Journal of Organometallic Chemistry, 382 (1990) 407–417
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20474

Synthesis, crystal structure and heterometallic derivatives of $[Mo_2Cp_2(\mu\text{-}\sigma,\pi\text{-}CN^tBu)(PPh_2CH_2PPh_2\text{-}P)(CO)_3]$ ($^tBu = C(CH_3)_3$, $Cp = \eta\text{-}C_5H_5$)

Víctor Riera *, **Miguel A. Ruiz,**

Departamento de Química Organometálica, Universidad de Oviedo, 33071 Oviedo (Spain)

Fernando Villafañe,

Química Inorgánica, Universidad de Valladolid, 47005 Valladolid (Spain)

Claudette Bois and Yves Jeannin *,

Laboratoire de Chimie des Métaux de Transition, UACNRS 419, Université Pierre et Marie Curie,
4 Place Jussieu, 75252 Paris cedex 05 (France)

(Received August 4th, 1989)

Abstract

The dppm ligand ($Ph_2PCH_2PPh_2$) in $[Mo_2Cp_2(CO)_4(\mu\text{-dppm})]$ ($Cp = \eta\text{-}C_5H_5$) undergoes ring-opening upon reaction with NCMe or CN^tBu ($^tBu = C(CH_3)_3$), to give $[MoCp(CO)(NCMe)(dppm)][MoCp(CO)_3]$ or $[Mo_2Cp_2(\mu\text{-}\sigma,\pi\text{-}CN^tBu)(dppm\text{-}P)(CO)_3]$, respectively. The crystal structure of the latter complex is described as well as its reactions with sources of the metal fragments ML_n [ML_n: $Fe(CO)_4$, $Mo(CO)_5$, $MnBr(CO)_4$, CuCl] to give the heterometallic species $[ML_n(\mu\text{-dppm})MoCp(CO)(\mu\text{-}\sigma,\pi\text{-}CN^tBu)MoCp(CO)_2]$.

Introduction

The study of the reactions of single metal–metal bonds present in dinuclear transition metal carbonyl species usually requires the presence of a bridging ligand in order to prevent dimer degradation. Bidentate phosphorus donor ligands of the type A_2PBPA_2 (A = R, OR; B = CR_2, NR, O; R = H, alkyl, aryl) and, particularly $Ph_2PCH_2PPh_2$ (dppm), have proved to be very useful for this purpose [1–4]. However, there are now some observations which show such ligands do not always play only a spectator role [4].

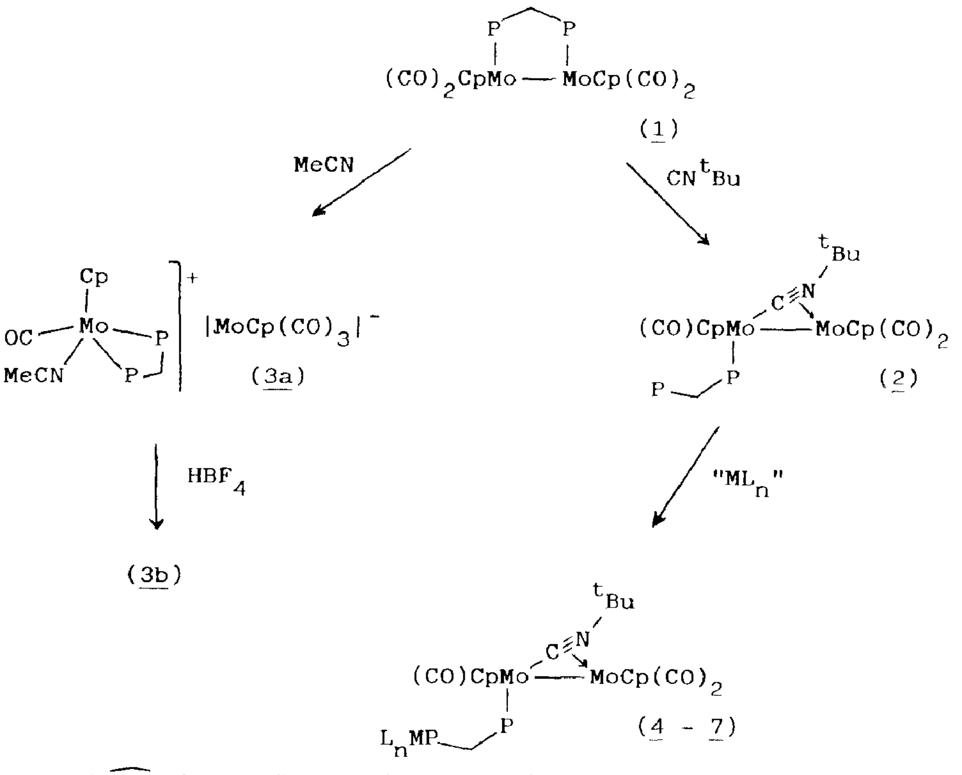
Although the dppm bridge in $[Mo_2Cp_2(CO)_4(\mu\text{-dppm})]$ (**1**) ($Cp = \eta\text{-}C_5H_5$) holds together the dimer through a number of reactions with electrophilic reagents [5], we have found some instances in which there is a chemical change in the dppm bridge as a result of a reaction. For example, a P–C(sp^3) cleavage in the ligand can be brought about by thermal treatment of compound **1** [6]. We report here some reactions of **1** which result in a change of the coordination of dppm ligand between bridging and chelated or monodentate modes. The uncoordinated phosphorus atom in the latter case can be utilized in the synthesis of new heterometallic species.

