Journal of Organometallic Chemistry, 236 (1982) 197—212
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

METAL—OLEFIN BONDING. THE PREPARATION AND PROPERTIES OF GROUP VI METAL CARBONYL COMPLEXES CONTAINING THE LIGANDS 1,6-BIS(DIPHENYLPHOSPHINO)-*trans*-HEX-3-ENE AND 1,6-BIS-(DIPHENYLARSINO)-*trans*-HEX-3-ENE. THE CRYSTAL AND MOLECULAR X-RAY STRUCTURE OF TRICARBONYL-1,6-BIS-(DIPHENYLPHOSPHINO)-*trans*-HEX-3-ENEMOLYBDENUM(0)

GEORGE R. CLARK *, CATHERINE M. COCHRANE
Department of Chemistry, University of Auckland, Auckland (New Zealand)

and PETER W. CLARK *
Department of Chemistry, University of Queensland, Brisbane 4067 (Australia)

(Received May 5th, 1982)

Summary

The complexes $M(CO)_3(BDPH)$ and $M(CO)_3(BDAH)$ (M = Cr, Mo or W, BDPH = 1,6-bis(diphenylphosphino)-*trans*-hex-3-ene and BDAH = 1,6-bis(diphenylarsino)-*trans*-hex-3-ene), have been prepared. These complexes have been characterised as octahedral complexes in which the tertiary unsaturated diphosphine and diarsine act as tridentate ligands. The complexes have been characterised by infrared, mass spectral, ^1H nuclear magnetic resonance, ^{13}C nuclear magnetic resonance and analytical data.

The crystal structure of $Mo(CO)_3(BDPH)$ has been determined by conventional X-ray diffraction techniques. The straw-coloured needles are orthorhombic, space group *Pbca*, a 16.991(2), b 20.073(4), c 17.333(2) Å, $Z = 8$. Refinement was by full-matrix least-squares methods and employed anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were included in calculated positions but were not refined. The final residuals are $R = 0.048$ and $R_w = 0.048$.

The compound is monomeric. The unsaturated phosphine ligand is tridentate, through the two phosphorus atoms (*trans*) and the olefin, and the octahedral coordination is completed by the three carbonyl groups. Distances and angles are Mo—P 2.450, 2.474(4) Å, Mo—CO 2.03, 2.01(1) Å (*trans* to CO) and 1.97(1) Å (*trans* to C═C). The olefin coordination has nearly symmetrical Mo—C, 2.504(12), 2.541(14) Å, a short olefin bond 1.38(2) Å, and a twisted olefin configuration.

---

* Present address: Department of Chemistry, Queensland, Institute of Technology, Brisbane 4000 (Australia).

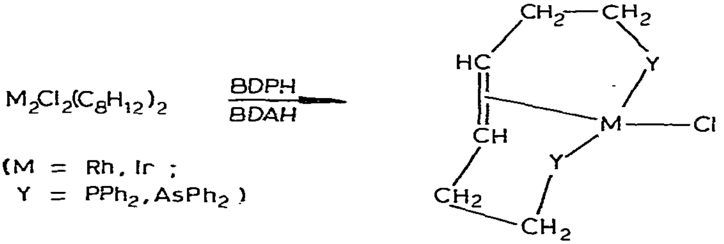
0022-328X/82/0000—0000/$02.75

Introduction

In recent years, there have been a number of papers describing the preparation and reactions of metal complexes containing tertiary unsaturated phosphines and arsines [1]. Interest has centred around the platinum metals, because of the known stability of d^8 metal olefin complexes and the associated homogeneous catalytic processes involving olefins, viz. the homogeneous hydrogenation, isomerization and hydroformylation reactions. For example, the ligands 1,6-bis(diphenylphosphino)-*trans*-hex-3-ene (BDPH) and 1,6-bis(diphenylarsino)-*trans*-hex-3-ene (BDAH) undergo normal substitution reactions with rhodium(I) and iridium(I) compounds to form square-planar complexes of the general formula MX(BDPH) and MX(BDAH), M = Rh or Ir and X = halide. The ligand in these complexes acts as a tridentate, bonding through the phosphorus or arsenic atoms and the olefin [2] (Scheme 1). The square planar complexes MCl(BDPH) undergo oxidative-addition reactions forming octahedral M(III) complexes of the formula M(XY)Cl(BDPH), M = Rh, XY = Cl_2 or Br_2; M = Ir, XY = H_2, Cl_2, HCl or Br_2 [3]. The X-ray structures of IrCl(BDPH), $IrH_2Cl(BDPH)$ and $IrCl_3(BDPH)$ have been published previously [2,3]. By way of comparison we describe herein the reactions of BDPH and BDAH with the Group VI metal carbonyls, and the completed X-ray structure of $Mo(CO)_3(BDPH)$.

SCHEME 1

Preparation of the complexes MX(BDPH) and MX(BDAH), M = Rh or Ir, X = Halide



Experimental

Chromium and tungsten hexacarbonyl were purchased from Pressure Chemical Company, and molybdenum hexacarbonyl from Fluka. Tris(acetonitrile)-tricarbonylchromium(0) and tris(acetonitrile)tricarbonyltungsten(0) were prepared according to the literature preparations [4] and were used in situ. The ligands, 1,6-bis(diphenylphosphino)-*trans*-hex-3-ene and 1,6-bis(diphenylarsino)-*trans*-hex-3-ene were prepared as described previously [1].

Infrared spectra were recorded on a JASCO IRA-2 spectrometer, ^1H NMR and ^{13}C NMR spectra were obtained using a Bruker HX-270 instrument. NMR samples were flushed with nitrogen before recording the spectra. The mass spectra were recorded on an AEI MS902S instrument. Analyses were obtained from the University of Queensland Microanalytical Service and the Australian Microanalytical Service, CSIRO, Melbourne, Australia. Molecular weights were

TABLE 1

CONDITIONS FOR PREPARATION OF THE COMPLEXES $M(CO)_3(BDPH)$ AND $M(CO)_3(BDAH)$ ($M = Cr$, Mo or W)

Complex	Starting materials	Solvent	Reflux time	Yield (%)
$Cr(CO)_3(BDPH)$	$Cr(CO)_6$ + BDPH	toluene	3.5 d	80
$Mo(CO)_3(BDPH)$	$Mo(CO)_6$ + BDPH	toluene	2.5 d	83
$W(CO)_3(BDPH)$	$W(CO)_6$ + BDPH	mesitylene	7 h	31
$Cr(CO)_3(BDAH)$	$Cr(CO)_3(CH_3CN)_3$ + BDAH	acetonitrile	2.0 d	67
$Mo(CO)_3(BDAH)$	$Mo(CO)_6$ + BDAH	toluene	16 h	90
$W(CO)_3(BDAH)$	$W(CO)_3(CH_3CN)_3$ + BDAH	acetonitrile	3 h	72

obtained by vapour pressure osmometry on solutions of the compounds dissolved in chloroform.

