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Synthesis and X-ray Analysis of the Tetranuclear Iridium Compounds HIr$_4$(CO)$_9$(μ_4-η^3-Ph$_2$PCCPh)(μ-PPh$_2$) and Ir$_4$(CO)$_7$(μ-CO)(μ_3-η^2-HCCPh)(μ-PPh$_2$)$_2$ and Multinuclear NMR Studies of the Latter Compound

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Reaction of HIr$_4$(CO)$_{10}$(μ-PPh$_2$) (1) with Ph$_2$PC≡CPh yields the CO-substituted compounds HIr$_4$(CO)$_{10-n}$(Ph$_2$PC≡CPh)$_n$(μ-PPh$_2$), n = 1 (2) and 2 (3). The monosubstituted species (2) undergoes facile P—C bond cleavage, followed by acetylide insertion into the Ir—H bond to give Ir$_4$(CO)$_7$(μ_3-η^2-HC$_2$Ph)(μ-CO)(μ-PPh$_2$)$_2$ (4) in high yields, and under more forcing conditions, HIr$_4$(CO)$_9$(μ_4-η^3-Ph$_2$PCCPh)(μ-PPh$_2$) (6) is also obtained. Compound 4 is also formed upon thermolysis of Ir$_4$(CO)$_{10}$(PPh$_2$H)(Ph$_2$PC≡CPh) (7), which is obtained from carbonyl substitution in Ir$_4$(CO)$_{11}$(PPh$_2$H) (8) with Ph$_2$PC≡CPh. Crystal data for 4: space group $P2_1/n$, a = 8.94(2) Å, b = 39.05(2) Å, c = 11.954(6) Å, β = 104.57(8)°, V = 4037.1 Å^3, Z = 4, and final R (R_w) value 0.069 (0.073), for 2108 unique reflections $[F_c > 4(F_o)]$. Compound 4 exhibits a tetrahedral metal framework, with two elongated edges bridged by the μ-PPh$_2$ ligands and a phenylacetylene bound to the cluster in the μ_3-η^2-$\|$ fashion. ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy studies have established that compound 4 is present in solution in the form of two isomers in a 1:2 ratio, which differ with respect to the orientation of the acetylene ligand and undergo two distinct dynamic processes: at low temperature, *ca.* 60° rocking of the acetylene with $\Delta G^{\ddagger}_{192}$ = 9.0 kcal mol^{-1}, and estimated $\Delta G^{\ddagger}_{169}$ = 5.4 kcal mol^{-1}, and interconversion of the two isomers at 82 °C, with $\Delta G^{\ddagger}$ = 21.8 kcal mol^{-1} *via* rotation of the acetylene by 120° steps. Crystal data for 6: space group $P2_1/n$, a = 11.840(3) Å, b = 18.745(9) Å, c = 18.695(8) Å, β = 100.63(3)°, V = 4077.9 Å^3, Z = 4; final $R(R_w)$ value 0.058 (0.060) for 2609 independent reflections observed $[F_c > 4(F_o)]$. Compound 6 exhibits a flat butterfly arrangement of metal atoms, with an elongated edge bridged by a PPh$_2$ ligand and all metal atoms interacting with Ph$_2$PCCPh, which acts as a 6-electron ligand.

Introduction

Reactions of phosphinoacetylenes R$_2$PC≡CR′ with di- and polynuclear carbonyl compounds of the iron subgroup have been the subject of numerous studies in the last years.[1–3] These molecules can behave as simple P donors,[4] as 4-electron (P+2π)[5] or 6-electron (P+4π)[6,7] ligands, as well as undergo cleavage of the P—C(alkyne) bond, which can be induced by thermolysis,[8] photolysis,[1] and chemical activation using Me$_3$NO,[9] to generate phosphido –PR$_2$ and –C$_2$R′ bridging fragments. The mechanism of the the P—C bond cleavage is unknown, but the formation of an intermediate with the acetylene π-interacting, followed by oxidative insertion into the P—C bond has been proposed.[1,10] Considering that HIr$_4$(CO)$_{10}$(μ-PPh$_2$) (1) is

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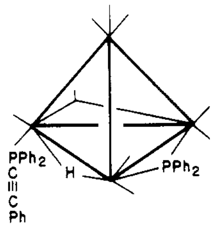
extremely reactive toward phosphines but inert toward acetylenes,[11] we thought it was worthwhile to investigate its reactions with $Ph_2PC{\equiv}CPh$, as an alternative route for obtaining acetylide- and acetylene-coordinated species. Indeed, the presence of a hydride ligand in 1 could extend the type of reactivity generally observed by the possible insertion of the C—C triple bond into the Ir—H bond. The literature gives only two precedents for this type of reaction with the clusters $HRu_3(CO)_9(\mu\text{-}PPh_2)$[3] and $[Ph_4P][HFe_3(CO)_{11}]$.[12]

We report here our studies on the rearrangements of the monosubstituted product from the reaction of 1 with $Ph_2PC{\equiv}CPh$, $HIr_4(CO)_9(Ph_2PC{\equiv}CPh)(\mu\text{-}PPh_2)$ (2), that yields $Ir_4(CO)_7(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}HC_2Ph)(\mu\text{-}PPh_2)_2$ (4) and, depending on the conditions, also $HIr_4(CO)_9(\mu_4\text{-}\eta^3\text{-}Ph_2PCCPh)(\mu\text{-}PPh_2)$ (6), by two distinct routes.[13]



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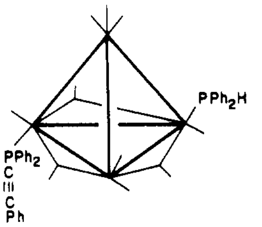
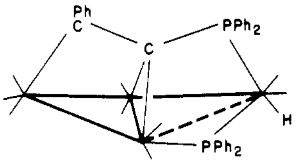


(7)



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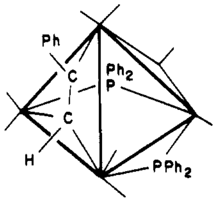

(4)

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–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 Bruker AC 200, 300, and WH 400 instruments using deuterated solvents as lock and reference [^1H and $^{13}C\{^1H\}$, $Si(Me)_4$ ($\delta = 0$); ^{31}P, 85% H_3PO_4 ($\delta = 0$); high frequency positive] in $C_6D_5CD_3$, CD_2Cl_2, and $CDCl_3$. Fast atom bombardment mass spectra (FAB MS) were obtained on a Kratos MS50, operating at 8 keV. The instrument was equipped with a standard Kratos FAB source and an Ion Tech Gun. The energy of the primary atom beam was 8 keV at an ion current at 40 μA. Xenon was used as the source of fast atoms. Spectra were obtained with a magnet scan rate in the range 30–100 s/decade using a magnet of 10 000 Da at 8-keV accelerating voltage. The source pressure was typically $\sim 1.3 \times 10^{-3}$ Pa. 3-Nitrobenzyl alcohol, purchased from Sigma Chemical Co. and distilled under vaccum, was used as a matrix. It was treated by bubbling either CO or Ar through it for 2 h prior to use. The sample was prepared by addition of a 10^{-3} M CH_2Cl_2 solution of the metal carbonyl compound (0.5 μL) to 2 μL of matrix on an acid-etched stainless steel probe tip and by thoroughly mixing. All *m/z* values are referred to ^{193}Ir. Micronalyses were carried out either at the University Chemical Laboratories, University of Cambridge, U.K., at the Instituto de Química, USP, São Paulo, or at the Instituto de Química, UNICAMP, Campinas, Brazil.

