Synthesis and Characterization of Cr, Mo and W Carbonyl Complexes of Bis(2-(diphenylphosphino)ethyl)benzylamine*

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(Received July 7, 1987)

Abstract

Various Cr, Mo and W carbonyl complexes of a tridentate ligand containing N and P as donor atoms, bis(2-(diphenylphosphino)ethyl)benzylamine (DPBA), have been synthesized. Reaction of $M(CO)_6$ (M = Cr, Mo and W) with DPBA in a 1:1 mole ratio in toluene or xylene, resulted in the formation of facial and meridional complexes of the type $[M(CO)_3(DPBA)]$ (M = Cr, Mo and W). Interaction of $Cr(CO)_6$ or $Mo(CO)_6$ with DPBA and PPh_3 in toluene yielded complexes of the composition $[Cr(CO)_3(DPBA)(PPh_3)]$ and $[Mo(CO)_2(DPBA)(PPh_3)]$, respectively. However reaction of $W(CO)_6$ with DPBA and PPh_3 yielded only $[W(CO)_3(DPBA)]$. Reaction of $Cr(CO)_6$ with DPBA and 1,2-bis(diphenylphosphino)ethane-(diphos) in toluene for 24 h resulted in the formation of a mixed ligand complex, $[Cr(CO)_4(DPBA)(diphos)]$ where both the ligands coordinate to the metal atom through only one of their donor atoms. A unique binuclear complex of the composition $[Mo(CO)_2(DPBA)(diphos)]_2$ resulted, with the tridentate ligand DPBA acting as a bidentate bridging ligand, by the reaction of $Mo(CO)_6$ with DPBA and diphos in refluxing xylene for 24 h. All the complexes are characterized by elemental analysis and infrared spectra. The $^{31}P\{^1H\}$ and ^1H NMR spectral data of the complexes gave valuable information in elucidating the structures of the complexes. The ligand DPBA has found to behave in a triligate monometallic, biligate monometallic, monoligate monometallic and biligate bimetallic manner.

Introduction

During recent years transition metal complexes of polydentate ligands having hard and soft donor groups have become very important due to the easy displacement of the weak donor atom at the approach of the incoming substrate molecule, which factor has an important bearing in the field of homogeneous catalysis [1–5]. Although considerable work has been done on the platinum group metal complexes of such bi- and polydentate ligands [3–10], relatively very little has been studied on the Cr, Mo and W carbonyl complexes and more so the ^{31}P NMR studies [11], which have become an important tool in probing the stereochemical behaviour of these complexes and a lot of structural information could be deduced from the chemical shifts values (δ) and spin–spin coupling constant values.

The present paper deals with the synthesis and characterization of Cr, Mo and W metal carbonyl complexes of a tridentate ligand containing N and P as donor groups, bis(2-(diphenylphosphino)ethyl)benzylamine (DPBA). The $^{31}P\{^1H\}$ NMR along with ^1H NMR and infrared spectra of these complexes are also presented.

Experimental

The Cr, Mo and W hexacarbonyls were obtained from Fluka Chemicals. The ligands triphenylphosphine and 1,2-bis(diphenylphosphino)ethane(diphos) were obtained from Aldrich Chemical Company. The ligand bis(2-(diphenylphosphino)ethyl)benzylamine (DPBA) was synthesized as reported in our earlier publication [7]. All solvents used in this work were of reagent grade and were purified and dried before use. All the preparations were carried out under an atmosphere of dry nitrogen gas. Microanalysis (C, H, N) were done on a Perkin-Elmer CHN analyzer. Infrared spectra were carried out on a Perkin-Elmer spectrophotometer and taken in KBr pellets. Proton NMR spectra were recorded on a JEOL FX90 spectrometer in $CDCl_3$ using TMS as internal reference. The phosphorus-31 NMR spectra of the complexes were taken in $CHCl_3$ on a JEOL FX100 spectrometer operating at 40.3 MHz in the Fourier transform mode with proton noise decoupling and a deuterium lock. The samples were placed in a 10 mm tube and a

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*RRL(H) Communication No. 2068.