Results and discussion

Ring opening reactions of [$Mo_2Cp_2(CO)_4(\mu$-dppm)] (1)

(a) Reaction with CN^{t}Bu. Reaction of compound **1** (Scheme 1) with a slight excess of CN^{t}Bu in CH_2Cl_2 proceeds smoothly at room temperature to give the red-brown [$Mo_2Cp_2(\mu$-σ,π-CN^{t}Bu)(dppm-P)$(CO)_3$] (**2**) in 78% yield. Spectroscopic data for **2** (Tables 1 and 2) firmly support the proposed structure in solution. Thus, ^{13}C resonances at 250.3, 247.6 and 243.4 ppm are assigned to three inequivalent terminal carbonyl ligands, which also give rise to ν(CO) bands at 1904, 1840, and 1811 cm^{-1} (CH_2Cl_2 solution); the unidentate coordination of the dppm ligand is evidenced by the chemical shifts in the $^{31}P\{^1H\}$ spectrum, that at -25.9 ppm being very close to the resonance in the free ligand.

Surprisingly, though, two bands (1658 and 1625 cm^{-1}) are present in the IR spectrum in the region expected for bridging (σ,π) isocyanides, whereas a single resonance for the coordinated C atom appears in the ^{13}C NMR spectrum. There are



Schema 1. $\widehat{P\ P}$ = dppm; "ML$_n$" = $Fe(CO)_4$ (**4**), $Mo(CO)_5$ (**5**), $MnBr(CO)_4$ (**6**), CuCl (**7**).

Table 1

Infrared and microanalytical data for new compounds

Compound	IR in CH_2Cl_2 solution		Analysis (Found (calcd.) (%))		
	ν(CO) (cm^{-1})	ν(CN)	C	H	N
2	1904vs, 1840m, 1811s	1658w, 1625vw	58.97	4.89	1.79
			(59.11)	(4.73)	(1.60)
3b	1881vs	1985wbr	56.60	4.19	1.91
			(56.52)	(4.31)	(2.00)
4	2047s, 1975m, 1936vsbr, 1907vs, 1836msh, 1815s	1654w, 1620vw	54.47	3.85	1.30
			(54.19)	(3.97)	(1.34)
5	2071m, 2017vw, 1990w, 1944vsbr, 1907vs, 1838msh, 1813s	1653w, 1620vw	51.88	3.62	1.18
			(51.95)	(3.72)	(1.26)
6	2088s, 2020s, 2002vs, 1963s, 1906vs, 1845m, 1812s	1655m, 1623w	50.50	3.96	1.25
			(50.37)	(3.69)	(1.25)
7	1909vs, 1851m, 1816m	1656w, 1624vw	50.14	4.18	1.41
			(49.96)	(4.10)	(1.33) [a]

[a] $7 \cdot CH_2Cl_2$.

some recent examples of single terminally bonded isocyanides giving rise to two ν(CN) bands [7a–d]. In one case [7a] this was attributed to the fact that a value for the C–N–C angle substantially lower than 180° allows the existence of distinct conformers. In contrast, the IR spectra of the closely related to **2** species $[Mo_2Cp_2(\mu\text{-}\sigma,\pi\text{-}CNR)(CO)_4]$ (R = Ph [8], ^{t}Bu [9]) exhibit a single ν(CN) band. In order to check whether this difference could be the result of a significant change in the bonding of the isocyanide ligand in **2** relative to that in the dimolybdenum compounds, we determined the crystal structure of **2**.

The molecular structure is depicted in Fig. 1, and some relevant distances and bond angles are listed in Table 3. The molecule consists of two molybdenum atoms

