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Synthesis and reactions of the cationic seven-coordinate complexes, $[MoI(CO)_3(NCR)\{Ph_2P(CH_2)_nPPh_2\}][BF_4]$ ($R = Me$, $n = 1$, 2 and 3; $R = Et$, $n = 1$). Crystal structures of $[MoI_2(CO)_2(PPh_3)\{Ph_2P(CH_2)PPh_2\}]$, $[MoI(CO)_2\{Ph_2P(CH_2)PPh_2\}_2][BF_4]\cdot CH_2Cl_2$, $[MoCl_3O\{Ph_2PO(CH_2)OPPh_2\}]$ and $[Mo_3(\mu_3\text{-}I)_2\{\mu_2\text{-}Ph_2P(CH_2)PPh_2\}_3]I$

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Abstract

Equimolar quantities of $[MoI_2(CO)_3\{Ph_2P(CH_2)_nPPh_2\}]$ ($n = 1$, 2 or 3) and $Ag[BF_4]$ were reacted in acetonitrile at room temperature to give the cationic seven-coordinate complexes, $[MoI(CO)_3(NCMe)\{Ph_2P(CH_2)_nPPh_2\}][BF_4]$, (**1**–**3**), in high yield. Reactions of $[MoI(CO)_3(NCMe)\{Ph_2P(CH_2)PPh_2\}][BF_4]$ (**1**) with one equivalent of L in CH_2Cl_2 at room temperature afford either $[MoI(CO)_3L\{Ph_2P(CH_2)PPh_2\}][BF_4]$, {L = NCEt **4**, $P(OMe)_3$ **5**, $P(OEt)_3$ **6**} or $[MoI(CO)_2(NCMe)L\{Ph_2P(CH_2)_nPPh_2\}][BF_4]$ {L = $P(OPr^i)_3$ **7**, $P(OPh)_3$ **8**, PPh_3 **9**}. Complex **9** reacts with NaI to give the crystallographically characterised complex, $[MoI_2(CO)_2(PPh_3)\{Ph_2P(CH_2)PPh_2\}]$ (**10**). Treatment of **1** with equimolar amounts of L^L {where L^L = 1,10-phen, 4,7-Me_2-1,10-phen, 2,2′-bipy, $Ph_2P(CH_2)_nPPh_2$ ($n = 1$, 2 and 3)} yielded the cationic complexes $[MoI(CO)(L\,\hat{}\,L)\{Ph_2P(CH_2)PPh_2\}][BF_4]$ (**11**–**16**). Complex **14**, {L^L = $Ph_2P(CH_2)PPh_2$}, has been crystallographically characterised. Equimolar quantities of **2**, **3** and $Ph_2P(CH)_2PPh_2$ give the complexes, $[MoI(CO)_2\{Ph_2P(CH_2)PPh_2\}\{Ph_2P(CH_2)_nPPh_2\}][BF_4]$ {$n = 2$, **17**, $n = 3$, **18**}. Reaction of equimolar amounts of **1** and $[S_2CX]^-$ affords the neutral complexes $[MoI(CO)_2(S_2CX)\{Ph_2P(CH_2)PPh_2\}]$, (where X = NMe_2 **19**, NEt_2 **20**, NC_4H_8 **21**). Reaction of **1** and NaX (X = F, Cl) or KSCN, in equimolar ratio, gave the neutral complexes $[MoXI(CO)_3\{Ph_2P(CH_2)PPh_2\}]$ (**22**–**24**) in good yield. Upon exposure to air of concentrated solutions of complex **1** in $CDCl_3$, the unusual crystallographically characterised species, $[MoCl_3O\{Ph_2PO(CH_2)OPPh_2\}]$ and $[Mo_3(\mu_3\text{-}I)_2\{\mu_2\text{-}Ph_2P(CH_2)PPh_2\}_3]I$, are obtained as decomposition products.

Keywords: Cationic; Seven-coordinate; Molybdenum(II); Iodide; Carbonyl; Phosphine; Nitrile; Crystal structure

1. Introduction

Seven-coordination is not commonly observed in transition metal chemistry. However, there are many examples of seven-coordinate complexes of molybdenum(II) and tungsten(II), which generally exhibit one of four geometries; capped octahedral, capped trigonal prism, pentagonal bipyramidal or the 4:3 geometry [1–5]. Both Bencze and co-workers [6,7] and, more recently, Baker and co-workers [8], have shown that complexes of the type $[MX_2(CO)_3(L)_2]$ (M = Mo, W; X = Cl, Br, I: L = NCMe, PPh_3, etc.) are active single component alkene metathesis catalysts. Although there are a large range of neutral, seven-coordinate halocarbonyl complexes of molybdenum(II) and tungsten(II) known [4,5,9–25], far fewer cationic complexes of this type have been reported [26–30].

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Until the work described in this paper, the only report of the use of silver salts to prepare cationic seven-coordinate complexes of Mo(II) and W(II), by halide abstraction, was by Beck and Rosendorfer in 1995 [31]. They treated $[MoBr_2(CO)_2(PPh_3)_2]$ with $Ag[CF_3SO_3]$ to give $[Mo(O_3SCF_3)_2(CO)_2(PPh_3)_2]$, which then gave the seven-coordinate cation $[Mo(CO)_2(NCMe)_3(PPh_3)_2]$-$[CF_3SO_3]_2$ in acetonitrile solution. The tungsten analogue, $[W(CO)_2(NCMe)_3(PPh_3)_2][CF_3SO_3]_2$ was also described [31]. Attempts by Beck and co-workers [32] to react $[MBr_2(CO)_2(PPh_3)_2]$ (M = Mo, W) with $Ag[BF_4]$ in CH_2Cl_2 gave the fluoro-bridged complexes, $[(Ph_3P)_2(CO)_2M(\mu\text{-}F)_3M(CO)_2(PPh_3)_2]$, which has been structurally characterised for M = Mo.

In 1986 [33,34], we described the synthesis and characterisation of the highly versatile seven-coordinate di-iodo complexes, $[MI_2(CO)_3(NCMe)_2]$ (M = Mo, W), and we have extensively investigated their chemistry [4,5]. In 1987 [35], we reported the high yield synthesis of the seven-coordinate complexes $[MI_2(CO)_3\{Ph_2P(CH_2)_nPPh_2\}]$ (M = Mo, W; $n = 1–6$). In this paper, the reactions of $[Mo_2(CO)_3\{Ph_2P(CH_2)_nPPh_2\}]$ ($n = 1–3$) with $Ag[BF_4]$ in NCMe to give the cationic complexes $[MoI(CO)_3(NCMe)\{Ph_2P(CH_2)_nPPh_2\}][BF_4]$ ($n = 1–3$) are detailed. The reactions of the bis(diphenylphosphino)methane (dppm) complex in particular, with a series of neutral and anionic ligands gave a range of products, including the crystallographically characterised complexes $[MoI_2(CO)_2(PPh_3)\{Ph_2P(CH_2)PPh_2\}]$ and $[MoI(CO)_2\{Ph_2P(CH_2)PPh_2\}_2][BF_4]$ which are described. Dissolving the cation, $[MoI(CO)_3(NCMe)\{Ph_2P(CH_2)PPh_2\}][BF_4]$, to give a concentrated $CDCl_3$ solution to afford the novel, structurally characterised complexes, $[MoCl_3O\{Ph_2PO(CH_2)POPh_2\}]$ and $[Mo_3(\mu_3\text{-}I)_2\{\mu_2\text{-}Ph_2P(CH_2)PPh_2\}_3]I$, as two separate decomposition products is also reported.

2. Results and discussion

The molybdenum(II) complexes $[MoI_2(CO)_3\{Ph_2P(CH_2)_nPPh_2\}]$ ($n = 1$, 2 or 3) were prepared by the reaction of equimolar amounts of $[MoI_2(CO)_3(NCMe)_2]$ and $Ph_2P(CH_2)_nPPh_2$, as previously reported [35]. Reaction of the neutral complexes $[MoI_2(CO)_3\{Ph_2P(CH_2)_nPPh_2\}]$ ($n = 1$, 2 or 3) with one equivalent of $Ag[BF_4]$ in acetonitrile at room temperature gave the cationic complexes $[MoI(CO)_3(NCMe)\{Ph_2P(CH_2)_nPPh_2\}][BF_4]$ ($n = 1$, 2 or 3) (**1**–**3**), in very good yields. The three cationic complexes have been fully characterised by elemental analysis (C, H, N), IR spectroscopy, ^1H-NMR spectroscopy, $^{11}B\{^1H\}$ and $^{31}P\{^1H\}$ spectroscopy (Tables 1–4) and $^{13}C\{^1H\}$-NMR spectroscopy {for (**1**) and (**2**) only} (Table 5).

Table 1
Physical and analytical data [a] for complexes **1**–**24**

	Complex	Colour	Yield (%)	Analysis (%)		
				C	H	N
1	$[MoI(CO)_3(NCMe)(dppm)][BF_4]$	Orange–brown	95	44.2 (44.0)	3.6 (3.1)	2.1 (1.7)
2	$[MoI(CO)_3(NCMe)(dppe)][BF_4]$	Orange–brown	87	44.9 (44.7)	3.8 (3.3)	1.7 (1.7)
3	$[MoI(CO)_3(NCMe)(dpppr)][BF_4]$	Orange–brown	74	45.8 (45.4)	4.0 (3.5)	1.7 (1.7)
4	$[MoI(CO)_3(NCEt)(dppm)][BF_4]$	Orange–brown	90	44.4 (44.7)	3.6 (3.3)	2.4 (1.7)
5	$[MoI(CO)_3\{P(OMe)_3\}(dppm)][BF_4]\cdot CH_2Cl_2$	Yellow	73	39.0 (39.0)	3.9 (3.4)	–
6	$[MoI(CO)_3\{P(OEt)_3\}(dppm)][BF_4]$	Yellow	73	43.3 (43.2)	4.8 (4.0)	–
7	$[MoI(CO)_2(NCMe)\{P(O^iPr)_3\}(dppm)][BF_4]\cdot 0.5CH_2Cl_2$	Yellow–brown	66	44.9 (44.9)	4.8 (4.6)	1.0 (1.4)
8	$[MoI(CO)_2(NCMe)\{P(OPh)_3\}(dppm)][BF_4]$	Yellow–brown	64	51.3 (51.3)	3.7 (3.7)	1.2 (1.3)
9	$[MoI(CO)_2(NCMe)(PPh_3)(dppm)][BF_4]$	Orange	72	54.1 (53.6)	4.1 (3.8)	1.6 (1.3)
10	$[MoI_2(CO)_2(PPh_3)(dppm)]$	Bright orange	64	50.8 (51.4)	3.8 (3.5)	–
11	$[MoI(CO)_2(1,10\text{-phen})(dppm)][BF_4]$	Dark brown	75	50.4 (50.2)	3.6 (3.5)	3.0 (3.0)
12	$[MoI(CO)_2(4,7\text{-}Me_2\text{-}1,10\text{-phen})(dppm)][BF_4]\cdot 0.5CH_2Cl_2$	Dark brown	70	50.2 (49.8)	3.6 (3.5)	3.0 (2.8)
13	$[MoI(CO)_2(2,2'\text{-bipy})(dppm)][BF_4]$	Dark brown	88	49.3 (49.0)	3.7 (3.3)	3.7 (3.1)
14	$[MoI(CO)_2(dppm)_2][BF_4]\cdot CH_2Cl_2$	Yellow	76	52.7 (52.2)	3.9 (3.8)	–
15	$[MoI(CO)_2(dppe)(dppm)][BF_4]$	Dark yellow	66	55.5 (55.4)	4.1 (4.0)	–
16	$[MoI(CO)_2(dpppr)(dppm)][BF_4]$	Dark yellow	69	55.7 (55.8)	4.3 (4.2)	–
17	$[MoI(CO)_2(dppm)(dppe)][BF_4]$	Dark yellow	67	55.5 (55.4)	4.3 (4.0)	–
18	$[MoI(CO)_2(dppm)(dpppr)][BF_4]$	Dark yellow	70	56.0 (55.8)	4.5 (4.2)	–
19	$[MoI(CO)_2(S_2CNMe_2)(dppm)]$	Brown	86	45.5 (46.0)	3.8 (3.6)	2.1 (1.8)
20	$[MoI(CO)_2(S_2CNEt_2)(dppm)]$	Brown	79	46.6 (47.4)	4.0 (4.0)	2.1 (1.7)
21	$[MoI(CO)_2(S_2CNC_4H_8)(dppm)]$	Brown	93	47.2 (47.5)	4.0 (3.7)	2.0 (1.7)
22	$[MoFI(CO)_3(dppm)]$	Brown–green	75	46.9 (47.3)	3.6 (3.1)	–
23	$[MoClI(CO)_3(dppm)]$	Dark brown	87	46.6 (46.3)	3.5 (3.1)	–
24	$[Mo(NCS)I(CO)_3(dppm)]$	Dark brown	70	46.8 (46.5)	3.5 (3.0)	1.9 (1.9)

[a] Calculated values in parentheses; dppm = $Ph_2P(CH_2)PPh_2$; dppe = $Ph_2P(CH_2)_2PPh_2$; dpppr = $Ph_2P(CH_2)_3PPh_2$.