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0020-1693/88/$3.50

TABLE I. Analytical, Physical and Infrared Spectral Data of the Complexes

Compound[a]	Colour	Melting point[b] (°C)	Elemental analysis (%)[c]			IR (ν(CO))[d]
			C	H	N	
$[Cr(CO)_3(DPBA)]$ (1)	yellow	210	68.36 (68.15)	5.24 (5.22)	2.09 (2.02)	1905(s), 1805(m), 1790(s)
$[Mo(CO)_3(DPBA)]$ (2)	yellow	187	64.14 (63.98)	4.92 (4.90)	1.97 (1.95)	1920(s), 1805(m), 1800(s)
$[W(CO)_3(DPBA)]$ (3)	yellow	217	57.08 (57.06)	4.38 (4.34)	1.75 (1.69)	1910(s), 1810(m), 1795(s)
$[Cr(CO)_3(DPBA)(PPh_3)$ (4)	yellow	159	72.26 (71.99)	5.37 (5.34)	1.51 (1.50)	1905(s), 1805(m), 1795(s)
$[Mo(CO)_2(DPBA)(PPh_3)$ (5)	yellow	188	69.77 (69.63)	5.29 (5.21)	1.48 (1.45)	1915(s), 1815(m), 1795(s)
$[Cr(CO)_4(DPBA)(diphos)]$ (6)	yellow	132	71.36 (71.30)	5.39 (5.31)	1.28 (1.25)	2000(s), 1910(s), 1885(s), 1870(s)
$[Mo(CO)_2(DPBA)(diphos)]_2$ (7)	yellow	95	69.94 (69.90)	5.46 (5.41)	1.30 (1.27)	1915(s), 1850(s), 1790(s)

[a] DPBA = $C_6H_5CH_2N(CH_2CH_2PPh_2)_2$, diphos = $Ph_2PCH_2CH_2PPh_2$. [b] Decomposition temperatures. [c] Found values are given in parentheses. [d] s = strong, m = medium.

capillary filled with deuterium oxide was placed for the lock. 85% H_3PO_4 was used as an external standard.

Microanalytical, melting point and infrared data are presented in Table I. The ^1H and $^{31}P\{^1H\}$ NMR data are presented in Table II.

Preparation of Cr, Mo and W Complexes

Tricarbonylbis(2-(diphenylphosphino)ethyl)-benzylaminechromium(0), [Cr(CO)$_3$(DPBA)] (1); Tricarbonylbis(2-(diphenylphosphino)ethyl)-benzylaminemolybdenum(0), [Mo(CO)$_3$(DPBA)] (2); Tricarbonylbis(2-(diphenylphosphino)ethyl)-benzylaminetungsten(0), [W(CO)$_3$(DPBA)] (3)

Complexes 1 and 2 were obtained by the reaction of $Cr(CO)_6$ (0.100 g, 0.45 mmol) and $Mo(CO)_6$ (0.100 g, 0.38 mmol) with the ligand DPBA (0.242 g, 0.45 mmol and 0.202 g, 0.38 mmol) in toluene respectively. Complex 3 was obtained by the interaction of DPBA (0.151 g, 0.28 mmol) with $W(CO)_6$ (0.100 g, 0.28 mmol) in xylene. On prolonged refluxing for about 20–24 h, a yellow coloured homogeneous solution resulted which was then concentrated to a small volume. n-Hexane was added to obtain yellow precipitates in all three cases. The complexes were recrystallized from chloroform–n-hexane mixture. Yield: **1**, 0.250 g (82%); 2, 0.162 g (60%); 3, 0.125 g (55%).

Tricarbonyltriphenylphosphinebis(2-(diphenylphosphino)ethyl)benzylaminechromium(0), [Cr(CO)$_3$(DPBA)(PPh$_3$)] (4); Bicarbonyltriphenylphosphinebis(2-(diphenylphosphino)ethyl)benzylaminemolybdenum(0), [Mo(CO)$_2$(DPBA)(PPh$_3$)] (5)

Complexes 4 and 5 were obtained by refluxing the toluene solutions of $Cr(CO)_6$ (0.100 g, 0.45 mmol), DPBA (0.242 g, 0.45 mmol), PPh_3 (0.24 g, 0.91 mmol) and $Mo(CO)_6$ (0.100 g, 0.38 mmol), DPBA (0.202 g, 0.38 mmol), PPh_3 (0.200 g, 0.76 mmol), respectively for about 20 h, under dry nitrogen gas. The resultant yellow solutions were then concentrated to a small volume and by the addition of n-hexane yellow complexes were precipitated in both cases. The precipitates were filtered, washed with n-hexane and recrystallized from chloroform–n-hexane mixture. Yield: 4, 0.210 g (50%); 5, 0.170 g (48%).

