

Group 6 homo-bimetallic carbonyl complexes containing polydentate phosphine ligands

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Abstract

The group 6 homo-bimetallic carbonyl complexes $[M(CO)_4(Pf-Pf-Pf)M(CO)_5]$ ($M = Cr, Mo$ or W ; $Pf-Pf-Pf = PhP(CH_2CH_2PPh_2)_2$) and $[M_2(CO)_8(P-Pf_3)]$ ($M = Cr, Mo$ or W ; $P-Pf_3 = P(CH_2CH_2PPh_2)_3$), were prepared by the chemical oxidation method with TMNO ($Me_3NO \cdot 2H_2O$) as initiator, and by the labile ligand substitution method with NBD (NBD = norbornadiene) as labile ligand. Crystals of the five-membered chelating ring compound, $[Cr(CO)_4(Pf-Pf-Pf)Cr(CO)_5]$ (**Ia**), are monoclinic, with space group $P2_1/c$, and with $a = 16.116(4)$, $b = 14.493(4)$, $c = 18.015(7)$ Å, $\beta = 96.33(3)^\circ$, $Z = 4$ and $R = 0.093$ for 1633 observed reflections. Crystals of the eight-membered chelating ring compound, $[Cr(CO)_4(Pf-Pf-Pf)Cr(CO)_5]$ (**II**), are monoclinic, with space group $P2_1/n$, and with $a = 12.812(2)$, $b = 22.807(4)$, $c = 15.611(2)$ Å, $\beta = 90.84(1)^\circ$, $Z = 4$ and $R = 0.050$ for 3907 observed reflections. Crystals of the double chelating ring compound $[W_2(CO)_8(P-Pf_3)]$ (**III**), are also monoclinic, with space group $P2_1/n$, and with $a = 11.618(2)$, $b = 17.526(3)$, $c = 26.080(3)$ Å, $\beta = 98.48(1)^\circ$, $Z = 4$ and $R = 0.033$ for 4936 observed reflections. The M–P bond lengths, M–P–C and P–C–C bond angles in the eight-membered ring were found to be greater than the corresponding ones in the five-membered ring, revealing the larger ring strain for the eight-membered chelating ring.

Keywords: Chromium; Molybdenum; Tungsten; Group 6 complexes; Homo-bimetallic complex; Metal carbonyl derivative

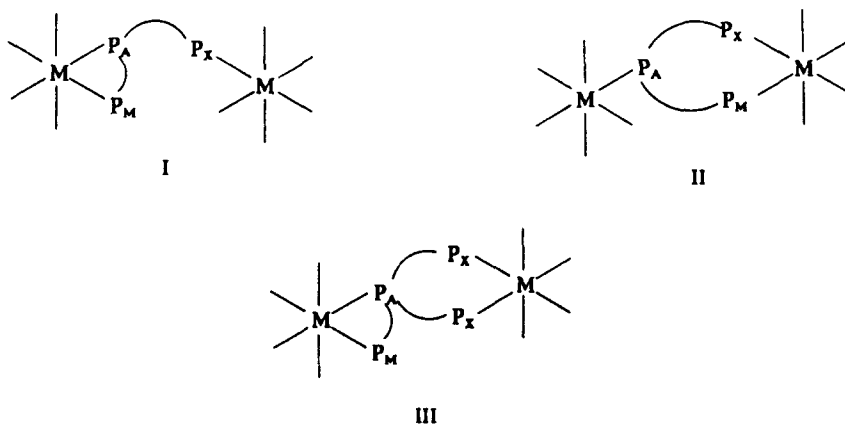
1. Introduction

There are in the literature some reports concerning the syntheses and structures of bimetallic complexes containing polydentate phosphine ligands. (1) Triphosphine ligands: $[Re_2Cl_3(dpmp)_2]X$ ($X = Cl$ or PF_6) ($dpmp = bis((diphenylphosphino)methyl)phenylphosphine$) [1]; $[(triphos)Co(\mu-S)_2Co(triphos)]$ [2] and other cobalt(II) complexes with triphos (triphos = 1,1,1-tris((diphenylphosphino)methyl)ethane) [3,4]; $[Fe_2(\mu-SH)_3(Pf-Pf-Pf)]X$ ($X = ClO_4$ or BF_4) ($Pf-Pf-Pf = bis(2-(diphenylphosphino)ethyl)phenylphosphine$) [5]. (2) Tripodal tetraphosphine ligand: $[Au_2(\mu-P-Pf_3)_2]Cl_2$ ($P-Pf_3 = tris(2-(diphenylphosphino)ethyl)phosphine$) [6]. (3) Linear tetraphosphine ligands: $[Rh_2Cl_2(CO)_2(eLTPP)]$ [7], $[Ni_2Cl_4(eLTPP)]$ [8]; and $[Co_2(\mu-CO)_2(CO)_2(eLTPP)]$ [9] ($eLTPP = bis((diethylphosphinoethyl)phenylphosphino)methane$). (4) Hexaphosphine ligands: $[Co_2(CO)_4(eHTP)]^{2+}$ and other binuclear

complexes with eHTP (eHTP = bis(bis(diethylphosphinoethyl)phosphino)methane) [10–14]. Recently, we have shown that the mixed bimetallic carbonyl complexes $[M(CO)_4(Pf-Pf-Pf)M'(CO)_5]$ and $[M(CO)_3(P-Pf_3)M'(CO)_5]$ ($M \neq M'$) [15] may be synthesized from $Pf-Pf-Pf$ or $P-Pf_3$ and Group 6 metal carbonyls. In this paper we report on the Group 6 homo-bimetallic carbonyl complexes $[M(CO)_4(Pf-Pf-Pf)M(CO)_5]$ and $[M_2(CO)_8(P-Pf_3)]$ ($M = Cr, Mo$ or W), which were prepared via the chemical oxidation of TMNO (TMNO = $(CH_3)_3NO \cdot 2H_2O$) [16–20] or substitution of NBD (NBD = norbornadiene) [15,21–23]. Three types of structures for the binuclear triligate octahedral and binuclear tetraligate octahedral complexes (**I**, **II**, **III**) are proposed.

I and **II** are configurational isomers, one having a five-membered chelating ring and the other possessing a eight-membered one. In order to elucidate the three-dimensional architecture, the crystal structures of $[Cr(CO)_4(Pf-Pf-Pf)Cr(CO)_5]$ (**Ia**), $[Cr(CO)_4(Pf-Pf-Pf)Cr(CO)_5]$ (**II**) and $[W_2(CO)_8(P-Pf_3)]$ (**IIIc**) were investigated by X-ray diffraction.

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2. Experimental

All reactions were performed under dinitrogen. All solvents were dried and distilled under dinitrogen prior to use: dichloromethane and acetonitrile (CaH₂). M(CO)₆ (M = Cr, Mo or W), Me₃NO · 2H₂O and all ligands were purchased from Aldrich Chemical Company. IR spectra were taken in potassium bromide pellets and recorded on a Jasco FT-IR 5300 spectrophotometer. NMR spectra (CDCl₃) were recorded on a Bruker 300 MHz spectrophotometer. Microanalyses were performed by the Northern Instrumentation Center, National Science Council, Taipei, Taiwan with a Perkin Elmer 2400 elementary analyzer. Melting points were determined in open capillaries with a Yamato MP-21 apparatus and are uncorrected.