Table 2
Infrared data [a] for complexes **1**–**24**

	$\nu(C\equiv N)$ cm^{-1}	$\nu(C\equiv O)$ cm^{-1}	$\nu(B{-}F)$ cm^{-1}
1	2252, w	2038, w, 1961, 1882 s, br	1069, 1028, s, br
2	2254, w	2046, w, 1957, 1890, s, br	1068, 1028, s, br
3	2274, w	1929, 1880, 1850, s, br	1067, 1028, s, br
4	2250, w	2041, w, 1960, 1888, s, br	1067, 1026, s, br
5	–	1988, 1954, 1908, s, br	1068, 1029, s, br
6	–	1982, 1953, 1901, s, br	1068, 1027, s, br
7	2280, w	1968, 1897, s, br	1062, 1024, s, br
8	2278, w	1978, 1911, s, br	1059, s, 1025, m
9	2271, w	1961, 1893, s	1066, 1027, s, br
10	–	1941, 1860, s, sh	–
11	–	1974, 1888, s, br	1064, 1026, s, br
12	–	1972, 1889, s, br	1065, 1027, s, br
13	–	1972, 1892, s, br	1065, 1028, s, br
14	–	1934, 1862, s, sh	1089, 1057, s, br
15	–	1950, s, sh, 1885, m, sh	1065, 1028, s, br
16	–	1946, s, sh, 1879, m, sh	1067, 1028, s, br
17	–	1950, s, sh, 1886, m, sh	1066, 1027, s, br
18	–	1946, s, sh, 1879, m, sh	1067, 1028, s, br
19	–	1946, m, 1882, s	ν(CS) 1786, m, br
20	–	1945, s, sh, 1880, s, br	ν(CS) 1792, 1771, m, s br
21	–	1946, 1880, s, br	ν(CS) 1789, m, br
22	–	2043, m, 1972, s, br, 1885, m, br	–
23	–	2040, m, 1950, s, br, 1871, m	–
24	ν(NCS) 2133, m	2071, 1955, 1880, s, br	–

[a] Spectra recorded as thin films in $CHCl_3$, between NaCl plates; s = strong, m = medium, w = weak, sh = sharp, br = broad.

Complexes **1**–**3** are soluble in acetone, acetonitrile, chloroform and dichloromethane, and are completely insoluble in hexane and diethyl ether as expected for cationic complexes. All three complexes **1**–**3** show a marked increase in air sensitivity compared to their neutral precursors [35], with deterioration of the complexes apparent within 1 h at room temperature, accompanied by a change in colour from orange–brown to dark brown. The cationic complexes can be stored under N_2 at −17 °C for up to 2 months with no signs of decomposition. Solution samples of complexes **1**, **2** and **3** were considerably more sensitive to decomposition, particularly upon exposure to air.

The IR spectra of **1**–**3** have a single weak $\nu(N\equiv C)$ stretching frequency at 2252, 2254 and 2274 cm^{-1}, respectively. Complexes **1**–**3** all have three carbonyl $\nu(C\equiv O)$ stretching bands; **1** and **2** have a weak band at 2038 and 2046 cm^{-1}, respectively, and two strong stretches at 1961, 1882 cm^{-1} for **1** and 1957, 1890 cm^{-1} for **2**, whilst complex **3** has three strong, broad carbonyl stretches at 1929, 1880 and 1850 cm^{-1}. The IR spectra of all three cationic complexes are distinct from their neutral precursors, which show three strong or medium intensity carbonyl bands at 2035 cm^{-1}, between 1967 and 1940 cm^{-1} and between 1920 and 1915 cm^{-1} [35]. The cationic nature of complexes **1**–**3** is confirmed by the presence of two strong, broad $\nu(B{-}F)$ stretching frequencies at 1069, 1028 cm^{-1} (**1**), 1068, 1028 cm^{-1} (**2**) and 1067, 1028 cm^{-1} (**3**), and by the characteristic singlet due to $[BF_4]^-$ in the $^{11}B\{^1H\}$-NMR spectra of **1** and **2** at −1.34 ppm and **3** at −1.20 ppm.

The ^1H-NMR spectra of **1**–**3** show the phenyl and methylene protons of the parent bidentate phosphine ligands (dppm, dppe or dpppr) in the expected regions, upon comparison with both the ^1H-NMR spectra of their neutral precursors [35], and the ^1H-NMR spectra of the phosphine ligands themselves ($CDCl_3$, 25 °C, referenced to $SiMe_4$). In addition, the methyl protons of the acetonitrile ligand are observed as broad singlets (Table 3). The $^{31}P\{^1H\}$-NMR spectra of complexes **1**–**3** have singlet resonances at −0.63 ppm (**1**), +76.34 ppm (**2**) and +32.12 ppm (**3**), which differ markedly from one another, but follow a similar pattern to that observed for the free bis(diphenylphosphino)alkane ligands [−23.03 ppm (dppm), −13.23 ppm (dppe) and −18.07 ppm (dpppr), in $CDCl_3$, referenced to 85% H_3PO_4]. The appearance of the two phosphorus atoms as a singlet, rather than two individual resonances, is indicative of the complex being fluxional at room temperature. The room temperature $^{13}C\{^1H\}$-NMR spectra of complexes **1** and **2** both show a triplet resonance due to the three carbonyl ligands, [223.06 ppm, $J_{P-C} = 22.6$ Hz (**1**) and 229.98 ppm, $J_{P-C} = 22.6$ Hz (**2**)], which also indicates that the complex is fluxional at room temperature. Resonances attributable to the dppm ligand in complex **1** were observed at 132.33–128.65 ppm ($\mathbf{Ph}_2P(CH_2)P\mathbf{Ph}_2$) and 37.66 ppm

