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Diolefin Derivatives of Tetrairidium Dodecacarbonyl. Synthesis and Crystal Structures of $Ir_4(CO)_9L(2,3\text{-}\eta\text{:}5,6\text{-}\eta\text{-norbornadiene})$ ($L = PMe_2Ph, PPh_3$)

Dario Braga,*[†] Fabrizia Grepioni,[†] Giuseppe Guadalupi,[‡] Alberto Scrivanti,[‡] Renzo Ros,*[‡] and Raymond Roulet*[§]

Istituto Chimico "G. Ciamician", Università di Bologna, 40126 Bologna, Italy, Istituto di Chimica Industriale dell'Università e Centro di Chimica Metallorganica del CNR, 35131 Padova, Italy, and Institut de chimie minérale et analytique de l'Université, 3, Place du Château, CH-1005 Lausanne, Switzerland

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The reaction of $Ir_4(CO)_{11}L$ ($L = PMe_2Ph, PMePh_2, PPh_3, AsPh_3$) with excess of diolefin (norbornadiene, 1,5-cyclooctadiene, cyclooctatetraene) and Me_3NO in THF yielded $Ir_4(CO)_9L(\eta^4\text{-diolefin})$ as well as the minor products $Ir_4(CO)_7L(\eta^4\text{-diolefin})_2$. For most of these mixed-ligand cluster compounds, two stereoisomers were observed in solution by ^{31}P and ^1H NMR with L occupying either an axial or a radial site of a basal Ir atom. The solid-state structures of $Ir_4(CO)_9(PMe_2Ph)(2,3\text{-}\eta\text{:}5,6\text{-}\eta\text{-norbornadiene})$ (**1**) and $Ir_4(CO)_9(PPh_3)(2,3\text{-}\eta\text{:}5,6\text{-}\eta\text{-norbornadiene})$ (**3**) show that the diolefin chelates a basal Ir atom in both species while the PMe_2Ph ligand in **1** is located on a radial site and the PPh_3 ligand in **3** occupies an axial site. Crystal data for **1**: space group $P2_1/n$, $a = 9.947$ (3) Å, $b = 13.677$ (2) Å, $c = 20.951$ (3) Å, $\beta = 96.18$ (2)°, $Z = 4$. Crystal data for **3**: space group $P2_1/n$, $a = 9.808$ (2) Å, $b = 33.682$ (4) Å, $c = 10.769$ (2) Å, $\beta = 103.12$ (2)°, $Z = 4$.

Introduction

The dodecacarbonyltetrairidium derivatives $Ir_4(CO)_{11}L$ bearing a ligand L more easily displaced than carbon monoxide are of interest as potential catalysts for a series of hydrocarbon reactions such as hydrogenation, contrary to $Ir_4(CO)_{12}$ which is rather insoluble in all common solvents.[1] We reported recently such derivatives ($L = C_2H_4, SO_2$)[2] where the ligand L is easily displaced by other olefins or CO and which react with hydrogen. Diolefin derivatives should also be of interest since they possess two potentially accessible coordination sites. For $M_4(CO)_{12}$ clusters, attempted substitution of CO by diolefins is complicated by dehydrogenation of the organic ligand (M = Ir)[3] or by changes in nuclearity of the cluster (M = Co, Rh).[4] The first well-characterized tetrairidium clusters with diolefins were $Ir_4(CO)_{12-2x}(cod)_x$ (cod = 1,5-cyclooctadiene; $x = 1\text{–}3$) obtained from the milder reaction of $Ir_4(CO)_{12}$ and cod in the presence of Me_3NO as an oxidative decarbonylating agent.[3] We have found that the soluble anionic cluster $[Ir_4(CO)_{11}Br]^-$ is a better starting material for selective introduction of mono- and diolefins giving $Ir_4(CO)_{11}(olefin)$ and $Ir_4(CO)_{10}(diolefin)$,[2] respectively, or of more basic ligands giving $Ir_4(CO)_{11}L$ (L = tertiary phosphines and arsines).[5,6] The olefin or diolefin is displaced from these cluster compounds by CO and other ligands under relatively mild conditions. We report now the first examples of mixed-ligand cluster compounds of the type $Ir_4(CO)_9L(diolefin)$, $Ir_4(CO)_8L_2(diolefin)$, and $Ir_4(CO)_7L(diolefin)_2$ (diolefin = norbornadiene, 1,5-cyclooctadiene, cyclooctatetraene; $L = PPh_3, PMePh_2, PMe_2Ph, AsPh_3$) whose stereochemistry in solution is amenable to study by NMR. The crystal structures of two representative examples are also reported.

Results and Discussion

The thermal reaction of $Ir_4(CO)_{11}PPh_3$ with excess diolefin in refluxing toluene leads to dehydrogenation of the coordinated diolefin and decomposition to unidentified cluster compounds. The milder reaction of $Ir_4(CO)_{11}L$ ($L = PMe_2Ph, PMePh_2, PPh_3, AsPh_3$)[6] with a large excess of norbornadiene (nbd) in the presence of 3 molar equiv of $Me_3NO{\cdot}2H_2O$ in THF gave after chromatography on silica gel the new complexes $Ir_4(Co)_9L(2,3\text{-}\eta\text{:}5,6\text{-}\eta\text{-nbd})$ ($L = PMe_2Ph$, **1**; $L = PMePh_2$, **2**; $L = PPh_3$, **3**; $L = AsPh_3$, **4**) and $Ir_4(CO)_7L(2,3\text{-}\eta\text{:}5,6\text{-}\eta\text{-nbd})_2$ ($L = PPh_3$, **10**; $L = PMePh_2$, **11**; $L = AsPh_3$, **12**). Higher yields of mono- or bis(nbd) compounds were obtained when 2 or 4 molar equiv of $Me_3NO{\cdot}2H_2O$, respectively, were used. The same procedure with cod gave $Ir_4(CO)_9L(1,2\text{-}\eta\text{:}5,6\text{-}\eta\text{-cod})$ ($L = PPh_3$, **5**; $L = AsPh_3$, **6**), $Ir_4(CO)_7L(1,2\text{-}\eta\text{:}5,6\text{-}\eta\text{-cod})_2$ ($L = PPh_3$, **13**; $L = AsPh_3$, **14**), as well as low yields of $Ir_4(CO)_8(AsPh_3)_2(1,2\text{-}\eta\text{:}5,6\text{-}\eta\text{-cod})$ (**9**). The latter compound was obtained in higher yield from the reaction of $Ir_4(CO)_{10}(cod)$[3] with excess $AsPh_3$ in the presence of 2 molar equiv of $Me_3NO{\cdot}2H_2O$. The reaction of $Ir_4(CO)_{11}L$ with excess cyclooctatetraene (cot) gave only the trisubstituted $Ir_4(CO)_9L(1,2\text{-}\eta\text{:}5,6\text{-}\eta\text{-cot})$ ($L = PPh_3$, **7**; $L = AsPh_3$, **8**) derivatives in low yield (10%). No evidence for the formation of $Ir_4(CO)_7L(cot)_2$ was found when a larger excess of cot and 4 molar equiv of $Me_3NO{\cdot}2H_2O$ were used. The related $Rh_4(CO)_8(cot)_2$ is however known.[4]

All the reported compounds are soluble in common organic solvents and thermally stable for several days under nitrogen. They show three IR bands characteristic of bridging CO's (Table I). The most relevant difference in the IR spectra is the successive lowering (ca. 15 cm^{-1}) of all $\nu(CO)$ frequencies on going from trisubstituted **1**–**8** to tetrasubstituted **9** and to pentasubstituted **10**–**14**.

The ^{31}P NMR spectrum of the phosphine derivatives may be used to assign the site of coordination (axial vs. radial with respect to the basal plane of the Ir_4 core) of the

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[†] Università di Bologna.

[‡] Università e Centro di Chimica Metallorganica del CNR.

[§] Université de Lausanne.

(1) Whyman, R. In *Transition Metal Clusters*; Johnson, B. F. G., Ed.; Wiley: New York, 1980; Chapter 8, p 563.