2.1. Synthesis of [M(CO)₄(Pf-Pf-Pf)M(CO)₅] (five-membered chelating ring) (M = Cr, **Ia**; M = Mo, **Ib**; M = W, **Ic**)

2.1.1. Labile ligand substitution method

For **Ia**: a mixture of [Cr(CO)₄NBD] which was prepared from [Cr(CO)₆] and NBD [15,21–23] (0.051 g, 0.20 mmol) and Pf-Pf-Pf (0.106 g, 0.20 mmol) was stirred in 15 ml CH₂Cl₂/MeCN (volume ratio = 1:1) solution at room temperature for 6 h, to give [Cr(CO)₄(Pf-Pf-Pf)]. A mixture of [Cr(CO)₆] (0.044 g, 0.20 mmol) and Me₃NO · 2H₂O (0.022 g, 0.20 mmol) dissolved in 15 ml or MeCN/CH₂Cl₂ (4:1) was stirred over a period of 30 min in an ice bath during which time the mixture gradually turned yellow. The previously prepared [Cr(CO)₄(Pf-Pf-Pf)] was added and the combined mixture was stirred for 24 h. The precipitate was filtered after the solvent volume had been reduced to a few milliliters and the crude product was separated by column chromatography with silica gel as packing material and n-hexane/CH₂Cl₂ (4:1) as eluent. The yellowish compound was collected and recrystallized

from CH₂Cl₂/n-hexane: 0.13 g, 58% yield; m.p. 170–171°C, IR (KBr, ν (cm⁻¹): 2064m, 2008m, 1989sh, 1933s, 1906s (CO). ³¹P NMR (CDCl₃) δ (ppm): 80.0 (P_A, dd, ²J_{XA} = 30.3 Hz, ²J_{MA} = 11.6 Hz), 79.0 (P_M, d, ²J_{AM} = 11.2 Hz), 50.0 (P_X, d, ²J_{AX} = 26.6 Hz), Anal. Found: C, 56.91; H, 3.70%. Calc. for C₄₃H₃₃Cr₂O₉P₃: C, 57.94; H, 3.73%.

For **Ib**: the procedure was similar to that for **Ia** except that the reaction period after [Mo(CO)₄(Pf-Pf-Pf)] had been added to the [Mo(CO)₅MeCN] solution was 8 h: 0.12 g, 63% yield; m.p. 159–160°C (decomposed). IR (KBr) ν (cm⁻¹): 2072m, 2020m, 1989sh, 1923s, 1894s (CO). ³¹P NMR (CDCl₃) δ (ppm): 56.5 (P_A, dd, ²J_{XA} = 36.8 Hz, ²J_{MA} = 5.1 Hz), 54.9 (P_M, d, ²J_{AM} = 5.8 Hz), 30.7 (P_X, d, ²J_{AX} = 34.6 Hz), Anal. Found: C, 53.67; H, 3.71%. Calc. for C₄₃H₃₃Mo₂O₉P₃: C, 53.73; H, 3.40%.

2.1.2. Chemical oxidation method

For **Ia**: a mixture of [Cr(CO)₆] (0.044 g, 0.20 mmol) and Me₃NO · 2H₂O (0.033 g, 0.30 mmol) dissolved in 15 ml MeCN/CH₂Cl₂ (4:1) was stirred over 30 min in an ice bath. The mixture gradually turned yellow. PhP(CH₂CH₂PPh₂)₂ (0.054 g, 0.10 mmol) was added and the solution was stirred at room temperature for 24 h. The steps for separation and purification were similar to those described for the labile ligand substitution method: 0.062 g, 67% yield.

For **Ib**: the procedure was similar to that for **Ia** except that the reaction period after PhP(CH₂CH₂PPh₂)₂ has been added was 8 h: 0.068 g, 72% yield.

For **Ic**: the procedure was similar to that for **Ia** except that the reaction period was after PhP(CH₂CH₂PPh₂)₂ has been added 36 h: 0.062 g, 51% yield. m.p. 174–175°C (decomposed). IR (KBr) ν (cm⁻¹): 2072m, 2016m, 1983sh, 1929s, 1888s (CO). Anal. Found: C, 46.01; H, 2.88%. Calc. for C₄₃H₃₃O₉P₃W₂: C, 44.69; H, 2.89%.

2.2. Synthesis of $[\text{Cr}(\text{CO})_4(\text{Pf-Pf-Pf})\text{Cr}(\text{CO})_5]$ (eight-membered chelating ring) (II)

This compound was prepared by the chemical oxidation method, the procedure was similar to that described for **Ia** and the colorless band was eluted prior to **Ia** during column chromatography: 0.012 g, 13% yield; m.p. 161–162°C; IR (KBr) ν (cm^{-1}): 2064m, 2008m, 1989sh, 1937s, 1906s (CO). ^{31}P NMR (CDCl_3) δ (ppm): 50.0 (P_A , dd, $^2J_{\text{XA}} = 13.2$ Hz, $^2J_{\text{MA}} = 14.4$ Hz), 80.0 (P_M , d, $^2J_{\text{AM}} = 15.3$ Hz), 79.0 (Px, d, $^2J_{\text{XM}} = 10.9$ Hz); Anal. Found: C, 56.51; H, 3.62%. Calc. for $\text{C}_{43}\text{H}_{33}\text{Cr}_2\text{O}_9\text{P}_3$: C, 57.94; H, 3.73%.

2.3. Synthesis of $[\text{M}_2(\text{CO})_8(\text{P-Pf}_3)]$ ($\text{M} = \text{Cr}$, **IIIa**; $\text{M} = \text{Mo}$, **IIIb**; $\text{M} = \text{W}$, **IIIc**)

2.3.1. Labile ligand substitution method

For **IIIa**: a mixture of $[\text{Cr}(\text{CO})_4\text{NBD}]$ (0.051 g, 0.20 mmol) and P-Pf_3 (0.067 g, 0.20 mmol) was dissolved in 15 ml $\text{CH}_2\text{Cl}_2/\text{MeCN}$ (volume ratio = 1:1) and the solution was stirred at room temperature for 24 h. The precipitate was filtered off after the solvent volume had been reduced to a few milliliters and crude products were separated by column chromatography with silica gel as packing material and n-hexane/ CH_2Cl_2 (6:1) as

Table 1

Crystallographic details for $[\text{Cr}(\text{CO})_4(\text{Pf-Pf-Pf})\text{Cr}(\text{CO})_5]$ (**Ia**) $[\text{Cr}(\text{CO})_4(\text{Pf-Pf-Pf})\text{Cr}(\text{CO})_5]$ (**II**) and $[\text{W}_2(\text{CO})_8(\text{P-Pf}_3)]$ (**IIIc**)

	Ia	II	IIIc
Empirical formula	$\text{C}_{43}\text{H}_{33}\text{Cr}_2\text{O}_9\text{P}_3$	$\text{C}_{43}\text{H}_{33}\text{Cr}_2\text{O}_9\text{P}_3 \cdot \text{CH}_2\text{Cl}_2$	$\text{C}_{50}\text{H}_{42}\text{O}_8\text{P}_4\text{W}_2 \cdot \text{CH}_2\text{Cl}_2$
M_r	890.64	975.57	1347.40
Color and form	yellowish needles	colorless needles	colorless needles
Diffraction meter	CAD4	CAD4	CAD4
Reflections for cell determination	25	25	25
2θ range ($^\circ$)	16.02–21.70	15.04–24.34	19.34–29.28
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$
a ($\text{\AA}$)	16.116(4)	12.812(2)	11.618(2)
b ($\text{\AA}$)	14.493(4)	22.807(4)	17.526(3)
c ($\text{\AA}$)	18.015(7)	15.611(2)	26.083(3)
β ($^\circ$)	96.33(3)	90.84(1)	98.48(1)
V ($\text{\AA}^3$)	4182(2)	4561(1)	5252(1)
Z	4	4	4
D_c (Mg m^{-3})	1.415	1.421	1.704
μ (mm^{-1})	0.67	0.62	4.74
Radiation ($\text{\AA}$)	Mo K α	Mo K α	Mo K α
$F(000)$	1824	1992	2624
Crystal size (mm)	$0.03 \times 0.10 \times 0.25$	$0.10 \times 0.20 \times 0.40$	$0.10 \times 0.20 \times 0.20$
Collection range, 2θ max ($^\circ$)	44.9	44.9	44.8
	$-17 < h < 17$	$-13 < h < 13$	$-12 < h < 12$
	$0 < k < 15$	$0 < k < 24$	$0 < k < 18$
	$0 < l < 19$	$0 < l < 16$	$0 < l < 28$
Scan speed ($^\circ \text{ min}^{-1}$)	1.27–5.49	1.27–8.24	0.82–5.49
Scan width ($^\circ$)	$0.70 \pm 0.35 \tan \theta$	$0.70 + 0.35 \tan \theta$	$0.70 + 0.35 \tan \theta$
Independent reflections	5543	5947	6858
Observed reflections	1633	3907	4936
$[I > 2.5\sigma(I)]$, m			
No. of parameters, P	255	542	605
Absorption correction	experimental Ψ rotation	experimental Ψ rotation	experimental Ψ rotation
Min. and max. transmission	0.926, 0.999	0.897, 0.998	0.818, 0.999
R_f^a (all reflections)	0.093(0.240)	0.050(0.086)	0.033(0.058)
R_w^b (all reflections)	0.061(0.088)	0.044(0.045)	0.030(0.031)
Δ/σ	0.001	0.001	0.185
Goodness of fit c	1.65	2.87	1.77
Secondary extinction (length in μm^{-1})	0.03(9)	0.5(2)	0.40(4)
Peaks in last D-map ($\text{e \AA}^{-3}$)	–0.61, 0.77	–0.80, 1.09	–0.96, 1.01
Graphics	ORTEP d [24]	ORTEP	ORTEP

^a $R_f = \sum [|F_o - F_c|] / \sum |F_o|$.^b $R_w = (\sum w(|F_o| - |F_c|)^2) / \sum [wF_o^2]^{1/2}$ where $w = 1/\sigma^2(F)$.^c $\text{Gof} = [\sum w(|F_o| - |F_c|)^2 / (m - p)]^{1/2}$.^d Ref. [24].