Table 3
Proton NMR data [a] for complexes **1**–**24**

	^{1}H (δ) ppm
1	7.65–7.10 (br s, 20H, $\mathbf{Ph_2}P(CH_2)P\mathbf{Ph_2}$); 4.50–4.35 (t, 2H, $P(\mathbf{CH_2})P$, $J_{P\text{–}H} = 11.1$ Hz); 2.10–1.95 (s, 3H, $\mathbf{CH_3}CN$).
2	7.70–7.30 (s, 20H, $\mathbf{Ph_2}P(CH_2)_2P\mathbf{Ph_2}$); 2.70–2.50 (d, 4H, $P(\mathbf{CH_2})_2P$, $J_{P\text{–}H} = 18.8$ Hz); 2.10–1.90 (s, 3H, $\mathbf{CH_3}CN$).
3	7.55–7.06 (m, 20H, $\mathbf{Ph_2}P(CH_2)_3P\mathbf{Ph_2}$); 2.78–2.15 (br m, 6H, $P(\mathbf{CH_2})_3P$); 2.05–2.00 (s, 3H, $\mathbf{CH_3}CN$).
4	7.53–7.25 (m, 20H, $\mathbf{Ph_2}P(CH_2)P\mathbf{Ph_2}$); 4.49–4.40 (t, 2H, $P(\mathbf{CH_2})P$, $J_{P\text{–}H} = 11.2$ Hz); 2.60–2.40 (m, 2H, $CH_3\mathbf{CH_2}CN$); 1.01–0.95 (t, 3H, $\mathbf{CH_3}CH_2CN$, $J = 7.5$ Hz).
5	7.59–7.20 (m, 20H, $\mathbf{Ph_2}P(CH_2)P\mathbf{Ph_2}$); 5.33 (s, 2H, CH_2Cl_2); 5.29–5.21 (t, 2H, $P(\mathbf{CH_2})P$, $J_{P\text{–}H} = 10.2$ Hz); 3.77–3.68 (m, 9H, $P(O\mathbf{CH_3})_3$).
6	7.60–7.10 (br m, 20H, $\mathbf{Ph_2}P(CH_2)P\mathbf{Ph_2}$); 5.35–5.25 (t, 2H, $P(\mathbf{CH_2})P$, $J_{P\text{–}H} = 10.3$ Hz); 4.25–4.15 (m, 6H, $P(O\mathbf{CH_2}CH_3)_3$); 1.40–1.25 (m, 9H, $P(OCH_2\mathbf{CH_3})_3$).
7	7.75–7.00 (br m, 20H, $\mathbf{Ph_2}P(CH_2)P\mathbf{Ph_2}$); 5.45 (s, 1H, $0.5CH_2Cl_2$); 4.95–4.85 (m, 1H, $P(\mathbf{CH_2})P$); 4.80–4.60 (m, 3H, $P(OC\mathbf{H}Me_2)_3$); 4.10–4.00 (m, 1H, $P(\mathbf{CH_2})P$); 1.95–1.85 (s, 3H, $\mathbf{CH_3}CN$); 1.40–1.25 (m, 18H, $P\{OCH(\mathbf{CH_3})_2\}_3$).
8	8.25–6.80 (br m, 35H, $\mathbf{Ph_2}P(CH_2)P\mathbf{Ph_2}/P(O\mathbf{Ph})_3$); 5.10–4.90 (m, 1H, $P(\mathbf{CH_2})P$); 4.55–4.40 (m, 1H, $P(\mathbf{CH_2})P$); 2.05 (s, 3H, $\mathbf{CH_3}CN$).
9	8.00–7.10 (br m, 35H, $\mathbf{Ph_2}P(CH_2)P\mathbf{Ph_2}/P\mathbf{Ph_3}$); 5.60–5.40 (m, 1H, $P(\mathbf{CH_2})P$); 4.80–4.60 (m, 1H, $P(\mathbf{CH_2})P$); 2.05 (s, 3H, $\mathbf{CH_3}CN$).
10	7.80–7.10 (br m, 35H, $\mathbf{Ph_2}P(CH_2)P\mathbf{Ph_2}/P\mathbf{Ph_3}$); 4.55 (br s, 2H, $P(\mathbf{CH_2})P$).
11	8.74 (d, 2H, $J = 4.3$ Hz); 8.56 (d, 2H, $J = 7.9$ Hz); 7.77 (d, 2H, $J = 5.2$ Hz); 7.57 (d, 2H, $J = 5.2$ Hz)–1,10-**phen**; 7.34–7.27 (m, 20H, $\mathbf{Ph_2}P(CH_2)P\mathbf{Ph_2}$); 4.72 (t, 2H, $P(\mathbf{CH_2})P$, $J_{P\text{–}H} = 10.4$ Hz).
12	8.62 (d, 2H, $J = 5.1$ Hz); 8.12 (s, 2H); 7.27 (s, 2H, 4,7-Me_2-1,10-**phen**); 7.62–7.31 (m, 20H, $\mathbf{Ph_2}P(CH_2)P\mathbf{Ph_2}$); 5.30 (s, 1H, $0.5CH_2Cl_2$); 4.66 (t, 2H, $P(\mathbf{CH_2})P$, $J_{P\text{–}H} = 10.3$ Hz); 2.85 (s, 6H, 4,7-$\mathbf{Me_2}$-1,10-phen).
13	8.49 (d, 2H, $J = 8.1$ Hz); 8.26 (s, 2H); 8.05 (d, 2H, $J = 7.7$ Hz)–2,2′-**bipy**; 7.47–7.26 (m, 20H, $\mathbf{Ph_2}P(CH_2)P\mathbf{Ph_2}$); 4.68 (t, 2H, $P(\mathbf{CH_2})P$, $J_{P\text{–}H} = 10.5$ Hz).
14	7.50–7.00 (m, 40H, 2 × $\mathbf{Ph_2}P(CH_2)P\mathbf{Ph_2}$); 5.25 (s, 2H, CH_2Cl_2); 4.45–4.30 (m, 4H, $P(\mathbf{CH_2})P$).
15	7.60–7.00 (m, 40H, $\mathbf{Ph_2}P(CH_2)P\mathbf{Ph_2}/\mathbf{Ph_2}P(CH_2)_2P\mathbf{Ph_2}$); 6.10–5.90 (br s, 1H, $P(\mathbf{CH_2})P$); 5.00–4.80 (br s, 1H, $P(\mathbf{CH_2})P$); 3.45–3.25 (br m, 2H, $P(\mathbf{CH_2})_2P$); 2.80–2.60 (br m, 2H, $P(\mathbf{CH_2})_2P$).
16	7.70–7.15 (m, 40H, $\mathbf{Ph_2}P(CH_2)P\mathbf{Ph_2}/\mathbf{Ph_2}P(CH_2)_3P\mathbf{Ph_2}$); 6.45–6.25 (m, 1H, $P(\mathbf{CH_2})P$); 5.20–5.00 (m, 1H, $P(\mathbf{CH_2})P$); 4.38–4.12 (m, 4H, $P\mathbf{CH_2}(CH_2)\mathbf{CH_2}P$); 3.15–2.85 (m, 2H, $PCH_2(\mathbf{CH_2})CH_2P$).
17	7.67–7.03 (m, 40H, $\mathbf{Ph_2}P(CH_2)P\mathbf{Ph_2}/\mathbf{Ph_2}P(CH_2)_2P\mathbf{Ph_2}$); 6.05–5.85 (br s, 1H, $P(\mathbf{CH_2})P$); 5.00–4.75 (br s, 1H, $P(\mathbf{CH_2})P$); 3.50–3.30 (br m, 2H, $P(\mathbf{CH_2})_2P$); 2.80–2.60 (br m, 2H, $P(\mathbf{CH_2})_2P$).
18	7.72–6.92 (m, 40H, $\mathbf{Ph_2}P(CH_2)P\mathbf{Ph_2}/\mathbf{Ph_2}P(CH_2)_3P\mathbf{Ph_2}$); 6.00–5.80 (m, 1H, $P(\mathbf{CH_2})P$); 4.80–4.55 (m, 1H, $P(\mathbf{CH_2})P$); 4.00–3.80 (m, 4H, $P\mathbf{CH_2}(CH_2)\mathbf{CH_2}P$); 2.70–2.50 (m, 2H, $PCH_2(\mathbf{CH_2})CH_2P$).
19	7.60–6.95 (m, 20H, $\mathbf{Ph_2}P(CH_2)P\mathbf{Ph_2}$); 4.45–4.30 (t, 2H, $P(\mathbf{CH_2})P$, $J_{P\text{–}H} = 11.1$ Hz); 3.55–3.45 (m, 6H, $(\mathbf{CH_3})_2NCS_2$).
20	7.73–7.01 (m, 20H, $\mathbf{Ph_2}P(CH_2)P\mathbf{Ph_2}$); 4.43–4.36 (t, 2H, $P(\mathbf{CH_2})P$, $J_{P\text{–}H} = 10.1$ Hz); 3.98–3.86 (m, 4H, $(CH_3\mathbf{CH_2})_2NCS_2$); 1.41–1.20 (m, 6H, $(\mathbf{CH_3}CH_2)_2NCS_2$).
21	7.70–6.90 (m, 20H, $\mathbf{Ph_2}P(CH_2)P\mathbf{Ph_2}$); 4.40–4.30 (t, 2H, $P(\mathbf{CH_2})P$, $J_{P\text{–}H} = 11.0$ Hz); 4.00–3.20 (br m, 8H, $C_4\mathbf{H_8}NCS_2$).
22	7.54–7.08 (m, 20H, $\mathbf{Ph_2}P(CH_2)P\mathbf{Ph_2}$); 5.05–4.90 (br s, 2H, $P(\mathbf{CH_2})P$).
23	7.80–7.10 (br m, 20H, $\mathbf{Ph_2}P(CH_2)P\mathbf{Ph_2}$); 5.10–4.90 (br s, 2H, $P(\mathbf{CH_2})P$).
24	7.80–7.00 (br m, 20H, $\mathbf{Ph_2}P(CH_2)P\mathbf{Ph_2}$); 5.05–4.90 (br s, 2H, $P(\mathbf{CH_2})P$).

[a] Spectra recorded in $CDCl_3$ at +25 °C, referenced to $SiMe_4$; s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, m = multiplet, br = broad.

($Ph_2P(\mathbf{C}H_2)PPh_2$). The acetonitrile resonances for complex **1** were observed at 130.96 ppm ($CH_3\mathbf{C}N$) and 4.14 ppm ($\mathbf{CH_3}CN$).

The majority of seven-coordinate complexes of molybdenum(II) and tungsten(II) have capped octahedral geometry [1,5], therefore it may be that the complexes **1**–**3** also have this geometry. Two possible structures for **1**–**3** are shown in Fig. 1(a) and (b). The proposed structure (Fig. 1(a)) is the most likely structure for **1**–**3**, as the acetonitrile ligand is arranged distally to the bulky phenyl groups of the bidentate phosphine ligand. The structure shown in (Fig. 1(b)), however, is least favoured as there would be considerable steric hindrance about the acetonitrile coordination site due to the phenyl groups of the bis(diphenylphosphino)alkane ligands. A number of unsuccessful attempts were made to grow suitable single crystals of **1**–**3** using a range of mixed solvents and temperatures to obtain crystals suitable for a single crystal X-ray diffraction study.

Equimolar quantities of $[MoI(CO)_3(NCMe)\{Ph_2P(CH_2)PPh_2\}][BF_4]$ (**1**) and L react at room temperature in CH_2Cl_2 to give either the acetonitrile displaced complexes $[MoI(CO)_3L\{Ph_2P(CH_2)PPh_2\}][BF_4]$, {L = NCEt (**4**); $P(OMe)_3$ (**5**); $P(OEt)_3$ (**6**)} or the carbonyl displaced products, $[MoI(CO)_2(NCMe)L\{Ph_2P(CH_2)PPh_2\}][BF_4]$, {L = $P(O^iPr)_3$ (7); $P(OPh)_3$ (**8**); PPh_3 (**9**)} in good yields. Complexes **4**–**9** have all been characterised by elemental analysis (C, H and N) (Table 1), IR spectroscopy (Table 2) and ^{1}H-, ^{11}B{^{1}H}- and ^{31}P{^{1}H}-NMR spectroscopy (Tables 3 and 4). Complex **4** has comparable air-sensitivity to complex **1**, is soluble in acetone, acetonitrile, chloroform and dichloromethane, and insoluble in diethyl ether and hexane. Complexes **5** and **6** are slightly more stable than complex **1**, but decompose within 2 h upon exposure to air at room temperature. Complexes **5** and **6** are very air-sensitive in solution and are very soluble in acetone, acetonitrile, dichloromethane and chloroform, but were completely

Table 4
Boron and phosphorus NMR data [a] for complexes **1**–**24**

[b]	$^{11}B\{^1H\}$ (δ) ppm	$^{31}P\{^1H\}$ (δ) ppm
1	-1.34, s	-0.63 (s, dppm)
2	-1.34, s	$+76.34$ (s, dppm)
3	-1.20, s	$+32.12$ (s, dppm)
4	-1.27, s	-0.87 (s, dppm)
5	-1.34, s	$+152.14$ (s, 1P, $P(OMe)_3$); -21.06 (s, 2P, dppm)
6	-1.34, s	$+149.18$ (s, 1P, $P(OEt)_3$); -21.38 (s, 2P, dppm)
7	-1.27, s	$+128.23$ (dd, 1P, $P(O^iPr)_3$, $J_{P1-P2} = 28.7$ Hz, $J_{P1-P3} = 217.8$ Hz); -7.51 (dd, 1P, dppm, $J_{P2-P1} = 28.7$ Hz, $J_{P2-P3} = 77.7$ Hz); -43.39 (dd, 1P, dppm, $J_{P3-P2} = 77.7$ Hz, $J_{P3-P1} = 217.8$ Hz)
8	-1.19, s	$+130.25$ (dd, 1P, $P(OPh)_3$, $J_{P1-P2} = 25.7$ Hz, $J_{P1-P3} = 231.7$ Hz); $+5.51$ (dd, 1P, dppm, $J_{P2-P1} = 25.7$ Hz, $J_{P2-P3} = 84.0$ Hz); 40.59 (dd, 1P, dppm, $J_{P3-P2} = 84.0$ Hz, $J_{P3-P1} = 231.7$ Hz)
9	-1.19, s	$+29.29$ (d, 1P, PPh_3, $J_{P1-P2} =$ N/O, $J_{P1-P3} = 132.93$ Hz); $+8.30$ (d, 1P, dppm, $J_{P2-P1} = 29.8$ Hz, $J_{P2-P3} =$ N/O); -34.81 (m, 1P, dppm)
10 [b]	–	$+21.35$ (s, 1P, PPh_3); -4.06 (s, 1P, dppm); -9.72 (s, 1P, dppm)
11	-1.13, s	-4.18 (s, dppm)
12	-1.20, s	-3.30 (s, dppm)
13	-1.19, s	-4.76 (s, dppm)
14	-0.46, s	-10.04 (s, 4P, dppm)
15	-1.28, s	$+53.74$ (d, 2P, dppe, $J_{P-P} = 89.6$ Hz); -14.73 (d, 2P, dppm, $J_{P-P} = 89.6$ Hz)
16	-1.33, s	$+2.89$ (d, 2P, dpppr, $J_{P-P} = 93.3$ Hz); -14.35 (d, 2P, dppm, $J_{P-P} = 93.3$ Hz)
17	-1.33, s	$+53.70$ (d, 2P, dppe, $J_{P-P} = 87.6$ Hz); -14.77 (d, 2P, dppm, $J_{P-P} = 87.6$ Hz)
18	-1.33, s	$+2.92$ (d, 2P, dpppr, $J_{P-P} = 95.0$ Hz); -14.32 (d, 2P, dppm, $J_{P-P} = 95.0$ Hz)
19	–	$+0.40$ (d, 1P, dppm, $J_{P-P} = 86.0$ Hz); -17.38 (d, 1P, dppm, $J_{P-P} = 86.0$ Hz)
20	–	$+0.17$ (d, 1P, dppm, $J_{P-P} = 86.0$ Hz); -17.34 (d, 1P, dppm, $J_{P-P} = 86.0$ Hz)
21	–	$+0.35$ (d, 1P, dppm, $J_{P-P} = 87.3$ Hz); -17.05 (d, 1P, dppm, $J_{P-P} = 87.3$ Hz)
23	–	-1.59 (s, dppm)
24	–	-10.98 (s, dppm)

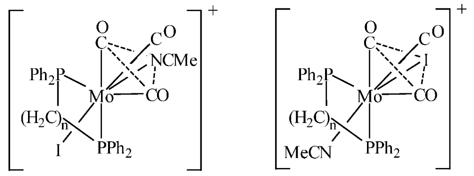
[a] Spectra recorded in $CDCl_3$ at +25 °C, referenced to $BF_3 \cdot OEt_2$.

