Chemistry of Tetrairidium Carbonyl Clusters. Part 1. Synthesis, Chemical Characterization, and Nuclear Magnetic Resonance Study of Mono- and Di-substituted Phosphine Derivatives. X-Ray Crystal Structure Determination of the Diaxial Isomer of [Ir$_4$(CO)$_7$(μ-CO)$_3$(Me$_2$PCH$_2$CH$_2$PMe$_2$)]†

Renzo Ros * **and Alberto Scrivanti**
Istituto di Chimica Industriale dell'Universita' e Centro di Chimica Metallorganica del C.N.R., Via Marzolo 9, 35131 Padova, Italy
Vincenzo G. Albano * **and Dario Braga**
Istituto Chimico 'G. Ciamician' dell'Universita', Via F. Selmi 2, 40126 Bologna, Italy
Luigi Garlaschelli
Dipartimento di Chimica Inorganica e Metallorganica, Universita' di Milano, Via Venezian 21, 20133 Milano, Italy

The reactions of the anionic cluster [NEt$_4$][Ir$_4$(CO)$_{11}$Br] with uni- and bi-dentate phosphines and arsines have been investigated. The bromide ligand is quantitatively displaced by 1 mol equivalent of phosphine or arsine at low temperature, the only complexes being formed under these mild conditions being the monosubstituted products [Ir$_4$(CO)$_{11}$L] (L = PPh$_3$, PPh$_2$Me, PPhMe$_2$, or AsPh$_3$), [Ir$_4$(CO)$_{11}$(L–L)] (L–L = trans-Ph$_2$PCH=CHPPh$_2$), and [(OC)$_{11}$Ir$_4$(L–L)Ir$_4$(CO)$_{11}$] [L–L = trans-Ph$_2$PCH=CHPPh$_2$ or Ph$_2$P(CH$_2$)$_n$PPh$_2$ (n = 3 or 4)]. Similar reactions with higher than stoicheiometric amounts of phosphine (L = PPh$_3$, PPh$_2$Me, or PPhMe$_2$) or diphosphine [L–L = Ph$_2$P(CH$_2$)$_n$PPh$_2$ (n = 1—4), Me$_2$P(CH$_2$)$_2$PMe$_2$, cis-Ph$_2$PCH=CHPPh$_2$, or o-Ph$_2$PCH$_2$C$_6$H$_4$-CH$_2$PPh$_2$] give in good yields the disubstituted compounds [Ir$_4$(CO)$_{10}$(L–L)] respectively. The stereochemical arrangements of the phosphine ligands and the dynamic processes occurring in solutions of these complexes are discussed on the basis of i.r. and n.m.r. data. The structure of the diaxial isomer of [Ir$_4$(CO)$_7$(μ-CO)$_3$(Me$_2$PCH$_2$CH$_2$PMe$_2$)] has been determined by X-ray diffraction. The complex crystallizes in the monoclinic space group $P2_1/c$, with cell constants a = 15.694(2), b = 10.403(2), c = 15.706(2) Å, β = 92.63(2)°, and Z = 4. The structure has been solved from 2 289 diffraction intensities collected by counter methods, and refined by least-squares calculations to R = 0.087 (R' = 0.091). The four iridium atoms define a tetrahedron with three bridging CO ligands around a triangular face. All remaining carbonyls are terminally bonded and the two P atoms of the Me$_2$PCH$_2$CH$_2$PMe$_2$ ligand are found in axial positions, generating a six-membered ring.

There is considerable current interest in the chemistry of metal carbonyl cluster compounds.[1-3] Among the most studied are tetranuclear complexes of iridium, with special interest in the stereochemical arrangement of the ligands,[4-8] fluxional processes in solution,[9-11] and kinetic studies of carbon monoxide substitution reactions.[11-15] It has been found that [Ir$_4$(CO)$_{12}$] requires elevated temperatures (80—120 °C) to promote carbonyl ligand substitution.[11-17] Several kinetic studies have pointed out the impossibility of isolating the mono- or di-substituted species by direct synthesis from [Ir$_4$-(CO)$_{12}$].[12 15] A 'co-operative' effect on the entering ligand (L) (L = phosphine, arsine, or isocyanide) has been invoked to explain the substantial progressive acceleration in the stepwise CO-subsitution processes [Ir$_4$(CO)$_{12}$] ⟶ [Ir$_4$(CO)$_{11}$L] ⟶ [Ir$_4$(CO)$_{10}$L$_2$] ⟶ [Ir$_4$(CO)$_9$L$_3$] ⟶ [Ir$_4$(CO)$_8$L$_4$]. Thus, only complexes [Ir$_4$(CO)$_9$L$_3$] and/or [Ir$_4$(CO)$_8$L$_4$], depending upon the bulkiness of the entering ligand, have easily been prepared.[1,12,16,17] The few examples of less substituted derivatives, [Ir$_4$(CO)$_{11}$L] and [Ir$_4$(CO)$_{10}$L$_2$], so far reported have been obtained by different routes such as

reduction of [Ir(CO)$_2$(H$_2$NC$_6$H$_4$Me-p)Cl] with metallic zinc in the presence of carbon monoxide and 0.25—0.5 equivalent of ligand (15—50% yields),[18] or from the reactions of [Ir$_4$H(CO)$_{11}$]$^-$ with ligands (60% yields).[19,20]

The availability of the more reactive anion [Ir$_4$(CO)$_{11}$-Br]$^-$ [21,22] has allowed the preparation of many tetranuclear substituted carbonyl complexes of iridium in a much easier way. In fact [Ir$_4$(CO)$_{11}$Br]$^-$ has been conveniently used in the synthesis of some monosubstituted species such as [Ir$_4$-(CO)$_{11}$(PF$_3$)][23] and [Ir$_4$(CO)$_{11}$(μ-SO$_2$)],[24] and of the mono- and di-olefin derivatives, [Ir$_4$(CO)$_{11}$(olefin)] and [Ir$_4$(CO)$_{10}$-(diolefin)].[24]

In this paper we describe the synthesis of a series of new substituted species such as [Ir$_4$(CO)$_{11}$L], [Ir$_4$(CO)$_{10}$L$_2$], [(OC)$_{11}$Ir$_4$(L–L)Ir$_4$(CO)$_{11}$], and [Ir$_4$(CO)$_{10}$(L–L)] [L = PPh$_3$, PPh$_2$Me, PPhMe$_2$, or AsPh$_3$; L–L = Ph$_2$P(CH$_2$)$_n$PPh$_2$, n = 1—4; cis-Ph$_2$PCH=CHPPh$_2$, trans-Ph$_2$PCH=CHPPh$_2$, Me$_2$PCH$_2$CH$_2$PMe$_2$, or o-Ph$_2$PCH$_2$C$_6$H$_4$CH$_2$PPh$_2$] via [Ir$_4$(CO)$_{11}$Br]$^-$. N.m.r. data on their structures in solution and the X-ray single-crystal structure determination of the diaxial isomer of the complex [Ir$_4$(CO)$_7$(μ-CO)$_3$(Me$_2$PCH$_2$CH$_2$-PMe$_2$)] are reported.

Results and Discussion

Reactions of [Ir$_4$(CO)$_{11}$Br]$^-$ *with Unidentate Phosphines and Arsines.*—The bromide ligand in [Ir$_4$(CO)$_{11}$Br]$^-$ is labile,
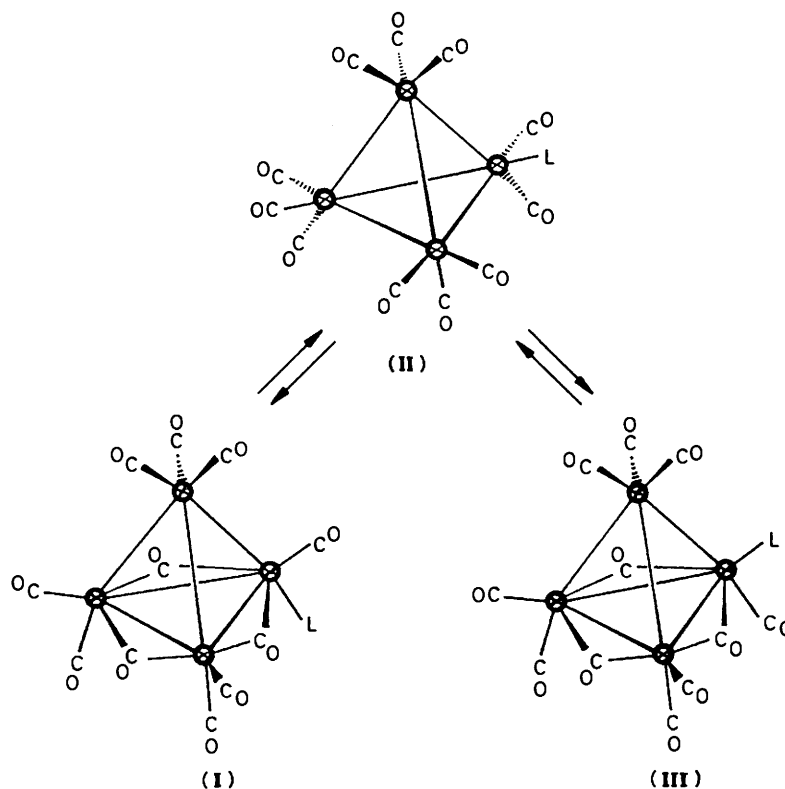
Figure 1. Ligand-site-exchange scheme for the (I) ⟷ (III) interconversion process in $[Ir_4(CO)_{11}L]$ complexes. The population ratio, (I):(III), obtained from ^{31}P n.m.r. data, at the lowest temperature increases with decreasing size of the phosphorus ligand in the sequence PPh_3 ($>50:1$) $> PPh_2Me$ (15:1) $> PEt_3^{27}$ (7:1) $> PPhMe_2$ (2:1) $> PMe_3^{11}$ (1:1)

being readily displaced by tertiary phosphines and triphenyl-arsine. Treatment of $[Ir_4(CO)_{11}Br]^-$ in dichloromethane or acetone solution with 1 mol equivalent of ligand at $-10\,^\circ C$ gives the monosubstituted derivatives $[Ir_4(CO)_{11}L]$ [L = PPh_3 (1), PPh_2Me (2), $PPhMe_2$ (3), or $AsPh_3$ (4)] in good yields ($>80\%$). The i.r. data, in the $\nu(CO)$ stretching region (Table 1), are in good agreement with other previously reported values for $[Ir_4(CO)_{11}(PR_3)]^{18}$ and $[Ir_4(CO)_{11}(AsPh_3)]^{14}$.