Table 2

Fractional atomic coordinates and isotropic thermal parameters with estimated standard deviations in parentheses, for **Ia**, **II** and **IIIc**

Atom	x	y	z	Biso ^a
Ia				
Cr1	0.1709(2)	0.7731(2)	0.2000(2)	2.9(2)
Cr2	0.5464(2)	0.5488(3)	0.2070(2)	3.6(2)
P1	0.1666(4)	0.6148(4)	0.1717(4)	2.9(3)
P2	0.0278(3)	0.7509(4)	0.2088(3)	2.7(3)
P3	0.4168(4)	0.4834(4)	0.2340(4)	2.7(3)
O1	0.173(1)	0.970(1)	0.248(1)	6.3(5)
O2	0.349(1)	0.790(1)	0.172(1)	6.2(5)
O3	0.136(1)	0.845(1)	0.041(1)	5.3(5)
O4	0.222(1)	0.709(1)	0.358(1)	6.4(5)
O5	0.697(1)	0.648(1)	0.167(1)	6.1(5)
O6	0.464(1)	0.614(1)	0.057(1)	8.0(6)
O7	0.604(1)	0.369(1)	0.141(1)	7.4(6)
O8	0.493(1)	0.711(1)	0.294(1)	5.8(5)
O9	0.644(1)	0.497(1)	0.355(1)	6.6(5)
C1	0.170(2)	0.892(2)	0.226(1)	5.5(7)
C2	0.280(1)	0.783(2)	0.185(1)	4.5(6)
C3	0.148(1)	0.813(2)	0.101(2)	4.8(7)
C4	0.204(1)	0.734(2)	0.298(2)	5.3(7)
C5	0.637(2)	0.610(2)	0.178(1)	5.1(7)
C6	0.495(2)	0.590(2)	0.115(2)	5.4(7)
C7	0.583(1)	0.437(2)	0.165(1)	4.4(7)
C8	0.513(1)	0.652(2)	0.258(1)	3.7(6)
C9	0.606(2)	0.512(2)	0.300(2)	5.0(7)
C10	0.242(1)	0.540(1)	0.224(1)	2.4(5)
C11	0.333(1)	0.567(1)	0.214(1)	1.9(5)
C12	0.068(1)	0.568(1)	0.192(1)	2.8(5)
C13	−0.004(1)	0.638(1)	0.166(1)	2.3(5)
C1A	0.176(1)	0.571(1)	0.076(1)	2.2(5)
C2A	0.219(1)	0.626(2)	0.029(1)	4.0(6)
C3A	0.229(2)	0.589(2)	−0.044(1)	5.1(7)
C4A	0.201(2)	0.502(2)	−0.061(2)	6.4(8)
C5A	0.164(2)	0.446(2)	−0.016(2)	6.1(7)
C6A	0.154(1)	0.481(2)	0.058(1)	4.9(7)
C1B	−0.006(1)	0.741(2)	0.303(1)	3.2(6)
C2B	−0.055(1)	0.672(2)	0.327(1)	3.8(6)
C3B	−0.077(1)	0.663(2)	0.399(2)	5.5(7)
C4B	−0.048(1)	0.729(2)	0.448(1)	5.5(7)
C5B	0.000(1)	0.800(2)	0.429(1)	5.1(7)
C6B	0.024(1)	0.808(2)	0.357(1)	3.3(6)
C1C	−0.052(1)	0.830(2)	0.164(1)	2.9(5)
C2C	−0.138(1)	0.803(2)	0.150(1)	3.6(6)
C3C	−0.193(1)	0.865(2)	0.110(1)	3.9(6)
C4C	−0.169(2)	0.946(2)	0.085(1)	5.4(7)
C5C	−0.086(1)	0.970(2)	0.096(1)	3.7(6)
C6C	−0.028(1)	0.913(2)	0.134(1)	3.3(6)
C1D	0.371(1)	0.384(2)	0.183(1)	2.7(5)
C2D	0.384(1)	0.378(2)	0.106(1)	4.6(6)
C3D	0.344(1)	0.310(2)	0.058(1)	4.7(6)
C4D	0.297(1)	0.246(2)	0.090(1)	3.9(6)
C5D	0.284(1)	0.252(2)	0.163(1)	4.8(6)
C6D	0.321(1)	0.320(2)	0.206(1)	3.7(6)
C1E	0.416(1)	0.450(2)	0.333(1)	3.3(5)
C2E	0.453(1)	0.371(2)	0.361(1)	3.1(5)
C3E	0.459(1)	0.349(2)	0.435(1)	4.3(6)
C4E	0.424(1)	0.411(2)	0.484(1)	3.8(6)
C5E	0.387(1)	0.492(2)	0.459(1)	3.4(6)
C6E	0.385(1)	0.513(2)	0.384(1)	4.0(6)

Table 2 (continued)

