4816 *Organometallics* **1997,** *16,* 4816−4823

Synthesis and Reactivity of $Ir(CO)(\eta^2\text{-}C_2R_2)(\eta^5\text{-}C_9H_7)$ (R = Ph, Tol). Alkyne Coupling and Arene C−H Bond Activation Forming a Substituted Butadiene Ligand

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Received July 8, 1997[⊗]

The reaction of $Ir(CO)(\eta^2\text{-}C_8H_{14})(\eta^5\text{-}C_9H_7)$ with excess C_2R_2 (R = Ph, Tol) in benzene at reflux leads to a mixture containing $Ir(CO)(\eta^2\text{-}C_2R_2)(\eta^5\text{-}C_9H_7)$ (**1a**, R = Ph; **1b**, R = Tol), $Ir_2(CO)_2(\mu\text{-}C_2R_2)(\eta^5\text{-}C_9H_7)_2$ (**2a**, R = Ph; **2b**, R = Tol), and $Ir(\eta^4\text{-}HC_4R_4R')(\eta^5\text{-}C_9H_7)$ (**3a**, R = Ph, R′ = Ph; **3b**, R = Tol, R′ = Ph). Conducting the reaction in benzene-d_6, toluene, or *m*-xylene leads to **1** and **2** and $Ir(\eta^4\text{-}DC_4R_4R')(\eta^5\text{-}C_9H_7)$ (**3c**, R = Tol, R′ = C_6D_5) or $Ir(\eta^4\text{-}HC_4R_4R')(\eta^5\text{-}C_9H_7)$ (**3d**, R = Ph, R′ = C_6H_4Me; **3e**, R = Ph, R′ = $C_6H_3Me_2$; **3f**, R = Tol, R′ = C_6H_4Me). The structures of compounds **2a** and **3b** have been determined by X-ray diffraction. Compound **2a** contains a dimetallacyclobutene framework with the CO ligands adopting a *trans* orientation with respect to the Ir_2C_2 mean plane. The indenyl ligands take positions opposite the carbonyls at each Ir center. Compound **3b** contains a 1-phenyl-1,2,3,4-tetratolyl-1,3-butadiene ligand formed through both alkyne coupling and CH bond activation of the solvent benzene. The direct reactions of **1** with excess $Ir(CO)(\eta^2\text{-}C_8H_{14})(\eta^5\text{-}C_9H_7)$ or C_2R_2 lead to higher yields of **2** or **3**, respectively.

Introduction

We have reported the synthesis of the indenyl iridium trimer $Ir_3(\mu\text{-}CO)_3(\eta^5\text{-}C_9H_7)_3$[1] and have attempted without current success to prepare alkyne derivatives of this cluster in analogy with the preparation of $Ir_3(\mu\text{-}CO)(\mu_3\text{-}C_2R_2)(\eta^5\text{-}C_5H_5)_3$ from $Ir_3(CO)_3(\eta^5\text{-}C_5H_5)_3$.[2] As an indirect approach to the same goal, we have investigated the formation of the mononuclear alkyne complex $Ir(CO)(\eta^2\text{-}C_2R_2)(\eta^5\text{-}C_9H_7)$. It appears that an appropriate precursor would be $Ir(CO)(\eta^2\text{-}C_8H_{14})(\eta^5\text{-}C_9H_7)$, since the cyclooctene ligand is readily replaced by ethylene,[3] C_{60},[4] and other π-bonding ligands.[5] We now report that the reaction of $Ir(CO)(\eta^2\text{-}C_8H_{14})(\eta^5\text{-}C_9H_7)$ with C_2R_2 (R = Ph, Tol) does indeed lead to the mononuclear alkyne compounds $Ir(CO)(\eta^2\text{-}C_2R_2)(\eta^5\text{-}C_9H_7)$ (**1a**, R = Ph; **1b**, R = Tol). Furthermore, subsequent reaction of **1** with $Ir(CO)(\eta^2\text{-}C_8H_{14})(\eta^5\text{-}C_9H_7)$ forms the dinuclear compounds $Ir_2(CO)_2(\mu\text{-}C_2R_2)(\eta^5\text{-}C_9H_7)_2$ (**2a**, R = Ph; **2b**, R = Tol). However, we have unexpectedly found that **1** also reacts with the aromatic solvent (e.g., benzene) as well as an additional molecule of C_2R_2 to form a complex with a substituted butadiene ligand, e.g., $Ir(\eta^4\text{-}HC_4R_4R')(\eta^5\text{-}C_9H_7)$ (**3a**, R = Ph, R′ = Ph; **3b**, R = Tol, R′ = Ph) (see Scheme 1).

Experimental Section

General Procedures. All reactions were conducted under an atmosphere of nitrogen by using standard Schlenk techniques, while purification procedures were done in air. $Ir(CO)(\eta^2\text{-}C_8H_{14})(\eta^5\text{-}C_9H_7)$[3] and C_2Tol_2[6] were prepared by literature methods. Diphenylacetylene (Aldrich) was used without further purification. Solvents for preparative use were dried by standard methods and distilled. The deuterated solvents, $(CD_3)_2CO$ and CD_2Cl_2 (Cambridge Isotope Laboratories), were used as received. Proton NMR spectra were recorded on General Electric spectrometers at 300 or 500 MHz and on Varian spectrometers at 500 or 750 MHz; the reference was a residual proton resonance in the deuterated solvent. Infrared spectra were recorded on a Perkin-Elmer 1750 FT-IR spectrometer. Field-desorption (FD) mass spectra were recorded on a Finnigan-Mat 731 spectrometer by the staff of the Mass Spectrometry Laboratory of the School of Chemical Sciences. Microanalyses were performed by the staff of the School Microanalytical Laboratory.

Proton correlation spectra (^{1}H COSY) were recorded on a GE GN500 spectrometer; data was collected in the absolute-value mode. A total of 4 transients of 512 data points were recorded for each of the 256 increments of t_1 with a relaxation delay of 0.3 s. The data matrix was zero-filled once in the f_2 dimension before transformation and symmetrized after transformation. Proton-detected $^1H-^{13}C$ correlation spectra were recorded on a Varian Unity Inova 500 MHz spectrometer by Dr. Vera Mainz.

Synthesis of $Ir(CO)(\eta^2\text{-}C_2R_2)(\eta^5\text{-}C_9H_7)$. Method A. A solution of C_2Ph_2 (200 mg, 1.12 mmol) in benzene (10 mL) was stirred and heated at reflux, and a benzene solution (10 mL) of $Ir(CO)(\eta^2\text{-}C_8H_{14})(\eta^5\text{-}C_9H_7)$ (50 mg, 0.112 mmol) was added slowly over 1 h through an addition funnel. The mixture was heated at reflux for an additional 7 h, resulting in a light orange solution. The solvent was removed under vacuum, and the residue was redissolved in dichloromethane. A small amount of neutral alumina I (Aldrich) was added, and the mixture was dried under vacuum and placed on a 20 cm × 1 cm column of neutral alumina I. Elution with hexane removed excess C_2Ph_2, and elution with a 4:1 mixture of hexane and dichloromethane removed a yellow band. The yellow fraction was concentrated on a rotary evaporator and placed on five

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[⊗] Abstract published in *Advance ACS Abstracts,* August 15, 1997.