(2) Ros, R.; Canziani, F.; Roulet, R. *J. Organomet. Chem.* **1984**, *267*, C9. Ros, R.; Scrivanti, A.; Roulet, R. *J. Organomet. Chem.* **1986**, *303*, 273. Braga, D.; Ros, R.; Roulet, R. *J. Organomet. Chem.* **1985**, *286*, C8.

(3) Stuntz, J. F.; Shapley, J. R.; Pierpont, C. G. *Inorg. Chem.* **1978**, *17*, 2596. Pierpont, C. G. *Inorg. Chem.* **1979**, *18*, 2972.

(4) Kitamura, T.; Joh, T. *J. Organomet. Chem.* **1974**, *65*, 235.

(5) Albano, V. G.; Braga, D.; Ros, R.; Scrivanti, A. *J. Chem. Soc., Chem. Commun.* **1985**, 866.

(6) Ros, R.; Scrivanti, A.; Garlaschelli, L.; Albano, V. G.; Braga, D. *J. Chem. Soc., Dalton Trans.*, in press.

0276-7333/87/2306-0056$01.50/0

Table I. IR and ^{31}P NMR Data of Diolefin Derivatives of $Ir_4(CO)_{12}$

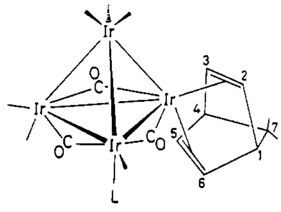
compd	$\nu(CO)$,[a] cm^{-1}	δ_P[b]	$\Delta\delta$,[c] ppm	axial/radial ratio
1, $Ir_4(CO)_9(PMe_2Ph)(nbd)$	2063 s, 2038 vs, 2015 s, 2009 s, 1990 s, 1977 m, 1862 w, 1823 s, 1795 s	−51.5, −27.2	−6.1, +18.2	0.1
2, $Ir_4(CO)_9(PMePh_2)(nbd)$	2064 vs, 2039 vs, 2011 s, 1999 m, 1992 m, 1984 w, 1870 w, 1824 s, 1798 m	−37.4, −8.9	−9.3, +19.2	1.4
3, $Ir_4(CO)_9(PPh_3)(nbd)$	2065 s, 2039 vs, 2014 s, 2001 s, 1996 sh, 1986 sh, 1865 w, 1827 s, 1797 s	−20.2	−13.4	>50
4, $Ir_4(CO)_9(AsPh_3)(nbd)$	2066 s, 2041 s, 2014 s, 2004 m, 1992 m, 1971 sh, 1870 w, 1826 s, 1797 s			>50[d]
5, $Ir_4(CO)_9(PPh_3)(cod)$	2063 s, 2037 vs, 2002 vs, 1994 sh, 1865 w, 1820 s br, 1798 s br	−17.3, +21.0	−10.4, +27.9	4.0
6, $Ir_4(CO)_9(AsPh_3)(cod)$	2065 vs, 2039 vs, 2004 vs, 1994 sh, 1865 w, 1818 s, 1797 s			
7, $Ir_4(CO)_9(PPh_3)(cot)$	2069 vs, 2045 vs, 2015 s, 2000 m, 1995 sh, 1875 vw, 1837 m, 1814 m	−17.7, +19.5	−10.8, +26.4	2.0
8, $Ir_4(CO)_9(AsPh_3)(cot)$	2070 vs, 2045 vs, 2012 vs, 1997 sh, 1874 vw, 1838 s, 1813 m			2.0[d]
9, $Ir_4(CO)_8(AsPh_3)_2(cod)$	2056 vs, 1893 vs, 1882 sh, 1870 s, 1840 vw, 1796 s, 1782 s			
10, $Ir_4(CO)_7(PPh_3)(nbd)_2$	2035 s, 2003 m, 1987 s, 1977 m, 1830 w, 1788 s, 1771 s	−26.7	−19.8	>50
11, $Ir_4(CO)_7(PMePh_2)(nbd)_2$	2036 s, 1998 m, 1989 w, 1976 s, 1835 vw, 1793 sh, 1785 s	−38.9, −8.8	−10.8, +19.3	2.4
12, $Ir_4(CO)_7(AsPh_3)(nbd)_2$	2037 s, 2002 m, 1988 s, 1975 m, 1829 w, 1787 s, 1771 m			>50[d]
13, $Ir_4(CO)_7(PPh_3)(cod)_2$	2039 vs, 2007 s, 1986 vs, 1978 vs, 1830 vw, 1790 sh, 1783 s	−22.5, +25.5	−15.6, +32.4	0.3
14, $Ir_4(CO)_7(AsPh_3)(cod)_2$	2038 vs, 1995 vs, 1987 m, 1972 s, 1832 vw, 1795 sh, 1781 s			

[a] In cyclohexane; **5** and **6** in dichloromethane. [b] $^{31}P\{^1H$ NMR$\}$ (32.20 MHz): in $CDCl_3$ for **7** and in CD_2Cl_2 for all others; at 223 K for **3**, **5**, and **10**, 210 K for **11**, 213 K for **7**, 193 K for **2** and **13**, and 183 K for **1**. [c] $\Delta\delta = \delta$(coordinated) − δ(free phosphine). [d] From ^1H NMR spectrum (Tables II and III); temperature is indicated in note *b*.

Table II. ^1H NMR Data for Norbornadiene–Tetrairidium Cluster Compounds[a]

	1		**2**					**11**		
type of proton[b,g]	axial isomer	radial isomer	axial isomer	radial isomer	**3**[h]	**4**	**10**	axial isomer	radial isomer	**12**
H(4)[c]	4.37		4.39		4.41	4.42	4.49	4.52		4.47
		4.50, 4.44		4.54, 4.46					4.48, 4.40	
H(1)[c]	4.23		4.21		4.18	4.21	4.00	4.17		4.17
H(2), H(3)[d]	4.27	4.39, 4.32	4.30	4.38, 4.33	4.25	4.29, 4.26	4.32, 4.03	4.08	4.36, 4.32	4.02, 3.97
H(5)[d]	3.59		3.68		3.74	3.75	3.71	3.80		3.91
		3.77, 3.66		3.84, 3.81					3.82, 3.72	
H(6)[d]	3.79		2.53		2.26	2.43	2.36	2.85		2.70
H(7)[e]	1.03, 0.95	1.12, 1.09	1.05, 0.97	1.12[c]	1.07, 0.97	1.06, 0.96	1.00, 0.91	1.04, 0.96	1.04	1.03, 0.98
PCH_3[f]	2.08, 1.73	2.40, 2.35	1.86	2.66				2.33	2.61	

[a] δ relative to Me_4Si; $CDCl_3$ at 220 K for **1** and **2** and at 230 K for all others. [b] See numbering in **i**. [c] Unresolved multiplet (see footnote *d*); $J(1,7_{anti}) \simeq J(1,7syn)$ = ca. 1 Hz. [d] Apparent triplet; selective decouplings gave $J(5,6) = J(2,3) = 3.9 \pm 0.2$ Hz; $J(1,6) = J(4,5) = 3.2 \pm 0.2$ Hz; $J(1,5) \simeq J(4,6)$ = ca. 0.5 Hz. [e] $J_{gem} = 9.3 \pm 0.2$ Hz. [f] J(P,H) = 9.6 Hz for **2**, 10.1 Hz for **1** (axial), 9.8 Hz for **2**, and 10.7 for **1** (radial isomer). [g] δ 7.8–7.2 for phenyl protons. [h] ^{13}C NMR data: see ref 2.



i

phosphine ligand (Table I). Compounds **3** and **10** present both at 220 and 300 K a single resonance with a coordination chemical shift $\Delta\delta = \delta$(coordinated) − δ(free phosphine) which seems characteristic of an axial position.[6] This axial substitution was unambiguously established by an X-ray analysis of **3** (see below). Two ^{31}P signals are observed for **1**, **2**, **5**, **7**, **11**, and **13** below room temperature, one with negative (−6 to −16 ppm) and the other with positive (18–32 ppm) $\Delta\delta$. The smaller $\Delta\delta$'s were attributed to the axial isomers of these six compounds, since in all reported $M_4(CO)_{12-x}L_x$ (M = Ir, Rh)[6-8] compounds the chemical shift (^{13}C or ^{31}P) of an axially coordinated ligand always appears at higher field than a radially coordinated CO or PR_3 ligand. The population ratio of the two stereoisomers (Table I) was directly determined from the