It is known that substitution of a CO ligand in $[Ir_4(CO)_{12}]^{25}$ with a good π-acceptor ligand, such as PF_3^{23} or isocyanide,^{6,11} leaves the overall T_d idealized symmetry unchanged, whereas substitution of ligands with poorer π-acceptor ability, such as phosphines,^{4,9,18} arsines,^{10,14} or olefins,^{24,26} shifts the ground-state structure to C_{3v} idealized symmetry with three edge-bridging carbonyl groups on a common face (basal plane) and the unique ligand bonded to an iridium atom of the basal plane. Thus for monosubstituted derivatives $[Ir_4(CO)_{11}L]$ two configurations are possible, (I) and (III), having the ligand L in axial and radial position respectively (Figure 1).

The ^{31}P n.m.r. spectrum of complex (3) in CD_2Cl_2 shows a single resonance at δ -41.5 p.p.m. at room temperature. On cooling the sharp singlet begins to broaden below $+10\,^\circ C$; at $-90\,^\circ C$ the signal splits into two sharp singlets at δ -24.2 and -45.3 p.p.m. with an intensity ratio of about 1:2. Similarly, $[Ir_4(CO)_{11}(PPh_2Me)]$ (2) displays a single ^{31}P resonance at δ -31.7 p.p.m. at room temperature, but on cooling two signals appear at δ -10.7 and -32.2 p.p.m. with an intensity ratio of 1:15. Instead complex (1) shows a single resonance at δ -12.8 p.p.m. which is unchanged over a similar temperature range (Table 2). These data suggest that compounds (2) and (3) exist in solution as a mixture of axial (I) and radial (III) isomers which interconvert rapidly at room temperature; for the

analogous PPh_3 derivative there is evidence for only the axial isomer. The assignment of the lower-field resonance to the radial rather than to the axial ligand is in agreement with the generally observed trend of ^{31}P n.m.r. signals displayed by phosphine derivatives $[Ir_4(CO)_{12-n}L_n]$ ($n = 1$—4) (see Tables 2 and 3 and related discussion). A similar dynamic behaviour was observed for $[Ir_4(CO)_{11}(PMe_3)]$ and $[Ir_4(CO)_{11}(PPh_2Me)]$, but detailed spectroscopic data were not reported.^{9,11} Recently, a more detailed ^{31}P and ^{13}C n.m.r. study on $[Ir_4(CO)_{11}(PEt_3)]^{27}$ in CD_2Cl_2 established that also for this complex the two interconverting radial and axial isomers may be distinguished at low temperature ($-90\,^\circ C$) with a population ratio of 1:7 respectively. Moreover a low-temperature ^{13}C n.m.r. study,^{27} using selective 180° pulses generated by the DANTE pulse sequence, was rationalized according to a Cotton merry-go-round mechanism.^{28,29} Such a mechanism involving two distinct low-energy processes (I) ⇌ (II) and (II) ⇌ (III) for carbonyl scrambling provided an explanation for the interconversion of (I) and (III) for $[Ir_4(CO)_{11}(PEt_3)]^{27}$ and $[Ir_4(CO)_{11}(PPh_2Me)]$.^{9}

Examination of the relative population ratios for (I):(III) of the two isomers in $[Ir_4(CO)_{11}L]$, by integration of the respective signals in the low-temperature ^{31}P n.m.r. spectra, reveals that they decrease in the order $PPh_3 > PPh_2Me > PEt_3 > PPhMe_2 > PMe_3$, following the decrease of the cone angle^{30} of the phosphine ligands (Figure 1). Thus these results indicate that the largest phosphines occupy preferentially the axial site, suggesting that for monosubstituted species the axial site is less crowded. Moreover the observation that the axial and radial isomers for the derivative with the less bulky phosphine PMe_3 possess the same population suggests that electronic factors are less important in determining the ligand

Table 1. Infrared data (cm^{-1}) of mono- and di-substituted derivatives of $[Ir_4(CO)_{12}]$

Complex		Solvent	v(CO) Terminal	Bridging
$[Ir_4(CO)_{11}L]$				
(1)	L = PPh$_3$[a]	Cyclohexane	2 087s, 2 069w, 2 052vs, 2 034s, 2 023s, 2 015s, 2 001m	1 888w, 1 854s, 1 829s
(2)	PPh$_2$Me	Cyclohexane	2 088s, 2 070w, 2 054vs, 2 033m, 2 024s, 2 014s, 2 001m	1 888w, 1 854s, 1 827s
(3)	PPhMe$_2$[a]	Cyclohexane	2 088s, 2 070w, 2 055vs, 2 030m, 2 023s, 2 014m	1 887w, 1 851s, 1 827s
(4)	AsPh$_3$[a]	Cyclohexane	2 093m, 2 089m, 2 052vs, 2 034s, 2 023s, 2 015s, 2 001m	1 888w, 1 854s, 1 827s
(5)	trans-Ph$_2$PCH=CHPPh$_2$	CHCl$_3$	2 085m, 2 054vs, 2 018vs, 1 998(sh)	1 885w, 1 842s, 1 825s
$[(OC)_{11}Ir_4(L-L)Ir_4(CO)_{11}]$				
(7)	L-L = trans-Ph$_2$PCH=CHPPh$_2$	CHCl$_3$	2 085m, 2 055vs, 2 018vs, 1 997(sh)	1 885w, 1 844s, 1 823s
(8)	Ph$_2$P(CH$_2$)$_3$PPh$_2$	thf[b]	2 087m, 2 056vs, 2 018vs, 1 996(sh)	1 883w, 1 844s, 1 819s
(9)	Ph$_2$P(CH$_2$)$_4$PPh$_2$	thf	2 086m, 2 056vs, 2 017vs, 1 997(sh)	1 883w, 1 884m, 1 818s
$[Ir_4(CO)_{10}(L-L)]$				
(10)	L-L = Ph$_2$PCH$_2$PPh$_2$[a]	thf	2 072s, 2 041s, 2 013vs, 1 982s	1 868w, 1 828s, 1 791s
(11)	Ph$_2$P(CH$_2$)$_2$PPh$_2$[a]	thf	2 067vs, 2 038vs, 2 007vs, 1 986w	1 868w, 1 831s, 1 787s
(12)	Me$_2$P(CH$_2$)$_2$PMe$_2$	thf	2 060s, 2 026vs, 2 008vs, 1 989vs	1 869vw, 1 835s, 1 795s
(13)	cis-Ph$_2$PCH=CHPPh$_2$	thf	2 067s, 2 036vs, 2 000vs, 1 993s	1 840m, 1 801m
(14)	Ph$_2$P(CH$_2$)$_3$PPh$_2$	thf	2 062s, 2 036vs, 2 005s, 1 982s	1 870w, 1 839s, 1 785s
(15)	Ph$_2$P(CH$_2$)$_4$PPh$_2$	thf	2 065s, 2 036s, 2 004vs, 1 980m	1 870w, 1 838s, 1 788s
(16)	o-Ph$_2$PCH$_2$C$_6$H$_4$CH$_2$PPh$_2$	thf	2 066vs, 2 037vs, 2 010vs, 1 996(sh), 1 983(sh)	1 871w, 1 833s, 1 802s
$[Ir_4(CO)_{10}L_2]$				
(17)	L = PPh$_3$[a]	Cyclohexane	2 065s, 2 040vs, 2 011vs, 1 995vs, 1 981(sh)	1 860w, 1 820m, 1 791s
(18)	PPh$_2$Me	Cyclohexane	2 066vs, 2 040vs, 2 010vs, 2 003vs, 1 999(sh), 1 990(sh)	1 870w, 1 827s, 1 798s
(19)	PPhMe$_2$[a]	Cyclohexane	2 064s, 2 037vs, 2 013(sh), 2 000vs, 1 979(sh)	1 864w, 1 829s, 1 793s

[a] Data in good agreement with the reported values: for complexes (1), (3), (11), (17), and (19) in cyclohexane solution, ref. 18; for (4) in decane solution, ref. 14; for (10) in CH$_2$Cl$_2$, ref. 32. [b] Tetrahydrofuran.

co-ordination site so that the two sites of the Ir$_4$ unit seem to have equivalent acceptor requirements.

From the limiting low-temperature ^{31}P n.m.r. data, diagnostic values are obtained for the co-ordination chemical shifts Δ $(= \delta_{co-ord.} - \delta_{free})$ which are close to zero or slightly negative for axially co-ordinated phosphines, but largely positive (in the range 17—24 p.p.m.) for radially co-ordinated phosphines. These values are in good agreement with the co-ordination chemical shifts of di-, and tri-, and tetra-substituted derivatives $[Ir_4(CO)_{12-n}(PR_3)_n]$ $(n = 2-4)$ (see Table 3) in which at least an axial and a radial phosphine are simultaneously present in the same molecule, as established by X-ray structural analysis[4] and by low-temperature $^{13}C-\{^1H\}$ n.m.r. spectra.[9]

Reactions of $[Ir_4(CO)_{11}Br]^-$ with Bidentate Phosphines.— The complex $[Ir_4(CO)_{11}Br]^-$ is also an ideal starting material for selective monosubstitution reactions with bidentate phosphines. We describe here the isolation of derivatives in which the diphosphine (L-L) is bound in a unidentate manner in $[Ir_4(CO)_{11}(trans-Ph_2PCH=CHPPh_2)]$ (5) and as a bridging bidentate ligand in complexes $[(OC)_{11}Ir_4(L-L)Ir_4(CO)_{11}]$ [L-L = trans-Ph$_2$PCH=CHPPh$_2$ (7), Ph$_2$P(CH$_2$)$_n$PPh$_2$, n = 3 (8) or 4 (9)]. Interestingly complex (5), which was obtained by treating $[Ir_4(CO)_{11}Br]^-$ with an excess of trans-Ph$_2$PCH=CHPPh$_2$, can be considered as a model of the first intermediate in the subsitution reaction with diphosphines (see Scheme 1). Compound (5) is the only product of this type which can be isolated in the solid state. The microanalysis, molecular-weight determination, and ^{31}P spectroscopy are in accord with the assigned structure. The $^{31}P-\{^1H\}$ n.m.r. spectrum in CDCl$_3$