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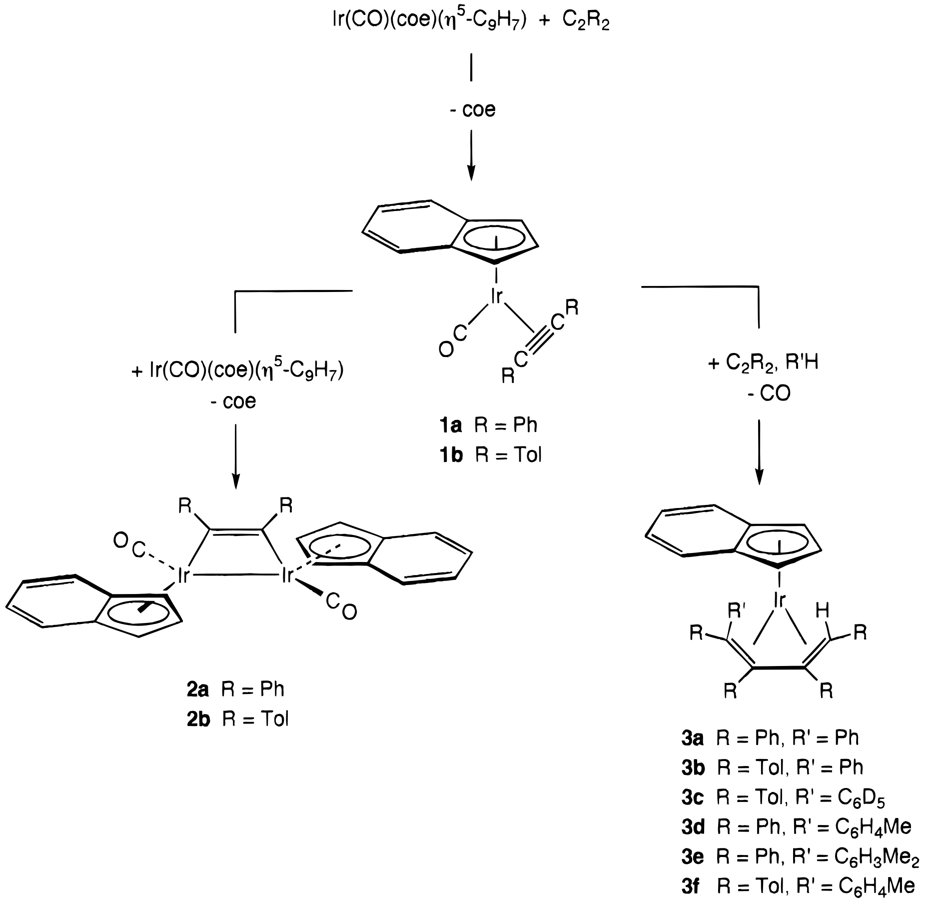
S0276-7333(97)00579-7 CCC: $14.00

Scheme 1



1a R = Ph
1b R = Tol

2a R = Ph
2b R = Tol

3a R = Ph, R' = Ph
3b R = Tol, R' = Ph
3c R = Tol, R' = C_6D_5
3d R = Ph, R' = C_6H_4Me
3e R = Ph, R' = $C_6H_3Me_2$
3f R = Tol, R' = C_6H_4Me

preparative silica gel TLC plates (Aldrich). Elution with hexane/ dichloromethane (4:1) provided, in order of elution, yellow **1a** (30.8 mg, 0.060 mmol, 53%), orange **2a** (trace, identified by infrared spectroscopy), and yellow **3a** (12.9 mg, 0.017 mmol, 15%).

Method B. A solution of C_2Ph_2 (200 mg, 1.12 mmol) and Ir(CO)(η^2-C_8H_{14})(η^5-C_9H_7) (50 mg, 0.112 mmol) in benzene (20 mL) was stirred and heated at reflux for 8 h, resulting in an orange solution. The reaction mixture was separated in the same manner as in method A, providing **1a** (18.9 mg, 0.037 mmol, 33%), **2a** (3.6 mg, 0.004 mmol, 4%), and **3a** (1.4 mg, 0.022 mmol, 20%).

Repeating method A using C_2Tol_2 (231 mg, 1.12 mmol) and Ir(CO)(η^2-C_8H_{14})(η^5-C_9H_7) (50 mg, 0.112 mmol) provided **1b** (22.0 mg, 0.041 mmol, 36%), **2b** (2 mg, 0.002 mmol, 2%), and **3b** (11.3 mg, 0.014 mmol, 13%).

Characterization data: **1a**, *m/z* 514 (M^+), ν_{CO} 1981 cm^{-1}, mp 153−154 °C. Anal. Calcd: C, 56.12; H, 3.34. Found: C, 56.12; H, 3.59. **1b**, *m/z* 542 (M^+), ν_{CO} 1981 cm^{-1}, mp 148−150 °C. Anal. Calcd: C, 57.65; H, 3.91. Found: C, 56.85; H, 3.83. **2a**, *m/z* 850 (M^+), ν_{CO} 1961 cm^{-1}, mp 190−192 °C. Anal. Calcd: C, 48.10; H, 2.75. Found: C, 47.67; H, 2.85. **2b**, *m/z* 878 (M^+), ν_{CO} 1961 cm^{-1}. **3a**, *m/z* 742 (M^+), mp 233−235 °C. Anal. Calcd: C, 69.61; H, 4.48. Found: C, 68.82; H, 4.58. **3b**, *m/z* 798 (M^+), mp 195−197 °C. Anal. Calcd: C, 70.74; H, 5.18. Found: C, 69.41; H, 5.16. Proton NMR data for compounds **1a**, **1b**, **2a**, **2b**, **3a**, and **3b** are collected in Table 1.

Carbon NMR data for compound **3b**: δ 140−125 (tolyl, phenyl, indenyl C_4−C_7), 107.0, 105.1 (indenyl C_8, C_9), 88.8, 88.2 (diene C_2, C_3), 81.5, 80.3, 79.4 (indenyl C_1−C_3), 60.4 (diene C_4), 51.9 (diene C_1−H), 21.0 (2C), 20.9 (1C), 20.8 (1C) (tolyl methyl).

Conducting the reaction of C_2R_2 with Ir(CO)(η^2-C_8H_{14})(η^5-C_9H_7) in C_6D_6, toluene, or *m*-xylene provided **1** and **2** and Ir(η^4-DC_4R_4R')(η^5-C_9H_7) (**3c**, R = Tol, R′ = C_6D_5) or Ir(η^4-HC_4R_4R')(η^5-C_9H_7) (**3d**, R = Ph, R′ = C_6H_4Me; **3e**, R = Ph, R′ = $C_6H_3Me_2$; **3f**, R = Tol, R′ = C_6H_4Me), respectively. Compounds **3c**, **3d**, **3e**, and **3f** were identified by comparing their TLC behavior with **3a** and **3b** and by the molecular ions in their FD-mass spectra (**3c**, *m/z* 804; **3d**, *m/z* 756; **3e**, *m/z* 770; **3f**, *m/z* 812).