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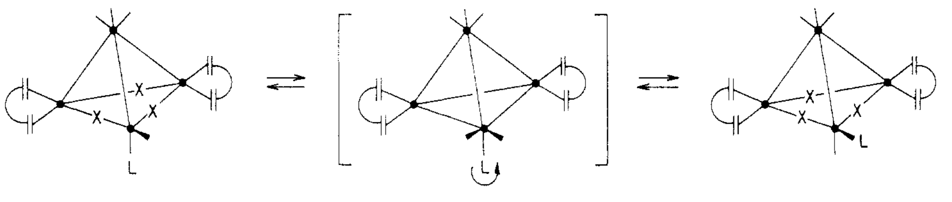
(7) Johnson, B. F. G., Ed. *Transition Metal Clusters*; Wiley: New York, 1980; Chapter 7.

(8) Heaton, B. T.; Longhetti, L.; Mingos, D. M. P.; Briant, C. E.; Minshall, P. C.; Theobald, B. R. C.; Garlaschelli, L.; Sartorelli, U. *J. Organomet. Chem.* **1981**, *213*, 333. Heaton, B. T.; Strona, L.; Della Pergola, R.; Garlaschelli, L.; Sartorelli, U.; Sadler, P. *J. Chem. Soc., Dalton Trans.* **1983**, 173.

Scheme I



X = μ-CO

integration ratio of the two ^{31}P signals. Likewise in the ^{1}H NMR spectra of the nbd complexes (Table II) the olefinic signals of the chelating diolefin that appear at high field were attributed to the double bond coordinated in an axial position. Evidence for this assignment is provided by the ^{1}H NMR spectrum of **3** which at 230 K exhibits two signals at δ 3.74 and 2.26 for the two magnetically inequivalent olefinic protons of the axially located double bond of nbd (the corresponding signals in **2** appear at δ 3.77 and 3.66). The unusually low δ value of the olefinic resonance at 2.26 ppm can be related to the close approach of a phenyl ring of PPh$_3$ to the axially located double bond. Indeed, NOE experiments showed a strong enhancement of the signal at 2.26 ppm on irradiating at the frequency of the phenyl protons of PPh$_3$. Further evidence for the steric interaction between the PPh$_3$ ligand and one double bond of the diolefin was found in the solid-state structure of **3** (see below). The $\Delta\delta$ criterion was also used for the assignment of the ^{1}H NMR spectra of the cot complexes (Table III). In the case of **7** the integration ratio of corresponding ^{1}H signals for the two stereoisomers was effectively in agreement with the ratio deduced from the ^{31}P NMR spectrum (Table I). The $\Delta\delta$ criterion was assumed to be also valid for the AsPh$_3$ derivatives.

The two stereoisomers of **1**, **2**, **5**, **7**, **11**, and **13** interconvert on the ^{31}P NMR time scale. For example two ^{31}P signals are observed for the trisubstituted complex **1** at 184 K with $\Delta\delta$ = −6.1 (axial) and +18.2 ppm (radial isomer) in a ratio of ca. 1:10. These signals coalesce at ca. 250 K, indicating the presence of two stereoisomers in solution which can interconvert via some carbonyl scrambling mechanism since there is no exchange between free and coordinated nbd or PR$_3$ at the NMR time scale. For the pentasubstituted complex **13**, the two ^{31}P signals coalesce above room temperature, indicating that the activation energy for the fluxional process increases in the Ir$_4$ cluster compounds with the degree of CO substitution. The population ratio was found to be temperature dependent, and the larger temperature range available for the slow-exchange domain in **13** allowed the evaluation of the thermodynamic parameters of the isomerization equilibrium **13** (axial) $\rightleftharpoons$ **13** (radial) (K = 3.0, 2.2, and 1.7 at 193, 223, and 273 K, respectively; $\Delta H = -2.5 \pm 0.9$ kJ mol^{-1}; $\Delta S = -3 \pm 2$ J mol^{-1} deg^{-1}). The axial → radial process is thus slightly exothermic, but thermodynamic data on Ir$_4$ cluster compounds are too scant at the moment to allow any discussion.

The fact that all three of the Ir atoms in the basal plane of **13** are terminally substituted allows a single CO scrambling mechanism for the axial ↔ radial interconversion to be postulated. Thus, mechanisms involving alternative bridging positions for basal CO's and effective formation of a new Ir$_3$ basal plane, such as that proposed for Ir$_4$(CO)$_9$(μ-CO)$_2$(μ-SO$_2$)[2], can be ruled out. Since there is no exchange between free and coordinated diolefin, the most likely mechanism of CO scrambling is a rotation in the unbridged intermediate of three terminal ligands about the pseudo C_3 axis passing through the Ir atom bearing the phosphine. This would interconvert the radial and axial positions on Ir (1) (Scheme I). Such intramolecular rotations have already been invoked to explain the scrambling of the apical CO's in cluster compounds such as Ir$_4$(CO)$_{11}$(PR$_3$).[9]

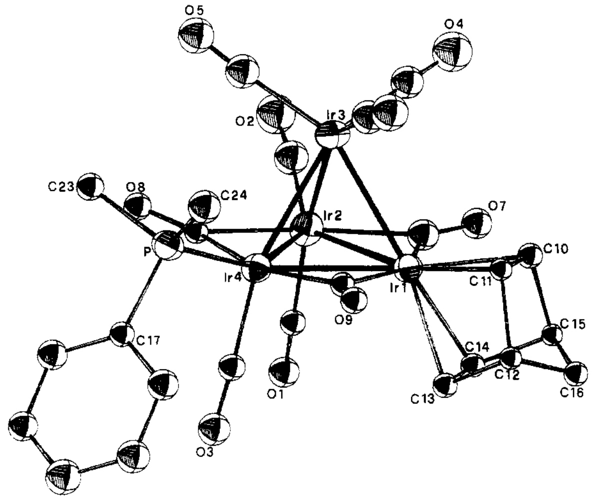


Figure 1. ORTEP diagram of **1** showing 50% probability thermal ellipsoids. The C atoms of the carbonyl groups bear the same numbering as the corresponding O atoms. H atoms have been omitted for clarity.

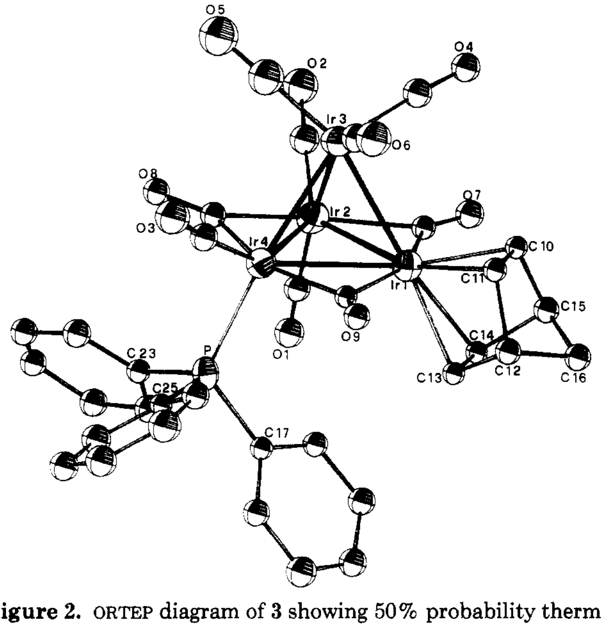


Figure 2. ORTEP diagram of **3** showing 50% probability thermal ellipsoids. The C atoms of the carbonyl groups bear the same numbering as the corresponding O atoms. H atoms have been omitted for clarity.