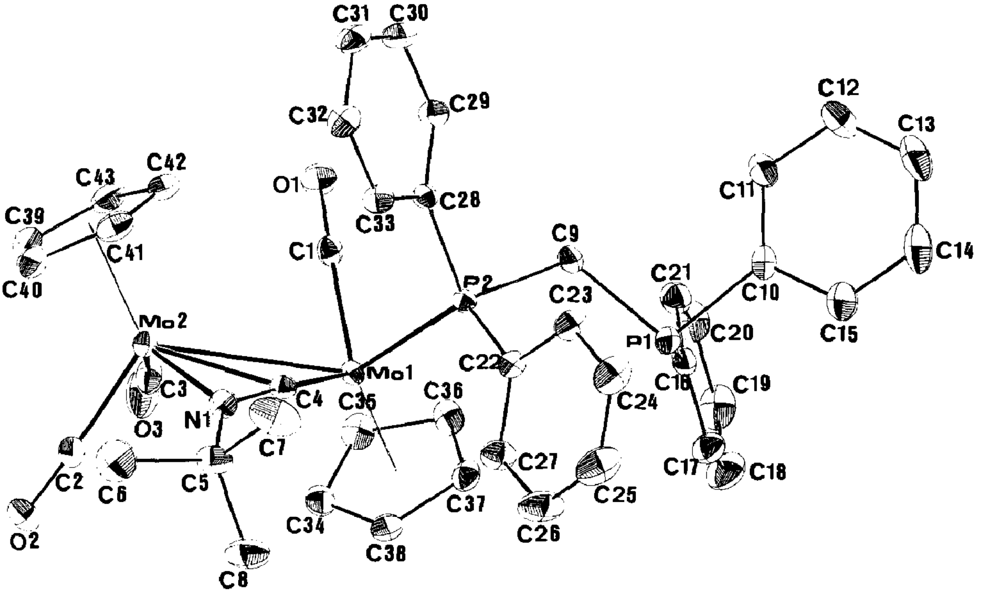


Fig. 1. Crystal structure of $[Mo_2Cp_2(\mu\text{-}\sigma,\pi\text{-}CN^tBu)(dppm\text{-}P)(CO)_3]$ (**2**).

Table 2

NMR data for new compounds. (shifts in ppm downfield relative to internal TMS (^1H, ^{13}C) or external 85% H_3PO_4 in H_2O (^{31}P); coupling constants in Hz; $CDCl_3$ solution unless otherwise stated)

Compound	^1H NMR	$^{31}P\{^1H\}$ NMR	$^{13}C\{^1H\}$ NMR
2	7.6–7.1 (m, C_6H_5, 20H), 5.18 (d, *J*(PH) 1, C_5H_5, 5H), 4.79 (s, C_5H_5, 5H), 3.41 (dd, *J*(PH) 8 and 3, CH_2, 2H), 1.18 (s, CH_3, 9H)	70.1 (d, *J*(PP) 73, $MoPCH_2P$), −25.9 (d, *J*(PP) 73, $MoPCH_2$*P*)	250.3 (s, MoCO), 247.6 (s, MoCO), 243.4 (d, *J*(PC) 20, MoCO), 209.7 (d, *J*(PC) 22, MoCN), 139.1–127.6 (C_6H_5), 94.0 (s, C_5H_5), 92.4 (s, C_5H_5), 59.7 (s, CMe_3), 37.3 (dd, *J*(PC) 32 and 22, CH_2), 31.6 (s, CH_3)
3b	8.0–6.6 (m, C_6H_5, 20H), 5.17 (d, *J*(PH) 2, C_5H_5, 5H), 4.57 and 4.46 (AB system of triplets, *J*(H_AH_B) 15, *J*(PH_A) 10, *J*(PH_B) 11, CH_2, 2H), 1.69 (d, *J*(PH) 3, CH_3, 3H)	24.4 (d, *J*(PP) 77), 15.4 (d, *J*(PP) 77)	239.4 (dd, *J*(PC) 20 and 3, MoCO), 140.2 (t, *J*(PC) 3, MoNC), 138.1–128.5 (C_6H_5), 92.9 (s, C_5H_5), 42.7 (dd, *J*(PC) 26 and 24, CH_2), 3.5 (s, CH_3)
4	7.6–7.1 (m, C_6H_5, 20H), 5.11 (s, C_5H_5, 5H), 4.77 (d, *J*(PH) 1, C_5H_5, 5H), 3.90 and 3.66 (AB system of triplets, *J*(H_AH_b) 16, *J*(PH) 7, CH_2, 2H), 1.22 (s, CH_3, 9H)	82.5 (d, *J*(PP) 35, MoP), 65.7 (d, *J*(PP) 35, FeP)	249.9 (s, MoCO), 247.7 (s, MoCO), 243.0 (d, *J*(PC) 19, MoCO), 213.7 (d, *J*(PC) 18, 4×FeCO), 209.4 (d, *J*(PC) 20, MoCN), 136.4–127.7 (C_6H_5), 94.6 (s, C_5H_5), 93.1 (s, C_5H_5), 59.7 (s, CMe_3), 40.4 (br, CH_2), 31.6 (s, CH_3) [a]
5	7.6–7.2 (m, C_6H_5, 20H), 4.89 (s, C_5H_5, 5H), 4.85 (d, *J*(PH) 1, C_5H_5, 5H), 3.72 and 3.66 (AB system, *J*(H_AH_B) 16; part A: dd, *J*(PH) 6 and 3; part B: t, *J*(PH) 5; CH_2, 2H), 1.16 (s, CH_3, 9H)	79.6 (d, *J*(PP) 26, MoCp(CO)P), 29.7 (d, *J*(PP) 26, $Mo(CO)_5P$)	
6	7.6–7.0 (m, C_6H_5, 20H), 4.97 (s, C_5H_5, 5H), 4.85 (d, *J*(PH) 1, C_5H_5, 5H), 4.22 and 4.08 (AB system of triplets, *J*(H_AH_B) 16, *J*(PH) 5, CH_2, 2H), 1.20 (s, CH_3, 9H)	82.3 (d, *J*(PP) 31, MoP), 35.7 (br, MnP)	
7	7.5–7.1 (m, C_6H_5, 20H), 5.05 (s, C_5H_5, 5H), 4.79 (d, *J*(PH) 1, C_5H_5, 5H), 3.53 and 3.40 (AB system, *J*(H_AH_B) 15; part A: t, *J*(PH) 7; part B: dd, *J*(PH) 9 and 6, CH_2, 2H), 1.28 (s, CH_3, 9H)	70.0 (d, *J*(PP) 46, MoP), −19.0 (br, d, *J*(PP) 46, CuP)	

[a] CD_2Cl_2 solution.