Reaction of Ir(CO)(η^2-C_2Ph_2)(η^5-C_9H_7) with Excess C_2Ph_2. A solution of **1a** (20 mg, 0.039 mmol) and C_2Ph_2 (69 mg, 0.39 mmol) in benzene (10 mL) was stirred and heated at reflux for 14 h, resulting in a yellow solution. The solvent was removed under vacuum, and the residue was purified in the same manner as above to give **3a** (23.7 mg, 0.032 mmol, 82%).

Reaction of Ir(CO)(η^2-C_2Ph_2)(η^5-C_9H_7) with excess Ir(CO)(η^2-C_8H_{14})(η^5-C_9H_7). A stirred solution of **1a** (20 mg, 0.039 mmol) and Ir(CO)(η^2-C_8H_{14})(η^5-C_9H_7) (26 mg, 0.059 mmol) in toluene (10 mL) was heated at reflux for 8 h, resulting in a dark orange solution. The solvent was removed under vacuum, and the residue was redissolved in dichloromethane and placed on four preparative silica gel TLC plates (Aldrich). Elution with hexane/dichloromethane (4:1) provided, in order of elution, Ir(CO)(η^2-C_8H_{14})(η^5-C_9H_7) (4.3 mg, 0.010 mmol, 17% recovery), **1a** (1.3 mg, 0.003 mmol, 6% recovery), and **2a** (14.0 mg, 0.016 mmol, 45% based on unrecovered **1a**).

X-ray Structure Determinations of 2a and 3b. X-ray quality crystals were grown by slowly evaporating hexane solutions of **2a** and **3b**. The crystals were mounted with oil (Paratone-N, Exxon) on thin glass fibers. Data were collected at 198 K on an Siemens Platform/CCD diffractometer. Crystal and refinement details are given in Table 2. Scattering factors and anomalous dispersion terms were taken from standard tables.[7] The structures were solved by direct methods using

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(7) *International Tables for X-ray Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Dordrecht, The Nethelands 1992; Vol. C, (a) scattering factors, pp 500−502; (b) anomalous dispersion corrections, pp 219−222.

Table 1. Selected ^1H NMR Data for Compounds 1−3

	indenyl[a]					
cmpd	H_2	H_1, H_3	H_4, H_7	H_5, H_6	aryl	methyl
1a[b,c]	6.62 t[d]	5.77 d[d]	7.45−7.23[e]	7.45−7.23[e]	7.45−7.23[e]	
1b[b,c]	6.61 t[f]	5.75 d[f]	7.37 m	7.23 m	7.31 d, 7.12 d[g]	2.36 s
2a[b,h,i]	4.84 m	6.31 m, 5.45m	7.43−6.77[e]	7.43−6.77[e]	7.43−6.77[e]	
2b[b,h,j]	4.81 m	6.33 m, 5.40 m	7.26 m, 7.39 m	6.92 m, 7.04 m	6.70 d, 6.85 d[k]	2.20 s
3a[h,l]	6.41 m	5.73 m, 4.85 m	7.59 m, 7.45 m	7.45 m, 7.40 m	7.09−6.14[m]	
3b[h,n]	6.34 m	5.58 m, 4.75 m	7.59 m, 7.44 m	7.44 m, 7.39 m	6.95−6.13[o]	2.05[p]

[a] The labeling scheme shown below was used for the indenyl proton resonances. [b] Recorded at 300 MHz. [c] In CD_2Cl_2 at 20 °C. [d] $J_{12} = 2.6$ Hz. [e] Signals for H_4−H_7 and the aryl protons appear throughout this region. See spectra included as Supporting Information. [f] $J_{12} = 2.5$ Hz. [g] $J = 8.1$ Hz. [h] In acetone-d_6 at 20 °C. [i] Simulation gives $J_{12} = 2.7$, $J_{23} = 2.9$, $J_{13} = 1.6$, $J_{17} = 0.8$, $J_{34} = 0.9$, $J_{67} = 8.4$, $J_{56} = 6.9$, $J_{45} = 8.4$, $J_{57} = 1.0$, $J_{46} = 1.0$, and $J_{47} = 1.0$ Hz. [j] Simulation gives $J_{12} = 2.6$, $J_{23} = 2.9$, $J_{13} = 1.5$, $J_{17} = 0.8$, $J_{34} = 0.8$, $J_{67} = 8.4$, $J_{56} = 6.8$, $J_{45} = 8.3$, $J_{57} = 1.1$, $J_{46} = 1.0$, and $J_{47} = 1.0$ Hz. [k] $J = 8.0$ Hz. [l] Recorded at 500 MHz. [m] Signals for alkyne phenyl substitutents appear throughout this region. Signals for groups derived from benzene: C_6H_5, δ 7.80 (1H), 7.37 (1H), 7.30 (1H), 7.25 (1H), 7.15 (1H), all multiplets; =CH, δ 2.55 (1H), singlet. [n] Recorded at 750 MHz. [o] Signals for the alkyne tolyl substitutents appear throughout this region. Signals for groups derived from benzene: C_6H_5, δ 7.76 (1H), 7.35 (1H), 7.24 (2H), 7.15 (1H), all multiplets; =CH, δ 2.47 (1H), singlet. [p] Overlap with acetone-d_5 signals; in CD_2Cl_2, δ 2.14, 2.13, 2.12, 2.10, all singlets.

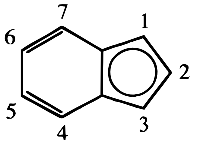

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Table 2. Crystallographic Data for 2a and 3b

compound	**2a**	**3b**
formula	$C_{34}H_{24}Ir_2O_2$	$C_{47}H_{41}Ir$
fw	848.93	798.00
temperature, K	198(2)	198(2)
λ, Å	0.710 73 (Mo Kα)	0.710 73 (Mo Kα)
space group, system	$P2_1/c$, monoclinic	*Pbca, ortho*rhombic
a, Å	12.7082(4)	9.7051(2)
b, Å	10.7592(3)	19.9195(4)
c, Å	19.4867(6)	37.2596(9)
α, deg	90	90
β, deg	94.09	90
γ, deg	90	90
V, Å^3	2657.64(14)	7203.1(3)
Z	4	8
ρ_{calcd}, g cm^{-3}	2.122	1.472
F(000)	1592	3200
cryst size, mm^3	0.20 × 0.22 × 0.24	0.10 × 0.20 × 0.36
θ range, deg	1.61−28.28	2.04−28.32
index ranges	$-15 \le h \le 16$, $-12 \le k \le 13$, $-25 \le l \le 25$	$-12 \le h \le 12$, $-18 \le k \le 26$, $-47 \le l \le 49$
I_{tot} (unique,R_i)	16 736 (6272, 0.0826)	43 896 (8794, 0.0608)
abs corr, μ, mm^{-1}	integration, 10.035	integration, 3.739
max/min *trans*mission	0.2324/0.1469	0.6936/0.4372
refinement method	full-matrix least-squares, F^2	full-matrix least-squares, F^2
data/restraints/parameters	6267/0/343	8779/0/433
goodness of fit (F^2)[a]	1.010	1.094
R1[b], wR2 [$I > 2\sigma(I)$][c]	0.0393, 0.1201	0.0431, 0.1296
R1[b], wR2 (all data)[c]	0.0497, 0.1365	0.0714, 0.1608
largest diff peak and hole, eÅ^{-3}	+1.791 and −2.391	+1.322 and −0.758