Scheme 1. Formation of diphosphine complexes from $[Ir_4(CO)_{11}Br]^-$. L-L = Ph$_2$P(CH$_2$)$_n$PPh$_2$ (n = 1—4), cis- or trans-Ph$_2$PCH=CHPPh$_2$, Me$_2$P(CH$_2$)$_2$PMe$_2$, or o-Ph$_2$PCH$_2$C$_6$H$_4$CH$_2$PPh$_2$. (i) $-Br^-$; (ii) $-Br^-$ + $[Ir_4(CO)_{11}Br]^-$; (iii) heat, $-CO$; (iv) heat, $-[Ir_4(CO)_{12}]$

(Table 2) showed two signals of equal intensities at δ -20.2 and -4.7 p.p.m. $[^3J(PP) = 9.8$ Hz] in the region expected for axially bonded (see later) and free PPh$_2$ groups respectively. Conclusive evidence that the signal at δ -4.7 p.p.m. is attributable to the unco-ordinated phosphorus comes from the oxidation reaction with H$_2$O$_2$; $[Ir_4(CO)_{11}\{trans-Ph_2PCH=CHP(O)Ph_2\}]$ (6) is quantitatively formed. The ^{31}P n.m.r. spectrum of (6) shows two doublets of equal intensity at δ 22.4 and -20.1 p.p.m. $[^3J(PP) = 43$ Hz] assignable to the P(O)Ph$_2$ and the PPh$_2$ groups respectively. The low-field chemical shift for the phosphine oxide in (6) is very similar to the value determined for the free ligand trans-Ph$_2$PCH=CHP(O)Ph$_2$ (δ 23.4 p.p.m., see Experimental section), and in

Table 2. ^{31}P N.m.r. data for phosphine derivatives of $[Ir_4(CO)_{12}]$

Cluster	Solvent	$\theta_c/°C$	$\delta(P)^a$	Configuration^b	Relative abundance
$[Ir_4(CO)_{11}L]$					
(1) L = PPh$_3$^{c}	CD$_2$Cl$_2$	30	-12.8 (P$_{ax}$)^d	(I)	
(2) PPh$_2$Me^c	CD$_2$Cl$_2$	30	-31.7 (P$_{ax}$ + P$_{rad}$)	(I) $\longleftrightarrow$ (III)	
		-90	$\{$ -32.2 (P$_{ax}$)	(I)	15
			$\{$ -10.7 (P$_{rad}$)	(III)	1
(3) PPhMe$_2$	CD$_2$Cl$_2$	30	-41.5 (P$_{ax}$ + P$_{rad}$)	(I) $\longleftrightarrow$ (III)	
		-90	$\{$ -45.3 (P$_{ax}$)	(I)	2
			$\{$ -24.2 (P$_{rad}$)	(III)	1
(5) trans-Ph$_2$PCH=CHPPh$_2$^{e}	CDCl$_3$	30	-20.2 (P$_{ax}$)^d	(I)	
(6) trans-Ph$_2$PCH=CHP(O)Ph$_2$^{f}	CDCl$_3$	30	-20.1 (P$_{ax}$)^d	(I)	
$[(OC)_{11}Ir_4(L-L)Ir_4(CO)_{11}]$					
(7) L–L = trans-Ph$_2$PCH=CHPPh$_2$	CDCl$_3$	30	-19.5 (P$_{ax}$)^d	(I)	
(8) Ph$_2$P(CH$_2$)$_3$PPh$_2$	CD$_2$Cl$_2$	-10	-18.2 (P$_{ax}$)^d	(I)	
(9) Ph$_2$P(CH$_2$)$_4$PPh$_2$	CD$_2$Cl$_2$	30	-14.7 (P$_{ax}$ + P$_{rad}$)	(I) $\longleftrightarrow$ (III)	
		-80	$\{$ -18.5 (P$_{ax}$)	(I)	8
			$\{$ 5.7 (P$_{rad}$)	(III)	1
$[Ir_4(CO)_{10}(L-L)]$					
(10) L–L = Ph$_2$PCH$_2$PPh$_2$	C$_6$D$_5$CD$_3$	11	-52.2 (P$_{ax}$)^d	(IV)	
(11) Ph$_2$P(CH$_2$)$_2$PPh$_2$	CD$_2$Cl$_2$	30	-16.2 (P$_{ax}$)	(IV) $\longleftrightarrow$ (IV$'$)	
		-80	$\{$ -17.6 (P$_{ax}$)	(IV)	(1:1)^g
			$\{$ -14.8 (P$_{ax}$)^g		
(12) Me$_2$P(CH$_2$)$_2$PMe$_2$	(CD$_3$)$_2$CO	30	-39.2 (P$_{ax}$)	(IV) $\longleftrightarrow$ (VI$'$)	3
			13.6 (P$_{ax}$ + P$_{rad}$)	(VI) $\longleftrightarrow$ (VI$'$)	2
		-95	-35.5 (P$_{ax}$)	(IV)	3
		-95	$\{$ 7.7 (P$_{ax}$)		
			$\{$ 25.2 (P$_{rad}$)	(VI)	2 (1:1)
(13) cis-Ph$_2$PCH=CHPPh$_2$	(CD$_3$)$_2$CO	30	-30.9 (P$_{ax}$)	(IV)	1
			31.2 (P$_{ax}$ + P$_{rad}$)	(VI) $\longleftrightarrow$ (VI$'$)	2
		-100	-27.3 (P$_{ax}$)	(IV)	1
		-100	$\{$ 21.7 (P$_{ax}$)		
			$\{$ 47.5 (P$_{rad}$)	(VI)	2 (1:1)
(14) Ph$_2$P(CH$_2$)$_3$PPh$_2$	CD$_2$Cl$_2$	30	-20.4 (P$_{ax}$)^a	(IV)	
(15) Ph$_2$P(CH$_2$)$_4$PPh$_2$	CD$_2$Cl$_2$	30	-21.1 (P$_{ax}$ + P$_{rad}$)	(VII) $\longleftrightarrow$ (VII$'$)	
	(CD$_3$)$_2$CO	-95	$\{$ -32.2 (P$_{ax}$)	(VII)	(1:1)
			$\{$ -7.4 (P$_{rad}$)^h		
(16) o-Ph$_2$PCH$_2$C$_6$H$_4$CH$_2$PPh$_2$	CD$_2$Cl$_2$	30	-19.5 (P$_{ax}$)	(IV)	
$[Ir_4(CO)_{10}L_2]$					
(17) L = PPh$_3$^{c}	CD$_2$Cl$_2$	-55	$\{$ -14.0 (P$_{ax}$)		
			$\{$ 18.9 (P$_{rad}$)^i	(VIII)	
(18) PPh$_2$Me^c	CD$_2$Cl$_2$	-30	$\{$ -28.8 (P$_{ax}$)	(VIII)	
			$\{$ -6.7 (P$_{rad}$)^j		
(19) PPhMe$_2$	CD$_2$Cl$_2$	-80	$\{$ -44.8 (P$_{ax}$)	(VIII)	
			$\{$ -26.2 (P$_{rad}$)^k		

^{a} ^{31}P-$\{^1$H$\}$ chemical shifts (δ) in p.p.m. relative to 85% H$_3$PO$_4$ (external), positive value, to high frequency. ^{b} As in Figures 1 and 2; (I) $\longleftrightarrow$ (III) indicates rapid interconversion of the two isomers (I) and (III). A prime indicates the same isomer with synchronous interchange of the phosphorus ligand from the axial to the radial position. ^{c} Ref. 9 reports δ -13.0 for (1), -31.5 for (2), -15.0 and 17.6 for (17), -28.2 and 5.7 p.p.m. for (18), but no spectroscopic conditions were quoted. ^{d} Identical resonances at lower temperatures. ^{e} The unco-ordinated phosphorus atom has δ -4.7 p.p.m. [d, ^3J(PP) = 9.8 Hz]. ^{f} Complex not isolated, see text; the unco-ordinated phosphine oxide group has δ 22.4 p.p.m. [d, ^3J(PP) = 43 Hz]. ^{g} The two signals with an intensity ratio 1:1 arise from the asymmetric arrangement of the diphosphine in the six-membered ring, see text. ^{h} ^3J(PP) = 3.7 Hz. ^{i} ^3J(PP) = 3.0 Hz. ^{j} ^3J(PP) = 2.2 Hz. ^{k} ^3J(PP) = 1.6 Hz.

the same region as previously reported values for some tertiary alkyldiarylphosphine oxides.[31]

Reactions of $[Ir_4(CO)_{11}Br]^-$ with the non-chelating diphosphine, trans-Ph$_2$PCH=CHPPh$_2$, or other diphosphines Ph$_2$P(CH$_2$)$_n$PPh$_2$ (n = 3 or 4) in 2:1 ratio at -10 °C in dichloromethane–methanol–acetone afford in good yield the complexes (7)—(9). Their formulation was confirmed by osmometric molecular-weight determination and on the basis of i.r. and ^{31}P n.m.r. spectroscopy. These compounds have solution i.r. spectra (Table 1) which are similar to those of (1)—(5), suggesting the same monosubstituted structural type. The presence of only one sharp resonance in the ^{31}P n.m.r. spectra

for compounds (7) and (8) and the values of their chemical shifts (see Table 2) clearly indicate that the diphosphine ligand is axially bridging two tetrahedral metal units. However compound (9) exhibits a dynamic behaviour of the type observed for (2) and (3). The ^{31}P n.m.r. resonance observed at δ -14.7 p.p.m. at room temperature splits at low temperature into two signals at δ 5.7 (P$_{radial}$) and -18.5 p.p.m. (P$_{axial}$) with an intensity ratio of 1:8. Compounds (7)—(9) are air stable in the solid state, while (8) and (9) disproportionate in solution on standing for some days at room temperature to insoluble $[Ir_4(CO)_{12}]$ and disubstituted derivatives $[Ir_4(CO)_{10}(L-L)]$ (14) and (15) respectively (Scheme 1).