The coordinated diolefin of all these cluster compounds can be displaced by other ligands, i.e., the reaction of **5** with

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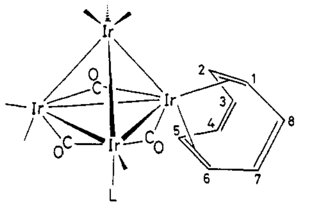
(9) Stuntz, G. F.; Shapley, J. R. *J. Am. Chem. Soc.* **1977**, *92*, 607.

Table III. ^{1}H NMR Data for Cyclooctatetraene Complexes 7 and 8[a]

	7[g]		8[h]	
type of proton[b,c]	axial isomer[d]	radial isomer[e]	axial isomer[d]	radial isomer[f]
H(3), H(8)	6.41 d	6.51, 6.48 d	6.41 d	6.47, 6.43 d
H(4)	5.87 dd		5.85 dd	
		6.01, 5.95 d		6.00, 5.94 d
H(7)	5.35 dd		5.34 dd	
H(1), H(2)	5.04, 4.96 dd	4.92 s	5.08, 4.98 dd	4.94 s
H(5)	4.03 dd		4.00 dd	
		4.34 s		4.29 m
H(6)	2.84 dd		3.05 dd	

[a] δ relative to Me_4Si; $CDCl_3$, 220 K. [b] See numbering in ii.



[c] 7.8–7.2 for phenyl protons. [d] $J(1,2) \simeq J(3,4) \simeq J(7,8) = 7.5$ Hz; $J(5,6) = 7.9$ Hz; $J(1,8) \simeq J(2,3) = 2.0 \pm 0.2$ Hz; $J(4,5) \simeq J(6,7) = 1.7 \pm 0.2$ Hz. [e] $J(3,4) = J(7,8) = 7.3$ Hz. [f] $J(3,4) \simeq J(7,8) = 7.0$ Hz; $J(4,5) \simeq J(6,7) =$ ca. 2 Hz. [g] Integration of corresponding signals for the two isomers gave an axial/radial ratio of 2.0. [h] Integration of signals at 3.05–4.00 and 4.29 ppm gave an axial/radial isomer ratio of 2.0.

Table IV. Fractional Atomic Coordinates and Thermal Parameters for 1

atom	x	y	z	U_{iso} or U_{eq}, Å^2
Ir(1)	0.16604 (9)	0.21661 (7)	0.46326 (4)	0.0294 (5)
Ir(2)	0.36295 (10)	0.11052 (7)	0.41167 (5)	0.0366 (6)
Ir(3)	0.32787 (10)	0.30318 (8)	0.38294 (5)	0.0411 (6)
Ir(4)	0.13994 (10)	0.16639 (7)	0.33654 (4)	0.0303 (6)
P	0.0558 (6)	0.2193 (5)	0.2362 (3)	0.037 (4)
C(1)	0.3145 (25)	−0.0218 (19)	0.4300 (11)	0.046 (7)
O(1)	0.2979 (18)	−0.0977 (14)	0.4408 (8)	0.065 (5)
O(2)	0.5518 (35)	0.1022 (23)	0.4130 (15)	0.081 (10)
O(2)	0.6615 (26)	0.0966 (17)	0.4072 (11)	0.108 (8)
C(3)	0.0280 (27)	0.0612 (19)	0.3338 (12)	0.051 (7)
O(3)	−0.0386 (20)	−0.0076 (14)	0.3308 (9)	0.074 (6)
C(4)	0.4636 (32)	0.3377 (22)	0.4514 (15)	0.074 (9)
O(4)	0.5310 (25)	0.3651 (17)	0.4896 (12)	0.111 (8)
C(5)	0.4311 (32)	0.3038 (23)	0.3075 (16)	0.082 (10)
O(5)	0.4868 (21)	0.3068 (15)	0.2679 (11)	0.090 (7)
C(6)	0.2268 (33)	0.4136 (24)	0.3801 (14)	0.078 (9)
O(6)	0.1482 (23)	0.4821 (16)	0.3769 (11)	0.094 (7)
C(7)	0.3508 (30)	0.1607 (20)	0.5039 (14)	0.069 (8)
O(7)	0.4089 (19)	0.1662 (13)	0.5555 (9)	0.066 (5)
C(8)	0.3000 (23)	0.0970 (16)	0.3101 (11)	0.040 (6)
O(8)	0.3657 (17)	0.0711 (11)	0.2677 (8)	0.054 (5)
C(9)	0.0208 (25)	0.2538 (16)	0.3843 (11)	0.041 (6)
O(9)	−0.0828 (16)	0.2997 (12)	0.3761 (7)	0.051 (4)
C(10)	0.1692 (25)	0.2905 (17)	0.5568 (11)	0.0456 (6)
C(11)	0.0584 (21)	0.3262 (16)	0.5134 (10)	0.036 (6)
C(12)	−0.0628 (24)	0.2594 (16)	0.5309 (10)	0.038 (6)
C(13)	−0.0208 (23)	0.1571 (17)	0.4996 (11)	0.042 (6)
C(14)	0.0962 (23)	0.1277 (17)	0.5407 (10)	0.041 (6)
C(15)	0.1138 (21)	0.2035 (15)	0.5964 (10)	0.032 (5)
C(16)	−0.0255 (24)	0.2389 (17)	0.6001 (11)	0.044 (6)
C(17)	−0.0877 (22)	0.1405 (16)	0.2055 (10)	0.042 (6)
C(18)	−0.2105 (25)	0.1573 (19)	0.2313 (12)	0.063 (8)
C(19)	−0.3108 (31)	0.0853 (20)	0.2129 (14)	0.077 (9)
C(20)	−0.2966 (32)	0.0172 (22)	0.1694 (14)	0.086 (10)
C(21)	−0.1835 (26)	0.0024 (19)	0.1440 (13)	0.059 (8)
C(22)	−0.0681 (28)	0.0634 (18)	0.1629 (12)	0.065 (8)
C(23)	0.1666 (24)	0.2117 (19)	0.1748 (11)	0.053 (7)
C(24)	−0.0129 (29)	0.3449 (19)	0.2323 (14)	0.076 (9)