[b] Spectrum recorded in $CDCl_3$ or in CD_2Cl_2 at +25 °C, referenced to 85% H_3PO_4; at +25 °C; s = singlet, d = doublet, m = multiplet; N/O = not observed.

Table 5
Carbon NMR data [a] for complexes **1** and **2**

	$^{13}C\{^1H\}$ (δ) ppm
1	223.06 (t, $3 \times$ **C**≡O, $J_{P-C} = 22.6$ Hz); 132.33–128.65 (m, **C**=**C**, **Ph**$_2$P(CH$_2$)**Ph**$_2$); 130.96 (s, CH$_3$**C**N); 37.66 (t, Ph$_2$P(**C**H$_2$)Ph$_2$, $J_{P-C} = 26.4$ Hz); 4.14, (s, **C**H$_3$CN).
2	229.98 (t, $3 \times$ **C**≡O, $J_{P-C} = 22.6$ Hz); 132.44–129.69 (m, **C**=**C**, **Ph**$_2$P(CH$_2$)$_2$**Ph**$_2$); 130.91 (s, CH$_3$**C**N); 27.46 (d, Ph$_2$**P**(**C**H$_2$)$_2$Ph$_2$, $J_{P-C} = 23.6$ Hz); 4.11 (s, **C**H$_3$CN).

[a] Spectra recorded in $CDCl_3$ at +25 °C, referenced to $SiMe_4$; s = singlet, d = doublet, t = triplet, m = multiplet.



(a) (b)

Fig. 1. Proposed structures of [MoI(CO)$_2$(NCMe){Ph$_2$P(CH$_2$)$_n$PPh$_2$}][BF$_4$] {$n = 1$ (**1**), 2 (**2**) and 3 (**3**)}.

insoluble in diethyl ether and hexane. They are much more soluble than their nitrile counterparts, **1**–**3**. Complexes **7** and **8** have similar solubility and stability to complexes **5** and **6**, with the triphenylphosphine complex **9** being the least soluble complex so far described.

The IR spectra (Table 2) of complexes **4**–**6** have three carbonyl stretching bands, whereas the acetonitrile complexes **7**–**9** have two carbonyl stretching bands and weak acetonitrile bands, as expected. All six complexes, **4**–**9**, have ν(B–F) stretching bands at approximately 1060 and 1030 cm^{-1}. The ^{1}H-NMR spectra of **4**–**9** all have the expected resonances shifted slightly downfield from the free ligands. It is interesting to note that the room temperature $^{31}P\{^1H\}$-NMR spectra of [MoI(CO)$_3${P(OR)$_3$}{Ph$_2$P(CH$_2$)PPh$_2$}][BF$_4$] (**5** and **6**) both show two phosphorus resonances at 152.14 and −21.06 ppm (**5**) and 149.18 and −21.38ppm

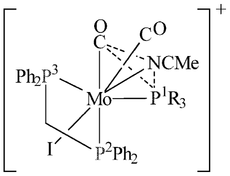


Fig. 2. Proposed structure of the cations, [MoI(CO)$_2$(NCMe)(PR$_3$)(dppm)]$^+$, (**7**–**9**), {R = (O^{i}Pr), (OPh) or Ph}.

(**6**), respectively, with no apparent phosphorus–phosphorus coupling which could result from poorly resolved spectra, or a fluxional process. The two singlets could result from phosphine dissociation (one for the phosphite's and also one resonance for the bidentate phosphine either in a symmetrical environment or rapidly equilibrating), whereby the coupling could diminish to zero. The room temperature $^{31}P\{^1H\}$-NMR spectra of complexes **7**–**9**, however, show three different chemical environments, for example, complex **7** has resonances at +128.23, −7.51 and −43.39 ppm. Using the proposed structure of complexes **7**–**9** (Fig. 2), for complex **7**, the lowfield doublet of doublets at +128.23 ppm is attributed to the $P(O^iPr)_3$ ligand, P^1, having *cis*-type coupling to one phosphorus of the dppm ligand, P^2, ($J_{P1-P2} = 28.7$ Hz) and *trans*-type coupling to the dppm phosphorus P^3 ($J_{P1-P3} = 217.8$ Hz). Similarly, the dppm phosphorus, P^3, shows a *trans*-type coupling to P^1 of the $P(O^iPr)_3$ ligand and a *cis*-type coupling to the other phosphorus of the dppm ligand, P^2, [−43.39 ppm, dd, $J_{P3-P2} = 77.7$ Hz, $J_{P3-P1} = 217.8$ Hz]. The P^2 phosphorus has *cis*-type couplings to both P^1 and P^3, [−7.51 ppm, dd, $J_{P2-P1} = 28.7$ Hz, $J_{P2-P3} = 77.7$ Hz]. The coupling constants for complex **8** are comparable with those of **7** (Table 4). A number of unsuccessful attempts to grow single crystals of **7**–**9** suitable for X-ray analysis were made, however, the $^{31}P\{^1H\}$-NMR data discussed above give evidence for the structure proposed in Fig. 2. It was surprising that the reaction of equimolar amounts of **1** with L {L = NCEt, $P(OR)_3$ (R = Me or Et)} and L {L = $P(OR)_3$ (R = ^{i}Pr or Ph), PPh_3} gave different products, but this was probably due to the increased steric bulk of the latter three ligands.

Treatment of the PPh_3 complex $[MoI(CO)_2(NCMe)(PPh_3)\{Ph_2P(CH_2)PPh_2\}][BF_4]$ (**9**), prepared in situ, with one equivalent of NaI in acetone gave the highly crowded neutral complex $[MoI_2(CO)_2(PPh_3)\{Ph_2P(CH_2)PPh_2\}]$ (**10**). Complex **10** was characterised in the usual manner (Tables 1–4). The $^{31}P\{^1H\}$-NMR of **10** also has three resonances, attributable to the PPh_3 and dppm ligands. Compared to the cationic precursor, complex **9**, there is an upfield shift for the PPh_3 ligand and the dppm phosphorus atom with higher chemical shift (P^1 and P^3), whereas the other dppm phosphorus atom (P^2) has moved downfield, [+21.35, −4.06, −9.72 ppm (**10**); +29.29, +8.30, −34.81 ppm (**9**)], which is probably due to the formation of a neutral complex upon addition of the iodide.

Single crystals suitable for X-ray crystallography of **10** were grown from a $CDCl_3$ solution (−17 °C), of $[MoI(CO)_2(NCMe)(PPh_3)\{Ph_2P(CH_2)PPh_2\}][BF_4]$ (**9**). Crystal data for all structures described in this paper, **10**, **14**, **25** and **26**, are given in Table 6. The associated bond lengths are given in Table 7. The crystal structure of **10** (Fig. 3) is comparable to the literature complexes $[MI_2(CO)_2\{P(OR)_3\}\{Ph_2P(CH_2)_nPPh_2\}]$ (M = Mo, R = Me, Et, $n = 1$; R = Et, ^{i}Pr, Ph, $n = 2$; M = W, R = Ph, $n = 1$; R = Me, Et, ^{i}Pr, $n = 2$) [36]. The mixed phosphite/phosphine complexes all have capped octahedral geometry, with one carbonyl ligand in the unique capping position over the face containing the other carbonyl, the phosphite ligand, and one phosphorus of the phosphine ligand. The crystal structure of complex **10** (Fig. 3) has a seven-coordinate molybdenum atom bonded to two carbonyl atoms, two iodine atoms, a triphenylphosphine ligand and a bidentate dppm ligand. The geometry is best considered as capped octahedral, with the carbonyl ligand [C(100)–O(100)] capping the face containing the other carbonyl ligand [C(200)–O(200)], the PPh_3 ligand [P(2)] and one phosphorus of the dppm ligand [P(1)]. The uncapped face contains the other phosphorus of the dppm ligand [P(3)] and the two iodine atoms. The PPh_3 ligand is positioned distally to the dppm ligand, which minimises steric hindrance between the two groups. The two carbonyl groups are mutually *cis*, which avoids competition between them for the metal *d*-electrons which are required for back bonding to the metal centre. The Mo–P bonds to the PPh_3 ligand [P(2)] and to the phosphorus atom of dppm which is essentially *trans* to the PPh_3 ligand, [P(3)], are identical [2.597(5) Å]. The remaining phosphorus atom of the dppm ligand has a slightly shorter Mo–P(1) bond [2.542(5) Å], and the iodine atom *trans* to P(1) has a shorter Mo–I(3) bond [2.873(3) Å], than the iodine *trans* to the non-capping carbonyl, [Mo–I(2) = 2.911(3) Å].

Reaction of $[MoI(CO)_3(NCMe)\{Ph_2P(CH_2)PPh_2\}][BF_4]$ (**1**), with equimolar quantities of L^L {L^L = 1,10-phen, 4,7-Me_2-1,10-phen, 2,2′-bipy, $Ph_2P(CH_2)_nPPh_2$ (n = 1–3)} in dichloromethane at room temperature, afforded the cationic dicarbonyl complexes, $[MoI(CO)_2(L\hat{}L)\{Ph_2P(CH_2)PPh_2\}][BF_4]$ (**11**–**16**). Similar reactions of $[MoI(CO)_3(NCMe)\{Ph_2P(CH_2)_2PPh_2\}][BF_4]$ (**2**), and $[MoI(CO)_3(NCMe)\{Ph_2P(CH_2)_3PPh_2\}][BF_4]$ (**3**), with one equivalent of $Ph_2P(CH_2)PPh_2$ in $CHCl_2$ at room temperature gave $[MoI(CO)_2\{Ph_2P(CH_2)PPh_2\}\{Ph_2P(CH_2)_nPPh_2\}][BF_4]$ (**17**) and (**18**), respectively, in high yield. Complexes **11**–**18** were all fully characterised by elemental analysis (C, H, N), IR spectroscopy, and ^1H-, $^{11}B\{^1H\}$- and $^{31}P\{^1H\}$-NMR spectroscopy (Tables 1–4). The complex, $[MoI(CO)_2\{Ph_2P(CH_2)PPh_2\}_2][BF_4]\cdot CH_2Cl_2$ (**14**) was also characterised by X-ray crystallography (Fig. 4). Complex **12** was confirmed as a $0.5CH_2Cl_2$ solvate and complex **14** as a CH_2Cl_2 solvate by repeated elemental analysis and ^1H-NMR spectroscopy. In the solid state, all the complexes showed deterioration after several hours when exposed to air. Solutions of complexes **11**–**18** decompose when exposed to air, with full decomposition observed within 12 h. The complexes can be stored under nitrogen at −17 °C in either solid or solution

Table 6
Crystal data and structure refinement for complexes **10**, **14**, **25** and **26**

	10	**14**	**25**	**26**
Empirical formula	$C_{45}H_{37}I_2MoO_2P_3$	$C_{52}H_{44}BF_4IMoO_2P_4\cdot 2CH_2Cl_2$	$C_{25.5}H_{28.5}Cl_{4.5}MoO_6P_2$	$C_{75}H_{66}I_3Mo_3P_6\cdot 1.5H_2O$
Formula weight	1052.4	1304.25	748.39	1848.64
Temperature (K)	293(2)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$	$P2_1/n$	$P2_1/n$
Unit cell dimensions				
a (Å)	11.867(12)	42.10(5)	16.66(2)	19.22(2)
b (Å)	13.111(15)	11.569(13)	8.647(13)	18.82(2)
c (Å)	14.160(17)	25.96(3)	23.09(2)	21.41(3)
α (°)	87.22(1)	–	–	–
β (°)	85.56(1)	115.97(1)	108.91(1)	90.35(1)
γ (°)	82.33(1)	–	–	–
V (Å^3)	2175(4)	11 366(21)	3147(7)	7747(15)
Z	2	8	4	4
Reflections collected	7179	16 624	10 116	16 839
Unique reflections	7179	9531	5477	11 485
R_{int}	–	0.036	0.0245	0.0466
Data/restraints/parameters	7179/0/479	9531/0/648	5477/4/349	11485/0/784
Final R indices R_1 [$I > 2\sigma(I)$], wR_2	0.1335, 0.2942	0.0742, 0.1969	0.1026, 0.2876	0.0905, 0.3240
R indices (all data) R_1, wR_2	0.1965, 0.3235	0.1130, 0.2191	0.1339, 0.3176	0.1224, 0.3732