Table 3

Selected distances (Å) and bond angles (°) in **2**

Distances (Å)		Angles (°)	
Mo(1)-Mo(2)	3.1950(5)	Mo(1)-C(4)-N(1)	164.7(3)
		C(4)-N(1)-C(5)	136.7(4)
Mo(1)-C(4)	1.951(4)		
C(4)-N(1)	1.239(5)	C(4)-Mo(1)-Mo(2)	44.7(1)
N(1)-C(5)	1.489(5)	C(4)-Mo(1)-P(2)	85.4(1)
		C(4)-Mo(1)-C(1)	105.9(2)
Mo(2)-C(4)	2.270(4)	P(2)-Mo(1)-Mo(2)	116.08(3)
Mo(2)-N(1)	2.186(3)	C(1)-Mo(1)-Mo(2)	78.1(1)
		P(2)-Mo(1)-C(1)	83.1(1)
Mo(1)-P(2)	2.396(1)		
Mo(1)-C(1)	1.940(4)	N(1)-Mo(2)-Mo(1)	69.11(9)
		N(1)-Mo(2)-C(2)	90.4(2)
Mo(2)-C(2)	1.928(5)	N(1)-Mo(2)-C(3)	127.3(2)
Mo(2)-C(3)	1.928(5)	C(4)-Mo(2)-Mo(1)	37.2(1)
		C(4)-Mo(2)-C(2)	106.6(2)
		C(4)-Mo(2)-C(3)	103.8(2)
		C(2)-Mo(2)-Mo(1)	113.6(2)
		C(3)-Mo(2)-Mo(1)	71.1(2)
		C(2)-Mo(2)-C(3)	75.5(2)

bridged by an isocyanide ligand in a σ,π fashion, while the Mo–Mo distance (3.1950(5) Å) is consistent with the presence of a single metal–metal bond. Angles and distances in the bridging region are very similar to those reported for the related dimolybdenum species mentioned above [8,9]. Thus the appearance of two ν(CN) in the IR spectrum of **2** cannot be due only to the presence of possible conformers caused by the C–N–C nonlinearity, but also in some way to the effect of the unidentate diphosphine.

It is noteworthy that, as for $[Cr(\eta\text{-}C_6H_5CO_2Me)(CN^tBu)(CO)_2]$ [7a], the relative intensities of the two ν(CN) bands for **2** are solvent dependent. The ratio of the high to low frequency band also decreases in the order $CHCl_3 > CH_2Cl_2 >$ toluene > thf > CCl_4; such a sequence cannot be correlated with any simple physical or chemical solvent property (e.g. dipolar moment, dielectric constant, or donor number), revealing the complexity of the factors involved.

(b) Reaction with MeCN. Whereas ^tBuNC promotes a ring opening of the bridging dppm in **1**, MeCN takes the process a step further, to bring about heterolytic cleavage of the Mo–Mo bond. Thus, heating compound **1** in acetonitrile at 60°C for 1.5 h results in the formation of [MoCp(CO)(NCMe)(dppm)]-[MoCp(CO)$_3$] (**3a**) (eq. 1). The cation can be isolated more conveniently as its BF_4^- salt **3b** after acidification of the mixture with $HBF_4 \cdot OEt_2$ (eq. 2).

$$[Mo_2Cp_2(CO)_4(\mu\text{-dppm})] \xrightarrow[60\,^\circ C]{MeCN} \underset{\textbf{(3a)}}{[MoCp(CO)(NCMe)(dppm)][MoCp(CO)_3]} \qquad (1)$$

$$\textbf{3a} \xrightarrow[MeCN]{HBF_4 \cdot OEt_2} \underset{\textbf{(3b)}}{[MoCp(CO)(NCMe)(dppm)]BF_4} + [MoCpH(CO)_3] \qquad (2)$$

Compound **3b** has been satisfactorily characterized by microanalysis and spectroscopic properties, but the coordination mode of the nitrile ligand, is not completely clear. In principle, nitrile ligands in mononuclear complexes can be bonded either "end-on" or "side-on" to the metal [10]. For compound **3b**, the ν(CN) band appears at 1985, 270 cm^{-1}, below that for free MeCN, thus suggesting a "side-on" coordination in terms of a criterion that must, however, be used with some caution [10]. The ^{13}C NMR spectra should also be informative, but relevant data are scarce and so likely to be less conclusive. In fact, δ(NCMe) for **3b** is found to be 140.2 ppm, which is intermediate between the values reported for (crystallographically confirmed) "bridging σ,π" (157.2 in $[Mn_2(\mu\text{-}\sigma,\pi\text{-}NCMe)(CO)_6(\mu\text{-dppm})]$ [11]) or "end-on" bridging (128.7 in $[WI_2(CO)(NCMe)(\eta^2\text{-}MeC{\equiv}CMe)_2]$ [12]), but equal to that reported for $[Mo_2Cp_2(CO)_3(NCMe)(\mu\text{-SPh})_2][BF_4]_2$ ("end-on", δ 138.9 ppm [13], but ν(CN) 2300 cm^{-1}). Clearly, spectroscopic correlations are still far from reliable.