[a] GOF = $[\sum[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$; n = number of reflections, p = total number of parameters refined. [b] R1 = $\sum||F_o| - |F_c||/^{-1}|F_o|$. [c] wR2 = $[\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

the Siemens SHELXTL package of programs;[8−10] correct positions for the metal atoms were deduced from *E*-maps. One cycle of isotropic least-squares refinement followed by an unweighted difference Fourier synthesis revealed positions for the remaining non-H atoms. Hydrogen atoms were included as fixed idealized contributors. H atom *U*s were assigned as 1.2*U*eq of adjacent C atoms. Non-H atoms were refined with anisotropic thermal coefficients. Successful convergence of the full-matrix least-squares refinements on F^2 were indicated by the maximum shift/error for the last cycle.[10] In both cases, the highest peaks in the final difference Fourier maps were in the vicinity of the metal atoms; the final maps had no other significant features. The refined positional parameters are given in the Supporting Information; selected structural data are displayed in Tables 3 and 4.

Results and Discussion

Synthesis of Compounds 1−3. The reaction of Ir(CO)(η^2-C_8H_{14})(η^5-C_9H_7) with 10 equiv of diphenylacetylene in benzene at reflux leads to a mixture of products identified as the mononuclear alkyne complex Ir(CO)(η^2-C_2Ph_2)(η^5-C_9H_7) (**1a**), the dinuclear alkyne complex $Ir_2(CO)_2(\mu$-$C_2Ph_2)(\eta^5$-$C_9H_7)_2$ (**2a**), and the mononuclear diene complex Ir(η^4-HC_4Ph_5)(η^5-C_9H_7) (**3a**). Infrared spectra obtained during the course of the reaction show

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Table 3. Selected Structural Data for 2a

Internuclear Distances (Å)

Ir1−Ir2	2.6750(4)	C30−C40	1.330(10)
Ir1−C40	2.069(7)	C30−C31	1.479(9)
Ir2−C30	2.078(7)	C40−C41	1.468(10)
Ir1−C11	2.279(7)	Ir2−C21	2.237(8)
Ir1−C12	2.241(8)	Ir2−C22	2.239(8)
Ir1−C13	2.250(7)	Ir2−C23	2.225(7)
Ir1−C14	2.359(7)	Ir2−C24	2.356(8)
Ir1−C19	2.355(8)	Ir2−C29	2.368(7)
Ir1−C1	1.840(7)	Ir2−C2	1.830(8)
C1−O1	1.141(9)	C2−O2	1.154(9)

Bond Angles (deg)

C40−Ir1−Ir2	70.4(2)	C40−C30−Ir2	107.2(5)
C30−Ir2−Ir1	71.6(2)	C30−C40−Ir1	110.3(5)
Ir1−Ir2−C30−C40	5.33(45)		

Angles between Vectors and Planes (deg)

C1, O1 vs Ir1, Ir2, C30, C40	85.9
C2, O2 vs Ir1, Ir2, C30, C40	81.6
C1, O1 vs C2, O2	172.5

Table 4. Selected Structural Data for 3b

Internuclear Distances

Ir1−C1	2.204(6)	C10−C11	1.489(8)
Ir1−C2	2.202(6)	C10−C20	1.445(8)
Ir1−C3	2.219(6)	C20−C21	1.501(8)
Ir1−C4	2.371(6)	C20−C30	1.449(7)
Ir1−C9	2.358(6)	C30−C31	1.498(7)
Ir1−C10	2.189(5)	C30−C40	1.483(7)
Ir1−C20	2.143(5)	C40−C41	1.526(7)
Ir1−C30	2.109(5)	C40−C51	1.518(7)
Ir1−C40	2.140(6)		

Bond Angles (deg)

C10−C20−C30	117.9(5)	C41−C40−C51	107.2(4)
C20−C30−C40	116.2(5)		

Angles between Vectors and Planes[a] (deg)

C10, C11 vs C10, C20, C30, C40	+ 8.9
C20, C21 vs C10, C20, C30, C40	+2.2
C30, C31 vs C10, C20, C30, C40	−1.8
C40, C41 vs C10, C20, C30, C40	+8.6
C40, C51 vs C10, C20, C30, C40	−46.6

[a] Signs of angles denote orientation of vectors above (+) or below (−) the mean C10, C20, C30, C40 plane with Ir1 above the plane.

the disappearance of the peak at 1957 cm^{-1} due to Ir(CO)(η^2-C_8H_{14})(η^5-C_9H_7) and the initial growth of a new peak due to **1a** at 1969 cm^{-1} followed by the appearance of a shoulder due to **2a** at 1953 cm^{-1}. Separation of the reaction mixture by preparative TLC provides light yellow **1a**, orange **2a**, and dark yellow **3a**, in order of decreasing R$_f$. An analogous reaction with ditolylacetylene leads to Ir(CO)(η^2-C_2Tol_2)(η^5-C_9H_7) (**1b**), Ir$_2$(CO)$_2$(μ-C_2Tol_2)(η^5-C_9H_7)$_2$ (**2b**), and Ir(η^4-HC_4Tol_4Ph)(η^5-C_9H_7) (**3b**). Similar reactions of Ir(CO)(η^2-C_8H_{14})(η^5-C_9H_7) with C_2R_2 (R = Ph, Tol) in toluene, benzene-d_6, or *m*-xylene also give products **1** and **2**, but the identity of **3** depends on the specific reaction solvent, as discussed below. These reactions are summarized in Scheme 1.

The reaction leading to compounds **1**−**3** is very sensitive to reagent concentration and reaction time, and these parameters can be manipulated to change product yields. For example, when a 1:10 mixture of Ir(CO)(η^2-C_8H_{14})(η^5-C_9H_7) and C_2R_2 are present together at the start of the reaction, significant yields of **2** are obtained. In contrast, adding Ir(CO)(η^2-C_8H_{14})(η^5-C_9H_7) slowly to a solution of C_2R_2 at reflux gives only trace amounts of **2**. Furthermore, if the reaction is allowed to continue after complete consumption of Ir(CO)(η^2-C_8H_{14})(η^5-C_9H_7), higher yields of **3** are obtained but the yield of **1** decreases. In fact, the direct reactions of isolated **1** with Ir(CO)(η^2-C_8H_{14})(η^5-C_9H_7) or **1** with C_2R_2 lead to higher yields of **2** or **3**, respectively.