Compounds $Ir_4(CO)_{12}$,[14] $Ir_4(^{13}CO)_{12}$ (*ca.* 25% enriched),[15] $Ir_4(CO)_{11}PPh_2H$,[16] $HIr_4(CO)_{10}(\mu\text{-}PPh)_2$,[17] and $Ph_2PC{\equiv}CPh$[18] were prepared according to published procedures; all other reagents were purchased from commercial sources. Trimethylamine *N*-oxide dihydrate was sublimed in vacuo; the other reagents were used as supplied.

Preparation of $HIr_4(CO)_9(Ph_2PC{\equiv}CPh)(\mu\text{-}PPh_2)$ (2). 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) was stirred with $Ph_2PC{\equiv}CPh$ (23.2 mg 0.08 mmol) for 4 h at 30 °C, after which time the solvent was evaporated *in vacuo* to about $^1/_5$. Purification by preparative TLC afforded two orange compounds: $HIr_4(CO)_9(Ph_2PC{\equiv}CPh)(\mu\text{-}PPh_2)$ (2) (85 mg, 0.06 mmol, 70%, R_f 0.25) and $HIr_4(CO)_8(Ph_2PC{\equiv}CPh)_2(\mu\text{-}PPh_2)$ (3) (42.0 mg, 0.024 mmol, 30%, R_f 0.07). Recrystallization of both compounds from CH_2Cl_2–hexane gave analytically pure samples of **2** and **3**. Anal. Calcd for $C_{41}H_{26}O_9P_2Ir_4$ (**2**): C, 33.0; H, 1.8. Found: C, 33.4; H, 2.1%. IR (hexane): $\nu_{C\equiv C}$ 2172 (w) cm^{-1}; ν_{CO} 2068 (s), 2032 (vs), 2004 (s), 1994 (m), 1982 (msh), 1830 (wbr) cm^{-1}. Anal. Calcd for $C_{60}H_{41}O_8P_3Ir_4$ (**3**): C, 43.5; H, 3.4. Found: C, 43.7; H, 3.2. IR (hexane): $\nu_{C\equiv C}$ 2172 (w) cm^{-1}; ν_{CO} 2068 (m), 2052 (m), 2022 (s), 1987 (mbr), 1805 (wbr) cm^{-1}.

Preparation of $Ir_4(CO)_8(\mu_3\text{-}\eta^2\text{-}HCCPh)(\mu\text{-}PPh_2)_2$ (4). A solution of **2** (40.0 mg 0.027 mmol) in CH_2Cl_2 (10 mL) was heated under reflux for 5 h, after which time the solvent was evaporated *in vacuo* to about 1 mL, and the mixture separated to afford yellow $HIr_4(CO)_9(\mu_4\text{-}\eta^3\text{-}Ph_2CCPh)(\mu\text{-}PPh_2)$ (6) (1.0 mg, 0.007 mmol, 2%, R_f 0.72), $Ir_4(CO)_8(\mu_3\text{-}\eta^2\text{-}HCCPh)(\mu\text{-}PPh_2)_2$ (4) (35.5 mg, 0.024 mmol, 70%, R_f 0.59), five red species in minute amounts **5a**, R_f 0.55; **5b**, R_f 0.39; **5c**, R_f 0.22; **5d**, R_f 0.11; **5e**, R_f 0.04, and unreacted **2** (4 mg, 0.03 mmol, 10%, R_f 0.48). Recrystallization of compounds **4** and **6** with CH_2Cl_2–hexane gave analytically pure samples of **4** and **6**. Anal. Calcd for $C_{40}H_{26}O_8P_2Ir_4$ (**4**): C, 32.8; H, 1.8. Found: C, 33.9, H, 2.1. IR (hexane): ν_{CO} 2062 (w), 2042 (s), 2034 (vs), 2004 (vw), 1990 (w), 1853 (whr) cm^{-1}. Anal. Calcd for $C_{41}H_{26}O_9P_2Ir_4$ (**6**): C, 33.0; H, 1.8. Found: C, 33.2, H, 2.0. IR (hexane): ν_{CO} 2078 (m), 2052 (vs), 2034 (s), 2018 (vs), 1968 (mbr), cm^{-1}.

Conversion of 2 into 4. When the reaction described above was investigated under the same conditions except for the temperature, which was kept at 25 °C for 5 h, only **4** (17.8, 0.017 mmol, 50%) and starting material **2** were obtained. Bubbling CO through the solution under the same reaction conditions did not result in any reaction.

Preparation of $Ir_4(CO)_{10}(Ph_2PC{\equiv}CPh)(PPh_2H)$ (7). A yellow solution of $Ir_4(CO)_{11}(PPh_2H)$ (8) (150.0 mg, 0.12 mmol) and $Ph_2PC{\equiv}CPh$ (34.0 mg, 0.12 mmol) in CH_2Cl_2 (20 mL) was heated under reflux for 48 h, after which time the solvent was

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Table I. Crystal Data and Details of Measurements for 4 and 6

	4	**6**
formula	$C_{41}H_{26}Ir_4O_8P_2$	$C_{41}H_{25}Ir_4O_9P_2$
M_r	1465	1492
cryst size (mm)	0.13 × 0.15 × 0.12	0.10 × 0.15 × 0.12
system	monoclinic	
space group	$P2_1/n$	
a (Å)	8.94(2)	11.840(3)
b (Å)	39.05(2)	18.745(9)
c (Å)	11.954(6)	18.695(8)
β (deg)	104.57(8)	100.63(3)
V (Å^3)	4037.1	4077.9
Z	4	4
$F(000)$	2672	2724
D_{calcd} (g cm^{-3})	2.41	2.43
λ(Mo Kα) (Å)	0.710 69	
μ(Mo Kα) (cm^{-1})	127.8	126.5
θ range (deg)	2.5–20	
scan mode	$\omega/2\vartheta$	
ω-scan width (deg)	1.50	0.90
requested counting $\sigma(I)/I$	0.02	
prescan rate (deg min^{-1})	6	5
prescan acceptance $\sigma(I)/I$	0.5	
max scan time (s)	90	100
no. of measd reflns	4085	6464
no. of unique obsd reflns		
no. of reflns used in the refinement [$I > 2.0\sigma(I)$]	2108	2609
no. of refined params	188	297
R, R_w[a]	0.069, 0.073	0.058, 0.060
S[b]	1.65	1.27
k, g	1.49, 0.0032	1.00, 0.0026

[a] $R_w = \Sigma[(F_o - F_c)w^{1/2}]/\Sigma F_o w^{1/2})$, where $w = k/[\sigma(F) \rightarrow \sigma^2(F)]$. [b] $S = \Sigma[(F_o - F_c)/\sigma]^2/(n - m)$.

concentrated *in vacuo* and the product purified by TLC affording $Ir_4(CO)_{10}(Ph_2PC{\equiv}CPh)(PPh_2H)$ (7) (144 mg, 0.09 mmol, 80%, R_f 0.43) and starting material only. Recrystallization of the yellow solid with CH_2Cl_2–hexane gave an analytically pure sample of 7. Anal. Calcd for $C_{42}H_{26}O_{10}P_2Ir_4$: C, 33.1; H, 1.7. Found: C, 33.2; H, 1.8. IR (hexane): $\nu_{C{\equiv}C}$ 2172 (w) cm^{-1}; ν_{CO} 2066 (s), 2038 (vs), 2004 (vs), 1866 (wbr), 1801 (mbr) cm^{-1}.