Synthesis of heterometallic derivatives of $[Mo_2Cp_2(\mu\text{-}\sigma,\pi\text{-}CN^tBu)(CO)_3(dppm\text{-}P)]$ *(2)*

It has been shown above that ring opening of the dppm bridge in compound **1** can be readily brought about. We thought that this Mo–P bond lability could perhaps be used in the synthesis of heterometallic species through direct reaction of **1** with appropriate metallic complexes. Such a procedure proved, however, to be not very useful because complete dppm transfer to these metallic complexes was found to occur readily in several cases, as shown in eqs. 3 and 4:

$$\mathbf{1} + [MnBr(CO)_5] \xrightarrow[\text{r.t.}]{\text{toluene}} [MnBr(CO)_3(dppm)] + [Mo_2Cp_2(CO)_6] \qquad (3)$$

$$\mathbf{1} + [MoCpCl(CO)_3] \xrightarrow[40\,^\circ C]{\text{toluene}} \tfrac{1}{2}[Mo_2Cp_2Cl_2(CO)_4(\mu\text{-dppm})] + [Mo_2Cp_2(CO)_6] \qquad (4)$$

The halogeno complexes shown in the above equations were characterized spectroscopically, by use of previously reported data [14,15].

We thus turned our attention to compound **2**, which contains an unidentate dppm ligand. This type of species has been successfully used in the synthesis of heterometallic complexes by Shaw and coworkers [4,16]. We examined some reactions of **2** with transition metal complexes, in order to see what effect coordination of the heterometal (to the unligated phosphorus atom) would have on the bridging isocyanide ligand.

Addition of a slight excess of $[Fe_2(CO)_9]$ to an Et_2O solution of **2** results in the coordination of a "$Fe(CO)_4$" fragment to its uncoordinated phosphorus atom, yielding $[Fe(CO)_4(\mu\text{-dppm})MoCp(CO)(\mu\text{-}\sigma,\pi\text{-}CN^tBu)MoCp(CO)_2]$ (**4**) in good yield. Microanalytical and spectroscopic data are consistent with the formulation proposed for this new compound, and indicate that little or no change has occurred in the ligands directly coordinated to molybdenum atoms. Thus $\delta(CN^tBu)$ or δ(MoCO) remain essentially unchanged compared with those for **2** (Table 2), and the ν(CO) and ν(CN) bands in **4** correspond roughly with a superimposition of those for **2** and $[Fe(CO)_4(dppm\text{-}P)]$ [17].

Similarly, treatment of **2** with appropriate sources of the "ML_n" fragments (see Experimental) yields the trimetallic complexes $[ML_n(\mu\text{-dppm})MoCp(CO)(\mu\text{-}\sigma,\pi\text{-}$

CN^{t}Bu)MoCp(CO)$_2$] (ML$_n$ = Mo(CO)$_5$ (**5**), MnBr(CO)$_4$ (**6**), CuCl (**7**)), which are isostructural with **4** in respect of the original dimolybdenum unit, i.e., they all retain the geometrical arrangement present in **2**. Interestingly, these complexes also exhibit two ν(CN) bands in their IR spectra, with a pattern similar to that for the parent **2**.

Complexes **4** to **7** may be precursors for new heterometallic clusters; for example through decarbonylation. Our studies in that direction have been unsuccessful, however, since we have found that complete dppm transfer competes effectively with CO loss, resulting in degradation of the trimetallic species.

Experimental

All reactions were performed under nitrogen. Solvents were purified by standard procedures [18], and distilled prior to use. Infrared spectra were recorded on a Perkin Elmer 883 spectrophotometer. ^{1}H, ^{31}P{^{1}H} and ^{13}C{^{1}H} NMR were recorded on a Bruker AC-300 spectrometer. Elemental analysis were performed with a Perkin Elmer 240 microanalyzer. Complexes [Mo$_2$Cp$_2$(CO)$_4$(μ-dppm)] [5], [Fe$_2$(CO)$_9$] [19a], [MnBr(CO)$_5$] [19b] and CuCl [20] were prepared by published methods. All other reagents were obtained from commercial suppliers. Spectroscopic data for compounds are given in Tables 1 and 2. All the compounds described are air-stable as solids unless otherwise stated.