Characterization of 1. The field-desorption mass spectra of **1a** and **1b** show clear molecular ions consistent with the formation of mononuclear alkyne compounds, Ir(CO)(C_2R_2)(C_9H_7). The infrared spectra of both **1a** and **1b** in hexane show one carbonyl stretching band at 1981 cm^{-1}; the tolyl substituents in **1b** do not noticeably affect the stretching frequency. The ^{1}H NMR spectra of both **1a** and **1b** (see Table 1 and Figure S-1 in Supporting Information) are consistent with symmetric molecules that possess a mirror plane bisecting the indenyl ligand and passing through the iridium atom and the midpoint of the C≡C vector.

Compounds analogous to **1** containing both η^2-alkyne and carbonyl ligands are rare. Recently, the rhodium compound Rh(CO)(η^2-C_2Ph_2)(η^5-C_5H_5) was prepared from Rh(Sb^{i}Pr$_3$)(η^2-C_2Ph_2)(η^5-C_5H_5) upon reaction with CO at room temperature.[11] In the photochemical reaction of Co(CO)$_2$(η^5-C_5H_5) with C_2Ph_2 in toluene, a transient product with an IR peak in the carbonyl region at 1990 cm^{-1} was assigned to Co(CO)(η^2-C_2Ph_2)(η^5-C_5H_5).[12] The related compound Ir(P^{i}Pr$_3$)(η^2-C_2Ph_2)(η^5-C_5H_5) was made through reaction of IrCl(PR$_3$)(η^2-C_2R_2) with NaCp.[13] Also, cationic allyl−alkyne compounds of the form [Ir(η^3-C_3H_3)(η^2-C_2R_2)(η^5-C_5Me_5)]$^+$ have been reported.[14]

Characterization of 2. The mass spectra of **2a** and **2b** are fully consistent with the formulas Ir$_2$(CO)$_2$(C_2Ph_2)(C_9H_7)$_2$ and Ir$_2$(CO)$_2$(C_2Tol_2)(C_9H_7)$_2$, respectively, and the IR spectrum of each compound in hexane shows just one CO stretching band at 1961 cm^{-1}. The ^{1}H NMR spectra of both **2a** and **2b** (see Table 1 and Figure S-2) indicate that each indenyl ligand lies in an asymmetric site but that the respective ligands are equivalent.

The ^{1}H NMR assignments for **2a** and **2b** were aided by homonuclear decoupling experiments as well as by a ^{1}H−^{1}H COSY spectrum of **2a** (see Figure S-3). This spectroscopic information is consistent with a *trans* relationship of the Ir(CO)(η^5-C_9H_7) vertexes in the expected dimetallocyclobutene molecular core, as observed for a number of related compounds, M$_2$(CO)$_2$(μ-C_2R_2)(η^5-C_5H_5)$_2$ (M = Rh, Ir; R = CF_3, C_6F_5).[15−18] In comparison, the reaction of Ir(CO)(η^2-C_8H_{14})(η^5-C_9H_7) with HC_2Ph provided the dinuclear compound Ir$_2$(CO)$_2$(μ_2-C=CHPh)(η^5-C_9H_7)$_2$ containing a bridging vinylidene ligand.[5] The reactions of terminal alkynes with mononuclear reagents often lead to vinylidene products.[13,19]

The molecular structure of **2a**, as determined by X-ray crystallography, is shown in Figure 1; selected structural data are provided in Table 3. The two Ir atoms

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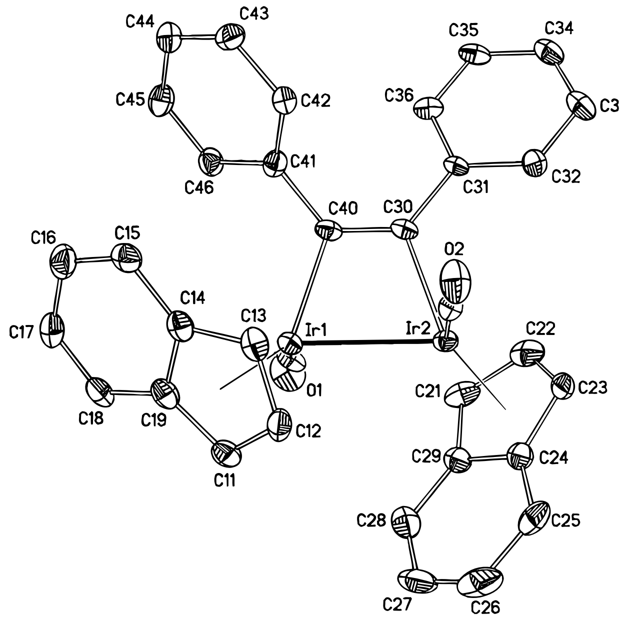

Figure 1. ORTEP diagram of the molecular structure of **2a**.

and the two alkyne carbon atoms form a nearly planar dimetallacyclobutene core; the C30−C40 vector is slightly twisted (ca. 5°) with respect to the Ir1−Ir2 vector. The CO ligands are nearly perpendicular to the Ir1, Ir2, C30, C40 mean plane and are nearly antiparallel to each other. The indenyl ligands take positions opposite the carbonyl ligands at each iridium vertex. The bond distances and angular orientations are very similar to those determined for the analogous compounds $Ir_2(CO)_2(\mu\text{-}C_6H_4)(\eta^5\text{-}C_5H_5)_2$ (Ir−Ir = 2.7166(2) Å, Ir−C = 2.045(3) Å, and C−C = 1.386(3) Å)[20] and *trans*-$Rh_2(CO)_2(\mu\text{-}CF_3C_2CF_3)(\eta^5\text{-}C_5H_5)_2$ (Rh−Rh = 2.682(1) Å and Rh−C = 2.054(10), 2.031(10) Å).[16c]

Although the two Cp ligands in *trans*-$Rh_2(CO)_2(\mu\text{-}CF_3C_2CF_3)(\eta^5\text{-}C_5H_5)_2$ and $Ir_2(CO)_2(\mu\text{-}C_6H_4)(\eta^5\text{-}C_5H_5)_2$ are related by (noncrystallographic) 2-fold axes, the two indenyl ligands in **2a** are not. They are both inclined at approximately 50° with respect to the Ir1, Ir2, C30, C40 mean plane, but they are not related by symmetry in the solid state. The long axis of the indenyl ligand attached to Ir1 is "horizontal" with respect to the Ir1−Ir2 vector while that for the ligand attached to Ir2 is "vertical". In solution, however, only one set of indenyl resonances is observed by ^1H NMR, consistent with free rotation of the $\eta^5\text{-}C_9H_7$ ligands. The structural details of indenyl ligand bonding can be described by the slip distortion parameter (Δ), the fold angle, and the hinge angle.[21] For the indenyl ligands attached to Ir1 and Ir2 in **2a**, these parameters have the values $\Delta = 0.09$ and 0.13 Å, fold angles = 4.58° and 6.15°, and hinge angles = 3.25° and 6.26°, respectively, which are fully consistent with their characterization as η^5-indenyl ligands.