Tetracarbonyl-1,2-bis(diphenylphosphino)ethane-bis(2-(diphenylphosphino)ethyl)benzylamine-chromium(0), [Cr(CO)$_4$(DPBA)(diphos)] (6)

A suspension of the complex $Cr(CO)_6$ (0.100 g, 0.45 mmol) in toluene was refluxed with DPBA (0.242 g, 0.45 mmol) and diphos (0.181 g, 0.45 mmol) for 24 h, under a nitrogen atmosphere. The solution was concentrated to a small volume and the complex precipitated with n-hexane to give a yellow precipitate, which was then filtered, washed

TABLE II. $^{31}P\{^{1}H\}$ and ^{1}H NMR Spectral Data

Compound	^{31}P NMR[a]								^{1}H NMR δ (ppm)		
	Chemical shift δ (ppm)			Coordination chemical shift Δ			J(P–P) (Hz)	J(M–P) (Hz)	–Ph	$-CH_2-$	$-CH_2CH_2-$
	DPBA	PPh_3[b]	diphos	DPBA	PPh_3	diphos					
$C_6H_5CH_2N(CH_2CH_2PPh_2)_2$	–19.3(s)								7.2(m)	3.5(s)	2.58(m), 2.10(m)
$Ph_2PCH_2CH_2PPh_2$			–12.5(s)						7.3(s)		2.1(t)
$[Cr(CO)_3(DPBA)]$ (1)	32.2(s)			51.5					7.3(m)	4.5(s)	3.3(m), 2.7(m)
	56.4(s)			75.7							
$[Mo(CO)_3(DPBA)]$ (2)	32.3(s)			51.6					7.3(m)	4.5(s)	3.2(m), 2.7(m)
	37.8(s)			57.1							
$[W(CO)_3(DPBA)]$ (3)	31.7(s)			51.0				163.5	7.3(m)	4.4(s)	3.2(m), 2.6(m)
	33.1(s)			52.4				244.2			
$[Cr(CO)_3(DPBA)(PPh_3)]$ (4)	–19.5(s)	32.2(d)		75.8	38.8		38.0		7.3(m)	4.5(s)	3.0(m), 2.6(bm), 2.5(m)
	56.5(d)										
$[Mo(CO)_2(DPBA)(PPh_3)]$ (5)	56.1(d)	37.8(t)		75.4	43.8		27.0		7.2(m)	4.5(s)	3.3(m), 2.6(m)
$[Cr(CO)_4(DPBA)(diphos)]$ (6)	–19.3(s)		–11.8(s)	53.6		46.1	30.1		7.2(m)	3.5(s)	3.0(bm), 2.5(m), 2.2(b)
	34.3(d)		33.6(d)								
$[Mo(CO)_2(DPBA)(diphos)]_2$ (7)	45.4(t)		65.7(t)	85.0		64.7	12.7		7.2(m)	3.5(s)	3.2(m), 2.2(m)

[a] Positive chemical shifts in $CHCl_3$ downfield from 85% H_3PO_4; s = singlet, d = doublet, t = triplet. [b] PPh_3 = –6.0 ppm (ref. 16). [c] Chemical shifts in $CDCl_3$ are related to internal Me_4Si; s = singlet, m = multiplet, b = broad.

repeatedly with n-hexane and recrystallized from chloroform–n-hexane mixture. Yield: 0.200 g (40%).

