromatography in the drybox on alumina III with a 4:1 (v:v) pentane/Et_2O eluant gave **13b** (17 mg, 0.035 mmol, 70% yield) as a yellow, pentane-miscible oil. Product **13b** may also be distilled in the same manner as compound **13a** at 50 °C, 10^{-2} Torr, onto a sublimation coldfinger. All NMR spectra of the chromatographed product indicated the presence of one pure compound. ^{1}H NMR (acetone-d_6): δ 7.34 (m, 1 H), 7.23 (m, 1 H), 7.09 (m, 1 H), 6.99 (m, 1 H), 6.39 (d, J_{tr} = 15.6 Hz, 1 H), 5.46 (br, 1 H), 5.43 (br, 1 H), 5.33 (m, 1 H), 4.86 (dd, J_{tr} = 15.6 Hz, J_{HP} = 1.8 Hz, 1 H), 1.18 (d, J = 10.5 Hz, 9 H), 0.87 (s, 9 H), 0.57 (d, J = 5.4 Hz, 3 H) ppm. ^{31}P{^{1}H} NMR (acetone-d_6): δ −37.9 ppm. ^{13}C{^{1}H} NMR (acetone-d_6): δ 145.2 (d, J = 4.9 Hz), 124.1 (s), 123.8 (s), 122.3 (s), 122.0 (s), 112.3 (s), 110.4 (s), 108.5 (d, J = 14.8 Hz), 98.7 (s), 69.2 (d, J = 7.5 Hz), 69.1 (s), 36.3 (s), 30.7 (s), 14.3 (d, J = 39.0 Hz), −31.5 (d, J = 7.9 Hz) ppm. IR (pentane): 3052, 3037, 3009, 1576, 1323, 1281, 951, 936, 738, 732, 678 cm^{-1}. High-resolution MS (oil) (EI): m/e calcd for $C_{19}H_{30}PIr$, 482.1716/480.1691 (M^+, ^{193}Ir/^{191}Ir); m/e found, 482.1718/480.1691 (M^+, ^{193}Ir/^{191}Ir).

(*E*)-(η^5-C_9H_7)Ir(PMe_3)(CH_3)[(CH_3)C=C(CH_3)H] (13c). Compound **13c** was prepared in a fashion similar to compound **13b** from 2-butyne. Thermolysis at 85 °C for 24 h and subsequent distillation at 50 °C, 10^{-2} Torr, onto a sublimation coldfinger gave **13c** (18 mg, 0.040 mmol, 79% yield) as a yellow, pentane-miscible oil. All NMR spectra of the distilled product indicate the presence of one pure compound. ^{1}H NMR (acetone-d_6): δ 7.32 (m, 1 H), 7.26 (m, 1 H), 6.99 (m, 2 H), 5.55 (m, 1 H), 5.40 (m, 1 H), 5.34 (m, 1 H), 4.94 (q m, $^2J_{HH}$ = 6.6 Hz, 1 H), 1.75 (br, 3 H), 1.53 (d m, $^2J_{HH}$ = 6.6 Hz, 3 H), 1.21 (d, J = 10.3 Hz, 9 H), 0.42 (d, J = 6.1 Hz, 3 H) ppm. ^{31}P{^{1}H} NMR (acetone-d_6): δ −38.3 ppm. ^{13}C{^{1}H} NMR (acetone-d_6): δ 124.1 (s), 123.8 (s), 122.6 (d, J = 4.1 Hz), 122.2 (s), 121.7 (s), 114.8 (d, J = 11.9 Hz), 112.6 (s), 112.1 (s), 99.5 (d, J = 2.0 Hz), 70.0 (d, J = 4.0 Hz), 68.5 (d, J = 12.2 Hz), 28.1 (d, J = 2.1 Hz), 16.3 (s), 14.6 (d, J = 38.2 Hz), −32.4 (d, J = 8.8 Hz) ppm. IR (KBr pellet): 2910, 1596, 1320, 1282, 952, 936, 740, 730, 678, 441 cm^{-1}. High-resolution MS (oil) (EI): calcd for $C_{17}H_{26}PIr$, 454.1402/452.13785 (M^+, ^{193}Ir/^{191}Ir); m/e found, 454.1392/452.1372 (M^+, ^{193}Ir/^{191}Ir).