(IV) diaxial bridging   (V) diradial bridging   (VI) axial - radial chelating

(VII) axial - radial bridging   (VIII) axial - radial unidentate phosphine
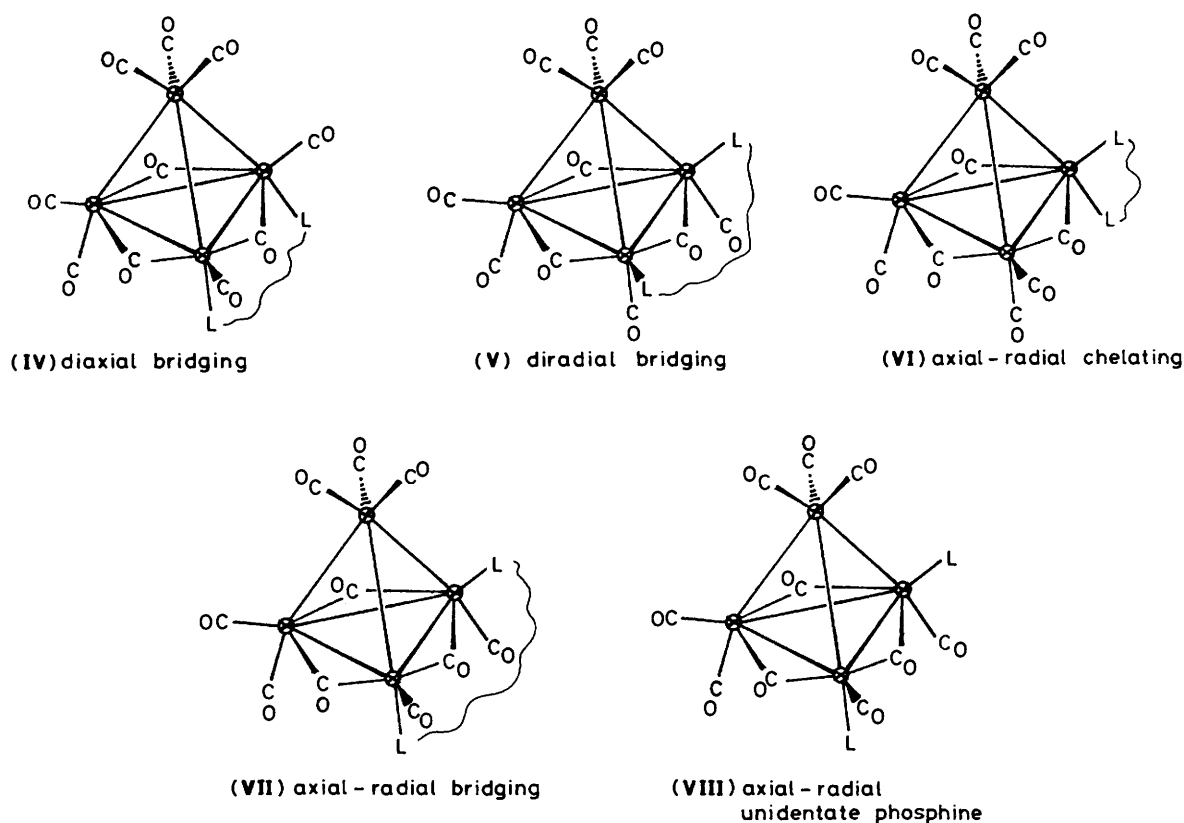
Figure 2. Possible arrangements of the ligands in disubstituted derivatives

Table 3. Lowest-temperature ^{31}P n.m.r. chemical shifts, $\delta,^a$ and co-ordination chemical shifts, Δ ($= \delta_{\text{co-ordinated}} - \delta_{\text{free ligand}}$), for mono-substituted derivatives of $[Ir_4(CO)_{12}]$

Cluster	$\theta_c/°C$	δ_{free}	δ_{ax}	δ_{rad}	Δ_{ax}	Δ_{rad}
$[Ir_4(CO)_{11}L]$						
(1) L = PPh₃	−55	−6.9	−12.2		−5.3	
(2) PPh₂Me	−90	−28.1	−32.2	−10.7	−4.1	17.4
(3) PPhMe₂	−90	−45.4	−45.3	−24.2	0.1	21.2
(5) trans-Ph₂PCH=CHPPh₂	15	−7.5	−20.2		−12.7	
(6) trans-Ph₂PCH=CHP(O)Ph₂	15	−5.6	−20.1		−14.5	
$[(OC)_{11}Ir_4(L-L)Ir_4(CO)_{11}]$						
(7) L-L = trans-Ph₂PCH=CHPPh₂	30	−7.5	−19.5		−12.0	
(8) Ph₂P(CH₂)₃PPh₂	−80	−19.6	−18.2		1.2	
(9) Ph₂P(CH₂)₄PPh₂	−80	−18.3	−18.5	5.7	−0.2	24.0
$[Ir_4(CO)_{10}L_2]^b$						
(17) L = PPh₃	−55	−6.9	−14.0	18.9	−7.1	25.8
(18) PPh₂Me	−30	−27.8	−28.8	−6.7	−1.0	21.1
(19) PPhMe₂	−80	−45.4	−44.8	−26.2	0.6	19.2
$[Ir_4(CO)_9(PPh_3)_3]^c$	—	−6.9	−17.4	20.0	−10.5	26.9
$[Ir_4(CO)_9(PPh_2Me)_3]^c$	—	−28.1	−25.0	−5.2	3.1	22.9
$[Ir_4(CO)_9(nbd)(PPh_3)]^d$	−50	−6.8	−20.2		−13.4	
$[Ir_4(CO)_9(nbd)(PPh_2Me)]^d$	−80	−28.1	−37.4	−8.9	−9.3	19.2
$[Ir_4(CO)_9(nbd)(PPhMe_2)]^d$	−90	−45.4	−51.5	−27.2	−6.1	18.2
$[Ir_4(CO)_8(PPh_2Me)_4]^{c,e}$	—	−28.1	−39.8	−7.4	−11.7	20.7

^{a} In CD_2Cl_2 solution except for complexes (5)—(7) in $CDCl_3$. ^{b} Configuration (VIII) (see Table 2). ^{c} Data from ref. 9, in which no spectroscopic conditions were reported. ^{d} Data from ref. 24 and unpublished works; for the PPh_2Me and $PPhMe_2$ derivatives, two isomers are present, having the phosphine ligand co-ordinated in an axial or a radial site to another iridium atom of the basal plane. ^{e} This cluster has an axial and two radial phosphines, while the fourth phosphine is co-ordinated in apical position ($\Delta_{ap} \leqslant -30$ p.p.m.).

Table 4. Low-temperature ^{31}P n.m.r. chemical shifts, δ, ^{a} co-ordination chemical shifts, Δ, and relative 'ring contribution,' Δ$_R$, ^{b} for disubstituted derivatives [Ir$_4$(CO)$_{10}$(diphosphine)]

Cluster	Configuration	δ$_{free}$^{c}	δ$_{ax}$	δ$_{rad}$	Δ$_{ax}$	Δ$_{rad}$	Δ$_R$
(10)	(IV)	−22.7	−52.2		−29.5		−28.5
(11)	(IV)	−14.3	−14.8		−0.5		0.5
			−17.6		−3.3		2.3
(12)	(IV)	−47.6	−35.5		12.1		13.1
	(VI)	−47.6	7.7	25.2	55.3	72.8	56.3, 51.7
(13)	(IV)	−23.1	−27.3		−4.2		3.2
	(VI)	−23.7	21.7	47.5	44.8	70.6	45.8, 49.5
(14)	(IV)	−17.3	−20.4		−3.1		−2.1
(15)	(VII)	−18.3	−32.2	−7.4	−13.9	10.9	−12.9, −10.2
(16)	(IV)	−13.9	−19.5		−5.6		−4.6
(18)	(VIII)	−27.8	−28.8	−6.7	−1.0^d	21.1^d	

^{a} Data from Table 2. ^{b} Δ$_R$ is the co-ordination chemical shift of a diphosphine complex minus the co-ordination chemical shift of an equivalent phosphorus in a non-chelated analogue, i.e. (18). ^{c} Data at the same temperature as δ$_{ax}$ and δ$_{rad}$. ^{d} Value of Δ used to calculate Δ$_R$.

Table 5. Fractional atomic co-ordinates with estimated standard deviations (e.s.d.s) in parentheses for complex (12)

Atom	x	y	z	Atom	x	y	z
Ir(1)	0.215 06(10)	0.075 81(16)	−0.050 99(10)	C(33)	0.338 2(20)	0.258 4(37)	−0.172 7(31)
Ir(2)	0.173 07(10)	−0.085 55(16)	−0.182 80(10)	O(33)	0.385 6(18)	0.334 6(29)	−0.146 4(23)
Ir(3)	0.256 70(11)	0.141 21(17)	−0.211 63(11)	C(41)	0.446 4(14)	−0.031 8(51)	−0.172 4(31)
Ir(4)	0.340 33(10)	−0.058 05(16)	−0.130 12(10)	O(41)	0.513 8(10)	−0.018 8(37)	−0.200 1(22)
P(1)	0.375 7(7)	−0.245 1(12)	−0.059 7(7)	C(1,2)	0.098 9(6)	0.040 5(30)	−0.114 8(18)
P(2)	0.130 8(7)	−0.268 6(11)	−0.115 5(7)	O(1,2)	0.023 8(6)	0.065 6(25)	−0.110 5(17)
C(11)	0.187 2(27)	0.240 5(14)	−0.019 6(20)	C(1,4)	0.345 6(5)	0.065 2(34)	−0.025 8(18)
O(11)	0.169 1(22)	0.347 2(12)	−0.005 3(20)	O(1,4)	0.402 2(17)	0.112 5(33)	0.018 8(19)
C(12)	0.193 7(33)	0.005 3(41)	0.053 3(13)	C(2,4)	0.282 4(4)	−0.165 9(24)	−0.225 7(14)
O(12)	0.178 1(27)	−0.044 1(34)	0.117 7(12)	O(2,4)	0.302 7(21)	−0.244 7(24)	−0.277 7(16)
C(21)	0.108 3(21)	−0.110 2(41)	−0.282 1(12)	C(1)	0.408 7(31)	−0.230 8(48)	0.054 7(27)
O(21)	0.071 2(18)	−0.122 0(34)	−0.348 1(11)	C(2)	0.462 8(32)	−0.335 2(48)	−0.103 4(31)
C(31)	0.158 4(15)	0.226 7(29)	−0.246 2(28)	C(3)	0.035 5(32)	−0.259 0(48)	−0.049 7(28)
O(31)	0.097 2(14)	0.287 9(31)	−0.262 9(25)	C(4)	0.109 7(30)	−0.410 0(44)	−0.188 5(28)
C(32)	0.304 7(23)	0.099 4(46)	−0.314 2(13)	C(5)	0.204 2(28)	−0.334 3(44)	−0.032 4(27)
O(32)	0.330 7(22)	0.071 8(36)	−0.379 7(12)	C(6)	0.292 9(28)	−0.366 5(43)	−0.061 7(29)
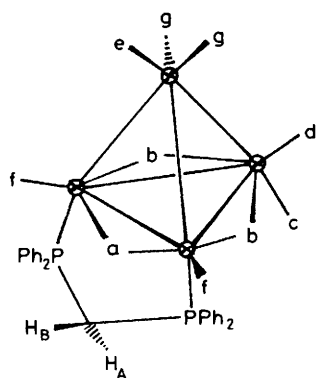
Figure 3. Proposed structure for [Ir$_4$(CO)$_{10}$(Ph$_2$PCH$_2$PPh$_2$)] (10). N.m.r.: ^{1}H (in CDCl$_3$ at 30 °C), δ(H$_A$) = 5.30, δ(H$_B$) = 2.82 p.p.m., J(H$_A$H$_B$) = 14.1, J(PH$_A$) = 10.7, J(PH$_B$) = 11.8 Hz; ^{13}C (in CD$_2$Cl$_2$ at −85 °C), 221.1 (1 C, a), 204.8 (2 C, b), 178.4 (2 C, f), 171.2 (1 C, d), 161.1 (1 C, e or c), 160.6 (1 C, c or e), 156.1 p.p.m. [t, 2 C, g, J(PC) = 17 Hz]

