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Synthesis and X-ray Structure of the Tetranuclear Butterfly Iridium Cluster $Ir_4(CO)_8L(\mu_3\text{-}\eta^3\text{-}Ph_2PC(H)CPh)(\mu\text{-}PPh_2)$ (L = PCy_3) and $^{13}C\{^1H\}$, ^1H, and $^{31}P\{^1H\}$ NMR Studies of the Compounds with L = CO, PCy_3, and $P(OMe)_3$

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Deprotonation of $HIr_4(CO)_{10}(\mu\text{-}PPh_2)$ (1) with DBU, which gives $[Ir_4(CO)_{10}(\mu\text{-}PPh_2)]^-$ (2), followed by reaction with $Ph_2PC{\equiv}CPh$ and immediate protonation affords $HIr_4(CO)_9(\mu_4\text{-}\eta^3\text{-}Ph_2PC_2Ph)(\mu\text{-}PPh_2)$ (3) and the novel species $Ir_4(CO)_9(\mu_3\text{-}\eta^3\text{-}Ph_2PC(H)CPh)(\mu\text{-}PPh_2)$ (4), in addition to the CO substitution products $HIr_4(CO)_{10-n}(Ph_2PC{\equiv}CPh)_n(\mu\text{-}PPh_2)$ (n = 1 (5), 2 (6)). Compound 4 undergoes facile CO substitution reactions with phosphines and phosphites (L) to yield $Ir_4(CO)_8L(\mu_3\text{-}\eta^3\text{-}Ph_2PC(H)CPh)(\mu\text{-}PPh_2)$ (L = PCy_3 (**7a**), $P(OMe)_3$ (**7b**), PPh_3 (**7c**), $PPhMe_2$ (**7d**)). The derivative **7a** has been structurally characterized by an X-ray diffraction analysis. Crystals of **7a** are triclinic, space group $P\bar{1}$, with a = 12.626(1) Å, b = 20.405(5) Å, c = 12.493(2) Å, α = 94.16(2)°, β = 90.44(1)°, γ = 77.02(1)°, V = 3128.0 $Å^3$, Z = 2, and 2θ range 5–50°, for 6698 measured reflections out of 6186 unique observed reflections ($I_0 > 2.0\sigma(I_0)$); R = 0.04, R_w = 0.04. The structure of **7a** consists of a butterfly arrangement of metal atoms, whose wingtips are bridged by a PPh_2 ligand, with the $Ph_2PC(H)CPh$ ligand interacting with a triangular metal face. The solution structures of compounds 4 and **7a**,**b** have been investigated by a combination of variable-temperature ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR studies, which have established that (i) 4 is isostructural with **7a**,**b**, with a CO in place of L, (ii) **7a**,**b** consist of two interconverting isomers in the ratio 3.9:1 at −20 °C and 1:5.9 at −60 °C, respectively, and (iii) the structure determined by X-ray analysis is that of the major isomer of **7a**, which is isostructural with the minor isomer of **7b**.

Introduction

We recently reported[1,2] the reaction of $HIr_4(CO)_{10}(\mu\text{-}PPh_2)$ (1) with the phosphinoacetylene $Ph_2PC{\equiv}CPh$, giving the CO replacement compound $HIr_4(CO)_9(Ph_2PC{\equiv}CPh)(\mu\text{-}PPh_2)$, which is readily converted to the cluster $Ir_4(CO)_7(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}HCCPh)(\mu\text{-}PPh_2)_2$, obtained in high yield as the main product of the reaction. A similar pattern of reactivity has also been observed by Carty and Sappa[3] for $HRu_3(CO)_9(\mu\text{-}PPh_2)$ and is proposed to involve cleavage of the P–C bond with formation of a coordinated acetylide species,[3–5] followed by hydride transfer onto the α-carbon to generate the alkyne-containing cluster. In rare cases no P–C bond cleavage is noted,[6] presumably due to a strong interaction of the alkynyl moiety with the cluster metal frame, as in $HIr_4(CO)_9(\mu_4\text{-}\eta^3\text{-}Ph_2PCCPh)(\mu\text{-}PPh_2)$, also formed in minute yields from the thermolysis of $HIr_4(CO)_9(Ph_2PC{\equiv}CPh)(\mu\text{-}PPh_2)$.[1,2]

The reactions of $Ph_2PC{\equiv}CR$ with the anionic hydrido compound $[Ph_4P][HFe_3(CO)_{11}]$, however, have been shown to give different types of products, whose nature depends on the R group. When R = ^tBu,[7] and C(O)OMe,[8] formation of the vinylidene-containing cluster $[Ph_4P][Fe_3(CO)_8(\mu\text{-}CCHR)(\mu\text{-}PPh_2)]$ is observed, *via* the intermediate $[Ph_4P][Fe_3(CO)_9(\mu_3\text{-}\eta^3\text{-}Ph_2PCCHR)]$, in the case of R = H. Herein is reported the reaction of the anionic compound $[Ir_4(CO)_{10}(\mu\text{-}PPh_2)]^-$ (2) with $Ph_2PC{\equiv}CPh$, followed by protonation, which gives $HIr_4(CO)_9(\mu_4\text{-}\eta^3\text{-}Ph_2PCCPh)(\mu\text{-}PPh_2)$ (3) and the novel compound $Ir_4(CO)_9(\mu_3\text{-}\eta^3\text{-}Ph_2PC(H)CPh)(\mu\text{-}PPh_2)$ (4) as a result of protonation on the metal frame and on the α-carbon of the phos-

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phinoacetylene ligand, respectively, both without cleavage of the P–C bond.

Experimental Section

Materials and Methods. All manipulations and reactions were performed under an atmosphere of dry argon, unless otherwise specified, by using Schlenk type glassware. Tetrahydrofuran (THF) was dried over sodium and benzophenone, dichloromethane, was dried over $LiAlH_4$, toluene and hexane were dried over sodium, and acetonitrile was dried over phosphorus pentoxide. All solvents were distilled under argon before use. The progress of the reactions was monitored by analytical thin-layer chromatography (0.5 mm thick, glass-backed silica gel plates prepared from silica gel GF 254 (Type 60, Fluka)). Preparative TLC was carried out in air by using ca. 1 mm thick glass-backed silica gel plates (20 × 20 cm) prepared as above and a mixture of CH_2Cl_2 and hexane (3:7) as eluent, unless otherwise specified. Infrared (IR) spectra were recorded on a JASCO IR 700 instrument scanning between 2200 and 1600 cm^{-1}. ^1H, ^{13}C, and ^{31}P NMR data were obtained on Brucker AC 200, AC 300, or WH 400 instruments using deuterated solvents as lock and reference (^1H and $^{13}C\{^1H\}$, $Si(Me)_4$ (δ 0); ^{31}P, 85% H_3PO_4 (δ 0); high frequency positive) in $C_6D_5CD_3$, CD_2Cl_2, or $CDCl_3$. Fast atom bombardment mass spectra (FAB MS) were obtained on a Kratos MS50, operating at 8 keV, equipped with a standard Kratos FAB source and an Ion Tech Gun by Dr. S. Naylor as previously described.[9] Microanalyses were carried out either at the University Chemical Laboratories, University of Cambridge, Cambridge, U.K., or at the Instituto de Química, UNICAMP, Campinas, Brazil.