Table 7
Bond lengths (Å) for complexes **10**, **14**, **25** and **26**

10		**14**	
Mo(1)–C(200)	1.91(2)	Mo(1)–C(200)	1.943(9)
Mo(1)–C(100)	1.943(16)	Mo(1)–C(100)	1.976(8)
Mo(1)–P(1)	2.542(5)	Mo(1)–P(1)	2.524(3)
Mo(1)–P(3)	2.597(5)	Mo(1)–P(4)	2.536(3)
Mo(1)–P(2)	2.597(5)	Mo(1)–P(3)	2.617(3)
Mo(1)–I(3)	2.873(3)	Mo(1)–P(6)	2.646(3)
Mo(1)–I(2)	2.911(3)	Mo(1)–I(1)	2.854(2)
25		**26**	
Mo(1)–O(12)	1.785(13)	Mo(1)–P(7)	2.455(5)
Mo(1)–O(11)	1.795(16)	Mo(1)–P(4)	2.461(5)
Mo(1)–Cl(11)	2.179(7)	Mo(1)–I(1)	2.938(3)
Mo(1)–O(1)	2.152(6)	Mo(1)–I(2)	3.023(3)
Mo(1)–O(3)	2.163(7)	Mo(2)–P(9)	2.483(5)
Mo(1)–Cl(12)	2.265(5)	Mo(2)–P(1)	2.498(5)
Mo(1)–Cl(2)	2.387(4)	Mo(2)–I(1)	2.962(3)
Mo(1)–Cl(1)	2.394(4)	Mo(2)–I(2)	3.032(3)
		Mo(2)–Mo(3)	3.155(4)
		I(1)–Mo(3)	2.919(3)
		I(2)–Mo(3)	3.009(3)
		Mo(3)–P(3)	2.496(6)
		Mo(3)–P(6)	2.505(5)

state for up to 2 months. All complexes **11**–**18** are soluble in polar chlorinated solvents such as CH_2Cl_2 or $CHCl_3$ and in acetone, but are insoluble in Et_2O and hydrocarbon solvents.

The IR spectra of complexes **11**–**16** all show two carbonyl stretching bands (Table 2). They also have two strong, broad ν(B–F) bands, confirming the cationic nature of the complexes. The ^{1}H-NMR spectra (Table 3) all show the expected features, with the coordinated ligand resonances shifted slightly downfield from the free ligands. The $^{11}B\{^1H\}$-NMR spectra all show single resonances as expected (Table 4). For example, the bidentate nitrogen donor complexes **11**–**13** have resonances at −1.13, −1.20 and −1.19 ppm, respectively.

Complexes **11**–**13** have a singlet resonance in their $^{31}P\{^1H\}$-NMR spectra (Table 4), similar to that of the precursor complex, **1**. The $^{31}P\{^1H\}$-NMR spectrum of the structurally characterised complex, $[MoI(CO)_2\{Ph_2P(CH_2)PPh_2\}_2][BF_4]\cdot CH_2Cl_2$ (**14**) has a single resonance at −10.04 ppm due to the four equivalent phosphorus atoms of the two dppm ligands (Fig. 4). This data is comparable to that of the related complex, $[MoI(CO)_2\{Me_2P(CH_2)PMe_2\}_2]I$ [37], which has a single resonance at −28 ppm.

The structure of $[MoI(CO)_2\{Ph_2P(CH_2)PPh_2\}_2][BF_4]\cdot 2CH_2Cl_2$ (**14**) (Fig. 4) is the first reported crystal structure of a seven-coordinate cation containing two dppm ligands, both of which are coordinated to the molybdenum centre in a bidentate manner. Complex **14** has capped trigonal prismatic geometry, with iodine capping the quadrilateral face containing the four phosphorus atoms. The four Mo–P bonds differ by a maximum of 0.122 Å [P(1) = 2.524(3) Å; P(3) = 2.617(3) Å; P(4) = 2.536(3) Å; P(6) = 2.646(3) Å] and the Mo–I bond is 2.854(2) Å.

Neutral seven-coordinate complexes containing two dppm ligands such as $[WI_2(CO)(dppm)_2]$ [38], prepared by reaction of $[\{W(\mu\text{-}I)I(CO)_4\}_2]$ and dppm in toluene at room temperature for 24 h, and $[MoBr_2(CO)_2(dppm\text{-}P)(dppm\text{-}P,P')]$ [39], prepared by addition of two equivalents of dppm (in CH_2Cl_2 or THF) to

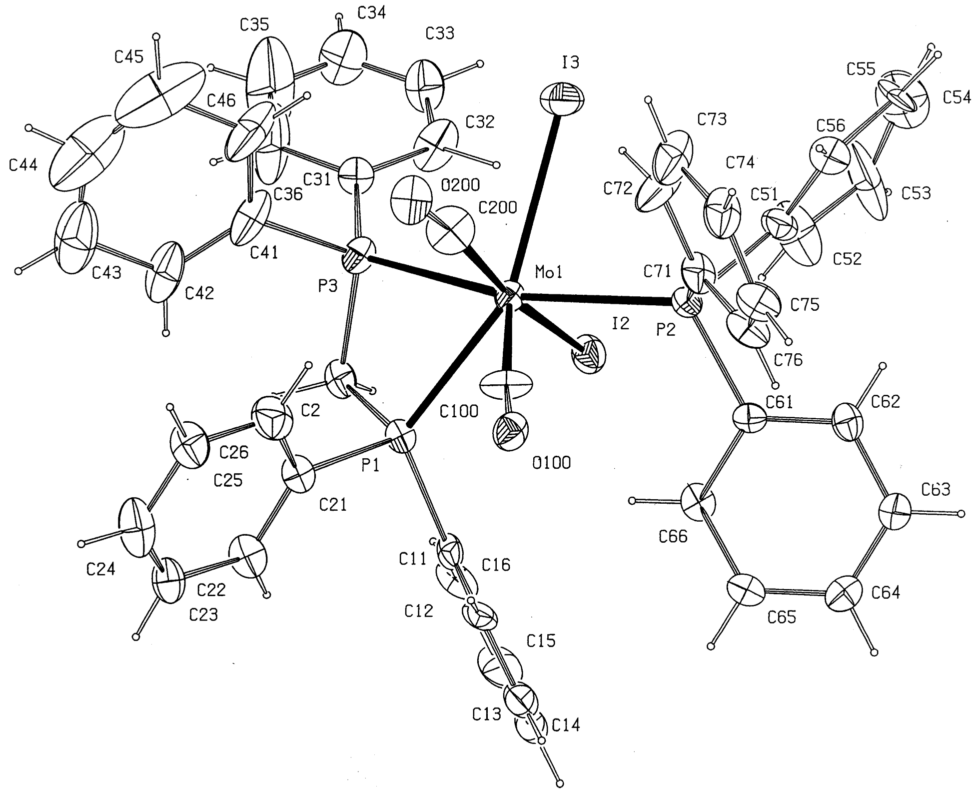


Fig. 3. Crystal structure of $[MoI_2(CO)_2(PPh_3)\{Ph_2P(CH_2)PPh_2\}]$ (**10**), with the atomic numbering scheme. Ellipsoids shown at 20% probability.

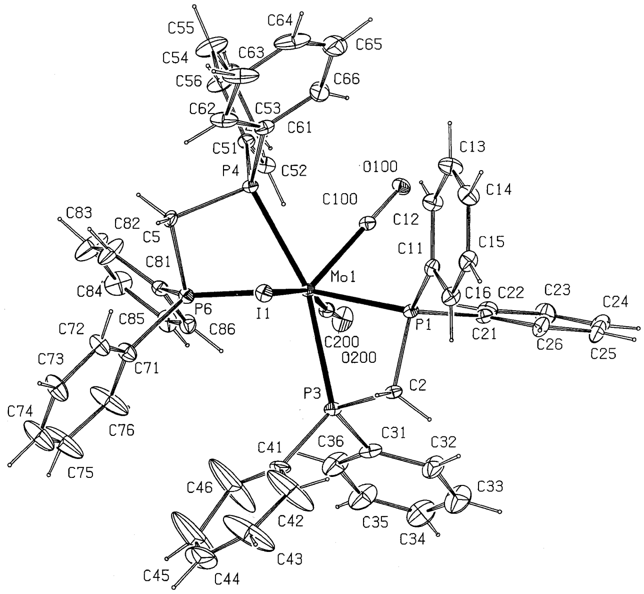


Fig. 4. Crystal structure of $[MoI(CO)_2\{Ph_2P(CH_2)PPh_2\}_2][BF_4]\cdot CH_2Cl_2$ (**14**), with the atomic numbering scheme. Ellipsoids shown at 20% probability.

$[MoBr_2(CO)(H_2CPz'_2)]$ in CH_2Cl_2 or THF at room temperature, have been previously reported [38,39]. Both of these complexes were structurally characterised by X-ray methods, with the former tungsten complex possessing two bidentately coordinated dppm ligands, and the latter molybdenum complex having one monodentate and one bidentate dppm ligand [39]. Cationic six-coordinate complexes, $[MI(CO)_2(dppe\text{-}P)(dppe\text{-}P,P')]I$ (M = Mo, W), have also been reported [10,40], containing one monodentate and one bidentate dppe ligand. Preparation of dppm complexes of the type $[MX(CO)_2(dppm\text{-}P)(dppm\text{-}P,P')]^+$, are well-represented [10,41–43]. However, seven-coordinate cations containing two bidentate dmpe ligands, namely $[MI(CO)_2(dmpe)_2]^+$ (M = Mo, W) [37] and $[MoCl(CO)_2(dmpe)_2]^+$ [44], have been reported, with the latter shown, by X-ray crystallography, to have capped trigonal prismatic geometry. The similar diars complex, $[MoCl(CO)_2(diars)_2]^+$, was also crystallographically determined and shown to have capped trigonal prismatic geometry [1].

Reaction of $[MoI(CO)_3(NCMe)\{Ph_2P(CH_2)PPh_2\}][BF_4]$ (**1**), with one equivalent of either sodium dithiocarbamates, $Na[S_2CNR_2]\cdot xH_2O$ (R = Me, Et), or $[NH_4][S_2CNC_4H_8]$, in CH_2Cl_2 at room temperature, gave the neutral complexes, $[MoI(CO)_2(S_2CX)\{Ph_2P(CH_2)PPh_2\}]$ (X = NMe_2, NEt_2, NC_4H_8) (**19**–**21**), respectively, in very good yields. The complexes **19**–**21** were characterised in the usual manner (Tables 1–4). Complexes **19**–**21** are moderately air-stable, decomposing within 24 h on exposure to air, with a more marked affect when in solution. The three complexes were stored under nitrogen at 17 °C for up to 2 months, with no

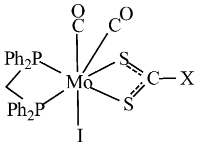


Fig. 5. Proposed structure of $[MoI(CO)_2(S_2CX)\{Ph_2P(CH_2)PPh_2\}]$ {X = NMe_2 (**19**), NEt_2 (**20**) and NC_4H_8 (**21**)}.

obvious deterioration. Single crystals of **19**–**21** were not obtained despite repeated attempts, therefore, the structure of the complexes can only be proposed (Fig. 5). The IR spectra for **19**–**21** have two carbonyl stretching frequencies at similar wavenumbers [1946 and 1882 cm^{-1} for **19**; 1945 and 1880 cm^{-1} for **20**; 1946 and 1880 cm^{-1} for **21**]. The ν(CS) stretch for **19** was observed at 1786 cm^{-1} and for **21** at 1789 cm^{-1}, whereas complex **20** showed a doublet at 1792 and 1771 cm^{-1} due to the ν(CS) stretch. A representation of the proposed structure of **19**–**21** is shown in Fig. 5. The *cis*-carbonyl arrangement was confirmed by the two different ν(C≡O) stretching frequencies observed in the IR spectra of complexes **19**–**21** (Table 2). As for the bis(dppm) complex **14**, it is possible that complexes **19**–**21** will have capped trigonal prismatic geometry, with the bidentate ligands occupying both edges of the face capped by the iodide ligand. The $^{31}P\{^1H\}$-NMR spectra of complexes **19**–**21** are also very similar [+0.40, −17.38 ppm, $J_{P-P} = 86.0$ Hz (**19**); +0.17, −17.34 ppm, $J_{P-P} = 86.0$ Hz (**20**); +0.35 ppm, −17.05 ppm, $J_{P-P} = 87.3$ Hz (**21**)], with the addition of the bidentate sulfur ligands resulting in the two phosphorus atoms of the dppm ligand appearing as two distinct singlets. Thus, the complexes are no longer fluxional at room temperature, as was observed for the cationic precursor, complex **1**.