Attempts to prepare monosubstituted derivatives of types [Ir$_4$(CO)$_{11}$(L–L)] or [(OC)$_{11}$Ir$_4$(L–L)Ir$_4$(CO)$_{11}$] with other diphosphines were unsuccessful. Because of the better chelating properties, only the stable disubstituted derivatives [Ir$_4$(CO)$_{10}$-

(L–L)] [L–L = Ph$_2$P(CH$_2$)$_n$PPh$_2$, n = 1 (10) or 2 (11); Me$_2$P(CH$_2$)$_2$PMe$_2$ (12); cis-Ph$_2$PCH=CHPPh$_2$ (13); or o-Ph$_2$PCH$_2$C$_6$H$_4$CH$_2$PPh$_2$ (16)] were obtained (Scheme 1). The i.r. spectra (Table 1) of diphosphine complexes (10)—(16) are in reasonable agreement with those of the phosphine complexes [Ir$_4$(CO)$_{10}$L$_2$] [L = PPh$_3$ (17), PPh$_2$Me (18), or PPhMe$_2$ (19)] and very similar to the previously reported spectra of [Ir$_4$(CO)$_{10}$(PR$_3$)$_2$]^{18} and [Ir$_4$(CO)$_{10}$(L–L)] (L–L = Ph$_2$-PCH$_2$CH$_2$PPh$_2$^{18} or o-Me$_2$AsC$_6$H$_4$AsMe$_2$^{10}). Several terminal bands and three bridging ν(CO) bands are observed for all these compounds, indicating a similar structural type. The most important difference in the i.r. spectra between the mono- and di-substituted derivatives is the lowering (ca. 20 cm^{-1}) of all the values of ν(CO) on going from [Ir$_4$(CO)$_{11}$L] to [Ir$_4$(CO)$_{10}$L$_2$] (L = unidentate phosphine or $\frac{1}{2}$ bidentate phosphine), regardless of their arrangements on the different sites of the basal iridium atoms (Figure 2). A possible cause of this effect may be that the addition of a second non-carbonyl ligand increases the electron density on the whole Ir$_4$ unit thereby increasing the π-back donation onto the remaining CO groups. Similar trends of progressive shifts to lower carbonyl stretching frequencies are observed on going from [M$_4$(CO)$_{10}$L$_2$] to [M$_4$(CO)$_9$L$_3$] and from these to [M$_4$(CO)$_8$L$_4$] (M = Ir^{14,23} or Rh^{32}) where L is a phosphorus donor ligand.

The stereochemistry and evidence for fluxional behaviour via CO scrambling of the disubstituted complexes are readily deducible from variable-temperature ^{31}P n.m.r. data, which are

Table 6. Bond distances (Å) and relevant angles (°) with e.s.d.s in parentheses for $[Ir_4(CO)_7(\mu\text{-}CO)_3(Me_2PCH_2CH_2PMe_2)]$

Ir(1)–Ir(2)	2.723(2)	P(1)–C(6)	1.81(4)	Ir(2)–C(21)	1.84(2)	Ir(1)–C(1,2)	2.07(2)
Ir(1)–Ir(3)	2.722(3)	P(2)–C(3)	1.86(5)	C(21)–O(21)	1.17(3)	Ir(2)–C(1,2)	2.08(2)
Ir(1)–Ir(4)	2.752(2)	P(2)–C(4)	1.86(5)	Ir(3)–C(31)	1.84(3)	C(1,2)–O(1,2)	1.21(2)
Ir(2)–Ir(3)	2.747(2)	P(2)–C(5)	1.83(4)	C(31)–O(31)	1.17(4)	Ir(1)–C(1,4)	2.07(1)
Ir(2)–Ir(4)	2.731(2)	C(5)–C(6)	1.52(5)	Ir(3)–C(32)	1.86(3)	Ir(4)–C(1,4)	2.08(2)
Ir(3)–Ir(4)	2.739(2)	Ir(1)–C(11)	1.84(2)	C(32)–O(32)	1.16(4)	C(1,4)–O(1,4)	1.21(4)
Ir(4)–P(1)	2.29(1)	C(11)–O(11)	1.17(2)	Ir(3)–C(33)	1.85(4)	Ir(2)–C(2,4)	2.05(1)
Ir(2)–P(2)	2.29(1)	Ir(1)–C(12)	1.84(3)	C(33)–O(33)	1.15(5)	Ir(4)–C(2,4)	2.05(2)
P(1)–C(1)	1.85(4)	C(12)–O(12)	1.17(4)	Ir(4)–C(41)	1.84(3)	C(2,4)–O(2,4)	1.21(3)
P(1)–C(2)	1.82(5)			C(41)–O(41)	1.17(4)		

Ir(4)–P(1)–C(1)	117(2)	Ir(2)–P(2)–C(5)	117(2)	Ir(3)–C(31)–O(31)	175(3)	Ir(2)–C(1,2)–O(1,2)	137(2)
Ir(4)–P(1)–C(2)	103(2)	P(2)–C(5)–C(6)	115(3)	Ir(3)–C(32)–O(32)	177(3)	Ir(1)–C(1,4)–O(1,4)	141(3)
Ir(4)–P(1)–C(6)	115(2)	P(1)–C(6)–C(5)	120(3)	Ir(3)–C(33)–O(33)	176(3)	Ir(4)–C(1,4)–O(1,4)	135(2)
Ir(2)–P(2)–C(3)	118(2)	Ir(1)–C(11)–O(11)	176(3)	Ir(4)–C(41)–O(41)	178(5)	Ir(2)–C(2,4)–O(2,4)	138(2)
Ir(2)–P(2)–C(4)	115(2)	Ir(1)–C(12)–O(12)	177(3)	Ir(1)–C(1,2)–O(1,2)	130(2)	Ir(4)–C(2,4)–O(2,4)	138(2)
		Ir(2)–C(21)–O(21)	176(3)				
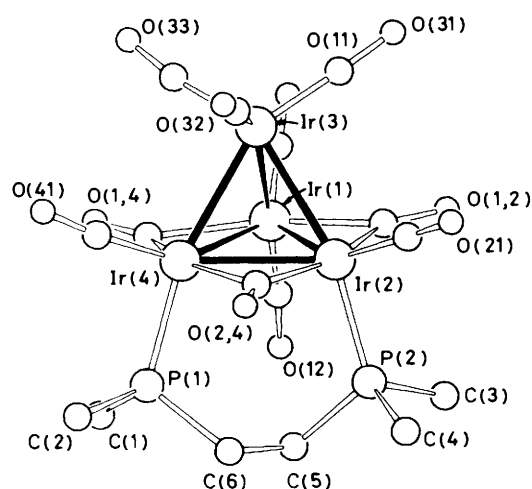
Figure 4. The molecular structure of the diaxial isomer $[Ir_4(CO)_7(\mu\text{-}CO)_3(Me_2PCH_2CH_2PMe_2)]$ (12) with the atom numbering scheme. The first digit(s) of each oxygen or carbon atom is that of the iridium atom to which the group is attached

summarized in Table 2. Singlet resonances were observed for derivatives (10), (14), and (16) over a large range of temperature, suggesting that the diphosphine ligands are symmetrically co-ordinated and are not involved in intramolecular site-exchange processes. For these complexes three possible structures can be proposed, (IV)—(VI) in Figure 2. The observed ^{31}P n.m.r. behaviour allows structure (VI) to be discarded because for such a configuration two ^{31}P n.m.r. signals are expected, at least at low temperature. The symmetrical structure [diradial (V)] seems unlikely on the basis of the value of the co-ordination chemical shift (Table 4) and because of the strain such a bridging mode would introduce. Thus the most likely configuration for compounds (10), (14), and (16) is the diaxial mode (IV). Compound (10) has recently been reported by other authors[33] but they did not propose a definite structure for this complex. Further support for the arrangement (IV) for complex (10) is provided by ^{1}H and ^{13}C n.m.r. data (Figure 3). The ^{13}C n.m.r. spectrum of (10) in CD_2Cl_2 solution at −85 °C shows seven carbonyl signals. This multiplicity is consistent with (IV) and not (VI) which would give only six signals. The resonance at δ 156.1 p.p.m., which appears as a triplet due to coupling with the two equivalent phosphorus atoms in a pseudo-*trans*

arrangement through an Ir–Ir bond, is assignable to the two equivalent apical carbonyls g. The spectrum is very similar to those previously reported for $[Ir_4(CO)_{11}L]$ (L = PPh_3[27] or PPh_2Me[9]) but not to those reported for disubstituted derivatives of type (VI), $[Ir_4(CO)_{10}(L–L)]$ (L–L = norbornadiene (nbd),[24] cyclo-octa-1,5-diene (cod),[26] or $Me_2AsC_6H_4AsMe_2$[10]). Further support of the assignment (IV) comes from the ^{1}H n.m.r. spectrum (Figure 3) which for the CH_2 group of the diphosphine ligand shows an ABX_2 pattern due to the inequivalence of the two methylene protons: whereas the H_B proton shows the expected chemical shift at δ 2.82 p.p.m., the H_A proton is abnormally deshielded (δ 5.30 p.p.m.). Space-filling models indicate that H_A in (IV) is located in the deshielding zone of the two phosphine aromatic rings, which are forced under the basal plane of the cluster in a rather coplanar mode with H_A. This further reinforces that structure (VI) is not adopted since in this case the protons in the PCH_2P group are arranged rather symmetrically.