Atom	x	y	z	Biso ^a
Ib				
Cr1	0.85324(8)	0.27994(5)	0.20713(7)	3.35(5)
Cr2	0.76965(8)	0.04771(5)	0.50966(7)	3.67(5)
P1	0.7509(1)	0.28853(7)	0.3357(1)	3.00(7)
P2	0.9618(1)	0.19999(7)	0.2532(1)	2.86(7)
P3	0.7168(1)	0.10975(7)	0.3955(1)	2.93(7)
O1	0.6862(4)	0.2019(3)	0.1327(3)	7.2(3)
O2	0.9690(4)	0.2836(2)	0.0416(3)	6.2(3)
O3	0.7302(5)	0.3753(3)	0.1202(4)	9.6(4)
O4	0.9903(4)	0.3760(2)	0.2833(4)	7.5(3)
O5	0.6157(5)	0.1068(3)	0.6259(4)	10.0(4)
O6	0.9301(5)	0.1377(3)	0.5636(4)	8.4(4)
O7	0.8379(5)	−0.0286(3)	0.6552(4)	9.3(4)
O8	0.9333(4)	−0.0109(3)	0.4006(4)	7.4(3)
O9	0.6013(4)	−0.0404(3)	0.4602(4)	8.1(4)
C1	0.7525(5)	0.2299(3)	0.1622(5)	4.3(4)
C2	0.9268(5)	0.2810(3)	0.1068(5)	4.0(3)
C3	0.7744(6)	0.3399(4)	0.1573(5)	5.5(4)
C4	0.9409(6)	0.3384(3)	0.2553(5)	4.6(4)
C5	0.6725(6)	0.0843(3)	0.5809(5)	5.4(4)
C6	0.8707(6)	0.1030(3)	0.5422(5)	5.0(4)
C7	0.8121(6)	0.0002(4)	0.5993(5)	5.3(4)
C8	0.8687(5)	0.0108(3)	0.4397(5)	4.5(4)
C9	0.6638(6)	−0.0078(3)	0.4771(5)	5.0(4)
C10	0.6539(4)	0.2312(3)	0.3663(4)	3.2(3)
C11	0.6917(5)	0.1847(3)	0.4324(4)	3.1(3)
C12	0.9115(4)	0.1500(3)	0.3362(4)	3.1(3)
C13	0.8090(5)	0.1217(3)	0.3071(4)	3.2(3)
C1A	0.8165(5)	0.3025(3)	0.4384(4)	3.1(3)
C2A	0.7593(5)	0.3193(3)	0.5115(4)	4.2(3)
C3A	0.8108(6)	0.3258(3)	0.5889(5)	5.3(4)
C4A	0.9160(6)	0.3152(4)	0.5969(5)	5.6(4)
C5A	0.9711(5)	0.2983(4)	0.5266(5)	5.5(4)
C6A	0.9214(5)	0.2930(3)	0.4481(4)	3.7(3)
C1B	0.6642(5)	0.3519(3)	0.3243(4)	3.7(3)
C2B	0.7015(6)	0.4081(3)	0.3449(5)	5.0(4)
C3B	0.6382(8)	0.4564(4)	0.3291(5)	6.5(5)
C4B	0.5421(9)	0.4499(4)	0.2930(6)	7.1(6)
C5B	0.5052(7)	0.3961(5)	0.2724(6)	7.1(5)
C6B	0.5648(6)	0.3467(3)	0.2866(5)	5.1(4)
C1C	0.9991(5)	0.1466(3)	0.1706(4)	3.1(3)
C2C	1.0818(5)	0.1086(3)	0.1883(4)	3.6(3)
C3C	1.1125(6)	0.0676(3)	0.1278(5)	5.0(4)
C4C	1.0613(6)	0.0643(3)	0.0512(5)	5.0(4)
C5C	0.9781(7)	0.1001(4)	0.0332(5)	5.5(4)
C6C	0.9470(5)	0.1411(3)	0.0938(5)	4.3(4)
C1D	1.0905(5)	0.2198(3)	0.2968(4)	3.4(3)
C2D	1.1288(5)	0.2029(3)	0.3760(4)	4.5(4)
C3D	1.2263(6)	0.2197(4)	0.4044(5)	5.9(4)
C4D	1.2886(6)	0.2541(4)	0.3544(7)	6.4(5)
C5D	1.2529(6)	0.2703(4)	0.2743(6)	6.1(5)
C6D	1.1537(5)	0.2542(3)	0.2462(5)	4.6(4)
C1E	0.5978(5)	0.0892(3)	0.3387(4)	3.4(3)
C2E	0.5017(5)	0.1106(3)	0.3613(5)	4.6(4)
C3E	0.4126(6)	0.0915(4)	0.3205(6)	6.2(5)
C4E	0.4158(6)	0.0513(4)	0.2574(6)	6.7(5)
C5E	0.5110(8)	0.0293(4)	0.2332(6)	7.9(6)
C6E	0.6008(6)	0.0477(4)	0.2740(5)	5.8(4)
Cl4	0.365(2)	0.9283(6)	0.002(2)	26(2)
Cl1	0.3512(4)	0.9970(3)	0.0016(3)	24.8(5)
Cl2	0.2874(5)	0.9066(3)	0.0937(5)	30.7(6)

Table 2 (continued)

Atom	x	y	z	Biso ^a
IIIc				
W1	0.62065(3)	0.65698(2)	0.09046(2)	2.95(2)
W2	0.38658(3)	1.01222(2)	0.15410(2)	3.29(2)
P1	0.5902(2)	0.7955(1)	0.0742(1)	2.9(1)
P2	0.7612(2)	0.6817(1)	0.0281(1)	3.5(1)
P3	0.2785(2)	0.9005(1)	0.1084(1)	3.0(1)
P4	0.5597(2)	0.9406(1)	0.2025(1)	3.3(1)
O1	0.6891(7)	0.4838(4)	0.1001(3)	7.8(5)
O2	0.4296(6)	0.6459(4)	0.1627(3)	5.9(4)
O3	0.4155(6)	0.6169(5)	0.0016(3)	7.4(5)
O4	0.7964(7)	0.6857(5)	0.1933(3)	7.8(5)
O5	0.4881(7)	1.1584(4)	0.2125(4)	8.9(5)
O6	0.1848(6)	1.1238(4)	0.1130(3)	8.0(5)
O7	0.5110(6)	1.0503(4)	0.0573(3)	5.7(4)
O8	0.2489(7)	0.9837(5)	0.2491(3)	8.1(5)
C1	0.6622(9)	0.5491(5)	0.0980(4)	5.0(5)
C2	0.5026(8)	0.6488(5)	0.1353(3)	3.9(5)
C3	0.4930(8)	0.6326(5)	0.0319(4)	3.9(5)
C4	0.7384(8)	0.6752(5)	0.1544(4)	4.6(5)
C5	0.4555(8)	1.1030(6)	0.1921(4)	5.1(5)
C6	0.2578(8)	1.0799(5)	0.1260(4)	5.1(5)
C7	0.4651(7)	1.0360(5)	0.0934(3)	3.6(4)
C8	0.3018(8)	0.9917(6)	0.2145(4)	5.0(5)
C9	0.6615(8)	0.8256(5)	0.0195(3)	3.4(4)
C10	0.7788(8)	0.7855(5)	0.0226(4)	3.9(5)
C11	0.4433(7)	0.8326(5)	0.0550(3)	3.4(4)
C12	0.3602(7)	0.8146(5)	0.0944(3)	3.4(5)
C13	0.6551(7)	0.8636(5)	0.1245(3)	3.4(4)
C14	0.6174(7)	0.8515(5)	0.1783(3)	3.4(4)
C1A	0.7118(7)	0.6527(5)	−0.0388(4)	4.0(5)
C2A	0.714(1)	0.6999(6)	−0.0804(4)	5.9(6)
C3A	0.677(1)	0.6727(7)	−0.1301(4)	7.7(8)
C4A	0.639(1)	0.5997(7)	−0.1383(4)	7.0(7)
C5A	0.636(1)	0.5520(6)	−0.0971(4)	6.2(6)
C6A	0.6721(9)	0.5786(6)	−0.0472(4)	5.3(6)
C1B	0.9123(7)	0.6501(5)	0.0402(4)	4.0(5)
C2B	0.974(1)	0.6569(9)	0.0876(5)	9.7(9)
C3B	1.091(1)	0.6353(9)	0.0982(5)	10.7(1)
C4B	1.1479(9)	0.6095(7)	0.0624(5)	7.8(8)
C5B	1.088(1)	0.603(1)	0.0169(6)	16(1)
C6B	0.971(1)	0.623(1)	0.0054(5)	13(1)
C1C	0.1934(7)	0.9139(5)	0.0444(3)	3.2(4)
C2C	0.1194(8)	0.8578(5)	0.0222(4)	4.3(5)
C3C	0.0601(8)	0.8653(6)	−0.0282(4)	5.2(5)
C4C	0.0769(8)	0.9281(6)	−0.0568(4)	5.0(6)
C5C	0.1514(9)	0.9848(6)	−0.0347(4)	5.7(6)
C6C	0.2088(8)	0.9782(6)	0.0150(4)	4.7(5)
C1D	0.1705(7)	0.8634(5)	0.1455(3)	3.4(4)
C2D	0.0667(8)	0.9011(6)	0.1456(4)	5.0(5)
C3D	−0.0114(8)	0.8793(7)	0.1775(4)	5.9(6)
C4D	0.0115(9)	0.8186(7)	0.2087(4)	7.3(7)
C5D	0.116(1)	0.7797(7)	0.2111(5)	8.0(8)
C6D	0.1941(9)	0.8013(6)	0.1782(4)	5.7(6)
C1E	0.6966(7)	0.9950(5)	0.2161(3)	3.7(4)
C2E	0.7225(8)	1.0513(5)	0.1829(4)	4.5(5)
C3E	0.8280(9)	1.0893(6)	0.1916(4)	5.7(6)
C4E	0.9096(8)	1.0700(6)	0.2323(4)	6.1(6)
C5E	0.8850(8)	1.0158(6)	0.2651(4)	5.5(6)
C6E	0.7813(8)	0.9761(6)	0.2576(4)	4.4(5)

Table 2 (continued)

Atom	x	y	z	Biso ^a
C1F	0.5334(8)	0.9116(6)	0.2668(4)	4.8(6)
C2F	0.4979(10)	0.8386(8)	0.2752(4)	7.8(8)
C3F	0.467(1)	0.814(1)	0.3230(6)	11(1)
C4F	0.478(1)	0.868(1)	0.3611(5)	13(1)
C5F	0.509(1)	0.942(1)	0.3544(5)	11(1)
C6F	0.537(1)	0.9625(8)	0.3065(4)	8.3(9)
CL1	0.6793(5)	0.2837(3)	0.1764(2)	17.1(5)
CL2	0.6913(8)	0.2271(3)	0.0795(2)	24.8(7)
C	0.669(2)	0.2982(8)	0.1146(5)	17(1)

$$^a \text{Biso} = (8/3)\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j.$$

2006m, 1915sh, 1890s, 1867s (CO); ³¹P NMR (CDCl₃) δ (ppm): 81.6 (P_A, dd, ²J_{XA} = 14.2 Hz, ²J_{MA} = 13.1 Hz), 79.9 (P_M, d, ²J_{AM} = 16.9 Hz), 51.5 (P_X, d, ²J_{AX} = 12.0 Hz). Anal. Found: C, 60.37; H, 4.33%. Calc. for C₅₀H₄₂Cr₂O₈P₄: C, 56.94; H, 4.01%.