The compounds $Ir_4(CO)_{12}$,[10] $Ir_4(^{13}CO)_{12}$ (*ca.* 25% enriched),[11] $Ir_4(CO)_{11}PPh_2H$,[12] $HIr_4(CO)_{10}(\mu\text{-}PPh_2)$,[13] and $Ph_2PC{\equiv}CPh$[14] were prepared according to published procedures; all other reagents were purchased from commercial sources. Triethylamine *N*-oxide dihydrate was sublimed *in vacuo*, and 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) was distilled *in vacuo*; the other reagents were used as supplied.

Preparation of $Ir_4(CO)_9(\mu_3\text{-}\eta^3\text{-}Ph_2PC(H)CPh)(\mu\text{-}PPh_2)$ (4). To an orange solution of $HIr_4(CO)_{10}(\mu\text{-}PPh_2)$ (1; 100.0 mg, 0.08 mmol) in CH_2Cl_2 (15 mL) were added the following compounds sequentially at room temperature with stirring: DBU (12 μL, 0.08 mmol), resulting in an instantaneous darkening of the solution, $Ph_2PC{\equiv}CPh$ (23.2 mg, 0.08 mmol), and CF_3COOH (6.2 μL, 0.08 mmol). At this stage an orange solution was obtained. The solvent was concentrated *in vacuo*, and purification by preparative TLC afforded four compounds, which were obtained as analytically pure samples after crystallization from CH_2Cl_2–hexane. $HIr_4(CO)_9(\mu_4\text{-}\eta^3\text{-}Ph_2PCCPh)(\mu\text{-}PPh_2)$ (**3**; 42 mg, 0.03 mmol, 30%, R_f 0.46): Anal. Calcd for $C_{41}H_{26}O_9P_2Ir_4$: C, 33.8; H, 1.8. Found: C, 33.2; H, 2.2. $Ir_4(CO)_9(\mu_3\text{-}\eta^3\text{-}Ph_2PC(H)CPh_2)(\mu\text{-}PPh_2)$ (**4**; 48 mg, 0.032 mmol, 40%, R_f 0.44): Anal. Calcd for $C_{41}H_{26}O_9P_2Ir_4{\cdot}0.35C_6H_{14}$: C, 33.9; H, 2.0. Found: C, 33.9; H, 2.1. IR (ν_{CO}, hexane): 2074 (m), 2044 (s), 2030 (s), 2014 (vs), 1972 (w), 1957 (vw) cm^{-1}. $HIr_4(CO)_9(Ph_2PC{\equiv}CPh_2)(\mu\text{-}PPh_2)$ (**5**; 24 mg, 0.016 mmol, 20%, R_f 0.25): Anal. Calcd for $C_{41}H_{26}O_9P_2Ir_4$: C, 33.0; H, 1.8. Found: C, 33.4: H, 2.1. $HIr_4(CO)_8(Ph_2PC{\equiv}CPh)_2(\mu\text{-}PPh_2)$ (**6**; 14 mg, 0.008 mmol, 10%, R_f 0.07): Anal. Calcd for $C_{60}H_{41}O_8P_3Ir_4$: C, 43.5; H, 3.4. Found: C, 43.7; H, 3.2.

Preparation of $Ir_4(CO)_8(L)(\mu_3\text{-}\eta^3\text{-}Ph_2PC(H)CPh)(\mu\text{-}PPh_2)$ (L = PCy_3 (7a), $P(OMe)_3$ (7b), PPh_3 (7c), $PPhMe_2$ (7d)). Method 1. A yellow solution of **4** (30.0 mg, 0.02 mmol) and L (0.02 mmol; L = PCy_3 (6 mg), $P(OMe)_3$ (2.5 μL), PPh_3 (5 mg), or $PPhMe_2$ (3 μL)) in CH_2Cl_2 (20 mL) was heated at reflux for 24 h, after which time the solvent was concentrated *in vacuo* and the mixture purified by preparative TLC as described above, affording $Ir_4(CO)_8(L)(\mu_3\text{-}\eta^3\text{-}Ph_2PC(H){=}CPh)(\mu\text{-}PPh_2)$, that after crystallization from CH_2Cl_2–hexane gave analytically pure samples (yield *ca.* 90%). L = PCy_3 (**7a**, R_f 0.3): Anal. Calcd for $C_{58}H_{59}O_8P_3Ir_4{\cdot}0.5C_6H_{14}$: C, 41.0; H, 3.7. Found: C, 41.3; H, 3.8. IR (ν_{CO}, hexane): 2044 (m), 2026 (s), 2002 (vs), 1969 (m), 1946 (w sh) cm^{-1}. L = $P(OMe)_3$ (**7b**, R_f 0.4): Anal. Calcd for $C_{48}H_{35}O_{11}P_3Ir_4{\cdot}0.6C_6H_{14}$: C, 34.1; H, 2.6. Found: C, 34.4; H, 2.7. IR (ν_{CO}, hexane): 2048 (w), 2034 (vs), 2008 (s), 1956 (m br) cm^{-1}. L = PPh_3 (**7c**, R_f 0.32): Anal. Calcd for $C_{58}H_{41}O_8P_3Ir_4{\cdot}0.5C_6H_{14}$: C, 41.3; H, 2.7. Found: C, 41.7; H, 2.9. IR (ν_{CO}, hexane): 2048 (w), 2036 (vs), 2010 (s), 1957 (m br) cm^{-1}. L = $PPhMe_2$ (**7d**, R_f 0.36): Anal. Calcd for $C_{48}H_{37}O_8P_3Ir_4{\cdot}0.4C_6H_{14}$: C, 36.9; H, 2.6. Found: C, 37.2; H, 2.7. IR (ν_{CO}, hexane): 2046 (w), 2030 (vs), 2002 (s), 1958 (w), 1943 (w) cm^{-1}.

Table I. Crystal Data and Details of Measurements for 7a

formula	$C_{58}H_{59}O_8P_3Ir_4$
cryst size (mm)	0.10 × 0.20 × 0.10
cryst syst	triclinic
space group	$P\bar{1}$
a (Å)	12.626(1)
b (Å)	20.405(5)
c (Å)	12.493(2)
α (deg)	94.16(2)
β (deg)	90.44(1)
γ (deg)	77.02(1)
V (Å^3)	3128.0
Z	2
F(000)	1648
D_{calcd} (g cm^{-3})	1.85
λ(Mo Kα) (Å)	0.710 69
μ(Mo Kα) (cm^{-1})	82.9
2θ range (deg)	5–50
ω-scan width (deg)	0.7
requested counting $\sigma(I)/I$	0.02
prescan rate (deg min^{-1})	8
max scan time (s)	100
no. of measd rflns	6698
no. of unique obsd rflns ($I_o > 2.0\sigma(I_o)$)	6186
no. of refined params	364
R, R_w,[a] S, K[a]	0.04, 0.04, 1.5, 1.9

[a] $R_w = \sum[(F_o - F_c)w^{1/2}]/\sum F_o w^{1/2})$, where $w = K/[\sigma(F) + |g|F^2]$.