(*E*)-(η^5-C_9H_7)Ir(PMe_3)(CH_3)[(C_2H_5)C=C(C_2H_5)H] (13d). Compound **13d** was prepared in a fashion similar to compounds **13b** and **13c** from 3-hexyne. Thermolysis at 85 °C for 48 h and subsequent distillation at 50 °C, 10^{-2} Torr, onto a sublimation coldfinger gave **13d** (30 mg, 0.042 mmol, 83% yield) as a yellow, pentane-miscible oil. All NMR spectra of the distilled product indicate the presence of one pure compound. ^{1}H NMR (acetone-d_6): δ 7.26 (m, 2 H), 7.02 (m, 2 H), 5.55 (m, 2 H), 5.29 (m, 1 H), 4.75 (t, $^2J_{HH}$ = 6.9 Hz, 1 H), 2.1–1.7 (m, 4 H), 1.19 (d, J = 10.4 Hz, 9 H), 0.87 (t, J = 7.4 Hz, 3 H), 0.81 (t, J = 7.5 Hz, 3 H), 0.48 (d, J = 5.9 Hz, 3 H) ppm. ^{31}P{^{1}H} NMR (acetone-d_6) δ −37.7 ppm. ^{13}C{^{1}H} NMR (acetone-d_6): δ 133.2 (d, J = 6.4 Hz), 124.3 (s), 123.7 (s), 123.1 (d, J = 13.1 Hz), 122.4 (s), 121.5 (s), 113.9 (s), 111.4 (s), 100.5 (d, J = 2.8 Hz), 69.1 (d, J = 5.4 Hz), 68.5 (d, J = 11.6 Hz), 29.6 (s), 24.4 (s), 15.7 (s), 15.0 (s), 14.0 (d, J = 39.2 Hz), −34.8 (d, J = 11.1 Hz) ppm. IR (KBr pellet): 2910, 1596, 1320, 1282, 952, 936, 740, 730, 678, 441 cm^{-1}. High-resolution MS (oil) (EI): m/e calcd for $C_{19}H_{30}PIr$, 482.1716/480.1691 (M^+, ^{193}Ir/^{191}Ir); m/e found, 482.1709/480.1685 (M^+, ^{193}Ir/^{191}Ir).

(η^5-C_9H_7)Ir(PMe_3)(CH_3)(C_2H_5) (14). In the drybox, 20 mg (0.05 mmol) of the hydridomethyl compound **6a** was dissolved in 1 mL of acetone-d_6 and placed in an 8-in. NMR tube. The NMR tube was fitted with a Cajon adaptor, and the solution was degassed with three freeze–pump–thaw cycles. From a known-volume bulb, 10 equiv of ethylene (138 Torr, 66.34 mL at 293 K. 0.50 mmol) was condensed into the solution at 77 K. The tube was flame-sealed under vacuum (Caution: thaw tube at −78 °C in a dry ice–2-propanol bath first; failure to dissolve ethylene in acetone would result in a gas pressure of about 10 bar), and the resulting mixture was heated to 45 °C for 40 h, at which time the reaction appeared to be complete. After the volatile materials wer removed under vacuum, distillation of the residue at 50 °C, 10^{-2} Torr, onto a sublimation coldfinger gave 14 mg of a yellow, pentane-miscible oil, the major component of which is complex **14**. ^{1}H NMR for **14** (acetone-d_6): δ 7.39 (m, 1 H), 7.26 (m, 1 H),

6.97 (m, 2 H), 5.48 (m, 2 H), 5.25 (m, 1 H), 1.4–1.1 (m, 5 H), 1.21 (d, J = 10.2 Hz, 9 H), 0.24 (d, J = 5.5 Hz, 3 H) ppm. $^{31}P\{^1H\}$ NMR for **14** (acetone-d_6): δ −39.5 ppm. $^{13}C\{^1H\}$ NMR for **14** (acetone-d_6): δ 123.7 (s), 123.4 (s), 121.8 (s), 121.6 (s), 112.6 (s), 110.4 (s), 97.7 (s), 70.3 (d, J = 3.7 Hz), 68.6 (d, J = 13.1 Hz), 23.2 (d, J = 4.6 Hz), 14.7 (d, J = 37.0 Hz), −13.9 (d, J = 7.1 Hz), −32.3 (d, J = 8.7 Hz) ppm. List of impurity peaks in the $^{13}C\{^1H\}$ NMR spectrum for **14** (acetone-d_6): δ 122.4 (s), 119.0 (s), 18.5 (d, J = 36.1 Hz), 9.9 (s) ppm. High-resolution MS (oil) (EI): m/e calcd for $C_{15}H_{24}PIr$, 428.1246/426.1222 (M^+, $^{193}Ir/^{191}Ir$); m/e found, 428.1230/426.1212 (M^+, $^{193}Ir/^{191}Ir$).