For **IIIb**: the procedure was similar to that for **IIIa** except that the reaction period was 8 h: 0.058 g, 65% yield; m.p. 179–180°C (decomposed). IR (KBr) ν (cm^{−1}): 2020m, 1929sh, 1883s, 1869s (CO); ³¹P NMR (CDCl₃) δ (ppm): 57.7 (P_A, dd, ²J_{XA} = 17.3 Hz, ²J_{MA} = 17.6 Hz), 55.6 (P_M, d, ²J_{AM} = 15.0 Hz), 33.2 (P_X, d, ²J_{AX} = 18.2 Hz); Anal. Found: C, 57.93; H, 4.38%. Calc. for C₅₀H₄₂Mo₂O₈P₄: C, 55.26; H, 3.90%.

2.3.2. Chemical oxidation method

For **IIIa**: a mixture of [Cr(CO)₆] (0.044 g, 0.20 mmol) and Me₃NO · 2H₂O (0.044 g, 0.40 mmol) was dissolved in 15 ml of MeCN/CH₂Cl₂ (4:1) in an ice bath and the solution was stirred over 50 min during which time it gradually turned to deep yellow. P(CH₂CH₂PPh₂)₃ (0.067 g, 0.10 mmol) was added and the mixture was stirred at room temperature for 24 h. The subsequent separation steps were the same as those described above for the labile ligand substitution method: 0.068 g, 66% yield.

For **IIIb**: the procedure was similar to that for **IIIa** except that the reaction period was 8 h following addition of P(CH₂CH₂PPh₂)₃: 0.079 g, 71% yield.

For **IIIc**: the procedure was similar to that for **IIIa** except that the reaction period was 36 h following addition of P(CH₂CH₂PPh₂)₃: 0.071 g, 52% yield; m.p. 184–185°C (decomposed). IR (KBr) ν (cm^{−1}): 2014m, 1927sh, 1881s, 1860s, (CO); ³¹P NMR (CDCl₃) δ (ppm): 41.2 (P_A, dd, ²J_{XA} = 13.0 Hz, ²J_{MA} = 14.1 Hz), 40.0 (P_M, d, ²J_{AM} = 13.6 Hz), 15.1 (P_X, d, ²J_{AX} = 15.5 Hz). Anal. Found: C, 50.27; H, 3.55%. Calc. for C₅₀H₄₂W₂O₈P₄: C, 47.56; H, 3.35%.

2.4. X-Ray structure determination

Crystals of **Ia**, **II** and **IIIc** were all obtained from CH₂Cl₂/n-hexane by the evaporation method. Details of crystal parameters, data collection and structure re-

eluent. The yellow compound was collected and recrystallized from CH₂Cl₂/n-hexane: 0.051 g, 52% yield; m.p. 152–153°C (decomposed). IR (KBr) ν (cm^{−1}):

Table 3

Selected bond lengths (Å) and angles (deg) with estimated standard deviations in parentheses for **Ia**, **II** and **IIIc**

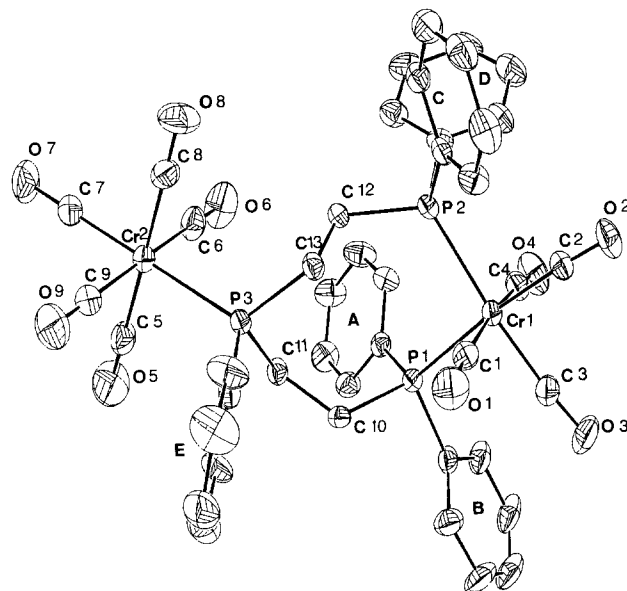
Ia			
Cr(1)–P(1)	2.349(7)	P(2)–C(1B)	1.85(2)
Cr(1)–P(2)	2.351(7)	P(2)–C(1C)	1.84(2)
Cr(1)–C(1)	1.78(3)	P(3)–C(11)	1.83(2)
Cr(1)–C(2)	1.81(2)	P(3)–C(1D)	1.83(2)
Cr(1)–C(3)	1.87(3)	P(3)–C(1E)	1.84(2)
Cr(1)–C(4)	1.87(3)	O(1)–C(1)	1.21(3)
Cr(2)–P(3)	2.392(7)	O(2)–C(2)	1.18(3)
Cr(2)–C(5)	1.83(3)	O(3)–C(3)	1.17(3)
Cr(2)–C(6)	1.86(3)	O(4)–C(4)	1.15(3)
Cr(2)–C(7)	1.90(3)	O(5)–C(5)	1.14(3)
Cr(2)–C(8)	1.86(3)	O(6)–C(6)	1.16(4)
Cr(2)–C(9)	1.91(3)	O(7)–C(7)	1.15(3)
P(1)–C(10)	1.81(2)	O(8)–C(8)	1.15(3)
P(1)–C(12)	1.80(2)	O(9)–C(9)	1.13(3)
P(1)–C(1A)	1.87(2)	C(10)–C(11)	1.54(3)
P(2)–C(13)	1.85(2)	C(12)–C(13)	1.57(3)
P(1)–Cr(1)–P(2)	82.8(2)	Cr(1)–P(1)–C(12)	109.0(7)
P(1)–Cr(1)–C(1)	176.3(9)	Cr(1)–P(1)–C(1A)	122.0(7)
P(1)–Cr(1)–C(2)	93.0(8)	C(10)–P(1)–C(12)	103.3(9)
P(1)–Cr(1)–C(3)	95.6(8)	C(10)–P(1)–C(1A)	98.9(9)
P(1)–Cr(1)–C(4)	84.8(8)	C(12)–P(1)–C(1A)	103(1)
P(2)–Cr(1)–C(1)	94.6(8)	Cr(1)–P(2)–C(13)	108.5(7)
P(2)–Cr(1)–C(2)	174.2(8)	Cr(1)–P(2)–C(1B)	117.3(7)
P(2)–Cr(1)–C(3)	90.6(7)	Cr(1)–P(2)–C(1C)	121.9(7)
P(2)–Cr(1)–C(4)	94.1(8)	C(13)–P(2)–C(1B)	103(1)
C(1)–Cr(1)–C(2)	90(1)	C(13)–P(2)–C(1C)	103(1)
C(1)–Cr(1)–C(3)	87(1)	C(1B)–P(2)–C(1C)	101.1(9)
C(1)–Cr(1)–C(4)	93(1)	Cr(2)–P(3)–C(11)	110.1(6)
C(2)–Cr(1)–C(3)	86(1)	Cr(2)–P(3)–C(1D)	121.5(8)
C(2)–Cr(1)–C(4)	90(1)	Cr(2)–P(3)–C(1E)	113.5(7)
C(3)–Cr(1)–C(4)	175(1)	C(11)–P(3)–C(1D)	100.2(9)
P(3)–Cr(2)–C(5)	172.2(8)	C(11)–P(3)–C(1E)	106(1)
P(3)–Cr(2)–C(6)	89.4(8)	C(1D)–P(3)–C(1E)	104(1)
P(3)–Cr(2)–C(7)	93.6(7)	Cr(1)–C(1)–O(1)	176(2)
P(3)–Cr(2)–C(8)	85.2(7)	Cr(1)–C(2)–O(2)	178(2)
P(3)–Cr(2)–C(9)	94.5(8)	Cr(1)–C(3)–O(3)	174(2)
C(5)–Cr(2)–C(6)	84(1)	Cr(1)–C(4)–O(4)	178(2)
C(5)–Cr(2)–C(7)	90(1)	Cr(2)–C(5)–O(5)	174(4)
C(5)–Cr(2)–C(8)	92(1)	Cr(2)–C(6)–O(6)	178(2)
C(5)–Cr(2)–C(9)	93(1)	Cr(2)–C(7)–O(7)	178(2)
C(6)–Cr(2)–C(7)	93(1)	Cr(2)–C(8)–O(8)	174(2)
C(6)–Cr(2)–C(8)	93(1)	Cr(2)–C(9)–O(9)	174(2)
C(6)–Cr(2)–C(9)	176(1)	P(1)–C(10)–C(11)	112(1)
C(7)–Cr(2)–C(8)	174(1)	P(3)–C(11)–C(10)	120(1)
C(7)–Cr(2)–C(9)	88(1)	P(1)–C(12)–C(13)	110(1)
C(8)–Cr(2)–C(9)	87(1)	P(2)–C(13)–C(12)	107(1)
Cr(1)–P(1)–C(10)	118.1(7)		
II			
Cr(1)–P(1)	2.421(2)	P(2)–C(1C)	1.842(6)
Cr(1)–P(2)	2.398(2)	P(2)–C(1D)	1.831(6)
Cr(1)–C(1)	1.853(8)	P(3)–C(11)	1.835(6)
Cr(1)–C(2)	1.840(7)	P(3)–C(13)	1.849(6)
Cr(1)–C(3)	1.863(8)	P(3)–C(1E)	1.814(7)
Cr(1)–C(4)	1.891(8)	O(1)–C(1)	1.154(9)
Cr(2)–P(3)	2.366(2)	O(2)–C(2)	1.161(8)
Cr(2)–C(5)	1.877(8)	O(3)–C(3)	1.14(1)
Cr(2)–C(6)	1.872(8)	O(4)–C(4)	1.15(1)
Cr(2)–C(7)	1.845(8)	O(5)–C(5)	1.14(1)
Cr(2)–C(8)	1.884(7)	O(6)–C(6)	1.15(1)
Cr(2)–C(9)	1.918(8)	O(7)–C(7)	1.14(1)