Method 2. A solution of **4** (30 mg, 0.02 mmol) in CH_2Cl_2 (15 mL) with L (0.02 mmol) was cooled to −70 °C and treated with a CH_2Cl_2 solution (2 mL) of Me_3NO (1.4 mg, 0.02 mmol). The reaction mixture was warmed to room temperature, the solvent was concentrated *in vacuo*, and the mixture was separated by preparative TLC as described above to afford **7a–d** in *ca.* 90% yields.

Preparation of $Ir_4(CO)_7(P(OMe)_3)_2(\mu_3\text{-}\eta^3\text{-}Ph_2PC(H)CPh)(\mu\text{-}PPh_2)$ (8b). A solution of **4** (30 mg, 0.02 mmol) in CH_2Cl_2 (15 mL) with L (0.04 mmol) was cooled to −70 °C and treated with a CH_2Cl_2 solution (2 mL) of Me_3NO (2.8 mg, 0.04 mmol). The same procedure as above was used to purify **8b** (90%, R_f 0.1). Anal. Calcd for $C_{45}H_{44}O_{13}P_4Ir_4{\cdot}0.5C_6H_{14}$: C, 32.9; H, 2.8. Found: C, 33.3; H, 2.9. IR (ν_{CO}, hexane): 2036 (s), 1999 (vs), 1936 (m br) cm^{-1}. ^1H NMR (CD_2Cl_2, −53 °C): δ 8.11–8.25 (m, H = $Ph_2PC(H)CPh$), 7.89–7.07 (m, Ph), 8.00 (d, J_{P-H} *ca.* 10.8 Hz $P(OMe)_3$ 3.62 (d), 3.52 (d, 2 $P(OMe)_3$), 3.4 (d), 3.31 (d), 2.9 (d), and 2.8 (d) (all J *ca.* 11.6 Hz).

X-ray Structure Determination. The diffraction data were collected at room temperature on an Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator (Mo Kα radiation, λ = 0.710 69 Å). The intensities were collected in the $\omega/2\theta$-scan mode at room temperature. Crystal data and details of the measurements are summarized in Table I. The structure was solved by using direct methods, followed by difference Fourier syntheses and subsequent least-squares refinement. Scattering

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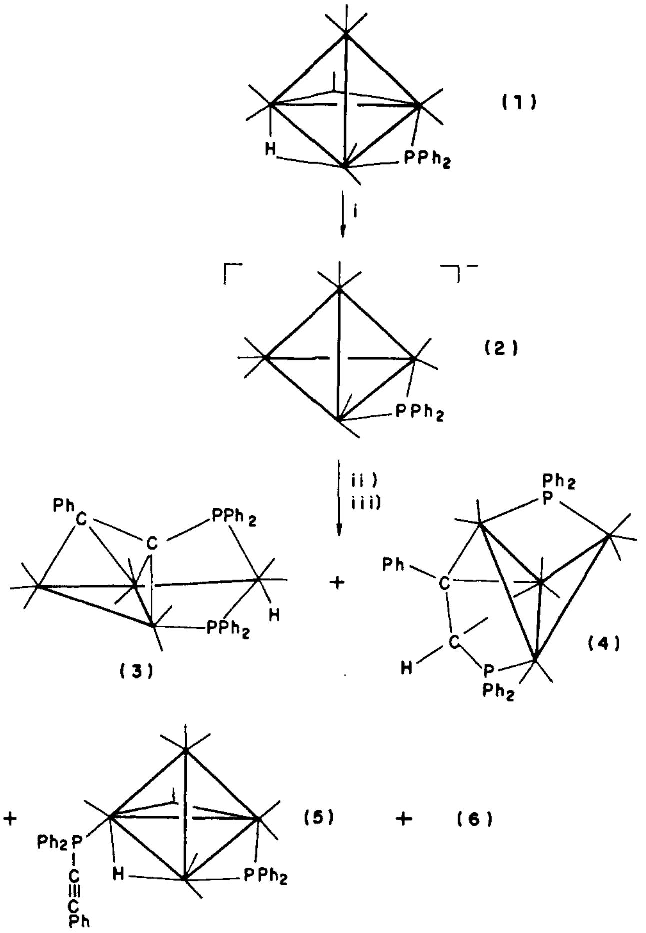
Scheme I[a]



[a] Legend: (i) DBU/CH_2Cl_2; (ii) $Ph_2PC{\equiv}CPh$; (iii) CF_3COOH.

factors for neutral atoms were taken from ref 15. For all calculations the SHELX76 program was used.[16] An absorption correction was applied by the Walker and Stuart method[17] once a complete structural model was available, and all atoms were refined isotropically (correction range 0.64–1.00).

All atoms, except the H and C atoms of the phenyl and cyclohexyl groups, were refined anisotropically. Single isotropic thermal factors were refined for the H(phenyl) and H(cyclohexyl) atoms (0.11(1), and 0.08(1) Å^2, respectively). The H atom of the C=C system in the $Ph_2PC(H){=}CPh$ ligand was located from the final Fourier maps. It was restrained in the observed position and refined in a "rigid group" with its C atom (C(39)). An isotropic thermal factor was also refined (0.07(4) Å). A rigid-body model (C–C–C = 120°, C–C = 1.395 Å) was adopted to refine the phenyl groups. The final difference Fourier map showed residuals of *ca.* 1 e/Å^3, close to the metal atoms of the cluster (0.12(3) Å^2).

Results and Discussion

Deprotonation of the orange compound $HIr_4(CO)_{10}(\mu\text{-}PPh_2)$ (**1**) with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in CH_2Cl_2 yields the bright red anion $[Ir_4(CO)_{10}(\mu\text{-}PPh_2)]^-$ (**2**),[2,13,18] which upon immediate addition of $Ph_2PC{\equiv}CPh$ in CH_2Cl_2 and protonation with trifluoroacetic acid affords four products, **3**–**6**, separated by TLC and fully characterized by elemental analysis and spectroscopic data. The bright yellow compound $HIr_4(CO)_9(\mu_4\text{-}\eta^3\text{-}Ph_2PC_2Ph)(\mu\text{-}PPh_2)$ (**3**) is produced in yields as high as 30% if the protonation step immediately follows addition of the phosphinoacetylene; otherwise, decomposition products are obtained instead. This compound was previously isolated in low yields from the thermolysis reaction of $HIr_4(CO)_9(Ph_2PC{\equiv}CPh)(\mu\text{-}PPh_2)$ (**5**).[1,2] The major product of this reaction, obtained in around 40% yield, is the golden yellow species $Ir_4(CO)_9(\mu_3\text{-}\eta^3\text{-}Ph_2PC(H)CPh)(\mu\text{-}PPh_2)$ (**4**), which is stable both in solution and in the solid state under argon. As expected on the basis of the analogous reaction with PPh_3,[18] the CO-substituted tetrahedral species $HIr_4(CO)_{10-n}L_n(\mu\text{-}PPh_2)$ (L = $Ph_2PC{\equiv}CPh$; n = 1 (**5**; 15%), 2 (**6**; 10%)) are also isolated from the reaction mixture. The characterization of compounds **3**, **5**, and **6** has been reported elsewhere.[1,6] Because compounds **3** and **4** run very closely on the TLC plates with a variety of solvent systems, they were initially isolated together as compound **3**.[1] Efficient separation of these species has since been achieved, and both have been characterized by spectroscopic and analytical methods.[2]