The reaction of **1** with one equivalent of the metal salts, NaF, NaCl and KSCN, in acetone at room temperature, afforded the neutral complexes $[MoXI(CO)_3\{Ph_2P(CH_2)PPh_2\}]$ {X = F (**22**), Cl (**23**) and NCS (**24**)}, in very good yields. All three complexes were characterised by elemental analysis, IR spectroscopy, ^1H- and $^{31}P\{^1H\}$-NMR spectroscopy (Tables 1–4) {$^{31}P\{^1H\}$-NMR spectra for complexes **23** and **24**}. The neutral complexes rapidly decompose upon exposure to air, within 30 min for solid samples and within 15 min for samples in solution. The complexes can be stored under nitrogen at −17 °C for up to 3 weeks without any obvious deterioration, both in solution and as solid samples. No crystals of **22**–**24** were obtained, despite repeated crystallisation attempts, but their structures should be comparable to the similar complex, $[MoBr_2(CO)_3(dppe)]$, which was shown to have distorted capped octahedral geometry [45]. Thus, a structure for the neutral complexes **22**–**24**, can be proposed (Fig. 6), having one carbonyl ligand capping the face containing one phosphorus of the dppm ligand and the other two carbonyl ligands, and an uncapped face, which contains the two halide atoms, or one halide and the thiocyanate ligand, plus the remaining phosphorus of the dppm ligand. The IR spectra of complexes **22** and **23** are comparable to the analogous di-iodide complexes, $[MI_2(CO)_3\{Ph_2P(CH_2)_nPPh_2\}]$ (M = Mo, W) [35], and the IR spectra of complex **1** (Table 2). Complexes **22** and **23** have three carbonyl stretching frequencies; a medium intensity band at 2043 cm^{-1} (**22**) or 2040 cm^{-1} (**23**), a strong band at 1972 cm^{-1} (**22**) or 1950 cm^{-1} (**23**), and a medium stretch at 1885 cm^{-1} (**22**) or 1871 cm^{-1} (**23**). The IR spectrum of complex **24** has three strong carbonyl stretches at 2071, 1955, 1880 cm^{-1} and a medium intensity band at 2133 cm^{-1}, which is indicative of an N-bonded thiocyanate ligand. The ^1H-NMR spectra of complexes **22**–**24** all show the expected resonances due to the coordinated dppm ligand. The room temperature $^{31}P\{^1H\}$-NMR spectra of complexes **23** and **24** both have one singlet resonance, at −1.59 and −10.98 ppm, respectively, which suggests that the complexes are fluxional at room temperature, as previously observed.

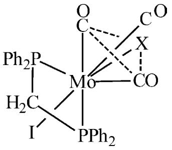


Fig. 6. Proposed structure of $[MoXI(CO)_3\{Ph_2P(CH_2)PPh_2\}]$ {X = F (**22**), Cl (**23**) and NCS (**24**)}.

A concentrated $CDCl_3$ solution of the cation $[MoI(CO)_3(NCMe)\{Ph_2P(CH_2)PPh_2\}][BF_4]$ (**1**), prepared for NMR analysis, gave two decomposition products upon standing, namely the Mo(V) complex, $[MoCl_3O\{Ph_2PO(CH_2)POPh_2\}]$ (**25**) and the unusual triangular complex, $[Mo_3(\mu_3\text{-}I)_2\{\mu_2\text{-}Ph_2P(CH_2)PPh_2\}_3]I$ (**26**), which have both been crystallographically characterised. Single crystals suitable for X-ray crystallography of these complexes were obtained from the NMR tube. The structures of **25** and **26** are shown in Figs. 7 and 8, respectively. In the crystal structure of complex **25** (Fig. 7), the terminal Cl(12) and O(11) sites are disordered with Cl(11) and O(12); the latter, however, is not represented in the structure shown in Fig. 7. Both disordered sites are *trans* to an oxygen atom bonded to a phosphorus atom of the dppm ligand. The bond lengths between molybdenum and the two oxygen atoms inserted into the Mo–P bonds, Mo–O(1) and Mo–O(3), are identical [2.15(7) and 2.163(7) Å, respectively]. The two ordered chlorine atoms also have equivalent bond lengths to the molybdenum centre [Mo–Cl(1) = 2.394(4) Å and Mo–Cl(2) = 2.387(4) Å].

The preparation of the homologue of complex **25**, namely $[MoCl_3O\{Ph_2PO(CH_2)_2OPPh_2\}]$, was reported by Lewis and Whyman in 1965 [46], from the treatment of $[Mo(CO)_4(dppe)]$ with excess chlorine in chloroform,

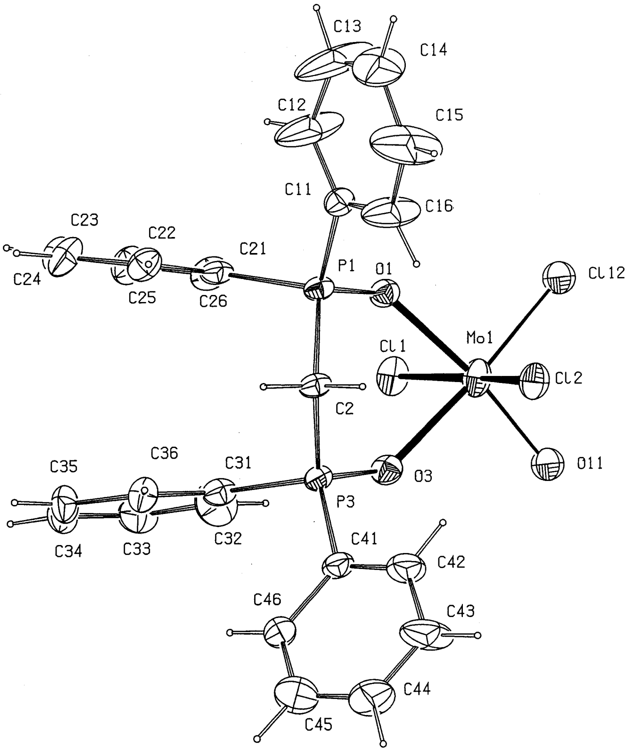


Fig. 7. Crystal structure of $[MoCl_3O\{Ph_2OP(CH_2)POPh_2\}]$ (**25**), with the atomic numbering scheme. Ellipsoids shown at 20% probability.

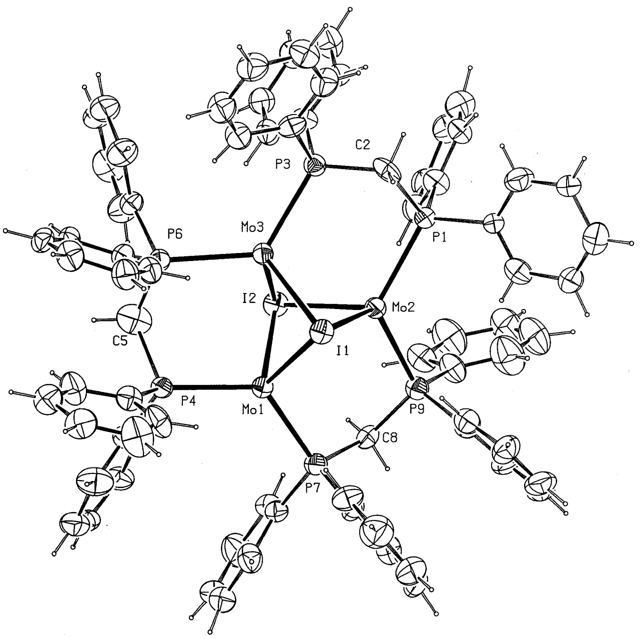


Fig. 8. Crystal structure of $[Mo_3(\mu^3\text{-}I)_2\{\mu^2\text{-}Ph_2P(CH_2)PPh_2\}_3]I$ (**26**), with atomic numbering scheme. Ellipsoids shown with 20% probability.

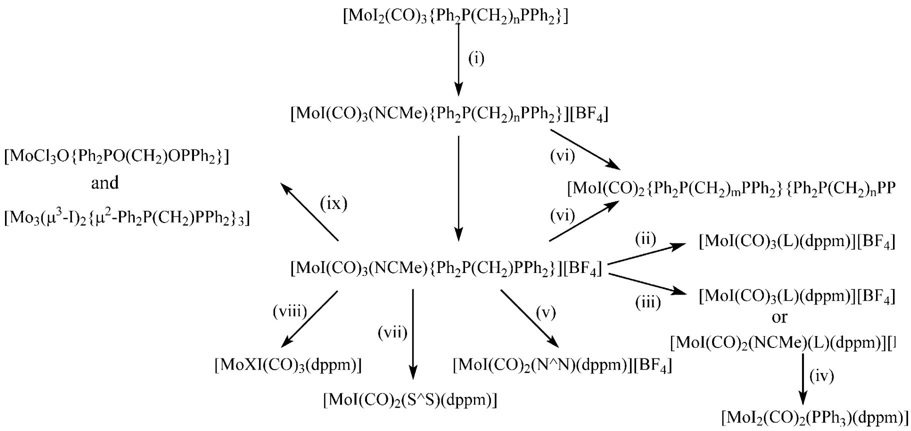
at room temperature. The preparation of the analogous molybdenum(V) oxotribromo-complex, $[MoBr_3O\{Ph_2PO(CH_2)_2OPPh_2\}]$, from the reaction of $[Mo(CO)_4(dppe)]$ and excess bromine, in chloroform at room temperature, has also been described [46]. However, reaction of the tungsten complex, $[W(CO)_4(dppe)]$, with excess bromine or chlorine gave the W(VI) complexes, $[WX_2O_2\{Ph_2PO(CH_2)_2OPPh_2\}]$ ($X = Cl$, Br), rather than the analogous tungsten(V) complexes [46]. Similar oxidised Mo(IV) complexes, $[MoX_2O\{Ph_2P(CH_2)_2PPh(CH_2)_2POPh_2\text{-}P,P',O\}]$ ($X = Br$, I), have been prepared and crystallographically characterised [47], by refluxing $[MoBr(CO)(L\text{-}P,P',P'')(\eta^2\text{-}RC_2R)]Br$, $\{L = Ph_2P(CH_2CH_2PPh_2)$, $R = Me$, Ph$\}$, in chloroform or by refluxing $[MoI_2(CO)(L\text{-}P,P')(\eta^2\text{-}MeC_2Me)]$ in wet acetonitrile, respectively [47].