Table 3 (continued)

P(1)–C(10)	1.871(6)	O(8)–C(8)	1.149(9)
P(1)–C(1A)	1.826(6)	O(9)–C(9)	1.12(1)
P(1)–C(1B)	1.829(7)	C(10)–C(11)	1.551(9)
P(2)–C(12)	1.849(6)	C(12)–C(13)	1.527(8)
P(1)–Cr(1)–P(2)	97.56(7)	Cr(1)–P(1)–C(1A)	119.6(2)
P(1)–Cr(1)–C(1)	88.9(2)	Cr(1)–P(1)–C(1B)	108.6(2)
P(1)–Cr(1)–C(2)	174.2(2)	C(10)–P(1)–C(1A)	101.4(3)
P(1)–Cr(1)–C(3)	89.4(2)	C(10)–P(1)–C(1B)	99.9(3)
P(1)–Cr(1)–C(4)	86.5(2)	C(1A)–P(1)–C(1B)	102.7(3)
P(2)–Cr(1)–C(1)	92.5(2)	Cr(1)–P(2)–C(12)	118.2(2)
P(2)–Cr(1)–C(2)	87.9(2)	Cr(1)–P(2)–C(1C)	116.6(2)
P(2)–Cr(1)–C(3)	172.7(2)	Cr(1)–P(2)–C(1D)	116.1(2)
P(2)–Cr(1)–C(4)	94.5(2)	C(12)–P(2)–C(1C)	100.3(3)
C(1)–Cr(1)–C(2)	92.8(3)	C(12)–P(2)–C(1D)	102.3(3)
C(1)–Cr(1)–C(3)	85.6(3)	C(1C)–P(2)–C(1D)	100.5(3)
C(1)–Cr(1)–C(4)	172.1(3)	Cr(2)–P(3)–C(11)	111.8(2)
C(2)–Cr(1)–C(3)	85.2(3)	Cr(2)–P(3)–C(13)	118.1(2)
C(2)–Cr(1)–C(4)	91.2(3)	Cr(2)–P(3)–C(1E)	116.3(2)
C(3)–Cr(1)–C(4)	87.9(4)	C(11)–P(3)–C(13)	102.4(3)
P(3)–Cr(2)–C(5)	89.7(2)	C(11)–P(3)–C(1E)	104.1(3)
P(3)–Cr(2)–C(6)	89.5(2)	C(13)–P(3)–C(1E)	102.4(3)
P(3)–Cr(2)–C(7)	179.1(3)	Cr(1)–C(1)–O(1)	175.6(6)
P(3)–Cr(2)–C(8)	91.1(2)	Cr(1)–C(2)–O(2)	176.3(6)
P(3)–Cr(2)–C(9)	90.1(2)	Cr(1)–C(3)–O(3)	174.0(7)
C(5)–Cr(2)–C(6)	90.1(4)	Cr(1)–C(4)–O(4)	176.5(7)
C(5)–Cr(2)–C(7)	90.1(3)	Cr(2)–C(5)–O(5)	178.0(8)
C(5)–Cr(2)–C(8)	179.0(3)	Cr(2)–C(6)–O(6)	177.8(7)
C(5)–Cr(2)–C(9)	88.8(3)	Cr(2)–C(7)–O(7)	179.2(8)
C(6)–Cr(2)–C(7)	89.7(3)	Cr(2)–C(8)–O(8)	176.1(6)
C(6)–Cr(2)–C(8)	89.4(3)	Cr(2)–C(9)–O(9)	178.3(7)
C(6)–Cr(2)–C(9)	178.8(3)	P(1)–C(10)–C(11)	116.4(4)
C(7)–Cr(2)–C(8)	89.1(3)	P(3)–C(11)–C(10)	118.8(4)
C(7)–Cr(2)–C(9)	90.7(3)	P(2)–C(12)–C(13)	111.1(4)
C(8)–Cr(2)–C(9)	91.8(3)	P(3)–C(13)–C(12)	113.3(4)
Cr(1)–P(1)–C(10)	121.6(2)		
IIIc			
W(1)–P(1)	2.481(2)	P(3)–C(12)	1.844(9)
W(1)–P(2)	2.508(3)	P(3)–C(1C)	1.824(9)
W(1)–C(1)	1.955(9)	P(3)–C(1D)	1.814(9)
W(1)–C(2)	1.935(9)	P(4)–C(14)	1.847(9)
W(1)–C(3)	2.011(9)	P(4)–C(1E)	1.844(9)
W(1)–C(4)	2.020(9)	P(4)–C(1F)	1.82(1)
W(2)–P(3)	2.528(2)	O(1)–C(1)	1.18(1)
W(2)–P(4)	2.543(3)	O(2)–C(2)	1.19(1)
W(2)–C(5)	1.98(1)	O(3)–C(3)	1.14(1)
W(2)–C(6)	1.97(1)	O(4)–C(4)	1.15(1)
W(2)–C(7)	1.983(9)	O(5)–C(5)	1.15(1)
W(2)–C(8)	2.01(1)	O(6)–C(6)	1.16(1)
P(1)–C(9)	1.830(9)	O(7)–C(7)	1.18(1)
P(1)–C(11)	1.826(8)	O(8)–C(8)	1.17(1)
P(1)–C(13)	1.850(8)	C(9)–C(10)	1.53(1)
P(2)–C(10)	1.839(9)	C(11)–C(12)	1.54(1)
P(2)–C(1A)	1.83(1)	C(13)–C(14)	1.55(1)
P(2)–C(1B)	1.823(9)		
P(1)–W(1)–P(2)	79.05(8)	C(9)–P(1)–C(13)	100.5(4)
P(1)–W(1)–C(1)	172.3(3)	C(11)–P(1)–C(13)	103.4(4)
P(1)–W(1)–C(2)	94.6(3)	W(1)–P(2)–C(10)	108.2(3)
P(1)–W(1)–C(3)	90.4(3)	W(1)–P(2)–C(1A)	115.4(3)
P(1)–W(1)–C(4)	92.8(3)	W(1)–P(2)–C(1B)	122.5(3)
P(2)–W(1)–C(1)	93.3(3)	C(10)–P(2)–C(1A)	103.0(4)
P(2)–W(1)–C(2)	173.1(3)	C(10)–P(2)–C(1B)	101.5(4)
P(2)–W(1)–C(3)	91.2(3)	C(1A)–P(2)–C(1B)	103.9(4)
P(2)–W(1)–C(4)	94.7(3)	W(2)–P(3)–C(12)	119.4(3)
C(1)–W(1)–C(2)	93.1(4)	W(2)–P(3)–C(1C)	119.7(3)
C(1)–W(1)–C(3)	90.9(4)	W(2)–P(3)–C(1D)	111.1(3)