Preparation of the complexes $M(CO)_3(BDPH)$ and $M(CO)_3(BDAH)$, ($M = Cr$, Mo or W)

The complexes were prepared either by the reaction of the metal hexacarbonyl or the tris(acetonitrile)metaltricarbonyl with the ligands BDPH or BDAH in refluxing solvent. The complexes were recrystallised from methylene chloride/methanol solution. The conditions for the preparation of the complexes are given in Table 1, and analytical results listed in Table 2. The preparation of one of the complexes $Mo(CO)_3(BDPH)$ is given as an example.

Preparation of tricarbonyl-1,6-bis(diphenylphosphino)-trans-hex-3-ene molybdenum(0)

1,6-Bis(diphenylphosphino)-*trans*-hex-3-ene (0.35 g, 0.77 mmol) and molybdenum hexacarbonyl (0.2 g, 0.76 mmol) were refluxed in 20 ml of toluene for 2.5 d giving a yellow solution. The solution was then cooled and

TABLE 2

ANALYTICAL RESULTS FOR THE COMPLEXES $M(CO)_3(BDPH)$ AND $M(CO)_3(BDAH)$ ($M = Cr$, Mo or W)

Complex	Analysis (Found (calcd.) (%))						
	C	H	P(As)	MW	M^+	MP	Colour
$Cr(CO)_3(BDPH)$	67.25 (67.34)	5.32 (5.14)	10.8 (10.5)	580 (588)	588	214	orange
$Mo(CO)_3(BDPH)$	63.50 (62.67)	5.36 (4.78)	9.9 (9.8)	635 (632)	632	196	yellow
$W(CO)_3(BDPH)$	55.10 (55.02)	4.23 (4.20)	8.7 (8.6)	850 (720)	720	188	yellow
$Cr(CO)_3(BDAH)$	59.00 (58.59)	4.71 (4.47)	21.7 (22.2)	704 (676)	676	136	yellow
$Mo(CO)_3(BDAH)$	55.05 (55.02)	4.49 (4.20)	20.5 (20.8)	740 (720)	720	168	yellow
$W(CO)_3(BDAH)$	48.97 (49.03)	3.86 (3.74)	17.9 (18.5)	790 (808)	808	180	yellow

the toluene removed at reduced pressure. The yellow solid was recrystallised from methylene chloride/methanol to give 0.40 g (83%) of straw coloured needle-like crystals of the complex $Mo(CO)_3(BDPH)$.

X-ray experimental

The crystals form as straw-coloured needles, elongated along the b axial direction. Preliminary X-ray photographs showed orthorhombic diffraction symmetry, with systematically absent reflections ($0kl$ when $k = 2n + 1$, $h0l$ when $l = 2n + 1$, $hk0$ when $h = 2n + 1$) corresponding to space group *Pbca* (No. 61). Unit cell dimensions were derived from a least-squares refinement of the setting angles of twelve high-theta reflections (theta range 15.2—17.3°) using a Hilger and Watts four-circle automatic diffractometer [5]. Details of unit cell parameters and intensity data collection procedures are summarised in Table 3. Data collection proceeded smoothly, with no nonstatistical variations being recorded in the intensities of three standard reflections remeasured after every 200 reflections. An attenuator was automatically inserted if the count rate exceeded 10 000 c s^{-1}. The data were corrected for Lorentz and polarization factors, but, because of the low value of the linear absorption coefficient, absorption corrections were not necessary. After averaging duplicate measurements, the data set comprised 1702 unique reflections for which $I > 3\sigma(I)$ ($\sigma(I) = [T + t^2B + (pI)^2]^{1/2}$, T = integrated peak count, B = average background count, t = ratio of scan to background times, p was assigned a trial value of 0.05, but as $\langle w(|F_o| - |F_c|)^2\rangle$ remained approximately constant across the range of data during the least-squares refinement, it did not require subsequent modification [6]).

Structure determination and refinement

The position of the molybdenum atom was deduced from a three-dimensional Patterson map, and subsequent electron density syntheses revealed the

TABLE 3

SUMMARY OF CRYSTAL DATA AND INTENSITY DATA COLLECTION FOR $Mo(CO)_3(BDPH)$

Compound: Tricarbonyl-1,6-bis(diphenylphosphino)-*trans*-hex-3-enemolybdenum(0)
Formula: $C_{33}H_{30}MoO_3P_2$ Molecular weight 632.5
Crystal colour and habit: Straw needles
a 16.991(2) Å b 20.073(4) Å
c 17.333(2) Å V 5911 $Å^3$
$Z = 8$
d_c 1.42 g cm^{-3} d_o 1.41 g cm^{-3} (by flotation in aqueous $ZnBr_2$)
Space group: *Pbca* D_{2h}^{15} (No. 61)
Crystal dimensions: 0.44 × 0.12 × 0.16 mm
X-radiation: Mo-K_α, λ 0.7107 Å, Zr filter
Collimators: Primary 2.0 mm Secondary 5.0 mm
Theta range: 0.5—27°
Scan speed: 0.01° in θ per second using $2\theta/\omega$ scan
Scan range: symmetric scan of 0.80° in θ
Background: 15 s stationary count at each end of scan range