A peculiar feature was observed in the variable-temperature ^{31}P n.m.r. spectra of complex (11). At room temperature a singlet occurs at δ −16.2 p.p.m. which broadens at lower temperature. At −80 °C this broadening disappears and two new peaks of the same intensity are observed at δ −17.6 and −14.7 p.p.m. It seems very likely that the molecular structure of (11) in solution, as deduced from the values of the co-ordination chemical shift (Table 4), is in agreement with (IV). The appearance of two signals at low temperature can be attributed to the two inequivalent axial arrangements of phosphorus atoms resulting from the conformation of the six-membered ring, as shown by X-ray analysis of (12), isomer (IV) (Figure 4). The single resonance observed at higher temperature arises from rapid conformational changes involving twisting of the bridged diphosphine ethane chain.

Complex (15) is also stereochemically non-rigid. The limiting low-temperature ^{31}P n.m.r. spectrum displays two resonances of equal intensities at δ −32.2 and −7.4 p.p.m. with $^2J(PP)$ = 3.7 Hz of similar magnitude to that observed for unidentate phosphine derivatives (17)—(19). Examination of their co-ordination chemical shifts (Table 4) suggests the peculiar structure (VII) in which the large size of the bridging diphosphine ligand allows an uncommon axial–radial bridging arrangement. This ground-state structure is not maintained at higher temperatures. At room temperature compound (15) shows a single resonance at δ −21.1 p.p.m. indicative of a rapid radial–axial synchronous interconversion for both phosphorus atoms, probably promoted by a carbonyl scrambling process over the Ir_4 skeleton.

The disubstituted derivatives (12) and (13), on the contrary, are both mixtures of two structurally different species (IV) and (VI) which could not be separated by t.l.c. or h.p.l.c. However, the presence of two isomers could be established by analytical h.p.l.c. using silica-gel columns (see Experimental section) and by variable-temperature ^{31}P n.m.r. studies. In their ^{31}P n.m.r. spectra at room temperature complexes (12) and (13) showed two resonances with 3:2 and 1:2 intensity ratios, respectively. On cooling, the downfield signal begins to broaden below -50 °C and then at -95 °C splits into two sharp singlets of equal intensity, while the high-field signal remains unchanged. Thus the high-field ^{31}P resonance can be assigned to the diaxial isomer (IV) and the downfield one to the chelate isomer (VI). The observed dynamic behaviour of the isomers (VI) of compounds (12) and (13) can be interpreted in terms of the mechanism proposed for carbonyl scrambling in [Ir$_4$(CO)$_{10}$-(o-Me$_2$AsC$_6$H$_4$AsMe$_2$)].[10]

It should be underlined that the ^{31}P n.m.r. co-ordination chemical shift (Δ) is a useful criterion for assigning the structures of the phosphine complexes [Ir$_4$(CO)$_{12-n}$L$_n$] ($n = 1$—4) (see Table 3) and a similar approach can be used for diphosphine complexes (10)—(16) (see Table 4) by calculating Δ_{ax} and Δ_{rad} (Δ_{ap} is not taken into account because substitution at the apical position occurs only for tetrasubstituted species).[4,7–9,32,34]

On the other hand, in order to rationalize the Δ_{ax} and Δ_{rad} values found for our complexes, we have calculated the 'ring contribution,' Δ_R, to the ^{31}P n.m.r. co-ordination chemical shift according to the method developed by Garrou.[35] These data are shown in Table 4. It appears that in our case these values are not useful in predicting the co-ordination mode of the ligands. (i) In the presence of large (6—8 membered) rings, Δ_R is very small as expected and does not allow ring-size predictions; (ii) in the case of five-membered rings [compound (10), and isomer (VI) of complexes (12) and (13)] unuseful scattered values are obtained. Evidently the method developed by Garrou[35] to calculate Δ_R does not seem useful for diphosphine derivatives of tetranuclear iridium cluster where the metal atoms have co-ordination sites which are conformationally and sterically different from those in mono- and bi-nuclear complexes.

Description of the Structure of [Ir$_4$(CO)$_{10}$(Me$_2$PCH$_2$CH$_2$-PMe$_2$)] (12), *Isomer* (IV).—The crystal consists of discrete units of [Ir$_4$(CO)$_{10}$(Me$_2$PC$_2$H$_4$PMe$_2$)] separated by normal van der Waals distances. The overall geometry of the molecules is shown in Figure 4. The four iridium atoms define an almost regular tetrahedron. Although they are all electronically equivalent, three kinds of ligand arrangement can be distinguished: atom Ir(3) bears three terminal carbonyl ligands, thus resembling an iridium atom in the parent [Ir$_4$(CO)$_{12}$];[25] atom Ir(1) is linked to two terminal and to two symmetrically bridging CO groups, while Ir(2) and Ir(4) form a six-membered ring with the bidentate diphosphinoethane ligand. The two phosphorus atoms replace two carbonyl ligands from the basal triangle. A third bridging and two terminal CO groups are also bonded to Ir(2) and Ir(4). The Ir–C and C–O distances for both terminal and bridging ligands [average 1.84(3), 1.17(3) and 2.07(2), 1.21(3) Å, respectively] are in the range reported for iridium clusters. The six-membered ring formed by the iridium atoms and the PCCP chain has a twist conformation. The two iridium atoms and the two phosphorus atoms are almost coplanar with a maximum deviation from the P(1)–Ir(4)–Ir(2)–P(2) plane of 0.085 Å. The two carbon atoms of the ethane group are on opposite sides of this plane, with deviations of 0.54 and 0.43 Å for C(5) and C(6), respectively. The rotational conformation about the C–C bond can be described as eclipsed, with the two phosphorus atoms in '*anti*' relative position (average P–C–C angle 117.5°). The overall geometry of the six-membered ring can be assimilated to that of a twisted

cyclohexane. The value of 1.52(5) Å for the C(5)—C(6) distance is within normal limits for a carbon–carbon single bond.

The average Ir–P distance of 2.29(1) Å agrees well with other reported Ir–P distances.[4,34] There are only slight differences in Ir–Ir bond lengths within the cluster [ranging from 2.722(2) to 2.752(2) Å] and none attributable to the presence of the bridging ligands. The average value of 2.736(2) Å is somewhat longer than the corresponding mean of 2.68 Å observed for [Ir$_4$(CO)$_{12}$],[25] although it is in good agreement with that observed for other phosphine-substituted iridium clusters such as [Ir$_4$(CO)$_9$(PPh$_3$)$_3$] and [Ir$_4$(CO)$_{10}$(PPh$_3$)$_2$] (2.73 Å).[4] The absence of significantly different patterns between the bridged and non-bridged iridium–iridium bonds seems to contradict the well established shortening effect of bridging carbonyls on metal–metal bonds, although the available data on iridium clusters are rather contradictory. For instance, while in [Ir$_4$(CO)$_{10}$(o-Me$_2$AsC$_6$H$_4$AsMe$_2$)][10] the symmetrically carbonyl-bridged Ir–Ir bond has a length of 2.694(2) Å and the non-bridged ones an average length of 2.726(2) Å, in [Ir$_4$(CO)$_{11}$Br]$^-$ (ref. 21) the bridged bonds [average 2.725(1) Å] are longer than the non-bridged [average 2.696(1) Å]. However, in both cases the presence of the substituents justifies the observed differences. In our case both steric and electronic effects may be invoked to account for the observed quasi-homogeneity in metal–metal bond distances.

Experimental

The salt [NEt$_4$][Ir$_4$(CO)$_{11}$Br] was prepared by the previously published method.[21] Samples of clusters enriched in ^{13}CO were prepared from [NEt$_4$][Ir$_4$(CO)$_{11}$Br] (25—30% ^{13}CO). Phosphines were obtained commercially and generally used without further purification, except for *cis*-Ph$_2$PCH= CHPPh$_2$ which was recrystallized from dichloromethane–ethanol. Silica gel (70—230 or 230—400 mesh) and preparative-scale t.l.c. plates (20 × 20 cm, thickness 1.0 or 2.0 mm; Merck) were used as received. H.p.l.c. analyses were made on a Perkin-Elmer series 2 chromatograph, using silica gel (10 μm) analytical columns and eluting with dichloromethane–hexane mixtures.

Preparation of Monosubstituted Complexes [Ir$_4$(CO)$_{11}$L] (1)—(6).—(a) L = PPh$_3$. Triphenylphosphine (0.2 g, 0.76 mmol) was added to [NEt$_4$][Ir$_4$(CO)$_{11}$Br] (1.02 g, 0.79 mmol) in dichloromethane (150 cm^3) at -10 °C, and the mixture stirred for 1 h. Solvent was removed at reduced pressure (0 °C) to give a volume of *ca.* 10 cm^3 and cold methanol (60 cm^3) was added to give a yellow precipitate. Recrystallization from dichloromethane–methanol gave the yellow compound [Ir$_4$(CO)$_{11}$(PPh$_3$)] (1) (0.98 g, 93%) (Found: C, 26.1; H, 1.2. C$_{29}$H$_{15}$Ir$_4$O$_{11}$P requires C, 26.0; H, 1.1%).

(b) L = PPh$_2$Me. Methyldiphenylphosphine (0.194 g, 0.97 mmol) was added to [NEt$_4$][Ir$_4$(CO)$_{11}$Br] (1.28 g, 0.99 mmol)

in acetone (50 cm^3) at $-15\,^\circ$C and the mixture stirred for 30 min at *ca.* $-10\,^\circ$C. Solvent was removed at reduced pressure ($<0\,^\circ$C) and the residue purified on a thermostatted ($0\,^\circ$C) column (60 $\times$ 3 cm) packed with silica gel (70—230 mesh). Elution with toluene gave a yellow band. The solvent was removed at reduced pressure and the residue recrystallized from dichloromethane–n-heptane, giving the yellow compound [Ir$_4$-(CO)$_{11}$(PPh$_2$Me)] (2) (1.13 g, 89%) (Found: C, 22.4; H, 1.1. C$_{24}$H$_{13}$Ir$_4$O$_{11}$P requires C, 22.6; H, 1.0%).

(*c*) L = PPhMe$_2$. This complex was prepared and purified in a similar manner to that of (2), using dichloromethane as solvent and a 5% excess of [NEt$_4$][Ir$_4$(CO)$_{11}$Br] over the dimethylphenylphosphine. Recrystallization from dichloromethane–methanol gave yellow crystals of [Ir$_4$(CO)$_{11}$-(PPhMe$_2$)] (3) (yield *ca.* 80%). (Found: C, 19.0; H, 0.95. C$_{19}$H$_{11}$Ir$_4$O$_{11}$P requires C, 18.8; H, 0.9%).