Table 3 (continued)

C(1)–W(1)–C(4)	86.7(4)	C(12)–P(3)–C(1C)	98.6(4)
C(2)–W(1)–C(3)	86.2(4)	C(12)–P(3)–C(1D)	103.3(4)
C(2)–W(1)–C(4)	88.1(4)	C(1C)–P(3)–C(1D)	102.1(4)
C(3)–W(1)–C(4)	173.7(4)	W(2)–P(4)–C(14)	123.2(3)
P(3)–W(2)–P(4)	98.81(8)	W(2)–P(4)–C(1E)	115.9(3)
P(3)–W(2)–C(5)	174.0(3)	W(2)–P(4)–C(1F)	111.5(3)
P(3)–W(2)–C(6)	89.6(3)	C(14)–P(4)–C(1E)	99.0(4)
P(3)–W(2)–C(7)	92.4(2)	C(14)–P(4)–C(1F)	101.4(4)
P(3)–W(2)–C(8)	87.9(3)	C(1E)–P(4)–C(1F)	103.0(4)
P(4)–W(2)–C(5)	85.2(3)	W(1)–C(1)–O(1)	176.6(9)
P(4)–W(2)–C(6)	170.6(3)	W(1)–C(2)–O(2)	178.2(8)
P(4)–W(2)–C(7)	94.4(2)	W(1)–C(3)–O(3)	174.5(8)
P(4)–W(2)–C(8)	88.0(3)	W(1)–C(4)–O(4)	173.5(9)
C(5)–W(2)–C(6)	86.1(4)	W(2)–C(5)–O(5)	174.9(9)
C(5)–W(2)–C(7)	91.8(4)	W(2)–C(6)–O(6)	174.2(9)
C(5)–W(2)–C(8)	87.7(4)	W(2)–C(7)–O(7)	179.6(7)
C(6)–W(2)–C(7)	89.4(4)	W(2)–C(8)–O(8)	176.0(9)
C(6)–W(2)–C(8)	88.1(4)	P(1)–C(9)–C(10)	109.2(6)
C(7)–W(2)–C(8)	177.5(4)	P(2)–C(10)–C(9)	110.6(6)
W(1)–P(1)–C(9)	110.3(3)	P(1)–C(11)–C(12)	113.4(6)
W(1)–P(1)–C(11)	119.9(3)	P(3)–C(12)–C(11)	110.9(6)
W(1)–P(1)–C(13)	118.5(3)	P(1)–C(13)–C(14)	114.5(6)
C(9)–P(1)–C(11)	101.3(4)	P(4)–C(14)–C(13)	111.1(6)

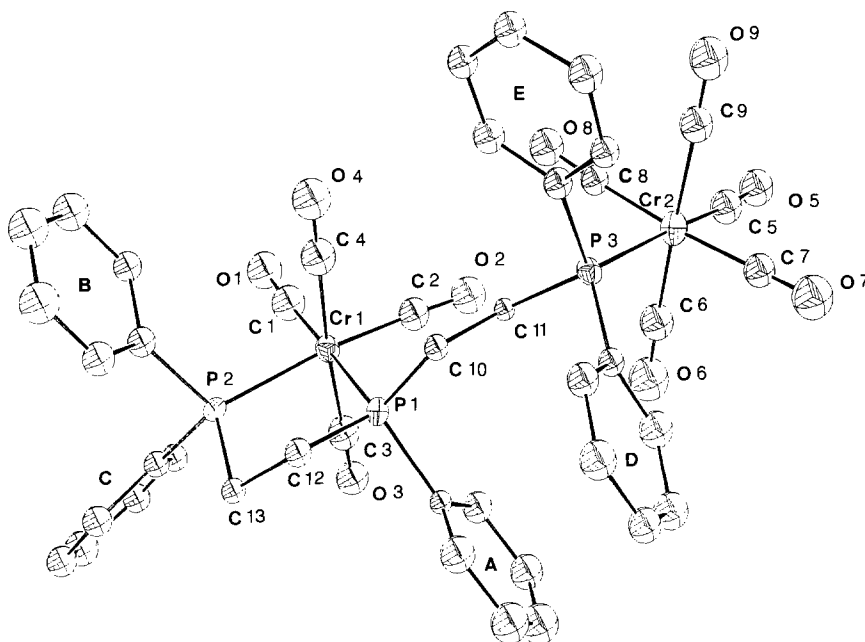
Fig. 2. Molecular structure of $[\text{Cr}(\text{CO})_4(\text{Pf-Pf-Pf})\text{Cr}(\text{CO})_5]$ (**II**).

finement are given in Table 1. All data reduction and structure refinement activities were performed using the NRCVAX package [25]. Structures were solved by the direct method with a solver program [25]. Atomic scattering factors were taken from the International Tables for X-ray Crystallography [26].

3. Results and discussion

Complexes **Ia**, **Ib**, **IIIa** and **IIIb** can be prepared by either the chemical oxidation method or the NBD labile

ligand substitution method. Complexes **Ic** and **IIIc** could only be prepared by chemical oxidation owing to the difficulty in preparing the $[\text{W}(\text{CO})_4\text{NBD}]$ intermediate for the labile ligand substitution method [21–23]. In the synthesis of **Ia** by the chemical oxidation method, **II** was the by-product the yield of **II** (13%) being lower than that of **Ia** (58%). A possible reason for this is that the bond strain for the five-membered chelating ring in compound (**Ia**) is less than that for eight-membered chelating ring in compound (**II**). Some unidentified products adhered to the silica gel and could not be washed out by elution during chromatographic separation in the preparations of all of the title complexes. For

Fig. 1. Molecular structure of $[\text{Cr}(\text{CO})_4(\text{Pf-Pf-Pf})\text{Cr}(\text{CO})_5]$ (**Ia**).

complexes of type **I** and **II**, $[\text{M}(\text{CO})_4(\text{Pf-Pf-Pf})\text{M}(\text{CO})_5]$, the IR spectra in the carbonyl stretching region show absorptions at 2064–2072m, 2008–2022m, 1983–1991sh, 1923–1937s and 1888–1906s cm^{-1} , and those of type **III**, $[\text{M}_2(\text{CO})_8(\text{P-Pf}_3)]$, at 2006–2014m, 1915–1929sh, 1881–1890s and 1860–1869sh cm^{-1} (KBr pellet), which are in accord with the CO stretching modes exhibited by $[\text{M}(\text{CO})_5\text{L}](\text{A} + \text{E} + \text{A}_1)$ and/or *cis*- $[\text{M}(\text{CO})_4\text{L}_2](\text{A} + \text{B}_1 + \text{B}_2 + \text{A}_1)$ species [15,17–30]. The ^{31}P NMR chemical shift for the disubstituting phosphorus atoms in five-membered chelating ring complexes are at ca. 80 Hz (Cr–P), ca. 55 (Mo–P) and ca. 40 (W–P) ppm, respectively. This trend has also been observed in the mixed Group 6 carbonyl complexes [15]. In complexes of type **I**, the coupling constants $^2J_{\text{PP}}$ are ca. 30 Hz when the two phosphorus atoms are coordinated to different metal atoms, and the relatively small value of $^2J_{\text{PP}}$ for phosphorus atoms coordinated to the same metal atom ($^2J_{\text{AM}}$, 5.8–11.2 Hz; $^2J_{\text{MA}}$, 5.1–11.6 Hz) is due to the chelate effect [15,31,32]. However, when the ring is eight-membered (complexes of type **II** and **III**) no coupling is found between the two chelating phosphorus atoms.