Reaction of 8 with $Ph_2PC{\equiv}CPh$ in the Presence of Me_3NO. A solution of 8 (25.0 mg, 0.02 mmol) in CH_2Cl_2 (10 mL) with $Ph_2PC{\equiv}CPh$ (6.0 mg, 0.02 mmol) was cooled to −70 °C and treated with a CH_2Cl_2 solution (2 mL) of Me_3NO (1.5 mg, 0.02 mmol). The reaction mixture was allowed to warm to room temperature, and the solvent was concentrated *in vacuo*. Separation of the mixture by TLC afforded 2 (8.0 mg, 0.005 mmol, 27%), 3 (3.0 mg, 0.002 mmol, 10%), and unreacted 8 (10.0 mg, 0.008 mmol, 40%), along with some decomposition (base line on the TLC plates).

Thermolysis of 7. A solution of 7 (100.0 mg, 0.066 mmol) in toluene (30 mg) was heated at 45 °C for 24 h. The solvent was then concentrated *in vacuo*, and the mixture separated by TLC affording $Ir_4(CO)_8(\mu_3\text{-}\eta^2\text{-}HCCPh)(\mu\text{-}PPh_2)_2$ (4) (77 mg, 0.053 mmol, 80%), along with starting material only.

X-ray Structural Analysis of 4 and 6. X-ray measurements were made 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. Fast decay under X-ray exposure prevented extension of both data collections beyond θ = 20°. Crystal data and details of measurements for 4 and 6 are summarized in Table I. Both structures were solved by direct methods, followed by difference Fourier synthesis and subsequent least-squares refinement. For all calculations the SHELX76 program was used.[19] An absorption correction in 6 was applied by the Walker and Stuart method[20] once a complete structural model was available, and all atoms were refined isotropically. Ir and P atoms in 4 and all atoms but H and phenyl carbon atoms in 6 were allowed to vibrate anisotropically. The H atoms of the phenyl groups were added in calculated positions [C–H 1.08 Å] and refined "riding" on their respective C atoms; a single isotropic thermal parameter was refined for the H atoms [0.15(6) and 0.14(4) Å^2 for 4 and 6, respectively].

Results and Discussion

The reaction of $HIr_4(CO)_{10}(\mu\text{-}PPh_2)$ (1) with 1 equiv of L = $Ph_2PC{\equiv}CPh$ in CH_2Cl_2 proceeds smoothly at room temperature to give the CO-substituted compound $HIr_4(CO)_9L(\mu\text{-}PPh_2)$ (2) in yields above 70%, along with some $HIr_4(CO)_8L_2(\mu\text{-}PPh_2)$ (3). Both compounds were characterized by analysis and spectroscopic data, as shown in Table II. Comparison of the ^1H and $^{31}P\{^1H\}$ NMR data for 2 with those reported for the analogous PPh_3 derivative (**2a**), whose molecular structure has been established by an X-ray analysis,[11] confirms that they possess the same structure, with L replacing an axial carbonyl bound to a basal Ir atom that does not interact with the μ-PPh_2 ligand in 1. It was noted that FAB MS of compound 2 in an argon-degassed matrix gives, instead of a molecular ion as previously observed for **2a**, an abundant peak at m/z 1465, due to $[M - CO]^+$, followed by sequential peaks at m/z $1465 - 28x$, x = 8, and that the molecular ion $[MH]^+$ at m/z 1494 is only observed when the matrix is saturated with CO. We have previously described saturation of the matrix with CO as a means of preventing CO dissociation in the matrix of labile carbonyl clusters, labile even in solution,[21] as is the case of compound 2. Compound 3 has been characterized only by analysis and its IR spectrum, which is very similar to that of the PPh_3 species **3b**.[11]

Stirring 2 in CH_2Cl_2 at 25 °C for 5 h results in its conversion into $Ir_4(CO)_7(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}HC_2Ph)(\mu\text{-}PPh_2)_2$ (4), which was isolated in 50% yield after crystallization from CH_2Cl_2–hexane and fully characterized by analysis, a combination of ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy described below, and an X-ray diffraction study.

The yields of this conversion and the products formed from it depend strongly on the conditions employed. Under 1 atm of CO, no reaction is observed under similar conditions. When compound 2 is heated in CH_2Cl_2 under reflux for 5 h, compound 4 is produced in 70% yield; minute amounts of five red species, **5a**–**5e** and the new yellow compound $HIr_4(CO)_9(\mu_4\text{-}\eta^3\text{-}Ph_2PCCPh)(\mu\text{-}PPh_2)$ (6), formed in 2% yield, are also isolated, besides a little unreacted 2. When heated together in CH_2Cl_2, only four of the five red species, **5a**–**5d**, slowly convert into compound 4, which seems to indicate that they may be intermediates in the formation of this species *via* alternative high temperature routes. After heating 2 under reflux in hexane for 4 h, all of 2 is consumed, **5e** is the major red species present, still in minute amounts, and compounds 4 and 6 are obtained in up to 75% and 5% yields, respectively, in addition to some decomposition. Furthermore, formation of 4 in 80% yield, is also observed if $Ir_4(CO)_{10}(PPH_2H)(Ph_2PC{\equiv}CPh)$ (7) is heated in toluene at 45 °C for 24 h.

Compound 7 is obtained in up to 80% yields from the reaction of $Ir_4(CO)_{11}(PPh_2H)$[11,12] (8) with equivalent amounts of $Ph_2PC{\equiv}CPh$ in refluxing CH_2Cl_2. Activation of compound 8 with equivalent amounts of Me_3NO, instead of thermolysis, however, results in the formation of only compounds 2 and 3, besides decomposition, and this is most probably due to the deprotonation of the PPh_2H

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Table II. ^1H, $^{31}P\{^1H\}$, and Carbonyl $^{13}C\{^1H\}$ NMR Data[a] for $HIr_4(CO)_9(Ph_2PC{\equiv}CPh)(\mu\text{-}PPh_2)$ (2), $Ir_4(CO)_8(HCCPh)(\mu\text{-}PPh_2)_2$ (4), $HIr_4(CO)_9(Ph_2PCCPh)(\mu\text{-}PPh_2)$ (6), and $Ir_4(CO)_{10}(Ph_2PC{\equiv}CPH)(PPh_2H)$ (7)