Table V. Fractional Atomic Coordinates and Thermal Parameters for 3

atom	x	y	z	U_{iso} or U_{eq}, Å^2
Ir(1)	0.30079 (11)	0.16536 (3)	0.76072 (11)	0.0353 (6)
Ir(2)	0.01602 (11)	0.17146 (3)	0.73643 (11)	0.0382 (7)
Ir(3)	0.12299 (12)	0.12242 (3)	0.58235 (11)	0.0428 (7)
Ir(4)	0.14537 (11)	0.10303 (3)	0.83150 (11)	0.0351 (6)
P	0.1601 (7)	0.0988 (2)	1.0514 (7)	0.037 (4)
C(1)	−0.0201 (30)	0.2010 (8)	0.8723 (30)	0.056 (8)
O(1)	−0.0377 (21)	0.2189 (6)	0.9564 (20)	0.069 (6)
C(2)	−0.1299 (34)	0.1846 (9)	0.6115 (32)	0.069 (9)
O(2)	−0.2300 (26)	0.1950 (7)	0.5255 (25)	0.096 (8)
C(3)	0.1394 (32)	0.0490 (9)	0.8113 (31)	0.062 (9)
O(3)	0.1385 (25)	0.0159 (7)	0.7890 (24)	0.095 (8)
C(4)	0.1357 (33)	0.1611 (9)	0.4604 (31)	0.066 (9)
O(4)	0.1390 (21)	0.1877 (6)	0.3932 (20)	0.067 (6)
C(5)	−0.0249 (44)	0.0909 (12)	0.5107 (41)	0.101 (13)
O(5)	−0.1390 (32)	0.0764 (8)	0.4667 (23)	0.122 (10)
C(6)	0.2553 (34)	0.0879 (9)	0.5591 (31)	0.065 (9)
O(6)	0.3538 (26)	0.0676 (7)	0.5457 (24)	0.098 (8)
C(7)	0.1655 (27)	0.2105 (8)	0.6949 (26)	0.046 (7)
O(7)	0.1598 (21)	0.2434 (6)	0.6509 (20)	0.063 (6)
C(8)	−0.0508 (30)	0.1146 (8)	0.7811 (27)	0.053 (8)
O(8)	−0.1708 (19)	0.1025 (5)	0.7732 (17)	0.055 (5)
C(9)	0.3591 (27)	0.1086 (7)	0.8385 (24)	0.039 (6)
O(9)	0.4609 (19)	0.0893 (5)	0.8621 (18)	0.055 (5)
C(10)	0.4325 (26)	0.1981 (7)	0.6706 (25)	0.040 (7)
C(11)	0.5024 (25)	0.1653 (8)	0.7149 (25)	0.045 (7)
C(12)	0.5989 (29)	0.1751 (8)	0.8475 (26)	0.053 (8)
C(13)	0.4796 (25)	0.1830 (7)	0.9189 (24)	0.039 (7)
C(14)	0.4147 (26)	0.2156 (7)	0.8761 (23)	0.038 (6)
C(15)	0.4787 (29)	0.2316 (8)	0.7649 (27)	0.053 (8)
C(16)	0.6385 (29)	0.2196 (8)	0.8241 (29)	0.057 (8)
C(17)	0.2777 (25)	0.1326 (6)	1.1522 (22)	0.041 (7)
C(18)	0.2804 (26)	0.1727 (6)	1.1216 (25)	0.048 (7)
C(19)	0.3673 (27)	0.2021 (8)	1.1957 (25)	0.059 (8)
C(20)	0.4579 (29)	0.1879 (8)	1.3026 (25)	0.061 (8)
C(21)	0.4630 (30)	0.1491 (7)	1.3406 (29)	0.072 (10)
C(22)	0.3734 (26)	0.1211 (8)	1.2623 (22)	0.057 (8)
C(23)	−0.0094 (25)	0.1049 (6)	1.0895 (23)	0.043 (7)
C(24)	−0.0392 (27)	0.1384 (7)	1.1538 (27)	0.060 (8)
C(25)	−0.1760 (25)	0.1408 (8)	1.1771 (23)	0.062 (9)
C(26)	−0.2755 (27)	0.1119 (6)	1.1405 (25)	0.055 (8)
C(27)	−0.2372 (26)	0.0781 (8)	1.0862 (27)	0.057 (8)
C(28)	−0.1035 (24)	0.0737 (8)	1.0563 (28)	0.063 (9)
C(29)	0.2276 (23)	0.0521 (7)	1.1220 (22)	0.039 (6)
C(30)	0.1683 (30)	0.0362 (8)	1.2167 (25)	0.069 (9)
C(31)	0.2292 (28)	0.0001 (8)	1.2745 (29)	0.067 (9)
C(32)	0.3463 (30)	−0.0142 (9)	1.2404 (30)	0.076 (10)
C(33)	0.4047 (34)	0.0010 (9)	1.1461 (30)	0.085 (11)
C(34)	0.3404 (26)	0.0356 (7)	1.0826 (27)	0.060 (8)

excess PPh_3 at room temperature gave $Ir_4(CO)_9(PPh_3)_3$.[10] The coordinated diolefin of **5** (or **13**) is also quantitatively displaced by CO giving $Ir_4(CO)_{11}PPh_3$, but not however by SO_2. The reaction of these complexes with H_2 is currently under study.

Crystal Structures of 1 and 3. The molecular structures of **1** and **3** have been established by single-crystal X-ray diffraction and are shown in Figures 1 and 2, respectively. The atomic coordinates for **1** and **3** are reported in Tables IV and V, and relevant bond distances and angles in Tables VI and VII, respectively. Because of the close relationship the two molecular geometries will be discussed together. The four Ir atoms define an almost regular tetrahedron. The overall ligand distribution is that common to the majority of substituted Ir_4 cluster species with three edge-bridging CO's defining a basal plane of the metal polyhedron and with the non-carbonyl ligands bonded to adjacent Ir atoms of this plane.

The metal–metal interactions do not appreciably differ in their mean values (2.722 (1) and 2.735 (1) Å for **1** and

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[10] Albano, V. G.; Bellon, P.; Scatturin, V. *J. Chem. Soc., Chem. Commun.* **1967**, 730.

[11] Malatesta, L.; Caglio, G. *J. Chem. Soc., Chem. Commun.* **1967**, *420*, 564.

Table VI. Selected Bond Distances (Å) for 1 and 3 (with Estimated Standard Deviations in Parentheses)

	1	3		1	3
Ir(1)–Ir(2)	2.749 (1)	2.753 (1)	Ir(1)–C(14)	2.20 (2)	2.24 (2)
Ir(1)–Ir(3)	2.720 (1)	2.702 (1)	C(1)–O(1)	1.08 (3)	1.13 (3)
Ir(1)–Ir(4)	2.723 (1)	2.800 (1)	C(2)–O(2)	1.11 (4)	1.24 (3)
Ir(2)–Ir(3)	2.714 (1)	2.715 (1)	C(3)–O(3)	1.15 (3)	1.14 (4)
Ir(2)–Ir(4)	2.687 (1)	2.717 (1)	C(4)–O(4)	1.05 (3)	1.16 (3)
Ir(3)–Ir(4)	2.745 (1)	2.721 (1)	C(5)–O(5)	1.05 (4)	1.21 (4)
Ir(4)–P	2.91 (5)	2.344 (7)	C(6)–O(6)	1.22 (3)	1.22 (4)
Ir(2)–C(1)	1.92 (2)	1.87 (3)	C(7)–O(7)	1.17 (3)	1.20 (3)
Ir(2)–C(2)	1.88 (3)	1.78 (2)	C(8)–O(8)	1.21 (2)	1.23 (3)
Ir(4)–C(3)	1.82 (2)	1.83 (3)	C(9)–O(9)	1.20 (2)	1.17 (3)
Ir(3)–C(4)	1.92 (2)	1.87 (3)	C(10)–C(11)	1.43 (3)	1.33 (3)
Ir(3)–C(5)	1.97 (3)	1.82 (3)	C(10)–C(15)	1.58 (3)	1.52 (3)
Ir(3)–C(6)	1.81 (3)	1.80 (3)	C(11)–C(12)	1.59 (3)	1.56 (3)
Ir(1)–C(7)	2.08 (2)	2.04 (2)	C(12)–C(13)	1.62 (3)	1.56 (4)
Ir(2)–C(7)	2.06 (2)	2.09 (2)	C(12)–C(16)	1.48 (3)	1.58 (3)
Ir(2)–C(8)	2.16 (2)	2.11 (2)	C(13)–C(14)	1.43 (3)	1.30 (3)
Ir(4)–C(8)	1.98 (2)	1.92 (2)	C(14)–C(15)	1.55 (3)	1.57 (4)
Ir(1)–C(9)	2.13 (2)	2.11 (2)	C(15)–C(16)	1.48 (3)	1.60 (3)
Ir(4)–C(9)	2.02 (2)	2.09 (2)	P–C(17)	1.85 (2)	1.80 (2)
Ir(1)–C(10)	2.20 (2)	2.10 (2)	P–C(23)	1.78 (2)	1.81 (2)
Ir(1)–C(11)	2.17 (2)	2.14 (2)	P–C(24)	1.85 (2)	
Ir(1)–C(13)	2.24 (2)	2.23 (2)	P–C(29)		1.81 (2)

Table VII. Selected Bond Angles (deg) for 1 and 3 (with Estimated Standard Deviations in Parentheses)