The deviations between elemental analyses are somewhat higher, especially for **IIIa** and **IIIc**, maybe as a result of incomplete exclusion of the crystallization solvent, which would be incorporated into the crystal during drying under diminished pressure.

Atomic position parameters, selected bond lengths and bond angles of **Ia**, **II** and **IIIc** are listed in Tables 2 and 3 and the molecular structures are shown in Figs. 1, 2 and 3, respectively.

Crystals of **Ia**, **II** and **IIIc** all belong to the monoclinic system with space group $P2_1/c$. Each molecule

of **Ia** and **II** consists of two metal atoms, a disubstituted metal coordinated by two chelating phosphine atoms, and a monosubstituted metal coordinated by only one phosphorus atom. The coordination sphere around the monosubstituted metal is a distorted octahedron with the bond angles of the three principle axes being $172.2(8)^\circ$ – $176(1)^\circ$ for **Ia** and $178.8(3)^\circ$ – $179.1(3)^\circ$ for **II**, the twelve mutually perpendicular angles being $84(1)^\circ$ – $94.5(8)^\circ$ for **Ia** and $88.8(3)^\circ$ – $91.8(3)^\circ$ for **II**, and dihedral angles between two of the three mutually perpendicular least-squares planes being $90.2(8)^\circ$, $91.6(7)^\circ$ and $86.9(6)^\circ$ for **Ia** and $89.1(2)^\circ$, $90.0(2)^\circ$ and $89.5(2)^\circ$ for **II**. It is obvious that the deviation from the theoretical octahedron around the monosubstituted metal for **Ia** is larger than that for **II**. This may be due to the steric effect of the two phenyl groups D and E in **Ia** being greater than that of the single phenyl Group E in **II**. The fact that the distortions from octahedral for the two disubstituted chelating coordination spheres (the three principle axes being $174.3(3)^\circ$ – $176.3(9)^\circ$ for **Ia** and $172.1(3)^\circ$ – $174.2(2)^\circ$ for **II** the twelve mutually perpendicular angles being $82.8(2)^\circ$ – $95.6(8)^\circ$ for **Ia** and $85.2(3)^\circ$ – $97.56(7)^\circ$ for **II** and the dihedral angles between two of the three mutually perpendicular least-squares planes being $91.7(7)^\circ$, $84.1(7)^\circ$ and $96.0(4)^\circ$ for **Ia**, and $91.0(2)^\circ$, $91.1(2)^\circ$ and $94.0(1)^\circ$ for **II**) are larger than those for the above monosubstituted ones is attributed to the formation of chelating rings. The two metals in **Ia** are located on the same side of the least-squares plane formed by three phosphorus atoms in the ligand, and those of **II** are located on different sides. The Cr–P bond lengths in the chelating ring for **II** are greater than those for **Ia** and the bond angles of M–P–C and P–C–C inside the chelating ring for **II** deviate from the typical sp^3 angle (109.5°) to a greater extent than those for **Ia** revealing the larger ring strain for the eight-membered chelating ring.

The molecule of **IIIc** also consists of two metal atoms which are both coordinated by two chelating phosphorus atoms and the coordination spheres are all rather distorted (the three principle axes being $172.3(3)^\circ$ – $173.7(4)^\circ$ for W(1), and $170.6(3)^\circ$ – $177.5(4)^\circ$ for W(2), the twelve mutually perpendicular angles being $79.05(8)^\circ$ – $94.7(3)^\circ$ for W(1) and $85.2(3)^\circ$ – $98.81(8)^\circ$ for W(2), and the dihedral angles between two of the three mutually perpendicular least-squares planes being $90.8(2)^\circ$, $89.5(2)^\circ$ and $81.6(2)^\circ$ for W(1) and $88.7(2)^\circ$, $89.9(2)^\circ$ and $84.8(2)^\circ$ for W(2)). Owing to the greater ring strain for the eight-membered chelating ring, the W–P bonds for W(2) are longer than those for W(1) and the bond angles inside the chelating ring for W(2) are obviously greater than those for W(1). Among the four W–P bonds, W(1)–P(1) (2.481(2) Å) is much shorter than the other three (2.508(2), 2.528(2) and 2.543(3) Å). This trend is a consequence of the lesser degree of phenyl substitution [15,33].

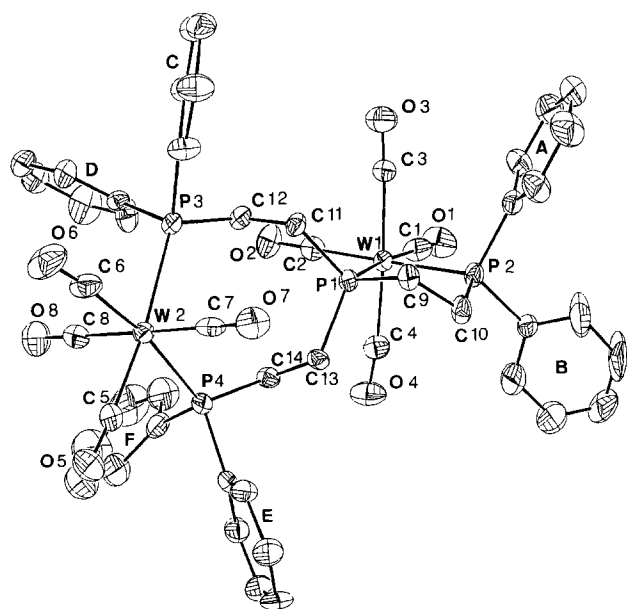


Fig. 3. Molecular structure of $[\text{W}_2(\text{CO})_8(\text{P-Pf}_3)]$ (**IIIc**).

The M–CO bond lengths (M = Cr or W) *trans* to the P atoms for each octahedron of **II** and **IIIc** are slightly less than those of the *cis* carbonyl. This feature is attributed to the π -acceptor ability of phosphorus being lower than that of the carbonyl group. This trend is not obvious for **Ia** since the crystallographic data obtained are not of such a good quality as those for the other two owing to the small size of the crystal of **Ia** (one of the dimensions was only 0.03 mm). The fact that the Cr–P length for **Ia** and **II** is less than the corresponding W–P length is due to the small atomic radius of Cr. The range of the P–C and C–C bond lengths in the phosphines is reasonable and there is no intermolecular contact of structural significance in any of these compounds.

Among the bimetallic complexes containing polydentate phosphine ligands reported in the literature, the coordination number and geometry around transition metal center are diverse. For example, the rhenium atoms are pentacoordinated or hexacoordinated, with distorted square-pyramidal or octahedral geometry [1]; cobalt atoms are pentacoordinated or hexacoordinated, with distorted trigonal bipyramidal [2–4,8,10] or cradle geometry [9]; iron atoms are hexacoordinated with confacial bioctahedral geometry [5]; gold atoms are tetracoordinated with distorted tetrahedral geometry [6]; rhodium platinum and nickel atoms are all tetracoordinated with distorted square-planar geometry [7,11,12]; the Group 6 metals are always hexacoordinate with distorted octahedral geometry [13,14]. Although the coordination sphere around the central metals in *fac, fac*-M₂(CO)₆(eHTP) (M = Cr, Mo or W) [14], [M(CO)₄(Pf-Pf)-M(CO)₅] and [M₂(CO)₈(P-Pf₃)] (M = Cr, Mo or W) all exhibit to-octahedral geometry, the deviation from the typical octahedron for *fac, fac*-M₂(CO)₆(eHTP) is greater than for the others. This phenomenon is caused by trichelated coordination and the short carbon chain between the two central phosphorus atoms in *fac, fac*-M₂(CO)₆(eHTP).

4. Supplementary material

Tables of anisotropic thermal parameters, hydrogen atom parameters, complete bond lengths and angles, and observed calculated structural factors can be obtained from the authors upon request.

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