The *trans* isomer of $Rh_2(CO)_2(\mu\text{-}CF_3C_2CF_3)(\eta^5\text{-}C_5H_5)_2$ exhibited CO site exchange between room temperature and −40 °C, as observed by ^{13}C NMR.[16b,d] The results were consistent with a pairwise CO bridge-closing and -opening mechanism coupled with shifts of the Cp rings, similar to the process proposed for the related compound $Rh_2(\mu\text{-}CO)(CO)_2(\eta^5\text{-}C_5H_5)_2$.[22] Scrambling of this type in **2a** and **2b** would lead to exchange of the H_1 and H_3 protons on the indenyl ligands, as observed for the related compound $Ir_2(\mu\text{-}CO)(CO)_2(\eta^5\text{-}C_9H_7)_2$.[1] This is not observed for **2a** or **2b**, presumably due to the difficulty of forming a triply bridged intermediate in the case of a bulky diarylacetylene.

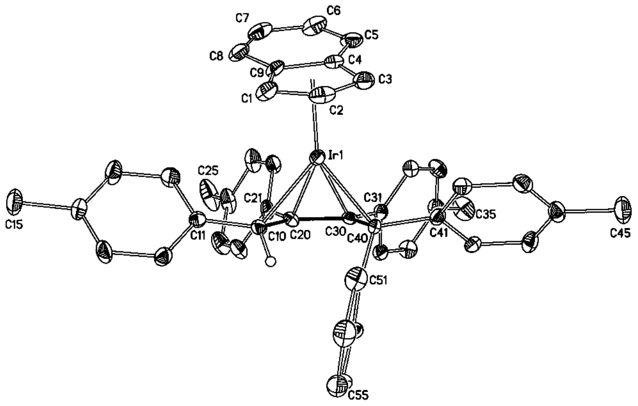

Figure 2. ORTEP diagram of the molecular structure of **3b**. The location of the H atom attached to C10 is assumed (see text).

Characterization of 3. The mass spectra of **3a** and **3b** contain molecular ions at *m/z* 742 and 798, respectively, with isotope patterns consistent with just one Ir atom. The mass difference clearly indicates the incorporation of 2 equiv of alkyne in the molecule, and the total mass suggests 1 equiv of benzene as well, resulting in a formula of $Ir(C_2R_2)_2(C_6H_6)(C_9H_7)_2$. Further support for a formula incorporating 1 equiv of solvent is provided by the results of analogous reactions in toluene and *m*-xylene, leading to **3d**, **3e**, and **3f**, with masses clearly reflecting the expected number of methyl groups. The reaction with ditolylacetylene also was conducted in benzene-d_6; the ^1H NMR spectrum of resulting **3c** is nearly identical to that of **3b** but lacks several multiplets in the arene region due to the coordinated "benzene" moiety. Nevertheless, the form of benzene incorporation into the molecule has only been defined by X-ray crystallography.

The molecular structure of **3b** is depicted in Figure 2 and selected structural details are provided in Table 4. The molecule contains an η^5-indenyl ligand and an η^4-1-phenyl-1,2,3,4-tetratolyl-1,3-butadiene ligand. Distances from the iridium center to the four carbons in the butadiene backbone, C10, C20, C30, and C40, are 2.189(5), 2.143(5), 2.109(5), and 2.140(6) Å, respectively. The bond vectors, C10−C11, C20−C21, C30−C31, and C40−C41 for the four tolyl substituents are all within 10° of being coplanar with the C10, C20, C30, C40 plane, but the C40−C51 vector for the phenyl substituent is displaced 46.6° below the plane (with the iridium atom defined as above the plane). An analogous position is presumed for the hydrogen atom attached to C10. The C_5 ring of the indenyl ligand attached to Ir1 makes an

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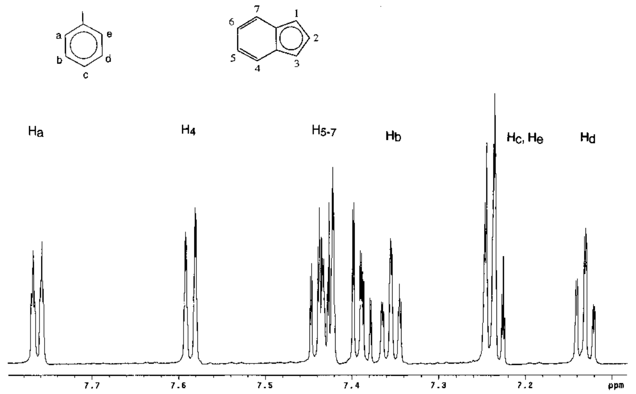


Figure 3. Partial ^{1}H NMR spectrum of **3b** recorded at 750 MHz. Assignment of the phenyl and indenyl ring signals derives in part from correlation data shown in Figure 4.

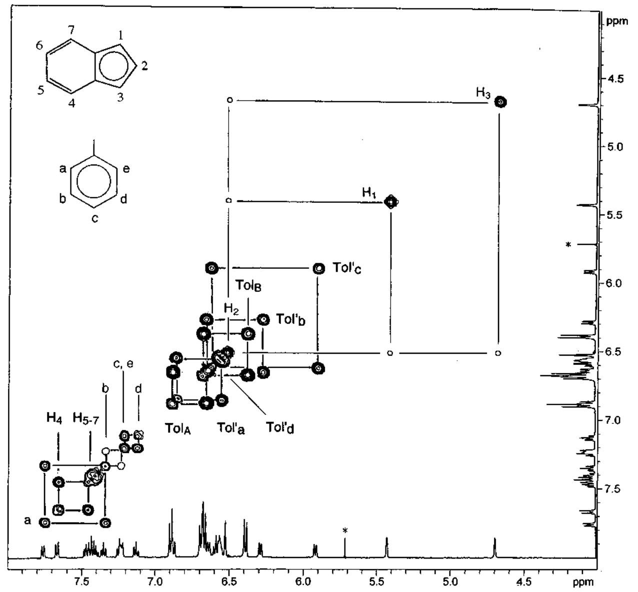


Figure 4. ^{1}H−^{1}H COSY spectrum of **3b** in acetone-d_6 at −50 °C. See text for explanation of labels. The peak marked with an asterisk is due to CH_2Cl_2.

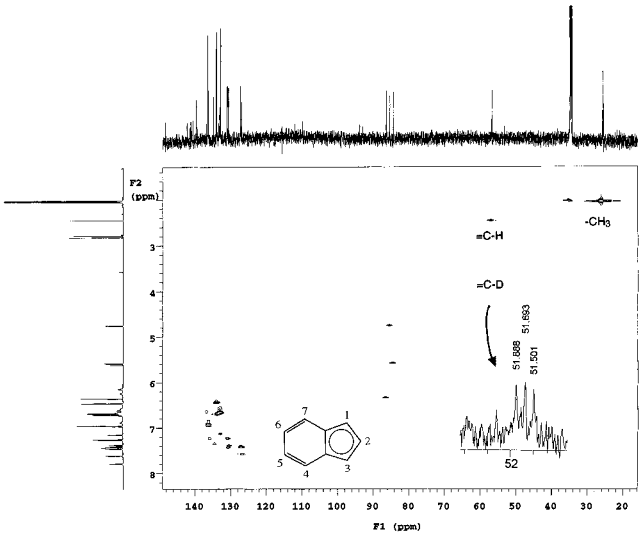


Figure 5. ^{1}H−^{13}C heteronuclear correlation spectrum of **3b** in acetone-d_6 at room temperature. The inset shows data from the corresponding spectrum of **3c**.