TABLE 4

ATOMIC POSITIONS FOR $Mo(CO)_3(BDPH)$

Atom	x/a	y/b	z/c
Mo	0.0626(1)	0.0231(1)	0.1979(1)
P(1)	−0.0192(2)	0.1234(2)	0.2054(2)
P(2)	0.1409(2)	−0.0799(2)	0.1823(2)
O(1)	0.0075(6)	−0.0101(5)	0.3672(6)
O(2)	0.1983(5)	0.0999(5)	0.2794(5)
O(3)	0.1293(6)	0.0744(6)	0.0388(6)
C(1)	−0.1077(8)	0.1095(7)	0.1476(7)
C(2)	−0.1262(8)	0.0352(7)	0.1489(8)
C(3)	−0.0571(8)	−0.0040(6)	0.1197(7)
C(4)	−0.0363(7)	−0.0636(7)	0.1532(9)
C(5)	0.0078(11)	−0.1159(8)	0.1062(9)
C(6)	0.0747(8)	−0.1479(6)	0.1546(8)
C(7)	0.0252(7)	−0.0016(6)	0.3057(9)
C(8)	0.1493(7)	0.0713(7)	0.2485(7)
C(9)	0.1032(7)	0.0537(7)	0.0949(8)
C(11)	0.0168(9)	0.2050(6)	0.1698(7)
C(12)	−0.0357(8)	0.2575(8)	0.1641(8)
C(13)	−0.0109(11)	0.3195(8)	0.1389(9)
C(14)	0.0667(13)	0.3283(8)	0.1195(9)
C(15)	0.1189(8)	0.2765(9)	0.1244(9)
C(16)	0.0939(9)	0.2134(7)	0.1494(10)
C(21)	−0.0547(8)	0.1477(5)	0.3008(8)
C(22)	−0.0020(8)	0.1683(8)	0.3559(9)
C(23)	−0.0248(11)	0.1859(8)	0.4292(9)
C(24)	−0.1026(12)	0.1844(9)	0.4500(10)
C(25)	−0.1559(9)	0.1623(8)	0.3972(10)
C(26)	−0.1327(9)	0.1445(8)	0.3220(8)
C(31)	0.1972(7)	−0.1168(7)	0.2630(8)
C(32)	0.2284(9)	−0.1815(7)	0.2543(9)
C(33)	0.2671(9)	−0.2111(8)	0.3148(11)
C(34)	0.2808(8)	−0.1769(9)	0.3825(10)
C(35)	0.2508(10)	−0.1136(10)	0.3910(9)
C(36)	0.2090(9)	−0.0839(8)	0.3297(9)
C(41)	0.2155(7)	−0.0760(7)	0.1057(7)
C(42)	0.2164(8)	−0.1185(8)	0.0418(8)
C(43)	0.2715(10)	−0.1103(9)	−0.0158(8)
C(44)	0.3268(9)	−0.0607(10)	−0.0117(9)
C(45)	0.3277(8)	−0.0177(9)	0.0515(10)
C(46)	0.2716(8)	−0.0272(8)	0.1094(8)

positions of all other non-hydrogen atoms [7]. Atomic scattering factors and dispersion corrections were from standard listings [8]. Refinement employed the full least-squares matrix to minimise the function $\Sigma w(|F_o| - |F_c|)^2$, with weights $w = 4|F_o|^2/(\sigma^2(F_o)^2)$. Residuals quoted are $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. With all atoms located, $R = 0.30$, but this reduced to 0.09 after the first isotropic cycle. In subsequent cycles, the molybdenum and phosphorus atoms were assigned anisotropic thermal parameters ($R = 0.078$), hydrogen atoms were included in the structure factor calculations in positions calculated assuming C—H 0.95 Å (at no stage were their positions or isotropic temperature factors (5.0 Å^2) refined), the carbonyl atoms and carbons 1—6 were allocated anisotropic temperature factors ($R = 0.053$),

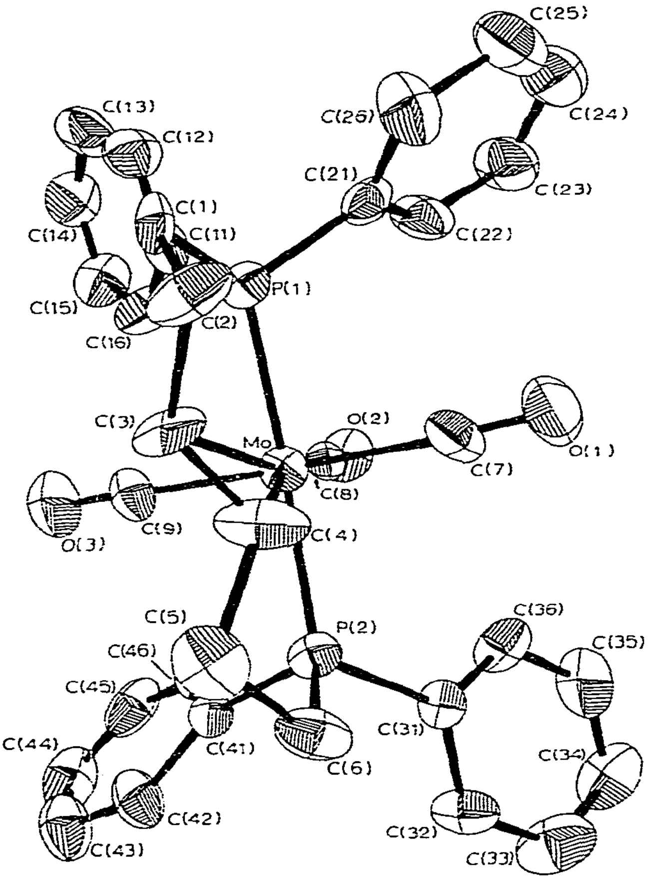


Fig. 1. The molecular geometry, atomic numbering, and anisotropic thermal ellipses (50% probability boundaries) for $Mo(CO)_3(BDPH)$.

and finally, all non-hydrogen atoms were made anisotropic (R = 0.048, R_w = 0.048). A final 'difference' map was featureless.

Final atomic positions are listed in Table 4. The atomic numbering scheme is outlined in Fig. 1. Tables of thermal parameters, calculated hydrogen positions, bond lengths and angles involving phenyl rings, and observed and calculated structure factors are available on request from the authors (G.R.C.).

Description of the structure of $Mo(CO)_3(BDPH)$

The complex is monomeric. The molybdenum atom is bonded to the three carbonyl groups and to the olefin and two phosphorus atoms of the BDPH moiety in an approximately octahedral arrangement, as evidenced by angles near 90° at molybdenum. The phosphorus atoms are mutually *trans*. The overall molecular geometry and numbering scheme are shown in Fig. 1. Important bond lengths and bond angles are listed in Table 5.