Kinetics of the Insertion Reaction of (η^5-C_9H_7)Ir(PMe$_3$)(CH$_3$)(H) (6a) with 3,3-Dimethyl-1-butyne. Samples were prepared in 5-mm thin-walled Wilmad 505-PS 8-in. NMR tubes. The volumes of the alkyne and cyclohexane-d_{12} were added to give a total volume of 0.60 mL, assuming a negligible (≤5%) change in the volume of mixing. For example, 4 mg (0.01 mmol) of **6a** was dissolved in 0.58 mL of cyclohexane-d_{12}, as measured by syringe, and the solution was loaded into an NMR tube fitted with a Cajon adaptor. Tetramethylsilane was vacuum-transferred (2.9×10^{-6} mol, 0.8 Torr, 66.34 mL, 293 K), into the NMR tubes as the internal standard for ^1H NMR spectra, and P(o-tol)$_3$ (6 mg, 2.0×10^{-5} mol) was added as a solid as the internal standard for $^{31}P\{^1H\}$ NMR spectra. The solution was degassed with three freeze–pump–thaw cycles, and 0.16 mmol (0.02 mL) of 3,3-dimethyl-1-butyne was condensed into the tube from a known-volume bulb. The tube was flame-sealed to give a solution with [**6a**] = 0.017 M and [alkyne] = 0.27 M. The tubes were heated in the appropriate Neslab constant-temperature baths and cooled rapidly in a 0 °C acetone bath. All NMR spectra were taken at 20 °C.

Acknowledgment. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, of the U.S. Department of Energy under Contract DE-AC0376SF00098. T.F. acknowledges the National Science Foundation for a predoctoral fellowship and the University of California for a Berkeley Fellowship. We are also grateful for a gift of iridium chloride from Johnson-Matthey, Aesar/Alfa.

Registry No. **4a**, 139377-84-7; **4b**, 139377-90-5; **4c**, 139377-91-6; **5a**, 139377-85-8; **5b**, 139377-92-7; **6a**, 139377-86-9; **8**, 139655-72-4; **9a**, 139655-73-5; **9b**, 139655-74-6; **9c**, 139655-75-7; **9d**, 139655-76-8; **9e**, 139655-77-9; **10a**, 139687-87-9; **10b**, 139687-86-8; **10c**, 139687-88-0; **13a**, 139687-89-1; **13b**, 139687-90-4; **13c**, 139687-91-5; **13d**, 139687-92-6; **14**, 139687-93-7; *t*-BuNC, 7188-38-7; acetylene, 74-86-2; *tert*-butylacetylene, 917-92-0; 2-butyne, 503-17-3; 3-hexyne, 928-49-4; ethylene, 74-85-1; 3,3-dimethyl-1-butyne, 917-92-0.

OM910645V

Reaction of Cyclopentadiene with (Alkylidyne)triruthenium Clusters. Syntheses of $Ru_3(\mu_3\text{-CPh})(\mu\text{-CO})_2(CO)_6(\eta^5\text{-}C_5H_5)$ and $(\mu\text{-H})_2Ru_3(\mu_3\text{-CPh})(\mu\text{-CO})(CO)_6(\eta^5\text{-}C_5H_5)$. Crystal Structures of $Ru_3(\mu_3\text{-CPh})(\mu\text{-CO})_2(CO)_6(\eta^5\text{-}C_5H_5)$ and $Ru_3(\mu_3\text{-CPh})(\mu\text{-CO})_3(\eta^5\text{-}C_5H_5)_3$

Leigh R. Nevinger, Jerome B. Keister,* Charles H. Lake, and Melvyn Rowen Churchill*

Department of Chemistry, University at Buffalo, State University of New York, Buffalo, New York 14214