angle of 16.69(35)° with the C_4 backbone of the butadiene ligand. The indenyl ligand's bonding parameters are $\Delta = 0.153$ Å, fold angle = 8.93°, and hinge angle = 7.03°, which are similar to those observed for **2a** and related compounds.[1,21]

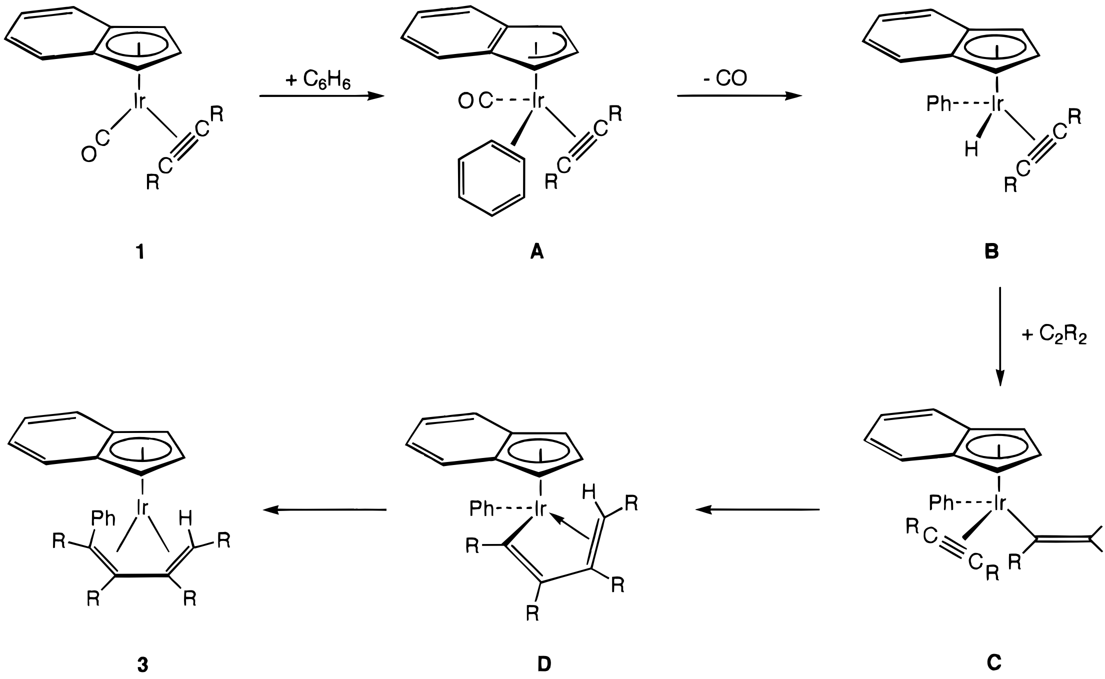
The ^{1}H NMR spectrum of compound **3b** has been investigated in detail. Figure 3 provides a portion of the spectrum recorded at 750 MHz, and Figure 4 shows the ^{1}H−^{1}H COSY spectrum at −50 °C. The resonances for the phenyl group are readily identified by their absence in the spectrum of C_6D_6-derived **3c**. The 1H doublet at lowest field is assigned to an *ortho* proton (labeled a), and a cross peak connects this peak to a 1H triplet assigned to a *meta* proton (labeled b). This *meta* proton is coupled to a 2H multiplet that contains peaks for both the *para* proton and the other *ortho* proton (labeled c and e). Finally, coupling between this multiplet and the 1H triplet at higher field identifies the latter as the other *meta* proton (labeled d). It is noteworthy that separate resonances are seen for both *ortho* as well as both *meta* positions on the phenyl ring. This is consistent with the asymmetry of the molecule and, therefore, gives no indication whether ring rotation is strongly hindered. No temperature-dependent effects are observed in this portion of the spectrum between room temperature and −50 °C, in contrast to the situation for the tolyl ring signals (*vide infra*).

From Figures 3 and 4 one can also readily identify the signals for the protons on the indenyl ring. An individual 1H multiplet at δ 7.59 (H_4) is correlated to a tightly coupled 3H pattern near δ 7.4 (H_5−H_7). Appropriate cross peaks are also observed to confirm the assignment of the indenyl H_1, H_2, and H_3 protons.

The tolyl ring resonances fall into two groups. One group consists of four 2H doublets that are pairwise correlated (labeled Tol_A and Tol_B in Figure 4) and show no temperature dependence. Each correlated pair is assigned to the (apparently equivalent) *ortho* and *meta* protons on a rapidly rotating tolyl ring. The other group is a set of eight 1H doublets distributed over the range δ 6.9−5.9 that show pairwise correlations (labeled Tol'_a-Tol'_d in Figure 4) and broaden as the temperature is raised from −50 °C to room temperature. Each of these correlated pairs is assigned to an *ortho*−*meta* proton pair on one side of a tolyl ring that is rotating slowly at −50 °C. The onset of higher rotation rates at higher temperatures will begin to cause observable exchange between *ortho*−*ortho* and *meta*−*meta* pairs on each ring. These two groups of tolyl rings presumably correspond to substituents on the two general types of positions on the butadiene ligand backbone, namely, at the terminal positions (C_1, C_4) or the inner positions (C_2, C_3). Unfortunately, it is not obvious from the crystal structure of **3b** (see Figure 2) which of the corresponding positions C10, C40 or C20, C30 might represent the more crowded sites.

The singlet resonance expected for the single proton attached to one terminal carbon of the butadiene ligand in **3b** does not appear in the lower field region shown in Figures 3 and 4. However, ^{1}H−^{13}C heteronuclear correlation spectra unambiguously establish that a 1H singlet at the higher field position of δ 2.47 is due to this proton. As shown in Figure 5, the singlet at this position in the ^{1}H spectrum is correlated with a signal at δ 51.7 in the ^{13}C spectrum. Most definitively, however, this carbon signal becomes a 1:1:1 triplet (J = 24.3 Hz) in the spectrum of **3c**, proving that it is due

Scheme 2



to a C−D moiety, with the deuterium atom derived from C_6D_6. High-field shifts for the signals of protons or carbons in ligands π-bonded to Ir(I) are not uncommon;[5] for comparison, the proton and carbon signals for the analogous position in the diene moiety of Ir(η^5-C_5H_5)(η^4-C_5H_6) occur at δ 3.13 and δ 23.9, respectively.[23]

The reaction of Ir(CO)(η^2-C_8H_{14})(η^5-C_9H_7) with C_2Ph_2 in toluene at reflux provided **3d**. The ^{1}H NMR spectrum contained more than one set of indenyl H_1−H_3 proton resonances. Also, three peaks in the tolyl methyl region were observed, suggesting the presence of isomeric compounds incorporating a toluene molecule attached at ring positions *ortho*, *meta*, and *para* to the methyl group. The ^{1}H NMR spectra of products **3f** and **3e** also were cluttered with what appeared to be a mixture of isomeric products.