			$^{13}C\{^1H\}^h$	
compd	^1H	$^{31}P\{^1H\}^b$	major isomer	minor isomer
2[c]	−11.8 (d, d), J(P—H) = 55.8 (PPh_2), J(P—H) = 6.0 ($Ph_2PC{\equiv}CPh$)	283.0 (s) (PPh_2), −41.0 (s) ($Ph_2PC{\equiv}CPh$)		
4[d–g]	major isomer: 7.5 (s) (HCCPh) minor isomer: 9.4 (s) (HCCPh), 7.2–7.8 (m, Ph)	major isomer: 32 (br) minor isomer: 54 (d), 1 (d), J(P—P) = 160	186.4 (1 CO), 173.2 (1 CO), 168.2 (2 CO), 158.1 (2 CO), 156.2 (2 CO)	187.0 (1 CO), 175.0 (1 CO), 168.8 (2 CO), 158.1 (2 CO), 157.5 (2 CO)
6[e,f]	−11.2 (d, d), J(P—H) = 90.0 ($Ph_2PC{\equiv}CPh$), J(P—H), 22.8 (PPh_2), 7.6–6.6 (m, Ph)	29.8 (d), −2.3 (d), J(P—P) = 42.2		
7[e,f]	7.3 (d), J(P—H) = 400.6, 7.0–8.0 (m, Ph)	isomer **7a**: −50.7 (s), −16.8 (s) isomer **7b**: −49.6 (d), −49.7 (d), J(P—P) = 3 isomer **7c**: **58**.3 (s), −20.6 (s)		

[a] Chemical shifts (δ) in ppm, coupling constants in Hz. [b] Chemical shifts positive to high frequency of 85% H_3PO_4 (external). [c] Measured in CD_2Cl_2. [d] Measured in $CD_3C_6D_5$. [e] Measured in $CDCl_3$. [f] −50 °C. [g] 70 °C. [h] 21 °C.

ligand by the Me_3N formed upon CO oxidation, thus catalyzing the formation of hydrido- and phosphido-bridged species.

Compound **6** is extremely air sensitive, and the purification procedure has to be fast to allow its isolation; however, it can be kept even in solution under an atmosphere of argon or CO for several days. It is also stable if heated in toluene at 40 °C under an O_2-free argon atmosphere or under a CO atmosphere for 48 and 6 h, respectively. Compounds **6** and **7** have been characterized by spectroscopic methods, as shown in Table II, and **6** has also been characterized by an X-ray diffraction study.

Compound **7** is present in solution in the form of three isomers in an approximate ratio of 16:4:1. Only absorptions characteristic of terminal CO ligands are observed in the ν_{CO} region of the IR spectrum of **6**, suggesting interaction of the acetylene moiety of the Ph_2PCCPh ligand with the metal frame. The ^1H NMR spectrum of **6**, except for the phenyl resonances, shows a doublet of doublets at δ −11.15, J(H-P) 90.0 and 22.8 Hz, attributed to a metal hydride, while the ^{31}P NMR spectrum exhibits two doublets at δ −29.8 and −2.32, J(P-P) 43 Hz, typical of coordinated phosphines and of phosphido ligands bound to iridium atoms that do not interact,[22] a proposal that has been confirmed by the X-ray analysis study.

Crystal Structures of Complexes 4 and 6. The molecular structure of **4** and the atomic labeling scheme are shown in Figure 1. Atomic coordinates and selected bond lengths and angles are shown in Tables III and IV, respectively. The molecule lies in a general position in the unit cell. The metal framework consists of a tetrahedron, with two elongated edges [Ir(1)–Ir(3) 3.180(3) and Ir(1)–Ir(2) 2.976(3) Å], which are spanned by the two 3-electron donor phosphido bridges. The remaining Ir–Ir distances fall in the range 2.696(3)–2.861(3) Å, commonly observed in a substituted Ir_4 carbonyl clusters. The phenylacetylene ligand is bound to the cluster in the μ_3-η^2-$\|$ fashion commonly observed in trimetallic clusters. The ligand formally contributes 4 electrons to the cluster, *via* two σ-interactions with Ir(2) and Ir(4) and one π-interaction with Ir(3). The C–C(alkyne) bond distance [1.51(6) Å] is close to the average values in alkanes, but longer than the distances reported for acetylene ligands capping cluster triangular faces (1.33–1.4).[23] However, the quality of diffraction data in **4** does not allow a confident discussion of these structural parameters.

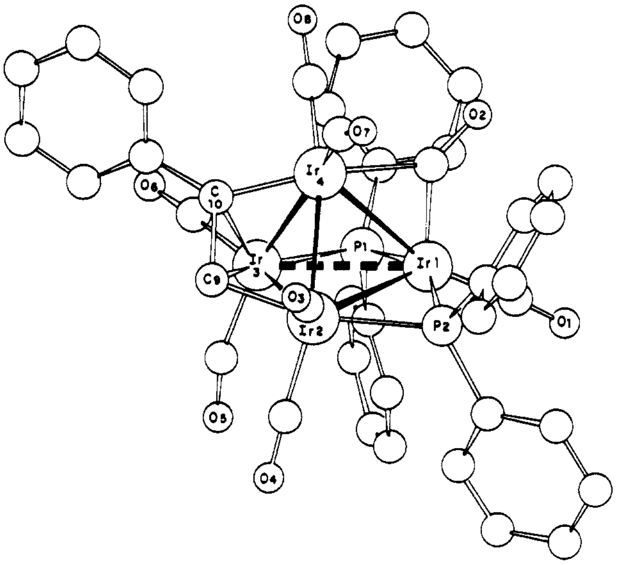

Figure 1. Molecular structure of $Ir_4(CO)_7(\mu\text{-}CO)(\mu\text{-}PPh_2)$-$(HCCPh)(\mu\text{-}PPh_2)_2$ (**4**) showing the atomic labeling scheme.

The molecule possesses seven terminal CO groups, distributed one on Ir(1) and two on each remaining Ir atom, and one bridging carbonyl, which asymmetrically spans the Ir(1)–Ir(4) edge [Ir(1)–C(2) 1.92(4) and Ir(4)–C(2) 2.15(5) Å]. To our knowledge, this is the first tetranuclear cluster bearing an acetylene ligand μ_3-η^2-bound to a triangular face. The most common mode of coordination of this ligand in such clusters is μ_4-η^2-bound to a M_4 butterfly,[24] although acetylene μ_2-η^2- and μ_4-η^2-bound modes to a M_4 square have been found in $Ir_4(CO)_8\{\mu_2\text{-}\eta^3\text{-}MeCO_2)_2C_2\}_2\{(\mu_4\text{-}\eta^2\text{-}MeCO_2)_2C_2\}_2$.[25]