Preparation of [Mo$_2$Cp$_2$(μ-σ,π-CN^{t}Bu)(dppm-P)(CO)$_3$] (2)

A solution of **1** (0.819 g, 1 mmol) and CN^{t}Bu (0.18 ml, 1.6 mmol) in CH$_2$Cl$_2$ (50 ml) was stirred at room temperature for 24 h. The solution was then transferred into an alumina column (activity II, 5 × 2 cm). Elution with CH$_2$Cl$_2$ (3 × 10 ml) gave a red-brown solution which after removal of solvent in vacuo and washing of the residue with hexane (3 × 10 ml) gave 0.685 g (78%) of compound **2** as a brown powder. The red crystals used in the X-ray study were obtained by recrystallization of this powder from Et$_2$O/hexane (2/1 in vol.) at −20 °C.

Preparation of [MoCp(CO)(NCMe)dppm)]BF$_4$ (3b)

A suspension of compound **1** (0.164 g, 0.2 mmol) in NCMe (10 ml) was stirred at 60 °C for 1.5 h and the resulting yellow solution then allowed to cool to room temperature and treated with HBF$_4$ · OEt$_2$ (0.028 ml, 0.2 mmol). The mixture was stirred for 5 min and the solvent then removed in vacuo to leave a yellow residue, which was washed with Et$_2$O (3 × 10 ml). Recrystallization from CH$_2$Cl$_2$/Et$_2$O (10/20) at −20 °C yielded 0.085 (61%) of salt **3b** as yellow microcrystals.

Preparation of [Fe(CO)$_4$(μ-dppm)MoCp(CO)(μ-σ,π-CN^{t}Bu)MoCp(CO)$_2$] (4)

A solution of **2** (0.175 g, 0.2 mmol) and [Fe$_2$(CO)$_9$] (0.146 g, 0.4 mmol) in Et$_2$O (20 ml) was stirred at room temperature for 5 h, then filtered through Celite, to give a brown solution. After partial removal of the solvent in vacuo, hexane (10 ml) was added to this solution, and the mixture was kept at −20 °C for 24 h. The brown microcrystalline **4** obtained was separated from the solution, washed with hexane (5 ml), and dried in vacuo (0.135 g, 65%).

Preparation of [Mo(CO)$_5$(μ-dppm)MoCp(CO)(μ-σ,π-CN^{t}Bu)MoCp(CO)$_2$] (5)

A solution of [Mo(CO)$_6$] (0.053 g, 0.2 mmol) and Me$_3$NO (0.015 g, 0.2 mmol) was stirred in NCMe (5 ml) at room temperature for 15 min as N$_2$ was bubbled gently through the solution. Compound **2** (0.087 g, 0.1 mmol) was then added to the yellow solution, and the solvent was removed in vacuo. The residue was dissolved in CH_2Cl_2 (10 ml) and the solution stirred for one hour. Active carbon was then added and the mixture filtered through Celite to give a dark brown solution, which after work-up as for **4** gave 0.035 g (32%) of compound **5** as black crystals.

Preparation of $[MnBr(CO)_4(\mu\text{-}dppm)MoCp(CO)(\mu\text{-}\sigma,\pi\text{-}CN^tBu)MoCp(CO)_2]$ ***(6)***

A solution of **2** (0.087 g, 0.1 mmol), $[MnBr(CO)_5]$ (0.056 g, 0.2 mmol) and Me_3NO (0.015 g, 0.2 mmol) in CH_2Cl_2 (10 ml) was stirred at 0 °C for 10 min. Removal of the solvent in vacuo from the resulting mixture gave a brown residue which was extracted with toluene (15 ml). This solution was filtered through Celite and cooled at −20 °C for 24 h. An orange solid identificated as $[MnBr(CO)_3(dppm)]$ was first separated. Further crystallization at −20 °C from the mother liquor gave

Table 4

Crystal and structural data for compound **2**

Formula		$C_{43}H_{41}Mo_2NO_3P_2$
Mol. wt.		873.6
Crystal system		Triclinic
Space group		$P1$
a, Å		9.656(2)
b, Å		14.045(2)
c, Å		15.287(1)
α, deg.		71.928(6)
β, deg.		82.09(1)
γ, deg.		80.36(1)
V, Å^3		1935(1)
Z		2
ρ_{calc}, g cm^{-3}		1.50
Reflections for lattice	number	25
parameters	θ-range	16–17
$F(000)$		888
Temperature, °C		18
Crystal size, mm		0.40 × 0.30 × 0.25
Diffractometer		CAD4 Enraf–Nonius
Radiation		Mo-K_α
Monochromator		Graphite
Scan type		$\omega-2\theta$
Scan width		$1.0+0.34 \tan\theta$
θ range, deg		1–25
Standard reflections		Two, measured every 2h
μ, cm^{-1}		3.4
Absorption correction, min-max		1.00–1.15
No. of measured reflections		6807
No. of reflections used $I \geqslant 3\sigma(I)$		4312
Min-max height in final $\Delta\rho$, e A^{-3}		−0.35–0.32
No. of refined parameters		587
$R = [\Sigma\lvert\Delta F\rvert/\Sigma F_o]$		0.026
$R_w = [\Sigma w(\Delta F)^2/\Sigma wF_o^2]^{1/2}$		0.028
$w = 1$.		