Table II. ^1H and $^{31}P\{^1H\}$ NMR Data[a] for $Ir_4(CO)_9(\mu_3\text{-}\eta^3\text{-}Ph_2PC(H)(Ph)(\mu\text{-}PPh_2)$ (**4**), $Ir_4(CO)_8(PCy_3)(\mu_3\text{-}\eta^3\text{-}Ph_2PC(H)(Ph)(\mu\text{-}PPh_2)$ (**7a**), and $Ir_4(CO)_8(P(OMe)_3)(\mu_3\text{-}\eta^3\text{-}Ph_2PC(H)(Ph)(\mu\text{-}PPh_2)$ (**7b**)

compd[c]	^1H	$^{31}P\{^1H\}$[b]	
4	8.25 (d, d) J_{P-H} = 12 ($Ph_2PC(H)(Ph)$ J_{P-H} = 3.4 (PPh_2) 7.1–7.8 (m, Ph)	−58.5 (d) −63.5 (d) J_{P-P} = 20.3	
7a	major isomer 8.3 (d, d) J_{P-H} = 12 J_{P-H} = 4 7.1–7.8 (m, Ph)		
7b	7.1–7.9 (m, Ph) major isomer 8.3 (d) J_{P-H} = 12 3.6 (d) J_{P-H} = 12 minor isomer 3.3 (d) J_{P-H} = 12	major isomer 73.8 ($P(OMe)_3$) J_{P-P} = 28 −67.5 (PPh_2) J_{P-P} = 28 J_{P-P} = 20 J_{P2-Cg} = 118 J_{P2-Ci} = 33 −65.7 ($Ph_2PC(H)CPh$) J_{P-P} = 20	minor isomer 63.6 ($P(OMe)_3$) J_{P2-P3} = 23 J_{P3-P1} = 124 −50.7 (PPh_2) J_{P-P} = 20 J_{P-P} = 23 −60.4 ($Ph_2PC(H)CPh$) J_{P-P} = 20 J_{P-P} = 124

[a] Chemical shifts (δ) in ppm and coupling constants in Hz. [b] Chemical shifts positive to high frequency of 85% H_3PO_4 (external). [c] Measured in CD_2Cl_2.

Only absorptions characteristic of terminal CO ligands are observed in the ν_{CO} region of the IR spectrum of compound **4**, suggesting interaction of the acetylene moiety of the phosphinoacetylene ligand with the metal frame. The FAB MS shows an abundant molecular ion at 1494 $[M]^+$ and sequential peaks at 1494 − 28x (x = 1–9), resulting from the loss of nine carbonyl ligands. The ^1H NMR spectrum of **4** did not show any resonance in the hydride region. The low-frequency chemical shifts observed in the $^{31}P\{^1H\}$ NMR spectrum of **4** (see Table II) are typical of coordinated phosphines and of phosphido ligands bound to iridium atoms that do not interact. Indeed, just as in the case of structurally related phosphido dimers and clusters of other transition metals,[19] low-frequency shifts in $\delta(^{31}P)$ are found to be associated with increases in Ir–P–Ir angles of iridium clusters,[2,13,14,19] and a comparison with the ^{31}P resonance observed for the starting material

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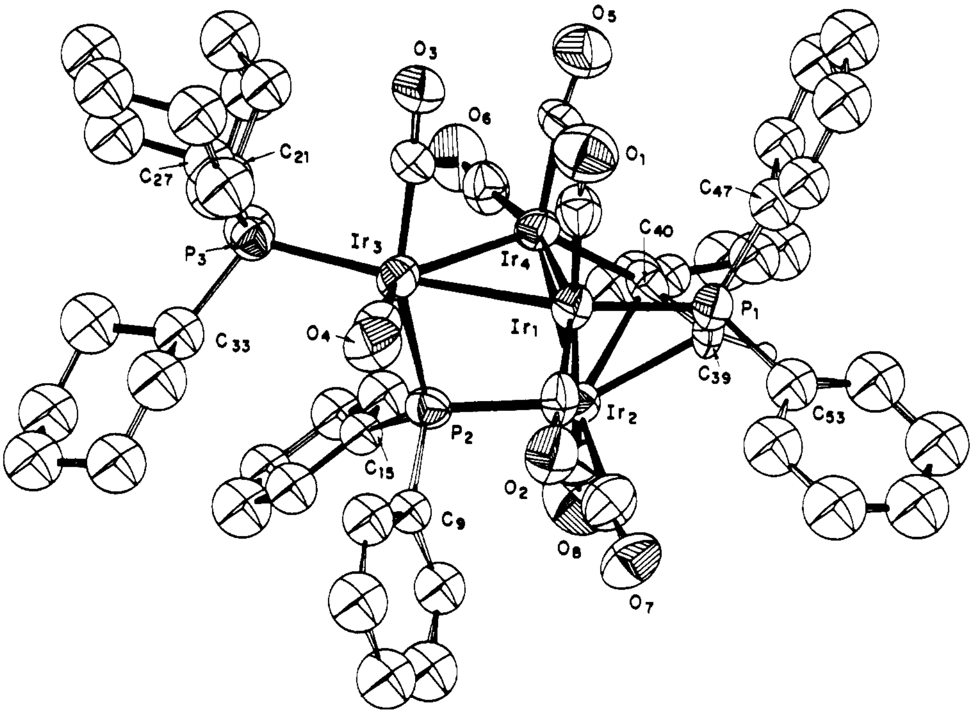

Figure 1. Molecular structure of $Ir_4(CO)_8(PCy_3)(\mu_3\text{-}\eta^3\text{-}Ph_2PC(H)CPh)(\mu\text{-}PPh_2)$ (**7a**) showing the atomic labeling scheme.

1 at δ 286.0[13,20] strongly suggests cleavage of the phosphido-bridged Ir–Ir bond in **4**. Crystals of **4** suitable for an X-ray analysis could not be obtained under a variety of conditions, and therefore its CO substitution reactions with a series of phosphines and phosphites were investigated, in an attempt to crystallize one of its derivatives. The solution structure of **4** is therefore discussed together with those of its derivatives.