The crystal structure of the unusual molybdenum 'trimer' $[Mo_3(\mu_3\text{-}I)_2\{\mu_2\text{-}Ph_2P(CH_2)PPh_2\}_3]I$ (**26**) is shown in Fig. 8. The cation consists of three molybdenum atoms, each bonded to two phosphorus atoms and two iodine atoms, in a tetrahedral arrangement, with both of the iodine atoms bonded to three molybdenum atoms each. The two phosphorus atoms of each dppm ligand are bonded to a different molybdenum atom, with each dppm forming a bridge between two molybdenum atoms. The crystal structure also contains one and a half molecules of water solvate (which is not included in Fig. 8), probably arising from slightly wet *d*-chloroform. The six Mo–P bond lengths are all between 2.455(5) and 2.498(5) Å, and are therefore very similar to one another. Similarly, the bonds between the three molybdenum atoms and I(1) are all comparable [2.938(3) Å to Mo(1), 2.962(3) Å to Mo(2) and 2.919(3) Å to Mo(3)] and are slightly shorter than those of Mo–I(2), [3.023(3) Å to Mo(1), 3.032(4) Å to Mo(2) and 3.009(3) Å to Mo(3)], which are comparable to one another. The two Mo–I bonds are longest for Mo(2), then Mo(1), with Mo(3)–I being the shortest. However, these differences are quite small (less than 0.05 Å), with the actual structure of **26** appearing to be symmetrical.

It is difficult to speculate on the formation of complexes **25** and **26** as they are both very different from the precursor cation **1**. It is probable that traces of water and/or air have got into the NMR solution affording the described complexes. However, unusual decompositions are very commonly observed in molybdenum chemistry [46,47].

3. Conclusions

In conclusion, as often observed in molybdenum chemistry, not only do new reactive starting materials such as the seven-coordinate cation, $[MoI(CO)_3(NCMe)\{Ph_2P(CH_2)PPh_2\}][BF_4]$ undergo predictable substitution chemistry as we report here (Scheme 1), but also unusual rearrangements are often observed, such as that of **1** in $CDCl_3$ to form the oxidised complex, $[MoCl_3O\{Ph_2PO(CH_2)POPh_2\}]$ (**25**) and the novel tri-



Scheme 1. A summary of the chemistry detailed in this paper. Reaction conditions: (i) one equivalent Ag[BF$_4$], NCMe, 4 h, under foil (**1**, **2** and **3**); (ii) one equivalent NCEt, CH$_2$Cl$_2$, 20 h (**4**); (iii) L = P(OR)$_3$, {R = Me, Et}, one equivalent P(OR)$_3$, CH$_2$Cl$_2$, 1 h (**5** and **6**); L = P(OR)$_3$, {R = ^{i}Pr, Ph} one equivalent P(OR)$_3$, CH$_2$Cl$_2$, 1 h, (**7** and **8**); L = PPh$_3$, one equivalent PPh$_3$, CH$_2$Cl$_2$, 2 h (**9**); (iv) one equivalent NaI, acetone, 2 h (**10**); (v) one equivalent 1,10-phen,4,7-Me$_2$-1,10-phen or 2,2′-bipy, CH$_2$Cl$_2$, 5 h, (**11**–**13**); (vi) $n = 1$, one equivalent dppm ($m = 1$), dppe ($m = 2$) or dpppr ($m = 3$), CH$_2$Cl$_2$, 2 h (**14**–**16**); $n = 2$, one equivalent dppm ($m = 1$), CH$_2$Cl$_2$, 2 h (**17**); $n = 3$, one equivalent dppm ($m = 1$), CH$_2$Cl$_2$, 2 h (**18**); (vii) one equivalent Na[S$_2$CNR$_2$] {R = Me, Et}, acetone, 18 h (**19** and **20**); one equivalent [NH$_4$][S$_2$CNC$_4$H$_8$], acetone, 18 h (**21**); (viii) one equivalent NaF, acetone, 2 h (**22**); one equivalent NaCl, acetone, 4 h (**23**); one equivalent KSCN, acetone, 20 h (**24**); (ix) the complex, [MoI(CO)$_3$(NCMe){Ph$_2$P(CH$_2$)PPh$_2$}][BF$_4$] (**1**), dissolved in CDCl$_3$ in an NMR tube.

angular complex [Mo$_3$(μ$_3$-I)$_2${μ$_2$-Ph$_2$P(CH$_2$)PPh$_2$}$_3$]I (**26**).

4. Experimental

4.1. General remarks

All reactions described in this paper were carried out under an atmosphere of dry nitrogen using standard vacuum/Schlenk line procedures. The starting materials, [MoI$_2$(CO)$_3${Ph$_2$P(CH$_2$)$_n$PPh$_2$}] ($n = 1$–3), were prepared by the published method [35]. All chemicals were purchased from commercial sources.

Elemental analyses (C, H, N) were performed using a Carlo Erba Elemental Analyser MOD 1108 (using helium as a carrier gas). Infrared spectra were recorded on a Perkin–Elmer 1600 series FTIR spectrophotometer. ^{1}H-, ^{11}B{^{1}H}-, ^{13}C{^{1}H}- and ^{31}P{^{1}H}-NMR spectra were recorded on a Bruker AC 250 CP/MAS NMR spectrometer. ^{1}H- and ^{13}C{^{1}H}-NMR spectra were referenced to SiMe$_4$, ^{11}B{^{1}H}-NMR spectra to BF$_3$·OEt$_2$ and ^{31}P{^{1}H}-NMR spectra to 85% H$_3$PO$_4$.

4.2. [MoI(CO)$_3$(NCMe){Ph$_2$P(CH$_2$)PPh$_2$}][BF$_4$] (1)

To a solution of [MoI$_2$(CO)$_3${Ph$_2$P(CH$_2$)PPh$_2$}] (7.500 g, 9.167 mmol) in MeCN (60 cm^3), in a foil-covered Schlenk tube, silver tetrafluoroborate Ag[BF$_4$], (1.784 g, 9.164 mmol) was added and the solution stirred for 4 h. The solvent was removed under vacuum and the crude product dissolved in CH$_2$Cl$_2$ (30 cm^3), then filtered three times over celite to remove all traces of silver iodide by-product. The solvent was removed in vacuo to yield the product, [MoI(CO)$_3$(NCMe){Ph$_2$P(CH$_2$)PPh$_2$}][BF$_4$] (**1**) as an orange–brown solid, yield = 7.661 g, 95%.

Cationic complexes [MoI(CO)$_3$(NCMe){Ph$_2$P(CH$_2$)$_2$PPh$_2$}][BF$_4$] (**2**) and [MoI(CO)$_3$(NCMe){Ph$_2$P(CH$_2$)$_3$PPh$_2$}][BF$_4$] (**3**) were prepared by similar reactions of equimolar quantities of the neutral complexes [MoI$_2$(CO)$_3${Ph$_2$P(CH$_2$)$_n$PPh$_2$}] ($n = 2$ and 3) with silver tetrafluoroborate in MeCN. Refer to Table 1 for physical and analytical data.

4.3. [MoI(CO)$_3$(NCEt){Ph$_2$P(CH$_2$)PPh$_2$}][BF$_4$] (4)

To a solution of [MoI(CO)$_3$(NCMe){Ph$_2$P(CH$_2$)PPh$_2$}][BF$_4$] (0.503 g, 0.614 mmol) in CH$_2$Cl$_2$ (30 cm^3), propionitrile (0.043 cm^3, 0.034 g, 0.617 mmol) was added and the solution stirred for 20 h. The resultant solution was filtered over celite and the solvent removed under vacuum to afford the product [MoI(CO)$_3$(NCEt){Ph$_2$P(CH$_2$)PPh$_2$}][BF$_4$] (**4**), as an orange–brown crystalline powder, yield = 0.463 g, 90%. Refer to Table 1 for physical and analytical data.

4.4. [MoI(CO)$_3${P(OEt)$_3$}{Ph$_2$P(CH$_2$)PPh$_2$}][BF$_4$] (6)

To a solution of [MoI(CO)$_3$(NCMe){Ph$_2$P(CH$_2$)PPh$_2$}][BF$_4$] (0.472 g, 0.576 mmol) in CH$_2$Cl$_2$ (30 cm^3), triethylphosphite (0.100 cm^3, 0.096 g, 0.577 mmol) was added and the solution stirred for 1 h. The resultant yellow–brown solution was filtered over celite and the solvent reduced under vacuum to minimum volume (3 cm^3). The concentrated solution was layered with Et$_2$O

(2 cm^3) and cooled to −17 °C. The product [MoI(CO)$_3${P(OEt)$_3$}{Ph$_2$P(CH$_2$)PPh$_2$}][BF$_4$] (**6**) was obtained as a yellow crystalline powder, yield = 0.398 g, 73%.

Complex **5**, [MoI(CO)$_3${P(OMe)$_3$}{Ph$_2$P(CH$_2$)PPh$_2$}][BF$_4$], and the related phosphite complexes, [MoI(CO)$_2$(NCMe){P(O^{i}Pr)$_3$}{Ph$_2$P(CH$_2$)PPh$_2$}][BF$_4$] (**7**) and [MoI(CO)$_2$(NCMe){P(OPh)$_3$}{Ph$_2$P(CH$_2$)PPh$_2$}][BF$_4$] (**8**), were prepared by the same method. Refer to Table 1 for physical and analytical data.

4.5. *[MoI(CO)$_2$(NCMe)(PPh$_3$){Ph$_2$P(CH$_2$)PPh$_2$}][BF$_4$] (**9**)*

To a solution of [MoI(CO)$_3$(NCMe){Ph$_2$P(CH$_2$)PPh$_2$}][BF$_4$] (0.512 g, 0.625 mmol) in CH$_2$Cl$_2$ (30 cm^3), triphenylphosphine (0.164 g, 0.625 mmol) was added and the solution stirred for 2 h. The resultant orange solution was filtered over celite and the solvent removed under vacuum to give [MoI(CO)$_2$(NCMe)(PPh$_3$){Ph$_2$P(CH$_2$)PPh$_2$}][BF$_4$] (**9**), as an orange crystalline powder, yield = 0.466 g, 72%. Refer to Table 1 for physical and analytical data.

4.6. *[MoI$_2$(CO)$_2$(PPh$_3$){Ph$_2$P(CH$_2$)PPh$_2$}] (**10**)*

To a solution of [MoI(CO)$_3$(NCMe){Ph$_2$P(CH$_2$)PPh$_2$}][BF$_4$] (0.500 g, 0.610 mmol) in CH$_2$Cl$_2$ (30 cm^3), triphenylphosphine (0.160 g, 0.610 mmol) was added, after stirring for 2 h, sodium iodide (0.092 g, 0.614 mmol) and acetone (30 cm^3) were added in situ and the resultant solution stirred for a further 20 h. The solvents were removed under vacuum, the crude product dissolved in CH$_2$Cl$_2$ (30 cm^3), then filtered three times over celite and the solvent removed to yield the product [MoI$_2$(CO)$_2$(PPh$_3$){Ph$_2$P(CH$_2$)PPh$_2$}] (**10**), as a bright orange powder, yield = 0.411 g, 64%. Refer to Table 1 for physical and analytical data.

4.7. *[MoI(CO)$_2$(1,10-phen){Ph$_2$P(CH$_2$)PPh$_2$}][BF$_4$] (**11**)*

To a solution of [MoI(CO)$_3$(NCMe){Ph$_2$P(CH$_2$)PPh$_2$}][BF$_4$] (0.507 g, 0.619 mmol) in CH$_2$Cl$_2$ (30 cm^3), 1,10-phenanthroline (0.112 g, 0.621 mmol) was added and the solution stirred for 5 h. The resultant dark brown solution was filtered over celite and the solvent removed under vacuum to afford the product (**11**), as dark brown crystalline powder, yield = 0.434 g, 75%. The novel complexes, [MoI(CO)$_2$(4,7-Me$_2$-1,10-phen){Ph$_2$P(CH$_2$)PPh$_2$}][BF$_4$] (**12**) and [MoI(CO)$_2$(2,2′-bipy){Ph$_2$P(CH$_2$)PPh$_2$}][BF$_4$] (**13**), were prepared by the same method. Refer to Table 1 for physical and analytical data.