Table 5

Atomic coordinates and thermal parameters for compound **2**

Atom	x	y	z	U_{equiv}
Mo(1)	−0.00606(4)	0.28734(2)	0.25386(2)	0.0307
Mo(2)	0.01146(4)	0.07522(3)	0.21395(3)	0.0402
P(1)	−0.2297(1)	0.60336(8)	0.27035(8)	0.0414
P(2)	−0.2203(1)	0.40032(7)	0.22094(7)	0.0303
O(1)	0.0577(4)	0.3512(3)	0.0410(2)	0.0587
O(2)	0.1495(5)	−0.1075(3)	0.3615(3)	0.0786
O(3)	0.3198(4)	0.1118(3)	0.2095(3)	0.0755
N(1)	−0.1707(4)	0.0974(3)	0.3110(2)	0.0423
C(1)	0.0282(4)	0.3252(3)	0.1202(3)	0.0400
C(2)	0.0945(6)	−0.0378(4)	0.3084(4)	0.0575
C(3)	0.2001(5)	0.1036(4)	0.2136(4)	0.0540
C(4)	−0.1255(4)	0.1800(3)	0.2877(3)	0.0343
C(5)	−0.2689(5)	0.0424(4)	0.3865(3)	0.0473
C(6)	−0.2585(8)	−0.0640(5)	0.3825(4)	0.0791
C(7)	−0.4173(6)	0.0987(5)	0.3704(4)	0.0703
C(8)	−0.2254(7)	0.0442(5)	0.4771(4)	0.0708
C(9)	−0.2094(5)	0.5379(3)	0.1799(3)	0.0395
C(10)	−0.3328(4)	0.7239(3)	0.2121(3)	0.0429
C(11)	−0.3387(6)	0.7644(4)	0.1180(4)	0.0621
C(12)	−0.4216(7)	0.8548(4)	0.0824(5)	0.0828
C(13)	−0.4979(6)	0.9065(4)	0.1388(5)	0.0771
C(14)	−0.4926(6)	0.8687(4)	0.2314(5)	0.0728
C(15)	−0.4104(5)	0.7774(4)	0.2686(4)	0.0639
C(16)	−0.0582(5)	0.6461(3)	0.2624(3)	0.0432
C(17)	−0.0105(6)	0.6430(4)	0.3449(4)	0.0602
C(18)	0.1146(7)	0.6759(5)	0.3468(4)	0.0758
C(19)	0.1942(6)	0.7122(5)	0.2659(5)	0.0711
C(20)	0.1514(5)	0.7161(4)	0.1836(4)	0.0638
C(21)	0.0249(5)	0.6831(4)	0.1814(3)	0.0549
C(22)	−0.3626(4)	0.3952(3)	0.3140(3)	0.0386
C(23)	−0.4947(5)	0.4508(4)	0.2986(3)	0.0516
C(24)	−0.5966(5)	0.4532(5)	0.3709(4)	0.0634
C(25)	−0.5653(6)	0.4022(6)	0.4593(4)	0.0739
C(26)	−0.4366(6)	0.3470(5)	0.4761(4)	0.0710
C(27)	−0.3358(5)	0.3432(4)	0.4036(3)	0.0537
C(28)	−0.3081(4)	0.3867(3)	0.1278(3)	0.0333
C(29)	−0.2762(5)	0.4414(3)	0.0363(3)	0.0444
C(30)	−0.3366(5)	0.4263(4)	−0.0342(3)	0.0536
C(31)	−0.4276(5)	0.3559(4)	−0.0156(3)	0.0533
C(32)	−0.4595(5)	0.3014(4)	0.0742(4)	0.0535
C(33)	−0.4007(5)	0.3155(3)	0.1458(3)	0.0454
C(34)	0.1789(5)	0.2304(4)	0.3517(3)	0.0507
C(35)	0.2182(5)	0.3111(4)	0.2749(4)	0.0528
C(36)	0.1255(5)	0.3986(3)	0.2795(4)	0.0486
C(37)	0.0292(5)	0.3715(4)	0.3581(3)	0.0477
C(38)	0.0645(5)	0.2678(4)	0.4023(3)	0.0523
C(39)	0.0661(6)	0.0042(4)	0.0953(4)	0.0631
C(40)	−0.0633(7)	−0.0257(4)	0.1386(4)	0.0612
C(41)	−0.1647(6)	0.0612(4)	0.1226(3)	0.0591
C(42)	−0.0991(6)	0.1450(4)	0.0718(3)	0.0524
C(43)	0.0443(6)	0.1088(4)	0.0558(3)	0.0593

black crystals of **6**, which were separated from the solution, washed with hexane (5 ml) and dried in vacuo (0.030 g, 27%).

Preparation of [CuCl(μ-dppm)MoCp(CO)(μ-σ,π-CN'Bu)MoCp(CO)$_2$] (7)

A mixture of **2** (0.087 g, 0.1 mmol), CuCl (0.010 g, 0.1 mmol) and toluene (10 ml) was stirred for 12 h at room temperature. After addition of active carbon, the resulting mixture was filtered through Celite to give a brown solution. Removal of the solvent in vacuo and recrystallization of the residue from CH_2Cl_2/hexane (20/10) at $-20\,°C$ yielded black crystals of **7**, which were separated, washed with hexane (5 ml), and dried in vacuo (0.025 g, 26%). Compound **7** decomposes even in the solid state when exposed to air.