Heating **4** in CH_2Cl_2 under reflux in the presence of 1 equiv of L or reacting **4** with 1 equiv of Me_3NO and L gives nearly quantitative yields of the canary yellow compounds $Ir_4(CO)_8L(\mu_3\text{-}\eta^3\text{-}Ph_2PC(H)CPh)(\mu\text{-}PPh_2)$ (L = PCy_3 (**7a**), $P(OMe)_3$ (**7b**), PPh_3 (**7c**), $PPhMe_2$ (**7d**)). Further CO substitution was also investigated in the case of $P(OMe)_3$. The reaction of **4** with 2 equiv of Me_3NO and $P(OMe)_3$ results in the formation of $Ir_4(CO)_7\{P(OMe)_3\}_2(\mu_3\text{-}\eta^3\text{-}Ph_2PC(H)CPh)(\mu\text{-}PPh_2)$ (**8b**) in 90% yield. All of these compounds have been characterized by spectroscopic and analytical methods (see Experimental Section and Tables II and III). Compounds **7b–d** exhibit IR spectra in the ν_{CO} region with band patterns that are similar, although shifted, due to the different electronic properties of the ligands, but rather different from that of compound **7a**, which contains the bulkiest of all ligands, PCy_3. This observation immediately suggested the presence of isomers in solution, confirmed by the NMR data discussed below. The ^1H NMR spectrum of compound **8b** also establishes the presence of at least four isomers in solution (see Experimental Section). Because the exact formulation of **4** and of these substituted complexes was impossible to ascertain on the basis of spectroscopic data alone, an X-ray analysis of compound **7a** was undertaken.

Table III. Carbonyl $^{13}C\{^1H\}$ NMR Data[a] for $Ir_4(CO)_9(\mu_3\text{-}\eta^3\text{-}Ph_2PC(H)CPh)(\mu\text{-}PPh_2)$ (4), $Ir_4(CO)_8(PCy_3)(\mu_3\text{-}\eta^3\text{-}Ph_2PC(H)CPh)(\mu\text{-}PPh_2)$ (7a), and $Ir_4(CO)_8(P(OMe)_3)(\mu_3\text{-}\eta^3\text{-}Ph_2PC(H)CPh)(\mu\text{-}PPh_2)$ (7b)

	$7a^{b,c}$		$7b^{b,c}$	
$4^{b,c}$	major isomer	minor isomer	major isomer	minor isomer
177.3	191.1	190.7	184.8	186.6
$J_{P-P} = 112$	$J_{P-C} = 8$	$J_{P-C} = 6$		
	$J_{P-C} = 117$	$J_{P-C} = 125$		
174.6	176.0	176.1	177.5	177.5
$J_{P-C} = 4$	$J_{P-C} = 5$	$J_{P-C} = 7$		
171.2	172.4	176.4	175.0	173.7
165.3	169.3	168.4	167.9	169.0
163.6	165.9	167.5	166.4	165.9
$J_{P-C} = 6$	$J_{P-C} = 10$	$J_{P-C} = 5$		
162.6	165.8	164.2	164.8	164.3
	$J_{P-C} = 4$	$J_{P-C} = 4$		
157.5	158.8	158.8	158.9	158.7
156.1	162.1	158.3	155.4	160.3
$J_{P-C} = 7$	$J_{P-C} = 11$	$J_{P-C} = 38$	$J_{P-C} = 33$	
	$J_{P-C} = 5$	$J_{P-C} = 6$		
		$J_{P-C} = 3$		
150.2				
$J_{P-C} = 5$				
$J_{P-C} = 30$				

[a] Chemical Shifts (δ) in ppm and coupling constants in Hz. [b] Measured in CD_2Cl_2. [c] –60 °C.

Crystal Structure of 7a. The molecular structure of **7a** in the solid state is sketched in Figure 1, together with the labeling scheme. Fractional atomic coordinates are reported in Table IV, and relevant bond distances and angles are listed in Table V. The metal atom framework of **7a** is spanned by a bridging PPh_2 ligand. Ir–Ir bond lengths range from 2.670(1) and 2.848(1) Å, the shortest bond corresponding to the hinge of the butterfly. The bridging PPh_2 ligand is slightly asymmetric (Ir(2)–P(2) = 2.350(3) Å; Ir(3)–P(2) = 2.385(3) Å). The PCy_3 ligand is terminally bound to one wingtip atom, while the $Ph_2PC(H){=}CPh$ ligand is located on the exterior of the butterfly framework bridging the butterfly wing not involved in the bonding to the PCy_3 ligand. Each iridium atom also bears

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[19] (a) MacLaughlin, S. A.; Nucciarone, D.; Carty, A. J. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis, Organic Compounds, and Metal Complexes*; Verkade, J. G.; Quinn, L. D., Eds.; VCH: New York, 1987; Chapter 16. (b) Randall, H. L.; Cherkas, A. A.; Carty, A. J. *Organometallics* **1989**, *8*, 568.

[20] Braga, D.; Grepioni, F.; Livotto, F. S.; Vargas, M. D. *J. Chem. Soc., Dalton Trans.* **1992**, 577.

Table IV. Fractional Atomic Coordinates for $Ir_4(CO)_8(PCy_3)(Ph_2PC(H)CPh)(PPh_2)$ (7a)