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Table III. Fractional Atomic Coordinates for 4

atom	*x*	*y*	*z*
Ir(1)	0.5568(2)	0.1436(1)	0.6780(2)
Ir(2)	0.8482(2)	0.1043(1)	0.7648(2)
Ir(3)	0.8011(2)	0.1272(1)	0.5325(2)
Ir(4)	0.6190(2)	0.0786(1)	0.5890(2)
P(1)	0.5869(16)	0.1636(3)	0.5061(11)
P(2)	0.6654(13)	0.1259(3)	0.8605(11)
C(1)	0.4501(50)	0.1805(9)	0.7225(41)
O(1)	0.3961(47)	0.2058(8)	0.7416(37)
C(2)	0.4214(52)	0.1068(11)	0.6110(38)
O(2)	0.2802(47)	0.1036(11)	0.5846(35)
C(3)	0.8869(96)	0.0654(14)	0.8602(62)
O(3)	0.9197(56)	0.0406(9)	0.9133(41)
C(4)	1.0264(52)	0.1295(16)	0.8352(59)
O(4)	1.1297(41)	0.1478(10)	0.8681(39)
C(5)	0.9705(43)	0.1575(11)	0.5654(47)
O(5)	1.0464(46)	0.1814(9)	0.5931(37)
C(6)	0.8018(63)	0.1239(15)	0.3762(20)
O(6)	0.8077(47)	0.1207(11)	0.2817(23)
C(7)	0.5790(73)	0.0390(11)	0.6661(50)
O(7)	0.5666(55)	0.0222(12)	0.7416(33)
C(8)	0.4880(51)	0.0683(13)	0.4445(26)
O(8)	0.4079(38)	0.0549(9)	0.3654(27)
C(9)	0.9403(53)	0.0850(12)	0.6421(40)
C(10)	0.8149(56)	0.0662(13)	0.5555(43)
C(12)	0.9736(37)	0.0561(8)	0.4078(33)
C(13)	1.0062(37)	0.0352(8)	0.3223(33)
C(14)	0.9250(37)	0.0047(8)	0.2917(33)
C(15)	0.8110(37)	−0.0049(8)	0.3467(33)
C(16)	0.7784(37)	0.0159(8)	0.4322(33)
C(11)	0.8597(37)	0.0465(8)	0.4628(33)
C(18)	0.6164(42)	0.2250(10)	0.3976(26)
C(19)	0.6641(42)	0.2589(10)	0.3929(26)
C(20)	0.7420(42)	0.2756(10)	0.4939(26)
C(21)	0.7722(42)	0.2584(10)	0.5996(26)
C(22)	0.7245(42)	0.2246(10)	0.6043(26)
C(17)	0.6466(42)	0.2078(10)	0.5033(26)
C(24)	0.4214(37)	0.1372(9)	0.2912(31)
C(25)	0.2888(37)	0.1330(9)	0.2013(31)
C(26)	0.1547(37)	0.1512(9)	0.2017(31)
C(27)	0.1534(37)	0.1738(9)	0.2920(31)
C(28)	0.2860(37)	0.1780(9)	0.3819(31)
C(23)	0.4200(37)	0.1597(9)	0.3815(31)
C(30)	0.6615(31)	0.0794(9)	1.0338(27)
C(31)	0.5970(31)	0.0542(9)	1.0897(27)
C(32)	0.4446(31)	0.0437(9)	1.0440(27)
C(33)	0.3567(31)	0.0585(9)	0.9424(27)
C(34)	0.4212(31)	0.0837(9)	0.8864(27)
C(29)	0.5737(31)	0.0942(9)	0.9322(27)
C(35)	0.7144(47)	0.1596(12)	0.9674(34)
C(36)	0.8094(47)	0.1858(12)	0.9458(34)
C(37)	0.8318(47)	0.2152(12)	1.0142(34)
C(38)	0.7591(47)	0.2184(12)	1.1042(34)
C(39)	0.6641(47)	0.1922(12)	1.1258(34)
C(40)	0.6417(47)	0.1628(12)	1.0574(34)

The molecular structure of **6** and the atomic labeling scheme are shown in Figure 2. Atomic coordinates and selected bond lengths and angles are given in Tables V and VI. The metal framework can be conveniently described either as a spiked triangle or as a flat butterfly [angle between Ir(1)—Ir(2)—Ir(4) and Ir(1)—Ir(2)—Ir(3) planes 17°] with an elongated edge [Ir(2)—Ir(3) 3.686(2) Å]. This long Ir—Ir edge is spanned by the 3-electron donor phosphido ligand. The phosphinoacetylene ligand interacts with all the iridium atoms, formally contributing a total of 6 electrons to the cluster *via* the 2-electron bond P(1)—Ir(3) and two σ- and one π-interactions from the acetylene system. Both the C—C bond length [C(22)—C(23) 1.33(4) Å] and the C(Ph)—C=C and C=C—P angles [128(3) and 130(2)°, respectively] indicate that the hybridization of the acetylene C atoms is essentially sp^2.

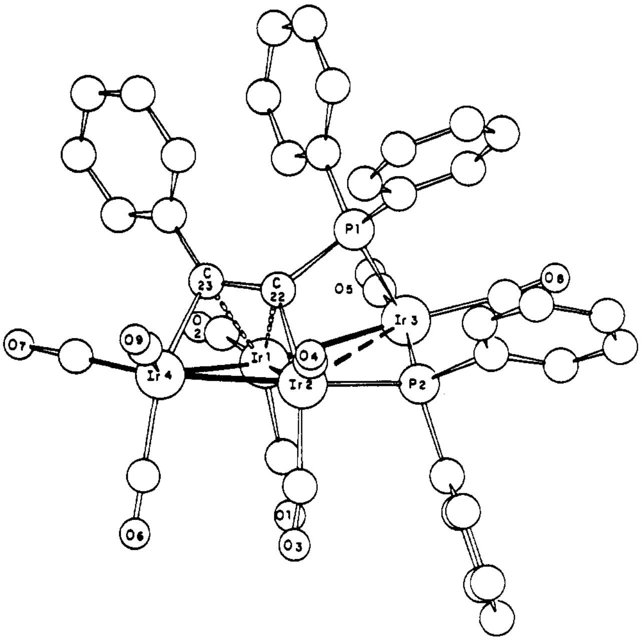

Figure 2. Molecular structure of $HIr_4(CO)_9(\mu_4\text{-}\eta^3\text{-}Ph_2PCCPh)(\mu\text{-}PPh_2)$ (**6**) showing the atomic labeling scheme.

Table IV. Relevant Bond Distances (Å) and Angles (deg) for 4

Ir(2)–Ir(1)	2.976(3)	Ir(3)–Ir(2)	2.847(3)
Ir(3)–Ir(1)	3.180(3)	Ir(4)–Ir(2)	2.730(3)
Ir(4)–Ir(1)	2.861(3)	Ir(4)–Ir(3)	2.696(3)
Ir(1)–P(1)	2.28(1)	Ir(1)–P(2)	2.26(1)
Ir(3)–P(1)	2.34(1)	Ir(2)–P(2)	2.37(1)
P(1)–C(17)	1.81(4)	P(2)–C(29)	1.81(4)
P(1)–C(23)	1.83(3)	P(2)–C(35)	1.81(5)
Ir(1)–C(1)	1.88(4)	Ir(3)–C(5)	1.88(4)
Ir(1)–C(2)	1.92(4)	Ir(3)–C(6)	1.87(3)
Ir(4)–C(2)	2.15(5)	Ir(4)–C(7)	1.88(5)
Ir(2)–C(4)	1.88(5)	Ir(4)–C(8)	1.87(3)
Ir(2)–C(4)	1.88(4)		
C(1)–O(1)	1.15(5)	C(5)–O(5)	1.15(5)
C(2)–O(2)	1.23(6)	C(6)–O(6)	1.15(4)
C(3)–O(3)	1.15(7)	C(7)–O(7)	1.15(7)
C(4)–O(4)	1.16(6)	C(8)–O(8)	1.16(5)
Ir(2)–C(9)	2.00(5)	Ir(4)–C(10)	1.95(5)
Ir(3)–C(9)	2.27(4)	C(9)–C(10)	1.51(6)
Ir(4)–C(9)	2.79(5)	C(10)–C(11)	1.48(7)
Ir(3)–C(10)	2.40(5)		
O(1)–C(1)–Ir(1)	171(4)	O(5)–C(5)–Ir(3)	162(4)
O(2)–C(2)–Ir(1)	133(4)	O(6)–C(6)–Ir(3)	177(5)
O(2)–C(2)–Ir(4)	138(4)	O(7)–C(7)–Ir(4)	158(5)
O(3)–C(3)–Ir(2)	174(8)	O(8)–C(8)–Ir(4)	165(4)
O(4)–C(4)–Ir(2)	172(5)		
Ir(3)–P(1)–Ir(1)	87.1(4)	Ir(2)–P(2)–Ir(1)	79.9(5)