Formation of 3. The formation of **3** requires the loss of a carbonyl ligand, linkage of two alkyne units and the incorporation of one arene solvent molecule. The timing of these steps is a key consideration.

The incorporation of the arene solvents in compounds **3a**−**f** requires the formal CH activation of the solvents and possibly proceeds through an intermediate of the form IrH(aryl)(CO)(η^5-C_9H_7). The analogous compound, IrH(C_6H_5)(CO)(η^5-C_5H_5), was observed spectroscopically in the reaction forming $Ir_2(CO)_2(\mu$-$C_6H_4)(\eta^5$-$C_5H_5)_2$.[20] Also, the photolysis of $Ir(CO)_2(\eta^5$-$C_5Me_5)$ in benzene produced IrH(C_6H_5)(CO)(η^5-C_5Me_5).[24] Furthermore, the reactions of Ir(H)(Me)(PMe_3)(η^5-C_9H_7) with RC_2R' provided the vinyl products, Ir(Me)(CR=CHR′)(PMe_3)(η^5-C_9H_7),[25] and kinetics studies were consistent with a mechanism involving reversible coordination of the alkyne followed by hydride migration, concurrent with η^5 to η^3 and η^3 to η^5 hapticity changes in the indenyl ligand. However, the reaction of **1** with excess acetylene leads to **3** in high yields. Therefore, the activation of the solvent and the formation of **3** probably proceeds through an alkyne-containing intermediate such as IrH(aryl)(η^2-C_2R_2)(η^5-C_9H_7). This idea leads to the set of steps proposed in Scheme 2, which includes the following: (i) Coordination of benzene in an η^2 fashion[26] to **1** with an indenyl η^5−η^3 ring slippage gives A, which is followed by oxidative addition, extrusion of CO, and subsequent η^3−η^5 recoordination, leading to the alkyne phenyl hydride product B. (ii) Insertion of the alkyne into the Ir−H bond and incorporation of another molecule of C_2R_2 would lead to a vinyl alkyne intermediate C, again, probably accompanied by indenyl slippage upon alkyne coordination followed by indenyl recoordination after insertion. (iii) Subsequent insertion of the alkyne into the Ir−vinyl bond gives the σ,π-vinyl olefin species D, and reductive elimination of the vinyl group with the Ph ligand provides the η^4-diene compound **3**.

Intermediates similar to D have been suggested for the reactions of [Ir(η^2-MeC_2Me)(η^3-C_3H_3)(η^5-C_5Me_5)$^+$] with alkynes, in which the coupling of the allyl ligand and two alkyne units led to compounds containing η^5-cycloheptadienyl ligands.[27] Also, the related insertion of 2-butyne into an intermediate iridacyclopentene complex has been proposed.[28] An alternative to the mechanism proposed in Scheme 2 could involve coordination of a second alkyne to **1** and subsequent CO loss before C−H bond oxidative addition. However, we observed none of the side products expected from such a metallocyclopentadiene pathway.

The reactions of acetylenes with $M(CO)_2(\eta^5$-L) (M = Co, Rh, Ir; L = C_5H_5, L = C_5Me_5) have often led to organometallic compounds containing oligomerized acety-

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lene units as ligands.[29] For example, the reactions of $M(CO)_2(\eta^5\text{-}C_5Me_5)$ (M = Co, Rh, Ir) with C_2R_2 (R = Me, CF_3) provided a variety of interesting products.[30] For M = Co or Rh, the cyclopentadienone compounds $M(\eta^4\text{-}C_4R_4CO)(\eta^5\text{-}C_5Me_5)$ were major products and the minor products observed were mononuclear complexes containing η^4-hexasubstituted benzene ligands or dinuclear compounds containing bridging pentadienone or hexa-1,5-diene-3,4-dione ligands. The reaction of $Ir(CO)_2(\eta^5\text{-}C_5Me_5)$ with $CF_3C_2CF_3$ led to a mononuclear compound containing a metallocyclobutenone unit as well as a dinuclear product containing a metallocyclopentadiene unit. Intriguingly, however, the reaction of $Rh(CO)_2(\eta^5\text{-}C_5H_5)$ with C_2Ph_2 in toluene provided a compound with the formula $Rh(C_2Ph_2)_2(C_7H_8)(C_5H_5)$, as determined by elemental analysis and mass spectrometry.[17] The ^1H NMR spectrum of this compound contained several singlets in the methyl region, apparently due to various tolyl isomers, so that it now appears that this product may be analogous to compound **3**, specifically **3d**, discussed here.

Conclusions

The mononuclear alkyne compounds $Ir(CO)(\eta^2\text{-}C_2R_2)(\eta^5\text{-}C_9H_7)$ (**1a**, R = Ph; **1b**, R = Tol) have been prepared through the reaction of $Ir(CO)(\eta^2\text{-}C_8H_{14})(\eta^5\text{-}C_9H_7)$ with excess C_2R_2. Subsequent reaction of **1** with $Ir(CO)(\eta^2\text{-}C_8H_{14})(\eta^5\text{-}C_9H_7)$ formed the dinuclear compounds $Ir_2(CO)_2(\mu\text{-}C_2R_2)(\eta^5\text{-}C_9H_7)_2$ (**2a**, R = Ph; **2b**, R = Tol), and the structure of **2a** was examined by X-ray diffraction. Alternatively, further reaction of **1** with C_2R_2 as well as one molecule of solvent (e.g., benzene) gave $Ir(\eta^4\text{-}HC_4R_4R')(\eta^5\text{-}C_9H_7)$ (**3a**, R = Ph, R′ = Ph; **3b**). The identities of **3a**−**f** were probed by mass spectrometry, confirming the proposed molecular formulas, $Ir(\eta^4\text{-}C_2R_2)_2(\text{arene})(\eta^5\text{-}C_9H_7)$, while the molecular connectivity of **3a**, **3b**, and **3c** was examined by $^1H-^1H$ COSY and $^1H-^{13}C$ HETCOR NMR experiments. The structure of **3b**, determined by X-ray diffraction, contains a 1-phenyl-1,2,3,4-tetratolyl-1,3-butadiene ligand formed through both alkyne coupling and CH bond activation of the benzene solvent.

Acknowledgment. This research was supported by National Science Foundation Grant No. CHE 94-14217. M.C.C. thanks the Department of Chemistry for a fellowship funded by the Lubrizol Corporation. NMR spectra were obtained using instruments in the Varian Oxford Instrument Center for Excellence in NMR Laboratory in the School of Chemical Sciences; external funding for this instrumentation was obtained from the Keck Foundation, NIH, and NSF. We thank VOICE NMR Lab Director Dr. Vera Mainz for collecting key spectral data. The purchase of the Siemens Platform/CCD diffractometer by the School of Chemical Sciences was supported by National Science Foundation Grant No. CHE 95-03145. We thank Drs. S. R. Wilson and T. Prussak-Wieckowska for collecting X-ray diffraction data for **2a** and **3b**.

Supporting Information Available: Complete tables of atom coordinates, anisotropic displacement parameters, and distances and angles for both **2a** and **3b** and ^1H NMR spectra of **2a** and **2b** (12 pages). Ordering information is given on any current masthead page.

OM970579I

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