(*d*) L = AsPh$_3$. This complex was prepared in an analogous manner to (1). Recrystallization from dichloromethane–isopropanol gave yellow microcrystals of [Ir$_4$(CO)$_{11}$(AsPh$_3$)] (4) (yield >85%) (Found: C, 25.7; H, 1.25. C$_{29}$H$_{15}$AsIr$_4$O$_{11}$ requires C, 25.2; H, 1.1%).

(*e*) L = *trans*-Ph$_2$PCH=CHPPh$_2$. To a solution of *trans*-1,2-bis(diphenylphosphino)ethene (0.198 g, 0.50 mmol) in dichloromethane (40 cm^3) was added at $-20\,^\circ$C a solution of [NEt$_4$][Ir$_4$(CO)$_{11}$Br] (0.215 g, 0.167 mmol) in methanol (70 cm^3). After stirring for 40 min at $-10\,^\circ$C the volume was reduced *in vacuo* ($<0\,^\circ$C) to 5 cm^3, and the yellow product was filtered off, washed with cold methanol (2 $\times$ 3 cm^3) and then with hexane (20 cm^3), affording [Ir$_4$(CO)$_{11}$(*trans*-Ph$_2$PCH= CHPPh$_2$)] (5) (0.184 g, 75%) (Found: C, 31.4; H, 1.7; P, 4.1%; *M* (osmometric) 1 508. C$_{37}$H$_{22}$Ir$_4$O$_{11}$P$_2$ requires C, 30.2; H, 1.5; P, 4.2%; *M* 1 473).

(*f*) L = *trans*-Ph$_2$PCH=CHP(O)Ph$_2$. A solution of compound (5) (0.065 g, 0.044 mmol) in [^{2}H]chloroform (0.5 cm^3) was treated at *ca.* 0 $^\circ$C with an excess of hydrogen peroxide (0.2 cm^3, 30%). The solution mixture was warmed to room temperature and its ^{31}P n.m.r. spectrum recorded. At *ca.* 30 $^\circ$C over a period of 1 h the resonances of complex (5) at δ -4.7 and -20.2 p.p.m. [^3J(PP) = 9.8 Hz] gradually decreased and two new signals of equal intensity appeared at δ 22.4 and -20.1 p.p.m. [^3J(PP) = 43 Hz]. The low-field resonance was attributed to the unco-ordinated P(O)Ph$_2$ group in the compound [Ir$_4$(CO)$_{11}${*trans*-Ph$_2$PCH=CHP(O)Ph$_2$}] (6), by comparison with those for free *trans*-Ph$_2$P(O)CH=CHP(O)Ph$_2$ (δ 21.8 p.p.m.) and *trans*-Ph$_2$PCH=CHP(O)Ph$_2$ [δ 23.4 and -5.6 p.p.m., ^3J(PP) = 19.7 Hz]. Attempts to isolate (6) as pure crystalline solid from the oily residue obtained by evaporation of solvent were unsuccessful.

Preparation of Bridged Diphosphine Complexes [(OC)$_{11}$-Ir$_4$(L–L)Ir$_4$(CO)$_{11}$] (7)—(9).—(*a*) L–L = *trans*-Ph$_2$PCH=CH-PPh$_2$. To a solution of [NEt$_4$][Ir$_4$(CO)$_{11}$Br] (0.20 g, 0.155 mmol) in dichloromethane–methanol (40 cm^3, 1:1) was added at $-10\,^\circ$C a solution of *trans*-1,2-bis(diphenylphosphino)-ethene (0.03 g, 0.076 mmol) in dichloromethane (10 cm^3). After stirring for 1 h at 0 $^\circ$C the volume was reduced *in vacuo* to 5 cm^3, and the solution left in a refrigerator overnight. Solvent was removed with a syringe, and the solid washed with cold methanol. Recrystallization from dichloromethane–n-heptane gave yellow microcrystals of [(OC)$_{11}$Ir$_4$(*trans*-Ph$_2$PCH=CH-PPh$_2$)Ir$_4$(CO)$_{11}$] (7) (0.152 g, 77%) [Found: C, 22.8; H, 1.0; P, 2.5%; *M* (osmometric) 2 505. C$_{48}$H$_{22}$Ir$_8$O$_{22}$P$_2$ requires C, 22.6; H, 0.9; P, 2.45%; *M* 2 550].

(*b*) L–L = Ph$_2$PC$_3$H$_6$PPh$_2$. The complex [(OC)$_{11}$Ir$_4$(Ph$_2$-PC$_3$H$_6$PPh$_2$)Ir$_4$(CO)$_{11}$] (8) was isolated as yellow microcrystals in analogous manner to (7), starting with [NEt$_4$][Ir$_4$-(CO)$_{11}$Br] and 0.5 mol equivalent of 1,3-bis(diphenylphosphino)propane (yield 65%) [Found: C, 23.6; H, 1.1; P,

2.5%; *M* (osmometric) 2 487. C$_{49}$H$_{26}$Ir$_8$O$_{22}$P$_2$ requires C, 22.9; H, 1.0; P, 2.4%; *M* 2 556].

(*c*) L–L = Ph$_2$PC$_4$H$_8$PPh$_2$. To a solution of [NEt$_4$][Ir$_4$-(CO)$_{11}$Br] (0.25 g, 0.194 mmol) in methanol (30 cm^3) was added dropwise at 0° C a solution of 1,4-bis(diphenylphosphino)-butane (0.04 g, 0.094 mmol) in dichloromethane–acetone (20 cm^3, 1:1). After stirring for 1 h, solvent was partially removed *in vacuo* to give a volume of 10 cm^3, and the suspension cooled in a refrigerator for 4 h. The precipitate was washed with cold methanol and dried *in vacuo* affording yellow microcrystals of [(OC)$_{11}$Ir$_4$(Ph$_2$PC$_4$H$_8$PPh$_2$)Ir$_4$(CO)$_{11}$] (9) (yield 0.185 g, 73%) [Found: C, 23.1; H, 1.1; P, 2.6%; *M* (osmometric) 2 596. C$_{50}$H$_{28}$Ir$_8$O$_{22}$P$_2$ requires C, 23.3; H, 1.1; P, 2.4%; *M* 2 580].

Preparation of Disubstituted Complexes [Ir$_4$(CO)$_{10}$(L–L)] (10)—(16).—(*a*) L–L = Ph$_2$PCH$_2$PPh$_2$ (10), Ph$_2$PC$_2$H$_4$PPh$_2$ (11), Me$_2$PC$_2$H$_4$PMe$_2$ (12), *cis*-Ph$_2$PCH=CHPPh$_2$ (13), or *o*-Ph$_2$PCH$_2$C$_6$H$_4$CH$_2$PPh$_2$ (16). (*i*) These complexes were prepared in high yield according to the following general procedure. A solution of [NEt$_4$][Ir$_4$(CO)$_{11}$Br] (0.30 g, 0.233 mmol) in tetrahydrofuran (50 cm^3) was added at $-10\,^\circ$C to a solution in slight molar excess of the diphosphine ligand (0.25— 0.30 mmol) in dichloromethane (80 cm^3). After stirring at room temperature (*ca.* 10 h) solvent was removed *in vacuo*. The residue was washed with n-heptane (2 $\times$ 5 cm^3), extracted with toluene (3 $\times$ 3 cm^3), and chromatographed on a 90 $\times$ 2 cm column packed with silica gel (230—400 mesh). Elution with toluene generated a main yellow fraction. Evaporation *in vacuo*, followed by recrystallization from dichloromethane–n-heptane, gave the expected disubstituted derivatives as yellow microcrystals (yields 65—95%) [Found: C, 29.2; H, 1.6. C$_{35}$H$_{22}$Ir$_4$O$_{10}$P$_2$, (10), requires C, 29.3; H, 1.55. Found: C, 29.8; H, 1.7; P, 4.3. C$_{36}$H$_{24}$Ir$_4$O$_{10}$P$_2$, (11), requires C, 29.9; H, 1.7; P, 4.3. Found: C, 16.1; H, 1.5. C$_{16}$H$_{16}$Ir$_4$O$_{10}$P$_2$, (12), requires C, 16.0; H, 1.3. Found: C, 29.8; H, 1.6; P, 4.2%; *M* (osmometric) 1 471. C$_{36}$H$_{22}$Ir$_4$O$_{10}$P$_2$, (13), requires C, 29.9; H, 1.5; P, 4.3%; *M* 1 445. Found: C, 33.6; H, 1.9. C$_{42}$H$_{28}$Ir$_4$O$_{10}$P$_2$, (16), requires C, 33.1; H, 1.85%].

The presence of two isomers [types (IV) and (VI) in Figure 2] for both complexes (12) and (13) as evidenced by ^{31}P n.m.r. studies (Table 2) was fairly well distinguished by h.p.l.c. using an analytical silica gel column and dichloromethane–n-hexane as eluant. Nevertheless many attempts to separate the two isomers by use of a preparative column were unsuccessful. Recrystallization of complex (12) from toluene–n-heptane gave a very few crystals suitable for *X*-ray structural characterization, together with some non-diffracting material. The latter was regarded as an amorphous residue of isomer (VI), only isomer (IV) being present as single crystals.

(*ii*) Complexes of type [Ir$_4$(CO)$_{10}$(L–L)] were the only diphosphine derivatives isolated from a similar reaction to the above, but starting with a L–L: [NEt$_4$][Ir$_4$(CO)$_{11}$Br] molar ratio of 1:2 and operating strictly at lower temperature ($< -10\,^\circ$C). After 5 h all the solvent was removed *in vacuo* and the residue extracted with cold methanol. The insoluble [Ir$_4$(CO)$_{10}$(L–L)] was filtered off. From the methanolic solution some unreacted [NEt$_4$][Ir$_4$(CO)$_{11}$Br] was recovered, and identified by its physical and spectroscopic properties.

(*iii*) Reaction as above, but with a large excess of diphosphine ligand (>5 mol equivalents), afforded [Ir$_4$(CO)$_{10}$(L–L)] in almost quantitative yield. No i.r. and ^{31}P n.m.r. evidence was found for a 'Ir$_4$(CO)$_{11}$' unit co-ordinated to a single phosphine ligand as in compound (5).