The molecule possesses nine terminal CO groups, distributed three on the wing-tip Ir(4) atom, which is σ-interacting with the acetylene ligand, and two on each remaining Ir atom. The hydride ligand is very likely bound in a terminal fashion to the Ir(3) atom, on which a free coordination site is available (see Figure 3). Altogether **6** is electron precise and can be seen as derived from a 60-electron tetrahedral cluster by addition of two electron pairs to the cluster orbitals and consequent "opening up" of two edges.

Compound **6** represents the second example of a phosphinoacetylene acting as a 6-electron donor to a carbonyl cluster, in which the bridged metal atoms are all linked by M—M bonds. In the case of the species

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Table V. Fractional Atomic Coordinates for 6

atom	*x*	*y*	*z*
Ir(1)	0.67016(10)	0.20950(6)	0.17430(8)
Ir(2)	0.45943(10)	0.21693(6)	0.19950(8)
Ir(3)	0.66605(10)	0.36010(6)	0.18210(8)
Ir(4)	0.53169(11)	0.09380(6)	0.14505(8)
P(1)	0.5369(7)	0.3283(4)	0.0741(5)
P(2)	0.5146(6)	0.3328(4)	0.2418(5)
C(1)	0.7406(24)	0.1995(16)	0.2794(20)
O(1)	0.7676(26)	0.1867(15)	0.3344(16)
C(2)	0.8077(25)	0.1943(15)	0.1396(22)
O(2)	0.8945(22)	0.1835(13)	0.1245(17)
C(3)	0.4739(35)	0.1791(16)	0.2969(24)
O(3)	0.4812(20)	0.1542(12)	0.3506(13)
C(4)	0.3057(34)	0.2158(13)	0.1769(17)
O(4)	0.2017(19)	0.2086(12)	0.1649(14)
C(5)	0.8070(29)	0.3593(17)	0.1501(22)
O(5)	0.8924(21)	0.3641(12)	0.1332(17)
C(6)	0.5624(22)	0.0427(16)	0.2437(20)
O(6)	0.5809(24)	0.0151(13)	0.2940(16)
C(7)	0.6070(30)	0.0236(16)	0.0983(21)
O(7)	0.6527(28)	−0.0220(12)	0.0722(19)
C(8)	0.6423(29)	0.4586(20)	0.1890(26)
O(8)	0.6497(19)	0.5189(12)	0.1930(16)
C(9)	0.3830(36)	0.0730(19)	0.1125(24)
O(9)	0.2870(25)	0.0569(12)	0.0936(17)
C(22)	0.5182(18)	0.2346(12)	0.1009(13)
C(23)	0.5469(25)	0.1739(17)	0.0715(23)
C(11)	0.3942(13)	0.4460(8)	0.0490(11)
C(12)	0.2896(13)	0.4798(8)	0.0235(11)
C(13)	0.1914(13)	0.4393(8)	−0.0015(11)
C(14)	0.1978(13)	0.3650(8)	−0.0009(11)
C(15)	0.3025(13)	0.3312(8)	0.0246(11)
C(10)	0.4006(13)	0.3717(8)	0.0496(11)
C(17)	0.5241(14)	0.3597(10)	−0.0720(14)
C(18)	0.5647(14)	0.3613(10)	−0.1375(14)
C(19)	0.6755(14)	0.3374(10)	−0.1400(14)
C(20)	0.7457(14)	0.3119(10)	−0.0770(14)
C(21)	0.7051(14)	0.3103(10)	−0.0115(14)
C(16)	0.5943(14)	0.3342(10)	−0.0090(14)
C(25)	0.6642(15)	0.1242(10)	−0.0173(12)
C(26)	0.6764(15)	0.1105(10)	−0.0888(12)
C(27)	0.5934(15)	0.1346(10)	−0.1466(12)
C(28)	0.4981(15)	0.1723(10)	−0.1328(12)
C(29)	0.4829(15)	0.1860(10)	−0.0613(12)
C(24)	0.5690(15)	0.1619(10)	−0.0035(12)
C(31)	0.4295(14)	0.4657(10)	0.2719(12)
C(32)	0.3470(14)	0.5191(10)	0.2699(12)
C(33)	0.2357(14)	0.5084(10)	0.2313(12)
C(34)	0.2070(14)	0.4442(10)	0.1947(12)
C(35)	0.2896(14)	0.3907(10)	0.1967(12)
C(30)	0.4008(14)	0.4015(10)	0.2353(12)
C(37)	0.6607(14)	0.3396(9)	0.3829(13)
C(38)	0.6759(14)	0.3399(9)	0.4587(13)
C(39)	0.5812(14)	0.3330(9)	0.4928(13)
C(40)	0.4712(14)	0.3257(9)	0.4511(13)
C(41)	0.4560(14)	0.3254(9)	0.3753(13)
C(36)	0.5507(14)	0.3324(9)	0.3412(13)

$Ru_4(CO)_{10}(\mu_4\text{-}PPh)(Ph_2PCCPh)$, obtained from the thermal decomposition of $Ru_3(CO)_{11}(Ph_2PC{\equiv}CPPh_2)$,[26] the μ_4-η^3 ligand interacts with the Ru_4 square metal frame, also capped by the phosphido fragment. In two instances this ligand has been shown to bridge two independent metal fragments: in $(\eta^5\text{-}C_5H_5)NiOs_3(\mu\text{-}H)_3(CO)_8\{(Ph_2PC_2\text{-}Pr^i)Co_2(CO)_6\}$[7] and in $(CO)_4Fe(PPh_2C_2Bu^t)Fe(CO)_4$.[5b]

Fluxional Behavior of Compound 4. The ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra at room temperature show the presence of two closely related isomers in approximately the intensity ratio 1:2. The ^1H NMR spectrum exhibits, besides the multiplet due to the phenyl protons, two singlets due to the acetylene hydrogen, at δ 9.7 for the minor isomer and at δ 7.8 for the major isomer; the latter signal is hidden under the signals of the phenyl protons, but at 70 °C in $C_6D_5CD_3$ it is shifted and appears at δ 7.52, with the minor isomer at δ 9.37. These signals exchange at 82 °C, and this was demonstrated using magnetization transfer; *vide infra*.

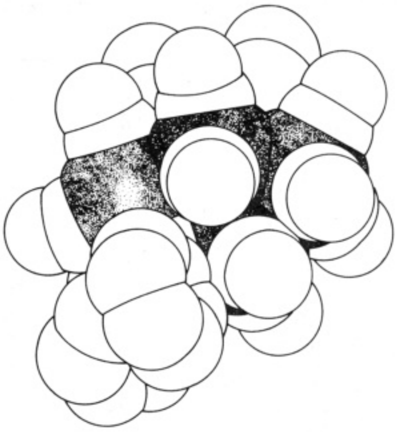

Figure 3. Space filling diagram of **6** showing the free coordination site on Ir(3).