The Mo—P distances of 2.450 and 2.474(4) Å lie within the normal range of

TABLE 5

BOND LENGTHS (Å) AND BOND ANGLES (degrees) FOR $Mo(CO)_3(BDPH)$

Mo—P(1)	2.450(4)	P(2)—C(31)	1.848(14)
Mo—P(2)	2.474(4)	P(2)—C(41)	1.836(13)
Mo—C(3)	2.504(12)	C(1)—C(2)	1.524(19)
Mo—C(4)	2.541(14)	C(2)—C(3)	1.499(18)
Mo—C(7)	2.034(13)	C(3)—C(4)	1.375(18)
Mo—C(8)	1.969(13)	C(4)—C(5)	1.522(20)
Mo—C(9)	2.011(13)	C(5)—C(6)	1.554(19)
P(1)—C(1)	1.828(14)	C(7)—O(1)	1.120(17)
P(1)—C(11)	1.854(14)	C(8)—O(2)	1.144(16)
P(1)—C(21)	1.828(13)	C(9)—O(3)	1.147(17)
P(2)—C(6)	1.835(14)		
P(1)—Mo—P(2)	176.3(2)	Mo—P(2)—C(31)	122.0(4)
P(1)—Mo—C(3)	75.3(3)	Mo—P(2)—C(41)	114.5(4)
P(1)—Mo—C(4)	101.8(3)	C(6)—P(2)—C(31)	102.6(6)
P(1)—Mo—C(7)	88.5(4)	C(6)—P(2)—C(41)	105.5(6)
P(1)—Mo—C(8)	89.8(4)	C(31)—P(2)—C(41)	102.0(6)
P(1)—Mo—C(9)	89.4(4)	P(1)—C(1)—C(2)	108.1(5)
P(2)—Mo—C(3)	101.3(3)	C(1)—C(2)—C(3)	110.4(7)
P(2)—Mo—C(4)	75.5(3)	Mo—C(3)—C(2)	109.8(5)
P(2)—Mo—C(7)	98.8(4)	Mo—C(3)—C(4)	75.7(6)
P(2)—Mo—C(8)	93.2(4)	C(2)—C(3)—C(4)	121.1(8)
P(2)—Mo—C(9)	88.5(4)	Mo—C(4)—C(3)	72.7(5)
Mo—P(1)—C(1)	108.2(4)	Mo—C(4)—C(5)	108.2(5)
Mo—P(1)—C(11)	121.5(4)	C(3)—C(4)—C(5)	120.1(8)
Mo—P(1)—C(21)	117.0(4)	C(4)—C(5)—C(6)	110.8(8)
C(1)—P(1)—C(11)	102.9(6)	P(2)—C(6)—C(5)	106.5(5)
C(1)—P(1)—C(21)	105.3(6)	Mo—C(7)—O(1)	174.0(5)
C(11)—P(1)—C(21)	100.1(6)	Mo—C(8)—O(2)	178.2(5)
Mo—P(2)—C(6)	108.6(4)	Mo—C(9)—O(3)	175.5(6)

approximately 2.42 to 2.52 Å [9]. The difference in the Mo—P bond lengths of six standard deviations is similar to the differences in metal—phosphorus bond lengths found in other complexes of chelating mono-olefin tertiary phosphines (see Table 6). It is considered unlikely that this difference is due to intermolecular interactions between the phenyl rings on the phosphorus atoms and neighbouring atoms of adjacent molecules, since lengthening the shorter Mo—P bond does not increase the number or extent of such interactions. Similarly, there appears to be no steric disadvantage in shortening the longer Mo—P bond.

The P(1)—Mo—P(2) angle of 176.3(2)° lies within the range 170—177° found in other chelating mono-olefin tertiary phosphine complexes (Table 5). If this deviation from linearity were due to intermolecular forces involving the phenyl rings further away from the hexene chain pushing the two phosphorus atoms close together, those phenyl rings would make more intermolecular contacts than phenyl ring carbon atoms closer to the hexene chain. Such is not observed, so it can be assumed that the reduction of the P—Mo—P angle from 180° is not due to intermolecular forces. It is more likely to be a result of either steric effects of other ligands in the metal coordination sphere, or else an attempt to reduce the strain imposed on the phosphorus atoms by the constraints of tridentate chelation. Transition metal complexes of monodentate tertiary phosphines generally exhibit metal—phosphorus—carbon angles of about 115° [10].

TABLE 6

GEOMETRY IN CHELATING MONO-OLEFIN TERTIARY PHOSPHINE COMPLEXES

Complex	M—C (olefin)	C=C	Olefin twist	M—P	P—$\hat{M}$—P	M—$\hat{P}$—C (alkene chain)	Ref.
(i) Square planar							
IrCl(BDPH)	2.092, 2.084(9)	1.42(2)	79.4	2.296, 2.272(2)	174.0(1)	105, 105	2
RhCl(BDPS) [a]	2.109, 2.117	1.436(6)	79	2.284, 2.281(2)	174.8(1)	103, 104	22
$RhCl[Bu^t_2P(CH_2)_2CH{=}]_2$	2.309, 2.323(5)	1.37(3)	74	2.323, 2.309(5)	176.0(2)	102, 104	11
(ii) Octahedral							
IrH_2Cl(BDPH)	2.343, 2.284(18)	1.34(2)	49.9	2.301, 2.283(4)	170.1(2)	107, 107	2
$IrCl_3$(BDPH)	2.274, 2.277(10)	1.352(14)	28.1	2.382, 2.389(2)		107, 107	3
$IrCl_3$(BDPS)		1.386(5)	15.5				22
$RhCl_3$(BDPS)		1.367(4)	14				22
$Mo(CO)_3$(BDPH)	2.504(12), 2.541(14)	1.38(2)	34.0	2.450, 2.474(2)	176.3(2)	109, 108	this work
$W(CO)_3$(BDPP) [b]	2.403(8), 2.387(9)	1.359(12)	23	2.450, 2.462(5)	176.0(2)	102, 104	21
$Mo(CO)_4(Ph_2PC_6H_4CH{=}CHMe)$	2.45(1), 2.52(2)	1.39(3)	0	2.517(3)		104	9

[a] BDPS is 2,2′-bis(diphenylphosphino)stilbene. [b] BDPP is 1,3-bis(2-diphenylphosphinophenyl)propene.

However, on tridentate chelation the angle to the carbon of the alkene chain is significantly reduced (to ca. 102—109°) (Table 6). There have been no reports of the phosphorus atoms bending away from the intervening alkene. The metal—phosphorus—carbon angle appears to be independent of other ligands in the metal coordination sphere since the values for $IrCl_3(BDPH)$ [3], $IrH_2Cl(BDPH)$ [2] and IrCl(BDPH) [2] are all equivalent. The phosphorus—metal—phosphorus angle may reduce slightly to minimise the extent to which the metal—phosphorus—carbon angle must change as a consequence of chelation. An apparent exception to this is the 13-membered ring complex, $RhCl(CO)[Bu^t_2P(CH_2)_4\text{-}C{=}C(CH_2)_4PBu^t_2]$ [11], which has a metal—phosphorus—carbon angle close to 115° (indicating little or no strain imposed on the phosphorus atoms by chelation), yet has a P—M—P angle of 171.6°, in the lower region of the 170—177° range. Ring strain has also been shown to be negligible in the complex $RhCl[Bu^t_2P(CH_2)_2CH{=}CH(CH_2)_2PBu^t_2]$ by comparison of rhodium—alkene lengths [11]. In both these cases the deviations may be due to the steric effects of the bulky tertiary butyl groups and not to any tendency to reduce the M—P—C angle.