Received September 3, 1991

The reaction of $(\mu\text{-H})_3Ru_3(\mu_3\text{-CPh})(CO)_{9-n}(NCMe)_n$ (n = 1, 2) with cyclopentadiene produces the new cluster $Ru_3(\mu_3\text{-CPh})(\mu\text{-CO})_2(CO)_6(\eta^5\text{-}C_5H_5)$, in addition to $Ru_3(\mu_3\text{-CPh})(\mu\text{-CO})_3(\eta^5\text{-}C_5H_5)_3$. Hydrogenation of $Ru_3(\mu_3\text{-CPh})(\mu\text{-CO})_2(CO)_6(\eta^5\text{-}C_5H_5)$ gives $(\mu\text{-H})_2Ru_3(\mu_3\text{-CPh})(\mu\text{-CO})(CO)_6(\eta^5\text{-}C_5H_5)$. The compound $Ru_3(\mu_3\text{-CPh})(\mu\text{-CO})_2(CO)_6(\eta^5\text{-}C_5H_5)$ crystallizes in the centrosymmetric monoclinic space group $P2_1/n$, with a = 9.039 (2) Å, b = 20.496 (5) Å, c = 11.896 (3) Å, β = 92.80 (2)°, V = 2201 (1) Å^3, and Z = 4. Diffraction data (Mo Kα, 2θ = 5–50°) were collected with a Siemens R3m/V diffractometer, and the structure was solved and refined to R = 5.09% for all 3901 data (R = 2.69% for those 2659 data with $F > 6.0\sigma(F)$). The structure contains a triangular arrangement of ruthenium atoms (Ru–Ru = 2.738 (1)–2.749 (1) Å) capped by a μ_3-CPh ligand (Ru–C = 2.055 (5)–2.086 (5) Å). Atoms Ru(1) and Ru(2) are each bound to three terminal CO ligands, while Ru(3) is linked to an η^5-C_5H_5 ligand. The structure is completed by two bridging CO ligands bonded more strongly to Ru(3) and somewhat less strongly to the remaining Ru atoms (Ru(3)–C(31) = 1.993 (6) Å, Ru(1)–C(31) = 2.167 (6) Å; Ru(3)–C(32) = 1.972 (6) Å, Ru(2)–C(32) = 2.225 (6) Å). The compound $Ru_3(\mu_3\text{-CPh})(\mu\text{-CO})_3(\eta^5\text{-}C_5H_5)_3$ crystallizes in the centrosymmetric monoclinic space group $P2_1/c$, with a = 10.465 (2) Å, b = 11.192 (2) Å, c = 18.444 (3) Å, β = 92.00 (2)°, V = 2158.8 (7) Å^3, and Z = 4. Diffraction data (Mo Kα, 2θ = 5–45°) were collected with a Siemens R3m/V diffractometer, and the structure was solved and refined to R_F = 3.24% for all 2716 unique data (R_F = 2.02% for those 2110 data with $|F_o| > 6\sigma(|F_o|)$). The three ruthenium atoms in the structure form an almost perfect equilateral triangle (Ru–Ru = 2.690 (1)–2.705 (1) Å), which is capped by a μ_3-CPh ligand (Ru–C = 2.019 (4)–2.023 (4) Å). Each edge of the triangle has a symmetrically bridging carbonyl attached. The structure is then completed by one η^5-C_5H_5 ring bonded to each ruthenium.

The alkylidyne trimetallic clusters $(\mu\text{-H})_3M_3(\mu_3\text{-CX})(CO)_{9-n}L_n$ (M = Ru, Os; X = H, alkyl, aryl, halide, CO_2R, OMe, etc.) have proved to be valuable for studies of cluster reactivity because of the numerous derivatives available in good yield, allowing ready modification of steric and electronic character of the cluster.[1] Cyclopentadienyl derivatives $H_{4-2n}Ru_3(CX)(CO)_{6+n}Cp$ would be desirable because (1) the neutral clusters would contain even num-

(1) (a) Keister, J. B. *Polyhedron* **1988**, *7*, 847. (b) Duggan, T. P.; Golden, M. J.; Keister, J. B. *Organometallics* **1990**, *9*, 1656. (c) Feighery, W. G.; Allendoerfer, R. D.; Keister, J. B. *Organometallics* **1990**, *9*, 2424.

0276-7333/92/2311-1819$03.00/0