Table VI. Relevant Bond Distances (Å) and Angles (deg) for 6

Ir(2)–Ir(1)	2.627(2)	Ir(3)–Ir(2)	3.686(2)
Ir(3)–Ir(1)	2.828(2)	Ir(4)–Ir(2)	2.723(2)
Ir(4)–Ir(1)	2.713(2)		
P(1)–Ir(1)	2.141(8)	P(2)–Ir(2)	2.361(7)
P(1)–Ir(3)	2.373(9)	P(2)–Ir(3)	2.337(9)
Ir(1)–C(1)	2.00(4)	Ir(4)–C(6)	2.05(4)
Ir(1)–C(2)	1.88(3)	Ir(4)–C(7)	1.89(4)
Ir(2)–C(3)	1.93(4)	Ir(3)–C(7)	1.89(4)
Ir(2)–C(4)	1.79(4)	Ir(4)–C(9)	1.80(4)
Ir(3)–C(5)	1.87(3)		
C(1)–O(1)	1.05(4)	C(6)–O(6)	1.06(3)
C(2)–O(2)	1.13(4)	C(7)–O(7)	1.17(4)
C(3)–O(3)	1.10(4)	C(8)–O(8)	1.14(4)
C(4)–O(4)	1.22(4)	C(9)–O(9)	1.17(4)
C(5)–O(5)	1.12(3)		
P(1)–C(10)	1.79(2)	P(2)–C(30)	1.85(2)
P(1)–C(16)	1.81(3)	P(2)–C(36)	1.83(3)
P(1)–C(22)	1.85(2)		
Ir(1)–C(22)	2.11(3)	Ir(4)–C(23)	2.07(4)
Ir(2)–C(22)	2.11(2)	C(22)–C(23)	1.33(4)
Ir(4)···C(22)	2.76(2)	C(23)–C(24)	1.49(5)
Ir(1)–C(23)	2.29(4)		
O(1)–C(1)–Ir(1)	170(3)	O(6)–C(6)–Ir(4)	178(2)
O(2)–C(2)–Ir(1)	174(3)	O(7)–C(7)–Ir(4)	177(3)
O(3)–C(3)–Ir(2)	176(3)	O(8)–C(8)–Ir(3)	167(3)
O(4)–C(4)–Ir(2)	174(2)	O(9)–C(9)–Ir(4)	177(3)
O(5)–C(5)–Ir(3)	175(3)		
Ir(3)–P(1)–Ir(1)	59.8(2)	Ir(3)–P(2)–Ir(2)	103.3(3)

The ^{13}C NMR spectrum of the ^{13}CO-enriched material shows two sets of only five carbonyl signals in the ratio 1:1:2:2:2, as shown in Table II and Figure 4, and the ^{31}P NMR spectrum exhibits only one resonance for each isomer. These data indicate that both isomers are fluxional and that this process leads to a time averaged plane of symmetry in the molecule, which results in the observation of only five carbonyls and of an average signal for the two μ-PPh_2 ligands for each isomer at room temperature. The ^{31}P NMR spectra at −81 and 104 °C are shown in Figure 5. At −81 °C, the minor isomer gives very broad ^{31}P NMR signals at *ca.* δ 54 and 1, with a line width of 250 Hz, corresponding to $\Delta G^{\ddagger}_{192} = 9.0$ kcal mol^{-1}, and on cooling to *ca.* −104 °C, it sharpens to give broad doublets at δ 54

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[26] Daran, J. C.; Jeannin, Y.; Kristianson, O. *Organometallics* **1985**, *4*, 1882.

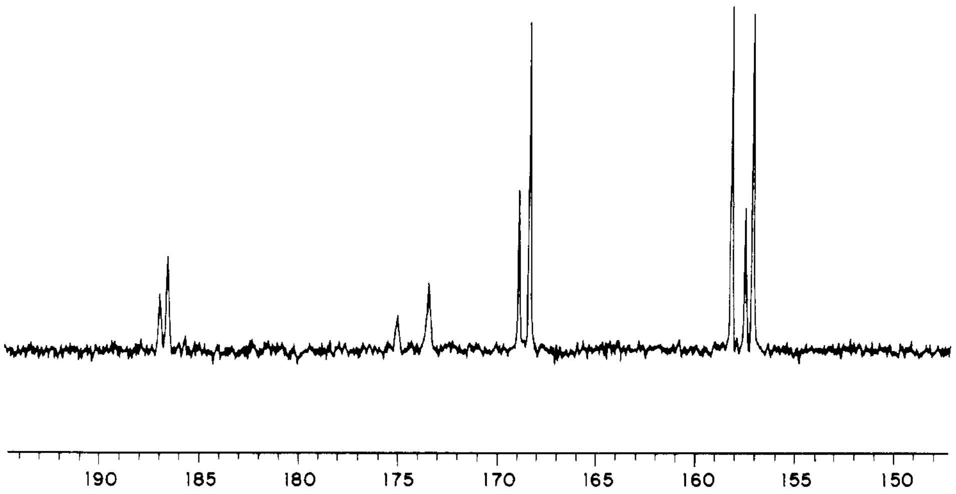

Figure 4. Carbonyl $^{13}C\{^1H\}$ NMR spectrum of $Ir_4(CO)_7(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}HCCPh)(\mu\text{-}PPh_2)_2$ (4) in CD_2Cl_2 at 21 °C.

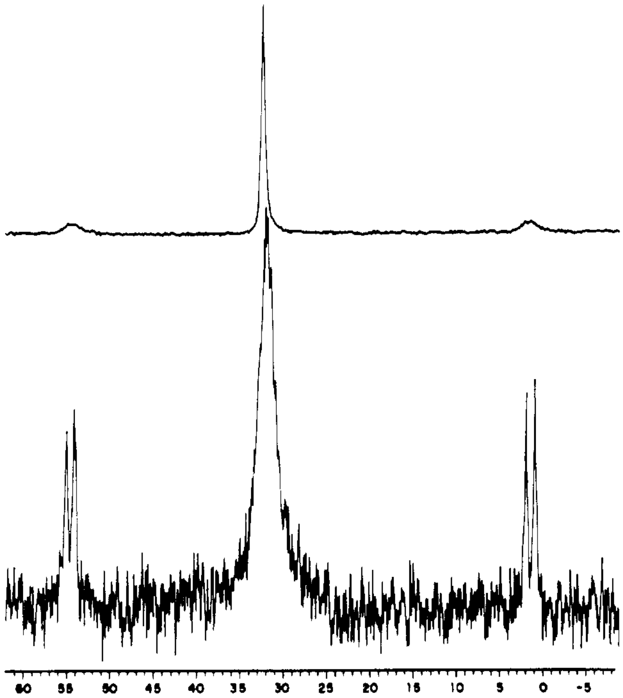

Figure 5. $^{31}P\{^1H\}$ NMR spectra of $Ir_4(CO)_7(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}HCCPh)(\mu\text{-}PPh_2)_2$ (4) in CD_2Cl_2 at −81 and −104 °C.