Bis(bicarbonyl-1,2-bis(diphenylphosphino)ethane-bis(2-(diphenylphosphino)ethyl)benzylamine-molybdenum(0)), [Mo(CO)$_2$(DPBA)(diphos)]$_2$ (7)

The reaction procedure is similar to that of **6** except that Mo(CO)$_6$ (0.100 g, 0.38 mmol), DPBA (0.202 g, 0.38 mmol) and diphos (0.151 g, 0.38 mmol) were refluxed in xylene for 24 h under nitrogen atmosphere. The resulting yellow solution was filtered, concentrated to a small volume by vacuum rotary evaporator and precipitated by the addition of n-hexane. The yellow precipitate was then filtered, washed repeatedly with n-hexane and recrystallized from chloroform–n-hexane mixture. Yield: 0.328 g (40%).

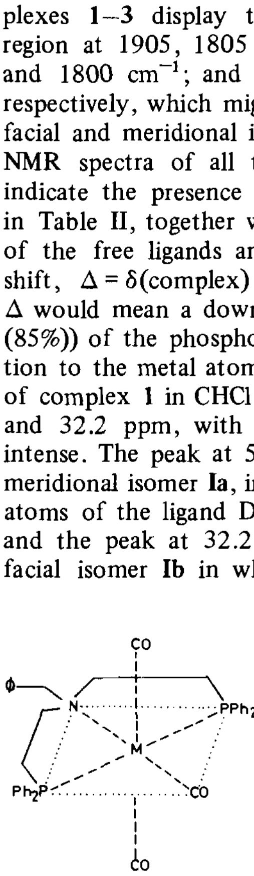
The interaction of W(CO)$_6$ with DPBA and diphos also resulted in the formation of complex **3**.

Results and Discussion

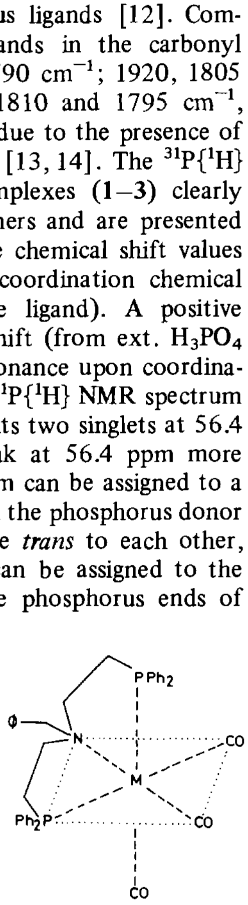
The tridentate ligands can complex with metal ions in all six possible ways: monoligate monometallic, biligate monometallic, triligate monometallic, biligate bimetallic, triligate bimetallic and triligate trimetallic [12]. In our earlier publications [7, 9] we reported that the ligand bis(2-(diphenylphosphino)-ethyl)benzylamine, (DPBA), which is potentially tridentate can act in two possible modes of coordination — triligate monometallic, and biligate monometallic. In the latter case, *i.e.* biligate monometallic, the coordination is either through nitrogen and one of the two phosphorus donor atoms [7] or through both the phosphorus atoms with the nitrogen end free [9]. It has been found, as described in this paper, that this tridentate ligand has the ability to bind the metal atom (Cr, Mo) in two more possible modes of coordination, (a) monoligate monometallic and (b) biligate bimetallic, in addition to the other two ways described earlier.

The Cr, Mo and W complexes of the ligand DPBA are synthesized as described in 'Experimental' and all the complexes (**1**–**7**) are air-stable and highly soluble in almost all organic solvents. Some of their physical characteristics, analytical and infrared spectral data are presented in Table I and ^{1}H and $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR spectral data which provides both gross and subtle structural information is presented in Table II.