	1	3		1	3
Ir(2)–C(1)–O(1)	174 (2)	177 (3)	C(13)–C(12)–C(16)	100 (6)	98 (2)
Ir(2)–C(2)–O(2)	172 (3)	177 (3)	C(12)–C(13)–C(14)	103 (3)	109 (2)
Ir(4)–C(3)–O(3)	176 (5)	174 (3)	C(13)–C(14)–C(15)	106 (6)	108 (2)
Ir(3)–C(4)–O(4)	172 (2)	173 (3)	C(10)–C(15)–C(14)	97 (2)	98 (2)
Ir(3)–C(5)–O(5)	177 (2)	166 (3)	C(10)–C(15)–C(16)	99 (2)	101 (2)
Ir(3)–C(6)–O(6)	173 (2)	173 (3)	C(14)–C(15)–C(16)	103 (7)	97 (2)
Ir(1)–C(7)–O(7)	132 (2)	142 (2)	C(12)–C(16)–C(15)	98 (4)	92 (2)
Ir(2)–C(7)–O(7)	144 (2)	133 (2)	Ir(4)–P–C(17)	109 (1)	117 (1)
Ir(2)–C(8)–O(8)	128 (3)	128 (2)	Ir(4)–P–C(23)	116 (3)	111 (1)
Ir(4)–C(8)–O(8)	149 (3)	146 (2)	Ir(4)–P–C(24)	115 (1)	
Ir(1)–C(9)–O(9)	137 (2)	136 (2)	Ir(4)–P–C(29)		114 (1)
Ir(4)–C(9)–O(9)	140 (2)	139 (2)	C(17)–P–C(23)	103 (1)	106 (1)
C(11)–C(10)–C(15)	107 (2)	108 (2)	C(17)–P–C(24)	104 (6)	
C(10)–C(11)–C(12)	102 (3)	108 (3)	C(17)–P–C(29)		100 (1)
C(11)–C(12)–C(13)	99 (5)	96 (5)	C(23)–P–C(24)	106 (3)	
C(11)–C(12)–C(16)	102 (2)	99 (2)	C(23)–P–C(29)		105 (1)

3, respectively). These values are strictly comparable with those reported for other di-, tri-, tri-, and tetrasubstituted Ir_4 species such as $Ir_4(CO)_9(PPh_3)_3$[10,11] (2.73 Å), $Ir_4(CO)_{10}(Me_2PCH_2CH_2PMe_2)$[6] (2.736 (1) Å), or $Ir_4(CO)_8(Ph_2PCH{=}CHPPh_2)_2$[5] (2.706 Å), confirming that all substituted species show a slight "swelling-up" of the metal core in comparison to the parent $Ir_4(CO)_{12}$ molecule (2.68 Å).[12] Other important mean values for **1** and **3** are Ir–C(terminal) = 1.89 (2) and 1.83 (3) Å, Ir–C(bridge) = 2.07 (2) and 2.06 (2) Å, C–O(terminal) = 1.11 (3) and 1.18 (4) Å, and C–O(bridge) = 1.19 (2) and 1.20 (3) Å, respectively. These values are in the range of other reported values for Ir cluster species. A further point of interest is the absence of any significant shortening effect on the Ir–Ir bonds due to the presence of the bridging CO's. More than that, while in **1** bridged and unbridged Ir–Ir bonds are almost identical in their mean values (2.720 (1) and 2.726 (1) Å, respectively), in **3** the bridged bonds appear to be longer than the unbridged ones (mean 2.757 (1) and 2.713 (1) Å, respectively). Similar behavior has been observed in other Ir_4 derivatives; for example, in $[Ir_4(CO)_{11}Br]^-$[13] the bridged bonds are also longer than the unbridged ones (mean 2.725 and 2.696 (1) Å, respectively) while in the aforementioned $Ir_4(CO)_{10}(Me_2PCH_2CH_2PMe_2)$[6] bridged and unbridged bonds are identical in their mean values (2.735 (1) and 2.736 (1) Å, respectively). However the available data on substituted Ir_4 species do not allow a rationalization of the phenomenon.[14]

In both molecules the diolefin occupies the radial and axial sites on Ir(1), therefore adopting a chelating mode of bonding. The most important single feature differentiating the solid-state structures of **1** and **3** is that in **1** the PMe_2Ph ligand occupies a radial position while in **3** the PPh_3 ligand is axial. The axial position occupied by PPh_3 in **3** is comparable with that in the series of $Ir_4(CO)_{11}L$ complexes (L = PPh_3, $PMePh_2$, PMe_2Ph, PMe_3) where the axially and radially substituted isomers are in thermodynamic equilibrium in solution, with the axial isomer always predominating.[6] Hence, it is the radial substitution of the PMe_2Ph ligand in **1** that may be considered unusual.

A comparison of the average lengths of the coordinated nbd double bonds in **1** and **3** (1.43 (3) and 1.32 (3) Å, respectively) suggests that the metal–olefin interaction is weaker in **3** (although this is not reflected in the corresponding Ir–C distances). A comparison of the dihedral angles between the tetrahedron base Ir(1)–Ir(2)–Ir(4) and the plane defined by Ir(1), C(13), and C(14) shows that the diolefin in **3** is pushed up by the axially bound PPh_3 ligand (121 (2)° in **1** and 128 (2)° in **3**). In the ligand sphere model of Johnson,[7] the axial PPh_3 ligand of **3** occupies a vertex adjacent to the axial C,C-double bond of nbd on the icosahedral surface. This is not so in **1**. Thus, steric

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[12] Churchill, M. R.; Hutchinson, J. P. *Inorg. Chem.* **1978**, *17*, 3528.

[13] Chini, P.; Ciani, G.; Garlaschelli, L.; Manassero, M.; Martinengo, S.; Sironi, A.; Canziani, F. *J. Organomet. Chem.* **1970**, *152*, C35. Ciani, G.; Manassero, M.; Sirohi, A. *J. Organomet. Chem.* **1980**, *199*, 271.

[14] Chini, P.; Heaton, B. T. *Top.-Curr. Chem.* **1977**, *71*, 1.

crowding between the PPh_3 and nbd ligands may account for the weaker metal–olefin interaction in 3 (further evidence of this crowding was found in its ^1H NMR spectrum, see above and Table II). The radial substitution of the PMe_2Ph ligand in 1 is difficult to rationalize since its cone angle is smaller than that of PPh_3.

It may be that, unlike $Ir_4(CO)_{11}L$ complexes where the axial site is the preferred position for the phosphine, in $Ir_4(CO)_9L$(diolefin) complexes the radial site may be preferred electronically with large phosphines being forced into an axial site. To sum up, the axial vs. radial substitution in $Ir_4(CO)_9L$(nbd) complexes may result from a delicate balance between the steric interactions of the phosphine with the C,C-double bond located in axial position and with the bridging CO's which are almost coplanar with the radial site on Ir(4).

Experimental Section

IR spectra were recorded on Perkin-Elmer 597 and/or 983 spectrophotometers and were calibrated with cyclohexane (2138.5 cm^{-1}) and polystyrene (1601.4 cm^{-1}). ^1H NMR spectra were obtained on a Bruker CXP-200 (200-MHz) or a Bruker WH-360 (360-MHz) spectrometer using Me_4Si, CH_2Cl_2 (δ 5.32), or $CHCl_3$ (7.27 ppm) as internal reference. ^{13}C and ^{31}P NMR spectra were recorded on a Bruker WH-360 (90.55 MHz) and a Varian FT-80A (32.20 MHz), respectively. ^{13}C and ^{31}P chemical shifts are in parts per million relative to Me_4Si and 85% H_3PO_4 (external), respectively, with shifts to high frequency taken as positive. Microanalyses were performed in the Institute of Analytical Chemistry (University of Padova).

The compounds $Ir_4(CO)_{11}L$ (L = PPh_3, $PMePh_2$, PMe_2Ph, $AsPh_3$) were prepared by displacement of bromide from $NEt_4[Ir_4(CO)_{11}Br]$[13] by a molar equivalent of ligand L.[6] Samples of cluster compounds enriched in ^{13}CO were prepared starting from $NEt_4[Ir_4(CO)_{11}Br]$ (25–35% ^{13}CO). Norbornadiene (nbd), cycloocta-1,5-diene (cod), and cyclooctatetraene (cot) (Merck) were passed over alumina prior to use. Other reagents, silica gel (230–400 mesh), and preparative TLC plates (20 × 20 cm, 1.0 or 2.0 mm thickness) (Merck) were used as received. All reactions were carried out under nitrogen or argon by using dry degassed solvents. In particular tetrahydrofuran (THF) was purified by distillation from sodium benzophenone under argon. All substituted Ir_4 cluster compounds were stored in Schlenk tubes under inert atmosphere in a refrigerator as they were found to be slightly air sensitive in the solid state.