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Ir1	0.65898(4)	0.36085(2)	0.53340(4)	C21	1.1154(11)	0.2025(6)	0.3609(10)
Ir2	0.62971(4)	0.23241(3)	0.52836(4)	C22	1.0881(11)	0.1360(7)	0.3781(11)
Ir3	0.84041(4)	0.30716(2)	0.40307(4)	C23	1.1832(13)	0.0818(8)	0.4074(13)
Ir4	0.81310(4)	0.26437(2)	0.61103(4)	C24	1.2429(15)	0.1066(8)	0.5097(13)
P1	0.5617(3)	0.3571(2)	0.6840(3)	C25	1.2723(14)	0.1764(8)	0.4960(14)
P2	0.7336(3)	0.2252(2)	0.3709(2)	C26	1.1673(12)	0.2294(7)	0.4631(11)
P3	1.0063(3)	0.2645(2)	0.3027(3)	C27	1.0751(11)	0.3347(7)	0.2798(11)
C1	0.7059(11)	0.4403(7)	0.5764(10)	C28	1.0059(13)	0.4009(8)	0.2442(13)
O1	0.7311(9)	0.4880(5)	0.6050(9)	C29	1.0636(13)	0.4572(8)	0.2437(13)
C2	0.5576(11)	0.3931(7)	0.4265(11)	C30	1.1712(14)	0.4342(9)	0.1833(14)
O2	0.4971(8)	0.4148(6)	0.3593(9)	C31	1.2418(14)	0.3713(9)	0.2223(15)
C3	0.9181(11)	0.3600(7)	0.4865(11)	C32	1.1806(12)	0.3123(8)	0.2153(13)
O3	0.9667(8)	0.3952(6)	0.5328(8)	C33	0.9885(10)	0.2215(6)	0.1698(10)
C4	0.7742(11)	0.3717(7)	0.3087(11)	C34	1.0854(12)	0.1731(7)	0.1128(11)
O4	0.7323(8)	0.4166(5)	0.2629(8)	C35	1.0491(14)	0.1346(8)	0.0173(13)
C5	0.8732(11)	0.3243(7)	0.6938(10)	C36	0.9850(16)	0.1834(9)	−0.0652(15)
O5	0.9067(9)	0.3593(6)	0.7534(8)	C37	0.8959(14)	0.2350(9)	−0.0068(14)
C6	0.9316(11)	0.1917(7)	0.6288(10)	C38	0.9313(13)	0.2707(7)	0.0898(12)
O6	1.0034(8)	0.1508(5)	0.6460(8)	C42	0.7876(7)	0.1073(4)	0.7246(6)
C7	0.4908(12)	0.2628(7)	0.4651(13)	C43	0.8066(7)	0.0532(4)	0.7897(6)
O7	0.4080(8)	0.2827(6)	0.4287(9)	C44	0.7605(7)	0.0611(4)	0.8922(6)
C8	0.6211(11)	0.1403(7)	0.5268(10)	C45	0.6954(7)	0.1230(4)	0.9297(6)
O8	0.6129(12)	0.0866(6)	0.5230(9)	C46	0.6764(7)	0.1771(4)	0.8646(6)
C39	0.5870(10)	0.2705(7)	0.7046(10)	C41	0.7225(7)	0.1693(4)	0.7620(6)
C40	0.6989(11)	0.2312(6)	0.6977(9)	C48	0.6691(8)	0.3709(3)	0.8799(8)
C10	0.5642(7)	0.1924(4)	0.2508(7)	C49	0.7026(8)	0.4087(3)	0.9659(8)
C11	0.4873(7)	0.1982(4)	0.1691(7)	C50	0.6630(8)	0.4784(3)	0.9773(8)
C12	0.4828(7)	0.2468(4)	0.0951(7)	C51	0.5901(8)	0.5103(3)	0.9027(8)
C13	0.5552(7)	0.2894(4)	0.1027(7)	C52	0.5566(8)	0.4725(3)	0.8168(8)
C14	0.6320(7)	0.2836(4)	0.1843(7)	C47	0.5961(8)	0.4028(3)	0.8053(8)
C9	0.6365(7)	0.2351(4)	0.2584(7)	C54	0.3516(8)	0.4070(5)	0.6041(7)
C16	0.8126(7)	0.1133(4)	0.2195(6)	C55	0.2384(8)	0.4205(5)	0.6104(7)
C17	0.8637(7)	0.0466(4)	0.1895(6)	C56	0.1875(8)	0.4078(5)	0.7029(7)
C18	0.9066(7)	0.0028(4)	0.2676(6)	C57	0.2497(8)	0.3816(5)	0.7891(7)
C19	0.8984(7)	0.0258(4)	0.3758(6)	C58	0.3629(8)	0.3681(5)	0.7829(7)
C20	0.8472(7)	0.0925(4)	0.4059(6)	C53	0.4139(8)	0.3808(5)	0.6904(7)
C15	0.8043(7)	0.1363(4)	0.3277(6)	H	0.5351	0.2537	0.7590

two terminal CO ligands. The $Ph_2PC(H){=}CPh$ ligand is bound to the metal cluster *via* one σ interaction (Ir(4)–C(40) = 2.07(1) Å), one P–Ir lone-pair donation (Ir(1)–P(1) = 2.270(3) Å), and one π interaction with the unsaturated C=C system (Ir(2)–C(39) = 2.31(1) Å; Ir(2)–C(40) = 2.28(1) Å). The structural parameters within the $Ph_2PC(H){=}CPh$ fragment are clearly indicative of an sp^2 hybridization of the two C atoms: the P—C=C—(Ph) system is planar, with P—C=C and C=C—C angles of 119(1) and 115(1)°, respectively. The C(39)–C(40) bond distance of 1.46(2) Å is in agreement with a double-bond character. Although direct location by X-ray diffraction of an H atom (see Experimental Section) in a molecule of such complexity is to be taken with great caution, it is worth noting that the H atom bound to C(39) is in the expected position for an sp^2-hybridized C atom dwelled in a sterically constrained environment (P(1)–C(39)–H 118.5(4)°, H–C(39)–C(40) = 115.3(7)°, C(39)–H = 1.07 Å). Altogether this ligand formally supplies five electrons to the cluster orbitals. Considering a three-electron donation from the bridging phosphine ligand and a two-electron contribution from the terminal PCy_3 ligand, the total number of electrons in **7a** is 62, as expected for a tetranuclear butterfly cluster, with all Ir atoms formally obeying the 18 e^- rule.

Solution Structures of 4 and 7a,b. The similarity of the ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra of ^{13}CO-enriched samples of compounds **4** and **7a,b** indicate that they possess similar structures, only with a carbonyl ligand in **4** in place of the $P(OMe)_3$ and PCy_3 ligands in compounds **7a,b** respectively.

The ^1H NMR spectra of **4** and **7a,b** show a signal at *ca.* δ 8.2 of intensity 1 with respect to the phenyl protons of intensity 25. For **4**, this signal is a doublet of doublets at δ 8.25 (see Figure 2). Selective ^{31}P decoupling showed that this signal is coupled to ^{31}P, and no significant ^1H–^1H coupling was detected to this signal. Decoupling at δ 63.5 results in the removal of the larger coupling J_{H-P} = 12 Hz from the signal at δ 8.25, while decoupling at δ −58.8 removes the smaller coupling J_{H-P} = 3.4 Hz from this signal.

For **7a**, at room temperature, the corresponding ^1H signal is broad at δ 8.30, but when the temperature is lowered to −20 °C, it separates into two signals at δ 8.30 (dd, J_{P-H} = 11.5, 2.5 Hz) and δ 8.35 (d, J_{P-H} = 12.5 Hz) in the ratio 3.9:1, corresponding to ΔG°_{253} = 0.68 kcal mol^{-1}. A similar behavior is observed for **7b**, with a broad doublet at δ 8.37 observed at room temperature, which separates into two overlapping doublets at −60 °C at 8.37 (J_{P-H} = 12 Hz) and δ 8.32 (J_{P-H} = *ca.* 12 Hz) in the approximate ratio of 6:1. For **7b** the presence of two isomers is more clearly demonstrated for the $P(OMe)_3$ ^1H NMR signal, which shows a broad doublet at room temperature at δ 3.56 (J_{P-H} = 12 Hz) that separates into two 12-Hz doublets at −60 °C at δ 3.63 and 3.41 in the intensity ratio 5.9:1, corresponding to ΔG°_{213} = 0.75 kcal mol^{-1}.