The C=C bond length of 1.375(18) Å is comparatively short (i.e. it is not very much longer than that in free ethylene, 1.337(2) Å [12]). The Mo—C (olefin) distances of 2.504(12) and 2.541(14) Å are neither similar enough to claim symmetrical bonding nor dissimilar enough to refute it, but it should be noted that the ^{13}C NMR contains only one olefin signal (see later) which is indicative of symmetrical bonding. The bonds are longer than those of 2.31(2), 2.38(1), 2.49(1) Å in $Mo(CO)_4[(C_6H_5)P{=}CHCH{=}CH_2]\cdot C_6H_6$ [13]; 2.23(2) Å in μ-allenebis(cyclopentadienyl)tetracarbonyldimolybdenum [14]; 2.23 and 2.25 Å in μ-dichlorobis[(π-benzene-π-allyl)molybdenum(II)] [15]; 2.354(5) Å in $(\eta^5\text{-}C_5H_5)Mo(CO)(CNCH_3)_2(CH_3)I$ [16], and the same as the Mo—C distances found in $Mo(CO)_4(Ph_2PC_6H_4CH{=}CHMe)$ of 2.45 and 2.52(2) Å [9]. The long Mo—C distances and short C=C bond length suggest that the extent of metal—olefin backbonding is minimal and that the CO groups in this complex have competed more successfully than the phosphines for π-electron density from the metal. The lack of metal—olefin backbonding removes the restriction on the orientation the olefin may adopt with respect to the coordination sphere of the metal and the olefin relaxes to assume an intermediate alignment with respect to the other donor atoms [17]. The angle between the planes defined by Mo, C(3), C(4) and Mo, P(1), P(2), C(8) is 34.0° (Fig. 2), which compares with those for corresponding planes in $IrH_2Cl(BDPH)$ [2] and $IrCl_3(BDPH)$ [3] of 50° and 28° respectively. In both these complexes, also, metal—olefin π-back-donation was found to be minimal. The C(1)—C(2), C(2)—C(3), C(4)—C(5) and C(5)—C(6) distances of 1.50 to 1.55(2) Å are normal for single carbon—carbon bonds.

The phosphorus—carbon lengths of 1.828 to 1.854(14) Å are equivalent, and are consistent with ranges of 1.815 to 1.846(9) Å in $IrCl_3(BDPH)$ [3]; 1.827(13) to 1.854(18) Å in $IrH_2Cl(BDPH)$ [2]; 1.80 to 1.84(1) Å in IrCl(BDPH) [2]; 1.82 to 1.86(1) Å in $Mo(CO)_4(Ph_2PC_6H_4CH{=}CHMe)$ [9]; and 1.83 to 1.92 Å in triphenylphosphorus [18]. Least squares plane calculations showed all benzene rings to be planar, with phosphorus atom displacements from the appropriate benzene ring planes of P(1)/C(11)—C(16) —0.035(4), P(1)/C(21)—C(26)

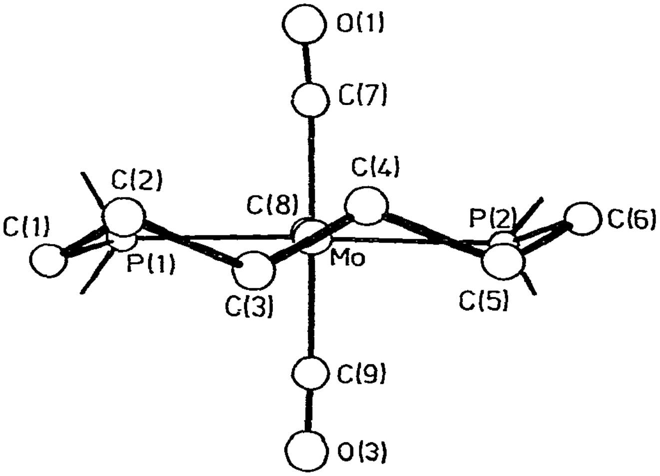


Fig. 2. Olefin configuration in $\mathrm{Mo(CO)_3(BDPH)}$. Atom O(2) is hidden behind C(8) and Mo.

−0.022(4), P(2)/C(31)—C(36) −0.041(4) and P(2)/C(41)—C(46) 0.106(4) Å. These displacements, and the configuration of the phenyl rings, are similar to those found in triphenylphosphorus [18]. The C—C distances and C—Ĉ—C angles in the phenyl rings are normal.

The molybdenum—carbonyl carbon distances of 2.03, 1.97 and 2.01(1) Å lie within the range 1.93 to 2.03 Å in $\mathrm{Mo(CO)_4[(C_6H_5)_3P{=}CHCH{=}CH_2]\cdot C_6H_6}$ [13]; 1.91 to 2.01 Å in $\mathrm{(CO)_2(Ph_4C_5O)Mo(Ph_2C_2)Mo(C_4Ph_4)(CO)}$ [19]; 1.96 to 2.05 Å in $\mathrm{Mo(CO)_4(Ph_2PC_6H_4CH{=}CHMe)}$ [9]; 2.06 Å in $\mathrm{Mo(CO)_6}$ [20], and 1.91 to 2.03(2) Å in $\mathrm{(EtP)_5Mo(CO)_4}$ [20]. The carbon—oxygen distances of 1.12, 1.14 and 1.15(2) Å and the Mo—C—O angles of 174.0, 178.2(5), and 175.5(6)° are very typical of those found in other metal—carbonyl complexes. The small deviations from 180° in the present complex are probably due to local packing forces, since O(1), O(2) and O(3) are involved in a number of intermolecular contacts shorter than 3.6 Å (Table 7). The arrangement of molecules in the crystal is shown in the stereopair diagrams of Fig. 3.

TABLE 7

INTERMOLECULAR APPROACHES <3.6 Å

Atom 1	Atom 2	Transformation of Atom 2			Distance
O(1)	C(13)	−x	1/2−y	1/2−z	3.42
O(1)	C(14)	−x	1/2−y	1/2−z	3.49
O(1)	C(45)	1/2−x	y	1/2−z	3.37
O(2)	C(1)	1/2+x	y	1/2−z	3.54
O(2)	C(2)	1/2+x	y	1/2−z	3.48
O(2)	C(26)	1/2+x	y	1/2−z	3.48
O(2)	C(43)	1/2−x	−y	1/2+z	3.59
O(3)	C(3)	−x	−y	−z	3.32
O(3)	C(5)	−x	−y	−z	3.52
O(3)	C(35)	1/2−x	−y	1/2+z	3.37
C(1)	C(43)	−x	−y	−z	3.59
C(15)	C(32)	1/2−x	1/2+y	z	3.54