Preparations. (a) $Ir_4(CO)_9(PMe_2Ph)$(nbd) (1), $Ir_4(CO)_9(PMePh_2)$(nbd) (2), and $Ir_4(CO)_7(PMePh_2)(nbd)_2$ (11). A solution of $Ir_4(CO)_{11}(PMe_2Ph)$ (500 mg, 0.41 mmol) and nbd (3.0 mL) in THF (50 mL) was treated at −5 °C with $Me_3NO{\cdot}2H_2O$ (125 mg, 1.12 mmol) and vigorously stirred. After 3 h the red-brown mixture was filtered through a silica gel pad (20 cm) and eluted with CH_2Cl_2 (60 mL). The red filtrate was evaporated to dryness in vacuo. The oily residue was dissolved in CH_2Cl_2 (3 mL) and chromatographed on a preparative-scale TLC plate. Elution with CH_2Cl_2/hexane (1/3) gave two fractions affording unreacted $Ir_4(CO)_{11}(PMe_2Ph)$ (35 mg) and orange-yellow $Ir_4(CO)_9(PMe_2Ph)$(nbd) (1) (311 mg, 60%) after recrystallization from CH_2Cl_2/MeOH. Anal. Calcd for $C_{24}H_{19}O_9PIr_4$: C, 23.04; H, 1.53. Found: C, 23.21; H, 1.48. No evidence for the formation of $Ir_4(CO)_7(PMe_2Ph)(nbd)_2$ was found when higher amounts of $Me_3NO{\cdot}2H_2O$ and/or nbd were used. 2 and 11: as for 1 starting with $Ir_4(CO)_{11}(PMePh_2)$ (400 mg, 0.31 mmol), nbd (3.0 mL), and $Me_3NO{\cdot}2H_2O$ (109 mg, 0.98 mmol). Elution with CH_2Cl_2/hexane (1/4) gave two fractions affording orange-yellow $Ir_4(CO)_9(PMePh_2)$(nbd) (2) (261 mg, 63%) and orange $Ir_4(CO)_7(PMePh_2)(nbd)_2$ (11) (53 mg, 12.5%) after recrystallization from CH_2Cl_2/MeOH. Anal. Calcd for $C_{29}H_{21}O_9PIr_4$ (2): C, 26.52; H, 1.61. Found: C, 27.10; H, 1.69. Anal. Calcd for $C_{34}H_{29}O_7PIr_4$ (11): C, 30.26; H, 2.17. Found: C, 30.45; H, 2.33.

(b) $Ir_4(CO)_9(PPh_3)$(nbd) (3) and $Ir_4(CO)_7(PPh_3)(nbd)_2$ (10). A solution of $Ir_4(CO)_{11}PPh_3$ (522 mg, 0.39 mmol) and nbd (2.0 mL) in THF (50 mL) was treated at 0 °C with $Me_3NO{\cdot}2H_2O$ (125 mg, 1.12 mmol) and vigorously stirred for 3 h. The red-brown mixture was filtered to remove unreacted $Me_3NO{\cdot}2H_2O$ and evaporated to dryness in vacuo. The residue was dissolved in toluene (10 mL) and chromatographed on a silica gel column (180 × 2.5 cm). Elution with toluene gave a first yellow fraction. Evaporation and recrystallization from CH_2Cl_2/MeOH gave 3 as yellow-orange microcrystals (169 mg, 32%). Anal. Calcd for $C_{34}H_{23}O_9PIr_4$: C, 29.69; H, 1.69. Found: C, 29.60; H, 1.80. Subsequent elution with toluene gave 10 which was recrystallized from CH_2Cl_2/MeOH as orange microcrystals (53 mg, 9.6%). Anal. Calcd for $C_{39}H_{31}O_7PIr_4$: C, 33.19; H, 2.21. Found: C, 32.82; H, 2.16. The yield of 10 may be increased to ca. 45% at the expense of 3 when 4 molar equiv of $Me_3NO{\cdot}2H_2O$ are used.

(c) $Ir_4(CO)_9(AsPh_3)$(nbd) (4) and $Ir_4(CO)_7(AsPh_3)(nbd)_2$ (12): as for (b) starting with $Ir_4(CO)_{11}(AsPh_3)$ (300 mg, 0.217 mmol), nbd (1.5 mL), and $Me_3NO{\cdot}2H_2O$ (67 mg, 0.60 mmol; stirring for 2 h). Chromatography on a silica gel column (180 × 2 cm) gave 4 (188 mg, 61%) and 12 (73 mg, 23%) which were recrystallized from CH_2Cl_2/MeOH as yellow microcrystals. Anal. Calcd for $C_{32}H_{23}AsO_9Ir_4$ (4): C, 28.77; H, 1.63. Found: C, 29.44; H, 1.83. Anal. Calcd for $C_{39}H_{31}AsO_7Ir_4$ (12): C, 32.19; H, 2.15. Found: C, 32.08; 2.24.

(d) $Ir_4(CO)_9(PPh_3)$(cod) (5) and $Ir_4(CO)_7(PPh_3)(cod)_2$ (13): as for (b) starting with $Ir_4(CO)_{11}(PPh_3)$ (402 mg, 0.30 mmol), cod (3.0 mL), and $Me_3NO{\cdot}2H_2O$ (87 mg, 0.78 mmol). Elution of the TLC plate with CH_2Cl_2/pentane (1/2) gave 5 (43 mg, 10%) and 13 (211 mg, 49%) after recrystallization from CH_2Cl_2/pentane as yellow and orange microcrystals, respectively. Anal. Calcd for $C_{35}H_{27}O_9PIr_4$ (5): C, 30.21; H, 1.96. Found: C, 30.29; H, 2.07. Anal. Calcd for $C_{41}H_{39}O_7PIr_4$ (13): C, 34.11; H, 2.72. Found: C, 33.60; H, 2.98.

(e) $Ir_4(CO)_9(AsPh_3)$(cod) (6), $Ir_4(CO)_7(AsPh_3)(cod)_2$ (14), and $Ir_4(CO)_8(AsPh_3)_2$(cod) (9): as for (a) starting with $Ir_4(CO)_{11}(AsPh_3)$ (251 mg, 0.181 mmol), cod (1.5 mL), and $Me_3NO{\cdot}2H_2O$ (60 mg, 0.54 mmol). Elution of the TLC plate with CH_2Cl_2/hexane (1/3) gave $Ir_4(CO)_8(cod)_2$[1] (11 mg), 6 (yellow-orange microcrystals, 43 mg, 16.5%), 9 (yellow-orange microcrystals, 22 mg, 7%), and 14 (orange microcrystals, 117 mg, 43%). Anal. Calcd for $C_{35}H_{27}AsO_9Ir_4$ (6): C, 29.29; H, 1.90. Found: C, 30.01; H, 2.14. Anal. Calcd for $C_{52}H_{42}As_2O_8Ir_4$ (9): C, 36.45; H, 2.47. Found: C, 36.70; H, 2.51. Anal. Calcd for $C_{41}H_{39}AsO_7Ir_4$ (14): C, 33.11; H, 2.64. Found: C, 33.35; H, 2.40. The yield of 9 may be increased to 70% when a solution of $Ir_4(CO)_{10}$(cod)[2,3] is stirred with an excess of $AsPh_3$ and 2 molar equiv of $Me_3NO{\cdot}2H_2O$ in THF at −10 °C for 3 h. Purification as above gave 9 and 6 as minor products (10%).