The ^{13}C NMR spectrum of **4** shows a double doublet at δ 70.5 (J_{P-C} = 17, 68 Hz), which with an INEPT detection gives J_{C-H} = 158 Hz, consistent with sp^2 hybridization at the carbon. The ^{13}C NMR spectra of **4** and **7a,b** are also similar in the carbonyl region (see Table III and Figure 3). The room-temperature $^{13}C\{^1H\}$ carbonyl NMR spectrum of **4** in CD_2Cl_2 shows the presence of six signals of

Table V. Relevant Bond Distances (Å) and Angles (deg) for $Ir_4(CO)_8(PCy_3)(Ph_2PC(H)CPh)(PPh_2)$ (7a)

Ir1–Ir2	2.724(1)	C1–O1	1.12(2)
Ir1–Ir3	2.787(1)	C2–O2	1.17(2)
Ir1–Ir4	2.670(1)	C3–O3	1.17(2)
Ir2–Ir4	2.720(1)	C4–O4	1.14(2)
Ir3–Ir4	2.848(1)	C5–O5	1.14(2)
Ir1–P1	2.270(3)	C6–O6	1.12(1)
Ir2–P1	3.052(3)	C7–O7	1.14(2)
Ir2–P2	2.350(3)	C8–O8	1.12(2)
Ir3–P2	2.385(3)	C21–C22	1.50(2)
Ir3–P3	2.404(3)	C22–C23	1.50(2)
C39–Ir2	2.31(1)	C23–C24	1.59(2)
C40–Ir2	2.28(1)	C24–C25	1.57(2)
C40–Ir4	2.07(1)	C21–C26	1.55(2)
P1–C39	1.76(1)	C25–C26	1.58(2)
P1–C47	1.82(1)	C27–C28	1.53(2)
P1–C53	1.82(1)	C28–C29	1.49(2)
P2–C9	1.85(1)	C29–C30	1.52(2)
P2–C15	1.88(1)	C30–C31	1.50(2)
P3–C21	1.83(1)	C27–C32	1.52(2)
P3–C27	1.87(1)	C31–C32	1.57(2)
P3–C33	1.86(1)	C33–C34	1.53(2)
Ir1–C1	1.89(1)	C34–C35	1.51(2)
Ir1–C2	1.89(1)	C35–C36	1.58(2)
Ir3–C3	1.87(1)	C36–C37	1.51(2)
Ir3–C4	1.88(2)	C33–C38	1.53(2)
Ir4–C5	1.83(2)	C37–C38	1.48(2)
Ir4–C6	1.88(1)	Ir2–C39	2.31(1)
Ir2–C7	1.91(2)	Ir2–C40	2.28(1)
Ir2–C8	1.90(1)	Ir4–C40	2.07(1)
		C39–C40	1.46(2)
		C40–C41	1.52(1)
		C39–H	1.07
P1–Ir1–Ir2	74.7(1)	P1–C39–Ir2	96(1)
P1–Ir1–Ir4	86.7(1)	C40–C39–P1	119(1)
P2–Ir2–Ir1	80.0(1)	C39–C40–Ir4	120(1)
P2–Ir2–Ir4	79.6(1)	O1–C1–Ir1	178(1)
C39–Ir2–Ir1	78.1(3)	O2–C2–Ir1	177(1)
C39–Ir2–Ir4	74.7(3)	O3–C3–Ir3	176(1)
C39–Ir2–P2	152.3(3)	O4–C4–Ir3	171(1)
C40–Ir2–Ir1	85.5(3)	O5–C5–Ir4	174(1)
C40–Ir2–Ir4	47.9(3)	O6–C6–Ir4	175(1)
C40–Ir2–P2	124.5(3)	O7–C7–Ir2	178(1)
P2–Ir3–Ir1	78.1(1)	O8–C8–Ir2	177(1)
P2–Ir3–Ir4	76.5(1)		
P3–Ir3–Ir1	175.0(1)		
P3–Ir3–Ir4	121.0(1)		
P3–Ir3–P2	105.9(1)		
C40–Ir4–Ir1	91.2(3)		
C40–Ir4–Ir3	139.3(3)		

equal intensity at δ 174.2, 170.7, 165,4, 163.2 (J_{P-C} = 5 Hz), 162.5, and 157.5 and a broad signal at δ 162. As the temperature is lowered to −60 °C, the six sharp signals remain virtually unchanged, but three new signals appear at δ 177.3 (J_{P-C} = 112 Hz), 156.1 (J_{P-C} = 7 Hz), and 150.2 (J_{P-C} = 30 and 5 Hz). At room temperature the ^{13}C (carbonyl) NMR spectra of **7a,b** are broadened but sharpen on cooling to show the presence of two isomers (see Table III), each isomer showing eight CO resonances. With the assistance of the crystal structure it is possible to assign some of these carbonyls as shown in Figure 3. The high-frequency signals with their large J_{P-C} values are consistent with a carbonyl *trans* to phosphorus. This carbonyl in 4 is involved in exchange with two other carbonyls. The most consistent assignment is as carbonyl g. This is also consistent with the ^{31}P NMR spectrum, which shows J_{P-C} = 106 Hz to the signal at δ −58.8, which is the signal with J_{P-H} = 3.4 Hz, and therefore more likely to be with the μ-PPh_2 group rather than the phosphorus of the $Ph_2PC(H)CPh$ ligand, which is expected to give the larger J_{P-H} value of 12 Hz. The fluxional process is a trigonal twist at Ir(3) exchanging carbonyls g, h, and i with ΔG^* = 12 kcal mol^{-1}.[21]