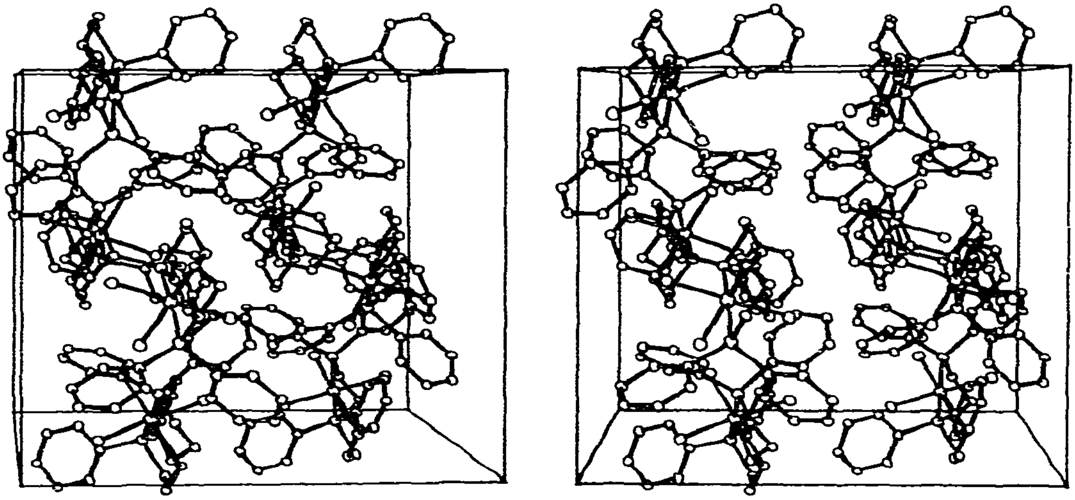


Fig. 3. A stereoscopic view of the molecular packing of $Mo(CO)_3(BDPH)$.

$Mo(CO)_3(BDPH)$ can be compared with the similar complex $W(CO)_3(BDPP)$, (BDPP = 1,3-bis[2-(diphenylphosphino)phenyl]propene [21]. Molybdenum is approximately the same size as tungsten (because of the lanthanide contraction) but W is the more electronegative. Even so, the metal—carbonyl distances in $W(CO)_3(BDPP)$ are not significantly different from those in $Mo(CO)_3(BDPH)$ and the two compounds have similar M—P distances, P—$\hat{M}$—P angles, M—CO distances and C=C bond lengths (Table 6 and ref. 22). The influence of differing electron configuration is difficult to estimate since the steric requirements of the ligands BDPP and BDPH probably play a large role in determining the tilt angle of the olefin, although the 5 *d* electrons of W could be expected to form more stable π bonds than the 4 *d* electrons of Mo. The similarity of the C=C distances suggests similar extents of metal—olefin π-backbonding in $W(CO)_3(BDPP)$ and $Mo(CO)_3(BDPH)$.

The central metals in $Mo(CO)_3(BDPH)$ and $IrCl_3(BDPH)$ share the same outer-shell electron configuration but differ in size. The smaller iridium forms shorter M—P bonds than molybdenum. The three π-accepting carbonyl ligands in $Mo(CO)_3(BDPH)$ withdraw π-electron density from Mo, reducing the amount available for metal—olefin π-backbonding. In contrast, the Cl ligands in $IrCl_3$-(BDPH) cannot withdraw π-electron density but the metal electrons are held more firmly by the more electron deficient iridium(III). Since the C=C bond lengths of $Mo(CO)_3(BDPH)$ and $IrCl_3(BDPH)$ are the same, the extent of π-backbonding must be very similar, the π-acceptance of the three carbonyl groups being balanced by the greater electron deficiency of iridium(III) to produce similar metal—olefin backbonding. This is further evidenced by the similar olefin twist angles in the two complexes.

Discussion

The ligand 1,6-bis(diphenylphosphino)-*trans*-hex-3-ene (BDPH) reacted smoothly with the Group VI metal hexacarbonyl complexes, displacing three carbon monoxide ligands to form $M(CO)_3(BDPH)$, (M = Cr, Mo or W). The ligand 1,6-bis(diphenylarsino)-*trans*-hex-3-ene(BDAH) reacted cleanly with $Mo(CO)_6$ to form $Mo(CO)_3(BDAH)$, but the chromium and tungsten complexes, $Cr(CO)_3(BDAH)$ and $W(CO)_3(BDAH)$ were best prepared from the corresponding tris(acetonitrile)-metaltricarbonyl compounds. The tungsten complex, $W(CO)_3(BDAH)$, could not be prepared from $W(CO)_6$ and the arsine ligand. All the complexes were stable in the solid state, and with the exception of $Cr(CO)_3(BDAH)$ were stable in solution. $Cr(CO)_3(BDAH)$ decomposed in solution when left to stand for extended periods, and we were unable to obtain its ^{13}C nuclear magnetic resonance spectrum.

Very little information regarding Group VI metal(0) carbonyl complexes containing tertiary unsaturated phosphines and arsines has so far been obtained. In most cases reported only two carbonyl ligands have been replaced by the unsaturated ligands [9, 23—26] e.g. in the reaction of *o*-styryl-diphenylphosphine (SP), but-3-enyldiphenylphosphine (mpb), bis(but-3-enyl)phenylphosphine(bpp) and tri(but-3-enyl)phosphine (tbp) with the Group VI metal(0) carbonyls, compounds of the formula $M(CO)_4$(ligand) are formed. The maximum possible chelation is not obtained. With the present ligands, BDPH and BDAH, maximum chelation is reached.

The mass spectra of the complexes $M(CO)_3(BDPH)$ and $M(CO)_3(BDAH)$, (M = Cr, Mo or W), are quite similar. Generally they consist of the parent ion with the stepwise loss of the three carbonyl ligands. Exceptions to this occurred in $Cr(CO)_3(BDAH)$ which consisted of only the parent ion (P^+) and the parent ion less three carbonyl ligands ($P^+ - 3CO$); and in $Cr(CO)_3(BDPH)$ which consisted of P^+ and $P^+ - 3CO$ and trace amounts of $P^+ - CO$ and $P^+ - 2CO$. The mass spectrum of $W(CO)_3(BDAH)$ was unusual in that it contained small peaks due to some dimeric species; notably $W_2(CO)_{10}(BDAH)$ —1188, $W_2(CO)_5(BDAH)$ —1048 and $W_2(CO)_4(BDAH)$ —1020, and a small amount of $W(CO)_4(BDAH)$ —836. The infrared spectra (Table 8) of $M(CO)_3(BDPH)$ in solution (methylene chloride) exhibit two carbonyl bands, a weak sharp band at ~1970 cm^{-1} and an intense broad band at ~1865 cm^{-1}, while the infrared spectra of $M(CO)_3(BDAH)$ in methylene chloride solution exhibit three bands; a very weak sharp band at ~1970—2000 cm^{-1}, a medium sharp band at ~1950 cm^{-1} and an intense broad band at ~1865 cm^{-1}. As in the case of rhodium(III) and iridium(III) octahedral

TABLE 8

INFRARED DATA FOR THE COMPLEXES $M(CO)_3(BDPH)$ AND $M(CO)_3(BDAH)$, (M = Cr, Mo or W) [a,b]