(f) $Ir_4(CO)_9(PPh_3)$(cot) (7) and $Ir_4(CO)_9(AsPh_3)$(cot) (8). A solution of $Ir_4(CO)_{11}PPh_3$ (400 mg, 0.30 mmol) and cot (1.0 mL) in THF (50 mL) was treated at −15 °C with $Me_3NO{\cdot}2H_2O$ (79 mg, 0.71 mmol). After being stirred for 4 h, the red-brown mixture was filtered through a silica gel pad (10 cm) and washed with THF (30 mL). Evaporation in vacuo gave an oily yellow residue which was dissolved in CH_2Cl_2 (3 mL) and chromatographed on a TLC plate. Elution with CH_2Cl_2/hexane (1/1) gave two main yellow fractions affording unreacted $Ir_4(CO)_{11}PPh_3$ (18 mg) and 7 (53 mg, 13%) after recrystallization from CH_2Cl_2//MeOH. Anal. Calcd for $C_{35}H_{23}O_9PIr_4$ (7): C, 30.30; H, 1.67. Found: C, 30.36; 1.60. No evidence for the formation of pentasubstituted products such as $Ir_4(CO)_7(PPh_3)(cot)_2$ was found when higher amounts of cot and $Me_3NO{\cdot}2H_2O$ were used. 8: as for 7 starting with $Ir_4(CO)_{11}AsPh_3$ (500 mg, 0.361 mmol), cot (1.5 mL), and $Me_3NO{\cdot}2HO$ (120 mg, 1.08 mmol). Purification by TLC gave unreacted $Ir_4(CO)_{11}AsPh_3$ (46 mg) and 8 (70 mg, 13.5%) after recrystallization from CH_2Cl_2/MeOH. Anal. Calcd for $C_{35}H_{23}AsO_9Ir_4$: C, 29.37; H, 1.62. Found: C, 30.14; H, 1.74.

Displacement Reactions of Coordinated Diolefins. (a) With PPh_3. In a typical experiment 5 (100 mg, 0.072 mmol) was dissolved in THF (15 mL). PPh_3 (150 mg, 0.57 mmol) was added and the solution stirred at room temperature for 48 h. Evaporation to dryness and recrystallization from CH_2Cl_2/hexane gave the known complex $Ir_4(CO)_9(PPh_3)_3$[9-11] (117 mg, 90%).

(b) With CO and SO_2. In a typical experiment 13 (105 mg, 0.073 mmol) was dissolved in THF (25 mL). The solution was saturated with CO and stirred at room temperature for 3 days. The solvent was removed at reduced pressure to give a yellow solid. Extraction with CH_2Cl_2 (3 mL) left insoluble $Ir_4(CO)_{12}$ (11 mg), and $Ir_4(CO)_{11}PPh_3$ (79 mg, 81%) was recovered from the filtrate. Exposure of a stirred solution of 5 or 13 in THF to a large excess

Table VIII. Crystal Data and Details of Measurements for 1 and 3

	1	3
formula	$C_{24}H_{19}O_9PIr_4$	$C_{34}H_{23}O_9PIr_4$
cryst system	monoclinic	monoclinic
space group[a]	$P2_1/n$	$P2_1/n$
a, Å	9.947 (3)	9.808 (2)
b, Å	13.677 (2)	33.682 (4)
c, Å	20.951 (3)	10.769 (2)
β, deg	96.18 (2)	103.12 (2)
V, Å^3	2833.7	3464.7
Z	4	4
d_{calcd}, g cm^{-3}	3.01	2.64
$F(000)$	2231	2487
cryst size, m	0.01 × 0.02 × 0.40	0.1 × 0.1 × 0.3
μ(Mo Kα), cm^{-1}	181.43	148.46
scan range, deg	$2.5 < \theta < 25$	$2.5 < \theta < 25$
scan method	$\omega/2\theta$	$\omega/2\theta$
scan interval, deg	$0.7 + 0.35 \tan \theta$	$1.0 + 0.35 \tan \theta$
prescan speed, deg min^{-1}	10	10
prescan acceptance $\sigma(I)/I$	0.3	0.5
required final $\sigma(I)/I$	0.01	0.01
bkgd measurements equal to	peak time	peak time
collected octants	$\pm h, +k, +l$	$\pm h, +k, +l$
no. of data collected	5256	6544
no. of data used ($F_0 > 5\sigma(F_o)$)	2604	2372
R (R_w)	0.041 (0.036)	0.042 (0.041)

[a] The space group assignment was based on systematic absences and confirmed by successful refinement of the structure models.

of SO_2 during several hours did not result in any displacement of the diolefin, and the starting complexes were recovered quantitatively.

X-ray Structural Determinations. Crystal data for 1 and 3 are summarized in Table VIII together with some experimental details. Single crystals suitable for X-ray analysis were grown by slow cooling (+30 to −40 °C) of a solution of 1 in CH_2Cl_2/2-propanol and of 3 in CH_2Cl_2/MeOH. Both data sets were collected at room temperature on an Enraf-Nonius CAD-4 diffractometer with Mo Kα radiation (λ = 0.71069 Å), reduced to F_o and corrected for crystal decay. For both crystals no azimuthal scan reflections could be measured. An absorption correction was applied by the Walker and Stuart method[15] once the complete structural models were obtained and all non-hydrogen atoms refined isotropically (correction ranges in ϕ and μ: 0.77–1.20 and 0.81–1.2 for 1 and 3, respectively). Both structures were solved by direct methods which afforded the positions of all Ir atoms. All C, O, and P atoms were located from subsequent difference Fourier syntheses. The refinements of the structural models were made by least-squares calculations, the minimized function being $\sum w(F_o - KF_c)^2$. The weighting scheme employed was $w = K/[\sigma^2(F) + |g|F^2]$ where both K and g were refined (1.54 and 0.0 for 1 and 1.34 and 0.0007 for 3). For all computations the SHELX package of crystallographic programs[16] was used with the analytical scattering factors, corrected for the real and imaginary parts of anomalous dispersion, taken from ref 17. Thermal vibrations were treated anisotropically only for Ir and P atoms, while all other atoms were treated isotropically. Geometrical constraints were applied to the phenyl rings imposing equality to ortho, meta, and para C–C bonds. Hydrogen atoms were added in calculated positions (C–H = 1.08 Å) and not refined although their contribution to the structure factors was taken into account. Residual electron density peaks lower than 2 e/Å^3 were found in the proximity of the metal atoms.

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Registry No. **1** (radial isomer), 105253-48-3; **1** (axial isomer), 105367-68-8; **2** (axial isomer), 105253-49-4; **2** (radial isomer), 105367-69-9; **3**, 91726-79-3; **4**, 105253-50-7; **5**, 105367-65-5; **6**, 105253-51-8; **7** (axial isomer), 105253-52-9; **7** (radial isomer), 105369-29-7; **8** (axial isomer), 105253-53-0; **8** (radial isomer), 105367-71-3; **9**, 105253-54-1; **10**, 105367-66-6; **11** (axial isomer), 105253-55-2; **11** (radial isomer), 105367-70-2; **12**, 105253-56-3; **13**, 105367-67-7; **14**, 105280-99-7; nbd, 121-46-0; cod, 111-78-4; cot, 629-20-9; $Ir_4(CO)_{11}(PMe_2Ph)$, 59532-78-4; $Ir_4(CO)_{11}(PMePh_2)$, 62034-94-0; $Ir_4(CO)_{11}(PPh_3)$, 53565-22-3; $Ir_4(CO)_{11}(AsPh_3)$, 78128-47-9; $Ir_4(CO)_9(PPh_3)_3$, 19631-23-3; Ir, 7439-88-5.

Supplementary Material Available: Complete listings of positional and thermal parameters, bond distances, and bond angles for $Ir_4(CO)_9(PMe_2Ph)$(norbornadiene) and $Ir_4(CO)_9(PPh_3)$(norbornadiene) (22 pages); listings of observed and calculated structure factors for $Ir_4(CO)_9(PMe_2Ph)$(norbornadiene) and $Ir_4(CO)_9(PPh_3)$(norbornadiene) (29 pages). Ordering information is given on any current masthead page.

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(15) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1983**, *39A*, 158.

(16) Sheldrick, G. M. SHELX76, Program for crystal Structure Determination; University of Cambridge: Cambridge, England, 1976.

(17) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1975; Vol. IV, pp 99–149.