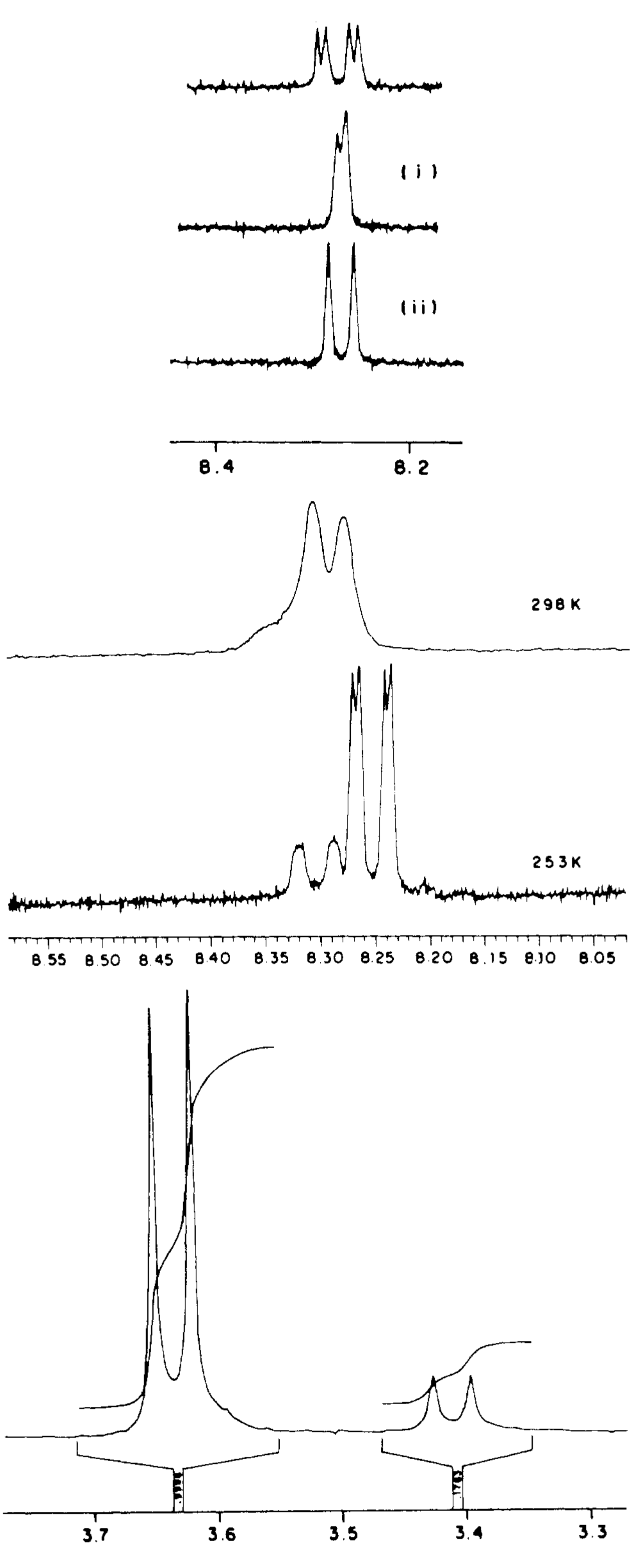

Figure 2. (a, top) ^1H NMR spectra (283 K) of $Ir_4(CO)_9(\mu_3\text{-}\eta^3\text{-}Ph_2PC(H)CPh)(\mu\text{-}PPh_2)$ (4) in the vinyl region with selective ^{31}P NMR decoupling at δ −63.5 (i) and δ −58.8 (ii). (b, middle) ^1H NMR spectra of $Ir_4(CO)_8(PCy_3)(\mu_3\text{-}\eta^3\text{-}Ph_2PC(H)CPh)(\mu\text{-}PPh_2)$ (**7a**) in the vinyl region at 298 and 253 K. (c) ^1H NMR spectrum of $Ir_4(CO)_8(P(OMe)_3)(\mu_3\text{-}\eta^3\text{-}Ph_2PC(H)CPh)(\mu\text{-}PPh_2)$ (**7b**) in the methyl region.

Comparison of the ^{13}C signals of the major and minor isomers of **7a,b** with those of 4 using both chemical shifts and J_{P-C} shows that the carbonyl signal which vanishes on replacement of a CO in 4 by a phosphorus ligand in

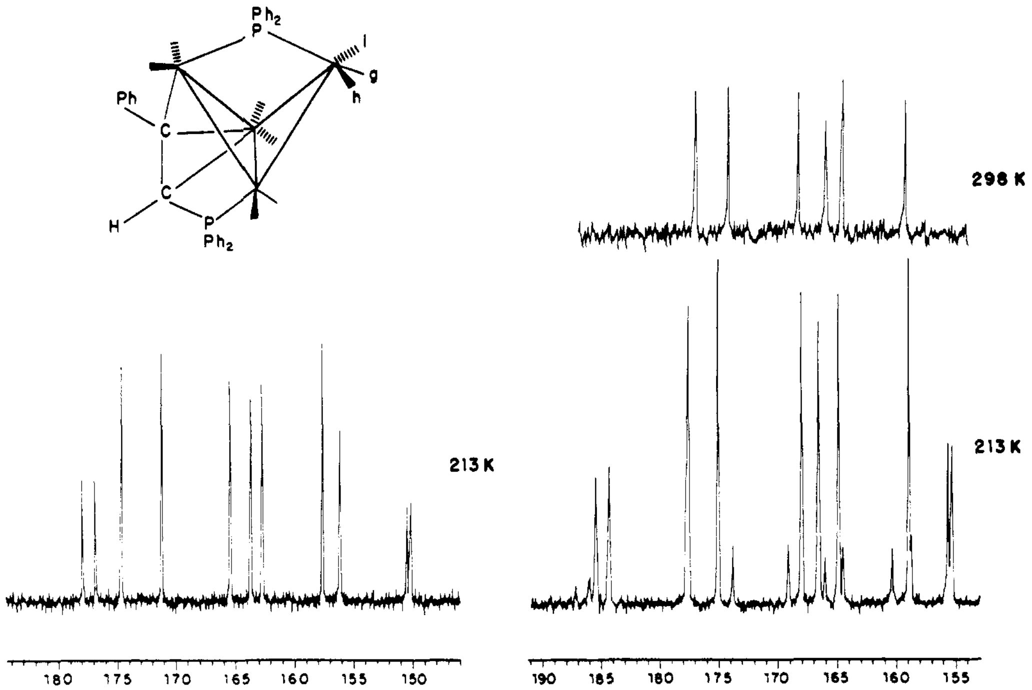

Figure 3. Carbonyl ^{13}C NMR spectra of $Ir_4(CO)_8L(\mu_3\text{-}\eta^3\text{-}Ph_2PC(H)(CPh)(\mu\text{-}PPh_2)$: (a, left) L = CO (4); (b, right) L = $P(OMe)_3$ (**7b**).

7a,b is the signal due to either carbonyl h or i. This is consistent with the X-ray structure, where carbonyl i is substituted by PCy_3. Consequently, the two isomers of **7a,b** differ by the positioning of the phosphorus ligand in either position h or i. Thus, interchange of the two isomers involves a 120° rocking of the three ligands in such a way that the g position is never occupied by the phosphorus ligand.

The ^{31}P NMR spectra of **7a,b** show the same temperature dependence; however, the major isomer of **7a** and the minor isomer of **7b** show a large coupling between P(1) and P(3). This large coupling is consistent with the nearly linear arrangement found in the crystal structure. Hence, the crystal structure established for **7a** is that of the major isomer, while the corresponding structure is found for the minor isomer of **7b**. An attempt was made to further assign the ^{13}CO signals of 4 by measuring the COSY-90 ^{13}C NMR spectrum, which showed J_{C-C} connectivity between signals at δ 174.6 and 157.5 and 171.2 and 163.6, but assignments to the other carbonyls were impossible.

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Supplementary Material Available: Tables of anisotropic thermal parameters and fractional atomic coordinates and isotropic thermal parameters for the non-hydrogen atoms, a table of fractional atomic coordinates for the hydrogen atoms, a complete list of bond lengths and angles, and additional figures of the molecular structure of **7a** (18 pages). Ordering information is given on any current masthead page.

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(21) The value of $\Delta G°$ was determined from line width measurements. $\Delta G^{\ddagger}$ was calculated using the Eyring equation: $\Delta G^{\ddagger} = RT(23.769 - \ln(k/T))$.