and 1, J(P–P) = 160 Hz. The major isomer gives a broad singlet at δ 32, with a line width of 325 Hz, at −104 °C, and considering the separation of the signals due to this isomer in the static form to be the same as for the minor isomer, then $\Delta G^{\ddagger}_{169}$ = 5.4 kcal mol^{-1}. This assumption seems valid, as we propose that the two isomers differ only with respect to the phenylacetylene orientation, as shown in Figure 6, and that the low energy dynamic process for both involves a *ca.* 60° rocking of this ligand on the Ir(2)Ir(3)Ir(4) face, with cleavage of only one Ir–C bond and concomitant elongation or shortening of the two Ir–Ir bonds bridged by the μ-PPh_2 groups. It is not possible to unambiguously determine which is the major isomer in solution. However, isomer **4b** appears to have more steric hindrance between the Ph and CO(8) than there is between the phenyl and CO(4) or CO(5) in **4a**, leading to a lower population, and this low energy dynamic process for **4b** would bring the phenyl close to CO(8) and CO(7), leading to a higher activation energy. It is therefore proposed that **4a** is the major isomer, and the minor isomer is **4b** found in the crystal structure. At 82 °C magnetization transfer shows interconversion of the major and minor isomers with $\Delta G^{\ddagger}$ = 21.8 kcal mol^{-1}. In this case the dynamic process observed seems to involve rotation of the acetylene on the triangular Ir(2)Ir(3)Ir(4) face, as shown in Figure 6. Evidence for such a process has been presented for $Os_3(C_6H_4)(CO)_7(PMe_3)_2$[27] and for a series of $(\mu\text{-}H)_2Os_3(alkyne)(CO)_9$ compounds.[28] Furthermore, on the basis of the calculations by Hoffmann et al.,[29] that have established the lowest energy paths for such a process in $(\mu\text{-}H)_2Os_3(\mu_3\text{-}\eta^2\text{-}HCCH)(CO)_9$, we propose that the equilibration of the two isomers of 4 involves 120° rotations (see Figure 6).

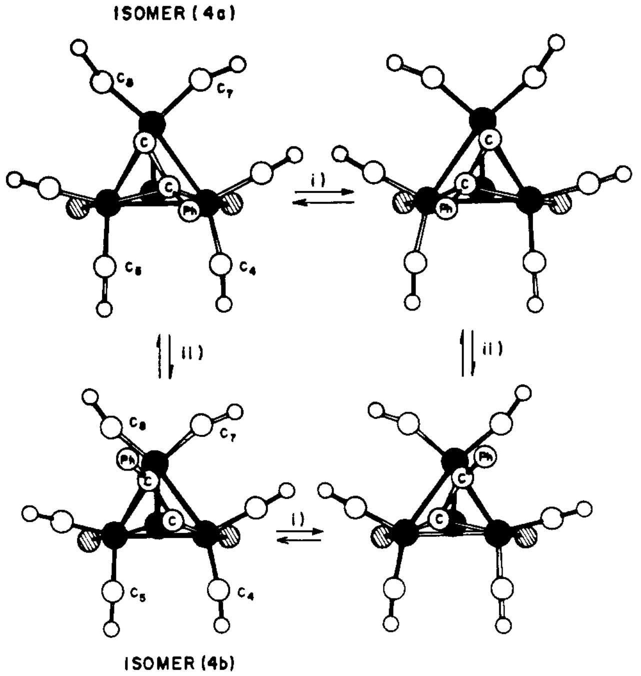

Figure 6. Dynamic processes observed for the two isomers, **4a** and **4b**, of $Ir_4(CO)_7(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}HCCPh)(\mu\text{-}PPh_2)_2$ (4): (i) low energy process involving ca. 60° rocking; (ii) high energy process involving 120° rotation.

Mechanisms of the Conversions of 2 into 4 and 6. Although P—C bond cleavage in phosphinoacetylene-

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[27] Deeming, A. J.; Kimber, R. E.; Underhill, M. *J. Chem. Soc., Dalton Trans.* **1973**, 2589.

[28] Deeming, A. J. *J. Organomet. Chem.* **1978**, *150*, 123.

[29] Schilling, B. E. R.; Hoffmann, R *Acta Chem. Scand., Ser B* **1979**, *33*, 231.

containing clusters is now a well-established phenomenon, this process is not usually observed under such mild conditions. Conversion of compound **2** into **4** can be envisaged as proceeding by (i) CO loss as a first step, (ii) transient interaction of the acetylene moiety with an electron poor Ir center, of the type observed in $(CO)_4Fe(Ph_2PC_2Bu^t)Fe(CO)_4$, which undergoes facile conversion into $Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^2\text{-}C_2Bu^t)$,[5b] (iii) probable formation of a reactive intermediate containing phosphido and acetylide ligands, and (iv) migration of the μ-hydride onto the α-carbon of the acetylide, thus generating the $\mu_3\text{-}\eta^2$-acetylene. Similar hydride migration has been observed in the reaction of $HRu_3(CO)_9(\mu\text{-}PPh_2)$ with $Ph_2PC{\equiv}CR$ (R = Ph, Bu^t, Pr^i),[3] while migration of the hydride ligand onto the β-carbon, generating the vinylidene ligand, has been shown to occur in the reaction of the anionic cluster $[HFe_3(CO)_{11}]^-$ with $Ph_2PC{\equiv}CCMe_3$.[12] It must be pointed out that several stable hydrido alkynyl species such as $(\mu\text{-}H)M_3(\mu_3\text{-}\eta^2\text{-}CCR)(CO)_9$ (M = Os,[30] Ru[31]) are known and do not show any tendency to convert to alkyne or vinylidene species, and therefore it may be the presence of the phosphido bridging ligands that somehow promote hydride migration in the case of the phosphinoalkyne-derived clusters.

Under more forcing conditions, it is evident that alternative pathways become available, both for the formation of **4**, as testified by the isolation of at least four compounds that undergo conversion into **4**, and for the production of different species, albeit in small yields, such as **5e** and **6**. The formation of **6** may be seen as resulting from the alternative cleavage of an Ir–Ir bond, rather than CO loss, which allows a type of interaction of the phosphinoacetylene ligand with all Ir atoms, similar to what was previously observed in $(\eta^5\text{-}C_5H_5)NiOs_3(\mu\text{-}H)_3(CO)_8\{(Ph_2PC_2Pr^i)Co_2(CO)_6\}$[7] and $Ru_4(CO)_{10}(\mu_4\text{-}PPh)(Ph_2PCCPh)$,[26] whose phosphinoalkyne P–C bond cleavages have unfortunately not been investigated yet. Our results indicate that rehybridization from P–C(sp) to P–C(sp^2), as a result of the interaction of the acetylene system with the metal frame, reduces drastically the lability of the P–C bond, and therefore rules out intermediates containing the Ph_2PCCPh ligand bound in such a way in the formation of **4**.

The conversion of compound **7** into **4** suggests that oxidative addition of the $Ph_2PC{\equiv}CPh$ ligand in **7** occurs before or concomitantly with that of the PPh_2H ligand, as compound **2** was not detected in the reaction.

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Supplementary Material Available: Tables of bond distances and angles for **4** and **6** (30 pages). Ordering information is given on any current masthead page.

OM920602U

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