Compound	Carbonyl stretching frequencies [c]	oop [d]
$Cr(CO)_3(BDPH)$	1962w 1859s	882m
$Mo(CO)_3(BDPH)$	1980w 1870s	884m
$W(CO)_3(BDPH)$	1976w 1864s	887m
$Cr(CO)_3(BDAH)$	2002w 1948s 1864s	[e]
$Mo(CO)_3(BDAH)$	1978vw 1952m 1866s	868m
$W(CO)_3(BDAH)$	1972vw 1950m 1860s	870m

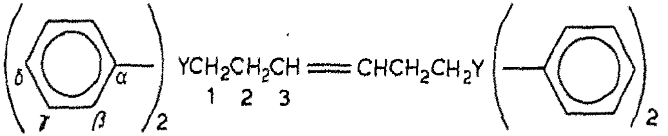
[a] All measurements are in cm^{-1}. [b] vw = very weak, w = weak, m = medium, s = strong. [c] Measured in methylene chloride solution. [d] Measured in Nujol mull, tentative assignment only. [e] Not observed.

TABLE 9

^{13}C AND ^{1}H NMR DATA FOR THE COMPLEXES $M(CO)_3(BDPH)$ AND $M(CO)_3(BDAH)$, (M = Cr, Mo or W)[a,b]

Compound	^{13}C Chemical shifts[c]								^{13}C Coupling constants[d]				
	α	β	γ	δ	C_1	C_2	C_3	CO	^{31}P—$^{13}C_\beta$	^{31}P—$^{13}C_\gamma$	^{31}P—$^{13}C_1$	^{31}P—$^{13}C_2$	$\delta(^1H)$[e]
$Cr(CO)_3(BDPH)$	[f]	132.4 130.9	128.6 128.5	129.5 128.9	36.4	32.4	95.9	[f]	4.9 4.9	3.9 3.9	8.9	7.9	~4.60
$Mo(CO)_3(BDPH)$	[f]	133.1 130.7	128.7 128.5	129.8 128.8	42.9	35.5	99.9	[f]	5.9 5.9	3.9 3.9	10.8	8.9	4.75
$W(CO)_3(BDPH)$	[f]	133.3 130.6	128.7 128.4	129.9 128.9	46.5	37.0	92.5	[f]	[g]	[g]	13.8	7.9	4.34
$Cr(CO)_3(BDAH)$[h]													4.60
$Mo(CO)_3(BDAH)$	141.0 140.6	132.6 131.7	129.1 128.9	129.5 129.3	42.7	35.6	99.5	226.1 212.1					4.61
$W(CO)_3(BDAH)$[i]	140.6 140.0	132.6 131.8	129.1 128.9	129.7 129.5	45.9	36.9	91.3	206.8					4.24

[a] The carbon atoms are labelled as follows



(Y = P or As)

[b] All compounds were dissolved in CD_2Cl_2, the spectra were recorded at ambient temperatures. [c] ^{13}C Chemical shifts in ppm relative to TMS, $\delta = 0$. [d] ^1H accurate to ±0.5 Hz. [e] ^1H Chemical shifts in ppm relative to TMS, $\delta = 0$. [f] Not observed. [g] Triplet nature evident, but not resolved. [h] ^{13}C NMR not recorded due to decomposition in solution. [i] It should be noted that the ^{13}C NMR spectrum of $W(CO)_3(BDAH)$ contained resonances due to some small impurity. In particular there are olefinic resonances at 85.6 and 85.9 ppm.

complexes, there is no out of plane deformation band for the complexes $M(CO)_3(BDPH)$ and $M(CO)_3(BDAH)$ in the 970 cm^{-1} region which characterises the *trans* distributed olefin [1,3,27]. However, there is a medium sharp band at ~880 cm^{-1} which could tentatively be assigned to this oop deformation band.

The ^1H NMR spectra (Table 9) of the compounds $M(CO)_3(BDPH)$ and $M(CO)_3(BDAH)$ exhibit quite complex coupling patterns associated with the rigidity of the coordinated ligand and consequent restricted rotation about the C—C bonds [28]. The upfield shift of the olefin in the ^1H NMR spectra in the complexes compared to the ligand is clear indication that the olefin is bonded to the metal [29]. However, the upfield shift of the olefinic proton is relatively small (0.75—1.26 ppm) compared to that in rhodium(I) (~2 ppm) and iridium(I) (~3 ppm) complexes containing these ligands [1].

The proton-decoupled ^{13}C NMR spectra are easily interpreted, and in many respects are similar to the spectra of the rhodium and iridium complexes containing these ligands (Fig. 4). In all cases, the spectra consisted of a phenyl region, an olefinic resonance (C_3) and two alkyl resonances (C_1 and C_2). The carbonyl resonances were only detected in two compounds, presumably due to their extremely long relaxation times. The phenyl resonances were assigned as previously [30] based on their chemical shifts and $^{31}P—^{13}C$ coupling constants (in the case of the BDPH complexes). The methylene carbons were assigned as previously [30] on the basis of $J(^{31}P—^{13}C) > J(^{31}P—^{13}C_2)$. The phenyl carbons and methylene carbons are triplets in the BDPH complexes arising from virtual coupling with the phosphorus atoms. No phosphorus coupling to the olefinic carbons was observed. The chromium complex, $Cr(CO)_3(BDAH)$ was not stable enough in solution for the relatively long periods required for the accumulation of data.

The coordination induced shifts $\Delta\delta(C)$ [30a] in the chromium complex $Cr(CO)_3(BDPH)$, the molybdenum complexes $Mo(CO)_3(BDPH)$ and $Mo(CO)_3$-(BDAH) and in the tungsten complexes $W(CO)_3(BDPH)$ and $W(CO)_3(BDAH)$ are 33.3, 29.3, 31.8, 36.7 and 40.0 ppm, respectively. The $\Delta\delta(C)$ values for the molybdenum(0) d^6 octahedral complex, $Mo(CO)_3(BDPH)$, and for the tung-