4.8. *[MoI(CO)$_2${Ph$_2$P(CH$_2$)PPh$_2$}$_2$][BF$_4$] (**14**)*

To a solution of [MoI(CO)$_3$(NCMe){Ph$_2$P(CH$_2$)PPh$_2$}][BF$_4$] (0.512 g, 0.625 mmol) in CH$_2$Cl$_2$ (30 cm^3), bis(diphenylphosphino)methane (0.240 g, 0.625 mmol) was added and the solution stirred for 2 h. The resultant yellow–brown solution was filtered over celite and the solvent volume reduced under vacuum to minimum volume (4 cm^3). The concentrated solution was layered with Et$_2$O (4 cm^3) and cooled to −17 °C for 1 week. The product, [MoI(CO)$_2${Ph$_2$P(CH$_2$)PPh$_2$}$_2$][BF$_4$] (**14**), was obtained as yellow crystals, suitable for X-ray crystallography, yield = 0.536 g, 76%.

Complexes, [MoI(CO)$_2${Ph$_2$P(CH$_2$)$_n$PPh$_2$}{Ph$_2$P(CH$_2$)PPh$_2$}][BF$_4$], {$n = 2$ (**15**) and 3 (**16**)}, were prepared from [MoI(CO)$_3$(NCMe){Ph$_2$P(CH$_2$)PPh$_2$}][BF$_4$] by the same method, and the related complexes, [MoI(CO)$_2${Ph$_2$P(CH$_2$)PPh$_2$}{Ph$_2$P(CH$_2$)$_n$PPh$_2$}][BF$_4$] {$n = 2$ (**17**) and 3 (**18**)}, were similarly prepared by reacting complexes **2** and **3**, [MoI(CO)$_3$(NCMe){Ph$_2$P(CH$_2$)$_n$PPh$_2$}][BF$_4$], ($n = 2$ and 3), with one equivalent of Ph$_2$P(CH$_2$)PPh$_2$ in CH$_2$Cl$_2$ at room temperature. Refer to Table 1 for physical and analytical data.

4.9. *[MoI(CO)$_2$(S$_2$CNMe$_2$){Ph$_2$P(CH$_2$)PPh$_2$}] (**19**)*

To a solution of [MoI(CO)$_3$(NCMe){Ph$_2$P(CH$_2$)PPh$_2$}][BF$_4$] (0.455 g, 0.555 mmol) in acetone (30 cm^3), Na[S$_2$CNMe$_2$]·2H$_2$O, (0.099 g, 0.554 mmol) was added and the solution stirred for 18 h. The solvent was removed in vacuo, the crude product dissolved in CH$_2$Cl$_2$ (30 cm^3) and filtered three times over celite. The solvent was removed, under vacuum, to give the neutral product, [MoI(CO)$_2$(S$_2$CNMe$_2$){Ph$_2$P(CH$_2$)PPh$_2$}] (**19**), as a brown solid, yield = 0.389 g, 86%. Complexes **20**, [MoI(CO)$_2$(S$_2$CNEt$_2$){Ph$_2$P(CH$_2$)PPh$_2$}], and **21**, [MoI(CO)$_2$(S$_2$CNC$_4$H$_8$){Ph$_2$P(CH$_2$)PPh$_2$}], were prepared by the same method. Refer to Table 1 for physical and analytical data.

4.10. *[MoFI(CO)$_3${Ph$_2$P(CH$_2$)PPh$_2$}] (**22**)*

To a solution of [MoI(CO)$_3$(NCMe){Ph$_2$P(CH$_2$)PPh$_2$}][BF$_4$] (0.520 g, 0.635 mmol) in acetone (30 cm^3), sodium fluoride, (0.027 g, 0.643 mmol) was added and the solution stirred for 2 h. The solvent was removed from the resultant cloudy brown–green solution, in vacuo, and the crude product dissolved in CH$_2$Cl$_2$ (30 cm^3). Filtration of the solution three times over celite, followed by removal of the solvent under vacuum, gave the neutral product, [MoFI(CO)$_3${Ph$_2$P(CH$_2$)PPh$_2$}] (**22**), as a brown–green solid, yield = 0.336 g, 75%. Neutral complexes, [MoClI(CO)$_3${Ph$_2$P(CH$_2$)PPh$_2$}] (**23**), and [Mo(NCS)I(CO)$_3${Ph$_2$P(CH$_2$)PPh$_2$}] (**24**), were prepared by the same method. Refer to Table 1 for physical and analytical data.

4.11. X-ray crystallographic study

Crystal data for the complexes **10**, **14**, **25** and **26** are given in Table 6, together with refinement details. Data were collected with Mo–K_α radiation using the MAR-research Image Plate System. The crystals were positioned at 70 mm from the Image Plate. 100 Frames were measured at 2° intervals with a counting time of 2 min. Data analyses were carried out with the XDS program [48]. The structures were solved using direct methods with the SHELXS86 program [49]. Default refinement details were as follows: the non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. Absorption corrections were carried out using the DIFABS program [50]. The structures were refined on F^2 to convergence using SHELXL [51]. The structure of **10** was refined using the default procedure. Complex **14** contained a disordered CH_2Cl_2 in which one chlorine was disordered over two positions. For complex **25**, a chlorine and oxygen atom bonded to the molybdenum centre were disordered over two positions. They were refined with distance constraints, common isotropic thermal parameters and with population factors x and $1-x$, x refined to 0.40(1). There was one solvent chloroform given 50% occupancy and four water molecules, two given full occupancy, two given 50% occupancy. For the structure of **26**, the Mo–I and P atoms were refined anisotropically. The carbon atoms were refined anisotropically, but with thermal factors constrained to remain similar using the SIMU instruction in SHELXL. There were three solvent water molecules, given 50% occupancy. In both **25** and **26**, the hydrogen atoms on the water molecules could not be located and were not included.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 184015 (**10**), 184016 (**14**), 184017(**25**) and 184018 (**26**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.uk).

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References

[1] M.G.B. Drew, Prog. Inorg. Chem. 23 (1977) 67 (and references cited therein).
[2] M. Melnick, P. Sharrock, Coord. Chem. Rev. 65 (1985) 49 (and references cited therein).
[3] C.W. Haigh, P.K. Baker, Polyhedron 13 (1994) 477 (and references cited therein).
[4] P.K. Baker, Adv. Organomet. Chem. 40 (1996) 45 (and references cited therein).
[5] P.K. Baker, Chem. Soc. Rev. 27 (1998) 125 (and references cited therein).
[6] L. Bencze, A. Kraut-Vass, J. Mol. Catal. 28 (1985) 369 (and references cited therein).
[7] L. Bencze, A. Kraut-Vass, L. Prókoi, J. Chem. Soc. Chem. Commun. (1985) 911.
[8] M. Al Jahdali, P.K. Baker, A.J. Lavery, M.M. Meehan, D.J. Muldoon, J. Mol. Catal. 159 (2000) 51.
[9] M.W. Anker, R. Colton, I.B. Tomkins, Rev. Pure Appl. Chem. 18 (1968) 23 (and references cited therein).
[10] R. Colton, Coord. Chem. Rev. 6 (1971) 269 (and references cited therein).
[11] R. Colton, I.B. Tomkins, Aust. J. Chem. 19 (1966) 1143.
[12] L. Mihichuk, M. Pizzey, B. Robertson, R. Barton, Can. J. Chem. 64 (1986) 991.
[13] H.C.E. Mannerskantz, G. Wilkinson, J. Chem. Soc. (1962) 4454.
[14] P. Planinić, H. Meider, Polyhedron 9 (1990) 1099.
[15] D. Sevdić, M. Ćurić, Lj.T. Božić, Polyhedron 8 (1989) 505.
[16] S.C.N. Hsu, W.-Y. Yeh, M.Y. Chiang, J. Organomet. Chem. 492 (1995) 121.
[17] P.K. Baker, E.M. Armstrong, Polyhedron 9 (1990) 801.
[18] P.K. Baker, D.J. Sherlock, Polyhedron 13 (1994) 525.
[19] P.K. Baker, S.G. Fraser, J. Coord. Chem. 20 (1989) 267.
[20] P.K. Baker, A.I. Clark, M.G.B. Drew, M.C. Durrant, R.L. Richards, J. Organomet. Chem. 549 (1997) 193.
[21] P.K. Baker, S.G. Fraser, D. ap Kendrick, J. Chem. Soc. Dalton Trans. (1991) 131.
[22] P.K. Baker, M.E. Harman, S. Hughes, M.B. Hursthouse, K.M.A. Malik, J. Organomet. Chem. 498 (1995) 257.
[23] E. Carmona, L. Contreras, E. Gutiérrez-Puebla, A. Monge, L. Sánchez, Inorg. Chem. 29 (1990) 700.
[24] B.J. Brisdon, A.G.W. Hodson, Inorg. Chim. Acta 141 (1988) 57.
[25] F.J. Arnaíz, G. García, V. Riera, Y. Dromzée, Y. Jeannin, J. Chem. Soc. Dalton Trans. (1987) 819.
[26] P. Chaudhari, K. Wieghardt, Y.-H. Tsai, C. Krüger, Inorg. Chem. 23 (1984) 427.
[27] S.D. Perera, M. Shamsuddin, B.L. Shaw, Can. J. Chem. 73 (1995) 1010.
[28] P.K. Baker, M. Bamber, G.W. Rodgers, J. Organomet. Chem. 367 (1989) 101.
[29] P.K. Baker, S.J. Coles, M.C. Durrant, S.D. Harris, D.L. Hughes, M.B. Hursthouse, R.L. Richards, J. Chem. Soc. Dalton Trans. (1996) 4003.
[30] P.K. Baker, M.C. Durrant, S.D. Harris, D.L. Hughes, R.L. Richards, J. Chem. Soc. Dalton Trans. (1997) 509.
[31] P. Rosendorfer, W. Beck, Chem. Ber. 128 (1995) 729.

[32] P. Rosendorfer, C. Robl, W. Beck, Gazz. Chim. Ital. 123 (1993) 145.
[33] P.K. Baker, S.G. Fraser, E.M. Keys, J. Organomet. Chem. 309 (1986) 319.
[34] P.K. Baker, M.M. Meehan, Inorg. Synth. 33 (2002) 239.
[35] P.K. Baker, S.G. Fraser, Inorg. Chim. Acta 130 (1987) 61.
[36] P.K. Baker, M.G.B. Drew, A.W. Johans, U. Haas, L. Abdol Latif, M.M. Meehan, S. Zanin, J. Organomet. Chem. 590/1 (1999) 77.
[37] J.A. Connor, G.K. McEwen, C.J. Rix, J. Chem. Soc. Dalton Trans. (1974) 589.
[38] F.A. Cotton, L.R. Falvello, R. Poli, Polyhedron 6 (1987) 1135.
[39] K.-B. Shiu, K.-H. Yih, S.L. Wang, F.-L. Liao, J. Organomet. Chem. 414 (1991) 165.
[40] M.W. Anker, R. Colton, C.J. Rix, I.B. Tomkins (in part), Aust. J. Chem. 22 (1969) 1341.
[41] R. Colton, C.J. Rix, Aust. J. Chem. 22 (1969) 2535.
[42] R. Colton, J.J. Howard, Aust. J. Chem. 22 (1969) 2543.
[43] R. Colton, J.J. Howard, Aust. J. Chem. 23 (1970) 223.
[44] L.K. Fong, J.R. Fox, B.M. Foxman, N.J. Cooper, Inorg. Chem. 25 (1986) 1880.
[45] M.G.B. Drew, J. Chem. Soc. Dalton Trans. (1972) 1329.
[46] J. Lewis, R. Whyman, J. Chem. Soc. (1965) 6027.
[47] P.K. Baker, M.G.B. Drew, M.M. Meehan, J. Chem. Soc. Dalton Trans. (1999) 765.
[48] W. Kabsch, J. Appl. Crystallogr. 21 (1988) 916.
[49] G.M. Sheldrick, Acta Crystallogr. Sect. A 46 (1990) 467.
[50] N. Walker, D. Stuart, Acta Crystallogr. Sect. A 39 (1983) 158.
[51] G.M. Sheldrick, SHELXL, Program for Crystal Structure Refinement, University of Göttingen, Göttingen, Germany, 1993.