(*b*) L–L = Ph$_2$PC$_3$H$_6$PPh$_2$. To a solution of 1,3-bis-(diphenylphosphino)propane (0.60 g, 1.45 mmol) in dichloromethane (120 cm^3) was added dropwise at $-20\,^\circ$C a solution of [NEt$_4$][Ir$_4$(CO)$_{11}$Br] (0.44 g, 0.342 mmol) in dichloromethane (140 cm^3). After stirring for 2 h at room temperature, the solvent

was removed *in vacuo*. The yellow residue was washed with heptane (3 × 5 cm^3), extracted with dichloromethane, and then chromatographed on preparative-scale t.l.c. plates. Elution with dichloromethane–n-hexane (1:3) gave a main yellow fraction. Extraction with dichloromethane, followed by recrystallization from n-heptane, gave microcrystals of [Ir$_4$(CO)$_{10}$(Ph$_2$PC$_3$-H$_6$PPh$_2$)] (14) (yield 0.41 g, 82%) (Found: C, 29.9; H, 1.8. C$_{37}$H$_{26}$Ir$_4$O$_{10}$P$_2$ requires C, 30.4; H, 1.8%).

(*c*) L–L = Ph$_2$PC$_4$H$_8$PPh$_2$. To a solution of 1,4-bis-(diphenylphosphino)butane (0.66 g, 1.55 mmol) in dichloromethane (150 cm^3) at 0 °C was added dropwise (1 h) a solution of [NEt$_4$][Ir$_4$(CO)$_{11}$Br] (0.20 g, 0.155 mmol) in dichloromethane–methanol (40 cm^3, 1:1). After stirring for 2 h at room temperature, the solvent was removed *in vacuo*. Extraction with cold benzene (15 cm^3) left insoluble 1,4-bis(diphenylphosphino)butane, which was filtered off. Benzene was removed at reduced pressure and the residue chromatographed on preparative-scale t.l.c. plates. Elution with dichloromethane–n-hexane (3:2) gave a main yellow fraction. Extraction followed by crystallization from dichloromethane–methanol gave yellow microcrystals of [Ir$_4$(CO)$_{10}$(Ph$_2$PC$_4$H$_8$PPh$_2$)] (15) (yield 0.105 g, 46%) [Found: C, 31.2; H, 2.0%; *M* (osmometric) 1 421. C$_{38}$H$_{28}$Ir$_4$O$_{10}$P$_2$ requires C, 30.9; H, 1.9%; *M* 1 475].

Preparation of Disubstituted Complexes [Ir$_4$(CO)$_{10}$L$_2$] [L = PPh$_3$ (17), PPh$_2$Me (18), *or* PPhMe$_2$ (19).—The general procedure is given for complex (18). A solution of [NEt$_4$]-[Ir$_4$(CO)$_{11}$Br] (0.3 g, 0.233 mmol) in dichloromethane (50 cm^3) was treated at 0 °C with methyldiphenylphosphine (0.078 g, 0.39 mmol). The yellow solution was warmed to room temperature, stirred for 1.5 h, and then the solvent was removed *in vacuo*. After washing with cold n-heptane (2 × 5 cm^3), the residue was dissolved in dichloromethane (5 cm^3) and then chromatographed on preparative-scale t.l.c. plates. Elution with dichloromethane–n-hexane (1:4) gave two main yellow fractions affording yellow [Ir$_4$(CO)$_{11}$(PPh$_2$Me)] (2) and yellow-orange [Ir$_4$(CO)$_{10}$(PPh$_2$Me)$_2$] (18), which were recrystallized from dichloromethane–methanol. The yields were 0.08 g (27%) and 0.185 g (55%), respectively.

The preparations of [Ir$_4$(CO)$_{12-n}$L$_n$] (*n* = 1 or 2, L = PPh$_3$ or PPhMe$_2$) proceeded analogously. For L = PPhMe$_2$ the additional orange cluster [Ir$_4$(CO)$_9$(PPhMe$_2$)$_3$] was separated in low yield (6%). Satisfactory carbon and hydrogen analyses were obtained for all these compounds.

Crystallography.—Crystal data. C$_{16}$H$_{16}$Ir$_4$O$_{10}$P$_2$, monoclinic, space group *P*2$_1$/*c* (no. 14), *a* = 15.694(2), *b* = 10.403(2), *c* = 15.706(2) Å, β = 92.63(2)°, *Z* = 4, *U* = 2 561 Å^3, *D$_c$* = 3.11 g cm^{-3}, *F*(000) = 2 120, Mo-*K$_\alpha$* radiation, λ = 0.7107 Å, μ(Mo-*K$_\alpha$*) = 201.3 cm^{-1}.

Intensity measurements. A suitable crystal of dimensions 0.2 × 0.18 × 0.1 mm was mounted on a Philips PW 1100 diffractometer. Diffraction intensities were measured in the range 3 < θ < 20°, by the ω–2θ scan method, with scan interval 1.0° and speed 3.0° min^{-1}. Fast decay of the crystal under *X*-ray exposure prevented extension of the data collection to higher θ. The background was measured on both sides of the reflections for a total time equal to the peak scanning time. 2 515 Reflections were collected, 2 289 of which [*I$_o$* > 3σ(*I$_o$*)] were used for structure solution and refinement. The integrated intensities were reduced to *F$_o$* values and an experimental absorption correction was applied. All computations were carried out by using the SHELX package of crystallographic programs.[36] The positions of three iridium atoms (defining a triangle) were found by Patterson synthesis. The remaining iridium atom and all the non-hydrogen atoms were found by subsequent Fourier difference synthesis. Refinement of the atomic positional and thermal parameters converged to a final

R of 0.087 and *R'* [= Σ(|*F$_o$*| − |*F$_c$*|)*w*$^{\frac{1}{2}}$/Σ|*F$_o$*|*w*$^{\frac{1}{2}}$] of 0.091. The weighting scheme employed was *w* = *K*/[σ^2(*F*) + |*g*|*F*^{2}], where both *K* and *g* were refined (0.61 and 0.015, respectively). Anisotropic thermal parameters were assigned to Ir and P atoms. Hydrogen atoms were added in calculated positions and not refined. A final Fourier difference synthesis showed a few residual peaks of *ca.* 3 e Å^{-3} in the vicinity of the metal atoms, confirming that, in spite of the attempts made to improve the final structural model, the data set was of a rather poor quality probably because of the mentioned decay and unsatisfactory absorption correction.

The atomic co-ordinates are given in Table 5, selected bond lengths and angles in Table 6.

Acknowledgements

References

1 P. Chini and B. T. Heaton, *Top. Curr. Chem.*, 1977, 71, 1.
2 B. F. G. Johnson (ed.), 'Transition Metal Clusters,' Wiley, New York, 1980.
3 H. Vahrenkamp, *Adv. Organomet. Chem.*, 1983, 32, 169.
4 V. G. Albano, P. L. Bellon, and V. Scatturin, *Chem. Commun.*, 1967, 730.
5 J. R. Shapley, G. F. Stuntz, M. R. Churchill, and J. P. Hutchinson, *J. Chem. Soc., Chem. Commun.*, 1979, 219.
6 M. R. Churchill and J. P. Hutchinson, *Inorg. Chem.*, 1979, 18, 2451; 1980, 19, 2765.
7 D. J. Darensbourg and B. J. Balwin-Zuschke, *Inorg. Chem.*, 1981, 20, 3846.
8 A. J. Blake and A. G. Osborne, *J. Organomet. Chem.*, 1984, 260, 227.
9 G. F. Stuntz and J. R. Shapley, *J. Am. Chem. Soc.*, 1977, 99, 607.
10 J. R. Shapley, G. F. Stuntz, M. R. Churchill, and J. P. Hutchinson, *J. Am. Chem. Soc.*, 1979, 101, 7425.
11 G. F. Stuntz and J. R. Shapley, *J. Organomet. Chem.*, 1981, 213, 389.
12 K. J. Karel and J. R. Norton, *J. Am. Chem. Soc.*, 1974, 96, 6812.
13 D. J. Darensbourg and M. J. Incorvia, *Inorg. Chem.*, 1980, 19, 2585; 1981, 20, 1911.
14 D. Sonnenberger and J. D. Atwood, *Inorg. Chem.*, 1981, 20, 3243; *Organometallics*, 1982, 1, 694; *J. Am. Chem. Soc.*, 1982, 104, 2113.
15 D. J. Darensbourg and B. J. Baldwin-Zuschke, *J. Am. Chem. Soc.*, 1982, 104, 3906.
16 A. J. Drakesmith and R. Whyman, *J. Chem. Soc., Dalton Trans.*, 1973, 362.
17 P. E. Cattermole, K. G. Orrell, and A. G. Osborne, *J. Chem. Soc., Dalton Trans.*, 1974, 328.
18 G. F. Stuntz, and J. R. Shapley, *Inorg. Chem.*, 1976, 15, 1994.
19 L. Malatesta and G. Caglio, *Chem. Commun.*, 1967, 420.
20 M. Angoletta, L. Malatesta, and C. Caglio, *J. Organomet. Chem.*, 1975, 94, 99.
21 P. Chini, G. Ciani, L. Garlaschelli, M. Manassero, S. Martinengo, A. Sironi, and F. Canziani, *J. Organomet. Chem.*, 1978, 152, C35.
22 G. Ciani, M. Manassero, and A. Sironi, *J. Organomet. Chem.*, 1980, 199, 271.
23 R. Ros, F. Canziani, A. Scrivanti, and L. Garlaschelli, *Atti Congr. Naz. Chim. Inorg.*, 1982, 78; *Chem. Abstr.*, 1984, 100, 166990f.
24 R. Ros, F. Canziani, and R. Roulet, *J. Organomet. Chem.*, 1984, 267, C9.
25 M. R. Churchill and J. P. Hutchinson, *Inorg. Chem.*, 1978, 17, 3528.
26 G. F. Stuntz, J. R. Shapley, and C. G. Pierpont, *Inorg. Chem.*, 1978, 17, 2596.
27 B. E. Mann, C. M. Spencer, and A. K. Smith, *J. Organomet. Chem.*, 1983, 244, C17.
28 F. A. Cotton, *Inorg. Chem.*, 1966, 5, 1083.
29 F. A. Cotton, L. Kruczynsky, B. L. Shapiro, and L. F. Johnson, *J. Am. Chem. Soc.*, 1972, 94, 6191.
30 C. A. Tolman, *Chem. Rev.*, 1977, 77, 313.
31 T. T. Derencsenyi, *Inorg. Chem.*, 1981, 20, 665.

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

33 D. F. Foster, B. S. Nicholls, and A. K. Smith, *J. Organomet. Chem.*, 1982, **236**, 395.

34 V. G. Albano, D. Braga, R. Ros, and A. Scrivanti, *J. Chem. Soc., Chem. Commun.*, 1985, 866.

35 P. E. Garrou, *Chem. Rev.*, 1981, **81**, 229.

36 SHELX 76 System of Computer Programs, G. M. Sheldrick, University of Cambridge, 1976.