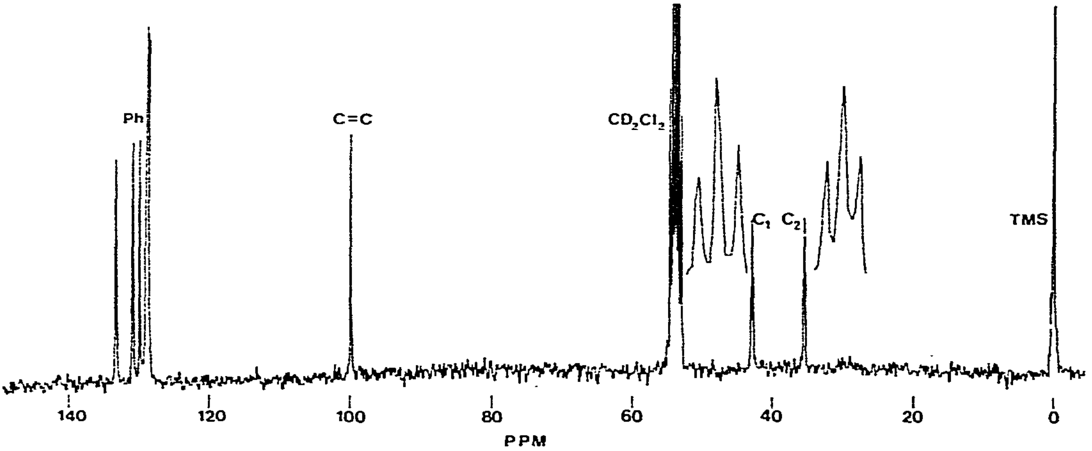


Fig. 4. ^{13}C NMR spectrum of $Mo(CO)_3(BDPH)$.

sten(0) d^6 octahedral complex $W(CO)_3(BDPH)$, are greater than those for the corresponding rhodium(III) d^6 octahedral complex $RhCl_3(BDPH)$ ($\Delta\delta(C)$ 15.0 ppm) and the iridium(III) d^6 octahedral complex $IrCl_3(BDPH)$ ($\Delta\delta(C)$ 30.5 ppm) respectively [30a]. We have shown earlier [30a] that the coordinated induced shift ($\Delta\delta(C)$) "is a complex function not only of M—C distance, but also of stereochemistry, oxidation state and the orientation of the olefin". One would expect that in the octahedral d^6 M(0) complexes of BDPH the amount of electron density on the metal and hence the amount of electron density available for back-bonding to the olefin would be greater than that in the octahedral d^6 M(III) complexes of BDPH. And therefore the coordination induced shifts in the octahedral d^6 M(0) complexes would be expected to be larger than in the analogous octahedral d^6 M(III) complexes. This is exactly what has been found and this reinforces our previous findings that the ^{13}C NMR parameters of BDPH complexes support the Dewar-Chatt-Duncanson model of metal—olefin bonding provided the oxidation state and stereochemistry of the complexes are considered [30a].

Acknowledgements

We thank Dr. Alan Jones and Mr. Peter Hanisch of the National NMR Centre, Australian National University for obtaining the ^1H- and ^{13}C-NMR spectra. This work (in part) was supported by a grant from the Australian Research Grant Committee.

References

1 P.W. Clark, J. Organometal. Chem., 137 (1977) 235 and references therein.
2 G.R. Clark, M.A. Mazid, D.R. Russell, P.W. Clark and A.J. Jones, J. Organometal. Chem., 166 (1979) 109.
3 G.R. Clark, P.W. Clark and K. Marsden, J. Organometal. Chem., 173 (1979) 231.
4 D.P. Tate, W.R. Knipple and J.M. Augl, Inorg. Chem., 1 (1962) 433.
5 W.R. Busing and H.A. Levy, Acta Crystallogr., 22 (1967) 457.
6 P.W.R. Corfield, R.J. Doedens and J.A. Ibers, Inorg. Chem., 6 (1967) 197.
7 All computing was carried out on the University of Auckland Burroughs B6700 computer. Major programs used were HILGOUT, FOURIER and CUCLS, written by R.J. Delaca of the University of Canterbury, New Zealand.
8 International Tables for X-ray Crystallography, Vol. III, Kynoch Press, Birmingham, 1962, pp. 202—214.
9 H. Luth and M.R. Truter, J. Chem. Soc., A, (1969) 28.
10 An example which clearly shows this trend is $Ir(PPh_2Me)_4BF_4 \cdot C_6H_{12}$, G.R. Clark, B.W. Skelton and T.N. Waters, J. Organometal. Chem., 85 (1975) 375.
11 R. Mason and G.R. Scollary, Aust. J. Chem., 31 (1978) 781.
12 L.S. Bartell, E.A. Roth, C.D. Hollowell, K. Kuchitsu and J.E. Young, Jr., J. Chem. Phys., 42 (1965) 2683.
13 I.W. Bassi and R. Scordamaglia, J. Organometal. Chem., 51 (1973) 273.
14 W.I. Bailey, M.H. Chisholm, F.A. Cotton, C.A. Murillo and L.A. Rankel, J. Chem. Soc., 100 (1978) 802.
15 K. Prout and G.V. Rees, Acta Cryst., B30 (1974) 2251.
16 R.D. Adams and D.F. Chodosh, J. Amer. Chem. Soc., 99 (1977) 6544.
17 S.D. Ittel and J.A. Ibers, Adv. in Organometal. Chem., 14 (1976) 33.
18 J.J. Daly, J. Chem. Soc., (1964) 3799.
19 J.A. Potenza, R.J. Johnson, R. Chirico and A. Efraty, Inorg. Chem., 16 (1977) 2354.
20 M.A. Bush and P. Woodward, J. Chem. Soc. (A), (1968) 1221.
21 M.A. Bennett, S. Corlett, G.B. Robertson and W.L. Steffen, Aust. J. Chem., 33 (1980) 1261.

22 Preliminary structural data by M.A. Bennett, P.W. Clark, G.B. Robertson and P.O. Whimp, J. Chem. Soc., Chem. Comm., (1972) 1011, and further described in Ref. 21.

23 L.V. Interrante, M.A. Bennett and R.S. Nyholm, Inorg. Chem., 5 (1966) 2213.

24 M.A. Bennett, R.S. Nyholm and J.D. Saxby, J. Organometal. Chem., 10 (1967) 301.

25 M.A. Bennett and I.B. Tomkins, J. Organometal. Chem., 51 (1973) 289.

26 P.E. Garrou and G.E. Hartwell, J. Organometal. Chem., 55 (1973) 331.

27 L.J. Bellamy, The Infrared Spectra of Complex Molecules, 2nd Ed., Methuen and Co., London, 1958, p. 45.

28 P.W. Clark and G.E. Hartwell, J. Organometal. Chem., 97 (1975) 117.

29 See for example: M.A. Bennett, Chem. Reviews, 62 (1962) 611.

30 (a) P.W. Clark, P. Hanisch and A.J. Jones, Inorg. Chem., 18 (1979) 2067; (b) J.-R. Llinas, E.-J. Vincent and G. Peiffer, Bull. Soc. Chim. France (1973) 3209; (c) P.S. Braterman, D.W. Milne, E.W. Randall and E. Rosenberg, J. Chem. Soc. Dalton, (1973) 1027; (d) B.E. Mann, J. Chem. Soc. Perkin II, (1972) 30.