Crystal structure determination of [Mo$_2$Cp$_2$(μ-σ,π-CN'Bu)(dppm-P)(CO)$_3$] (2)

Intensity data were collected with a Nonius CAD4. An empirical absorption correction was applied, using the psi-scan of two reflections. Further crystallographic data and details of the procedure are given in Table 4.

The two independent molybdenum atoms were found on a Patterson map and all other atoms in subsequent Fourier maps. All atoms except those of hydrogen had anisotropic thermal parameters. Least squares refinements were carried out in three blocks. Hydrogen atoms were refined with an overall isotropic temperature factor. Scattering factors were corrected for anomalous dispersion and a secondary extinction correction was applied. The final positional and thermal parameters are listed in Table 5.

All calculations were carried out with the CRYSTALS program [21]. Tables of hydrogen coordinates, anisotropic thermal parameters, bond lengths and angles, and observed and calculated structure factors can be obtained from the authors.

Acknowledgements

The authors thank the spanish Ministerio de Educación y Ciencia for a grant (M.A.R.) and the spanish C.A.I.C.Y.T. for financial support.

References

1 R.J. Puddephatt, Chem. Soc. Rev., 12 (1983) 99.

2 R.B. King, Acc. Chem. Res., 13 (1980) 243.

3 V. Riera and M.A. Ruiz, J. Chem. Soc., Dalton Trans., (1986) 2617.

4 B. Chaudret, B. Delavaux and R. Poilblanc, Coord. Chem. Rev., 86 (1988) 191.

5 V. Riera, M.A. Ruiz, F. Villafañe, Y. Jeannin and C. Bois, J. Organomet. Chem., 345 (1988) C4.

6 V. Riera, M.A. Ruiz, F. Villafañe, C. Bois and Y. Jeannin, J. Organomet. Chem., 375 (1989) C23.

7 (a) G.W. Harris, M.D. Albers, J.C.A. Boeyens and N.J. Coville, Organometallics, 2 (1983) 609; (b) V. Riera, J. Ruiz, Y. Jeannin and M. Philoche-Levisalles, J. Chem. Soc., Dalton Trans., (1988) 1591; (c) J.M. Martínez de Ilarduya, A. Otero and P. Royo, J. Organomet. Chem., 340 (1988) 187; (d) M. Vivanco, PhD Thesis, Universidad de Valladolid, Valladolid, Spain, 1989.

8 (a) R.D. Adams, D.A. Katahira and L.W. Yang, Organometallics, 1 (1982) 231; (b) I. Bernal, H. Brunner and J.W. Wachter, J. Organomet. Chem., 277 (1984) 395.

9 H. Adams, N.A. Bailey, C. Bannister, M.A. Faers, P. Fedorko, V.A. Osborn and M.J. Winter, J. Chem. Soc., Dalton Trans., (1987) 341.

10 B.N. Storhoff and H.C. Lewis Jr, Coord. Chem. Rev., 23 (1977) 319.

11 F.J. García-Alonso, M. García-Sanz, V. Riera, M.A. Ruiz, A. Tiripicchio and M.T. Camellini, Angew. Chem., Int. Ed. Eng., 27 (1988) 1167.

12 E.M. Armstrong, P.K. Baker and M.J.B. Drew, Organometallics, 7 (1988) 319.

13 M. El Khalifa, M. Guéguen, R. Mercier, F.Y. Pétillon, J.Y. Saillard and J. Tallarmin, Organometallics, 8 (1989) 140.

14 R.H. Reimann and E. Singleton, J. Organomet. Chem., 38 (1978) 113.

15 F. Villafañe, PhD Thesis, Universidad de Valladolid, Valladolid, Spain, 1989.

16 See for example, (a) G.B. Jacobsen, B.L. Shaw and M. Thornton-Pett, J. Chem. Soc., Dalton Trans., (1987) 1489; (b) S.W. Carr, B.L. Shaw and M. Thornton-Pett, ibid., (1987) 1763; (c) G.B. Jacobsen, B.L. Shaw and M. Thornton-Pett, ibid., (1987) 3079.

17 G.B. Jacobsen, B.L. Shaw and M. Thornton-Pett, J. Chem. Soc., Dalton Trans., (1987) 1509.

18 D.D. Perrin and W.L.F. Armarego, Purification of Laboratory Chemicals, Pergamon Press, 1988.

19 (a) R.B. King, Organometallic Synthesis, 1 (1965) 93; (b) R.B. King, ibid., 1 (1965) 641.

20 R.N. Keller and H.D. Wycoff, Inorg. Synth., 2 (1946) 1.

21 J.R. Carruthers and D.W. Watkin, CRYSTALS, an advanced crystallography computer program, 1985. Chemical Crystallographic Laboratory, Oxford University.