Treatment of M(CO)$_6$ (M = Cr, Mo and W) with one mole equivalent of the ligand DPBA in an aromatic hydrocarbon solvent resulted in the formation of mononuclear, yellow, 1:1 complexes of the composition, [M(CO)$_3$(DPBA)] (M = Cr (**1**), Mo (**2**), W (**3**)) by the displacement of three carbonyl groups by the ligand DPBA. Vigorous reaction conditions are needed for the substitution of these carbonyl groups and a mixture of isomers (facial and meridional) are formed in all three complexes, in which DPBA acts as a tridentate ligand with all its donor atoms coordinating to the metal atom. The infrared spectra of the metal–carbonyl complexes are taken in KBr pellets and as such the carbonyl frequencies have been shifted to lower frequencies in comparison to the solution spectra of similar types of tridentate phosphorus ligands [12]. Complexes **1**–**3** display three bands in the carbonyl region at 1905, 1805 and 1790 cm^{-1}; 1920, 1805 and 1800 cm^{-1}; and 1910, 1810 and 1795 cm^{-1}, respectively, which might be due to the presence of facial and meridional isomers [13, 14]. The $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR spectra of all the complexes (**1**–**3**) clearly indicate the presence of isomers and are presented in Table II, together with the chemical shift values of the free ligands and the coordination chemical shift, $\Delta = \delta(\text{complex}) - \delta(\text{free ligand})$. A positive Δ would mean a downfield shift (from ext. H$_3$PO$_4$ (85%)) of the phosphorus resonance upon coordination to the metal atom. The $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR spectrum of complex **1** in CHCl$_3$ exhibits two singlets at 56.4 and 32.2 ppm, with the peak at 56.4 ppm more intense. The peak at 56.4 ppm can be assigned to a meridional isomer **Ia**, in which the phosphorus donor atoms of the ligand DPBA are *trans* to each other, and the peak at 32.2 ppm can be assigned to the facial isomer **Ib** in which the phosphorus ends of the ligand are *trans* to the carbonyl groups. Similarly the $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR spectrum of complex **2** also exhibits two peaks, an intense singlet at 37.8 ppm and one more singlet at 32.3 ppm, indicative of the presence of meridional and facial isomers, respectively, as shown in **Ia** and **Ib**. The $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR of complex **3** displays two singlets of equal intensities with ^{183}W satellites. The peak at 33.1 ppm with $^{1}J(\mathrm{W{-}P}) = 244.2$ Hz, is assigned to the meridional isomer **Ia**, whereas the peak at 31.7 ppm is assigned to the facial isomer **Ib** with $^{1}J(\mathrm{W{-}P}) = 164$ Hz.



Ia



Ib

M = Cr, Mo, W

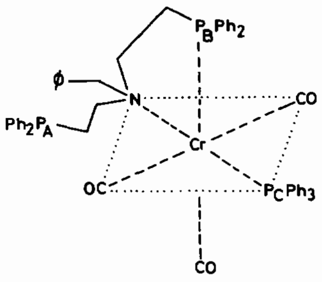
It has been observed in this work as well as in that reported earlier [15, 16] that there is a considerable downfield shift in the δ values of the phosphorus resonance upon coordination to the metal atom, due to ring contribution (ΔR). The coordination chemical shifts (Table II) of the meridional isomer of complexes **1–3** in which the phosphorus ends are *trans* to each other, are more downfield than those of facial isomers in which the P ends are *cis* to each other and *trans* to the carbonyl groups, as observed earlier [16]. The ^{31}P NMR chemical shifts (δ) of complexes **1–3** also reveal that there is a good correlation between the size of the metal atom and the chemical shifts [16]. The ^{31}P NMR chemical shifts of coordinated complexes are generally observed downfield as compared to that of the free ligand due to the strong σ-donor bond from phosphorus to metal with a small d_π–d_π back bonding. As the size of the metal increases and electronegativity decreases, the δ values are shifted less downfield due to the weak metal–phosphorus σ-bond and a strong metal to ligand d_π–d_π back bonding interaction [17]. This is also observed in the present work with δ values decreasing in the order Cr > Mo > W (Table II).

The magnitude of $^1J(M–P)$ coupling constants is generally dominated by the Fermi Contact term [18], which is directly proportional to the valence 's' orbital contribution at the respective nuclei and to direct or indirect bonding of the two nuclei. The s-character of the orbital at phosphorus used for M–P bonding is determined by the electronegativity of the groups attached to phosphorus and as well by the *trans* influence of the ligand *trans* to the phosphorus donor atom [19]. It is found that the $^1J(W–P)$ value of the meridional isomer of complex **3** is much higher (Table II) than that of the facial isomer which would mean a high *trans* influence of the ligand (CO) when *trans* to P (facial isomer) due to the formation of a strong bond between the ligand CO and the metal, which in turn would also demand more 's' and 'd' character for the bond leaving less 's' and 'd' and more 'p' character for the bond to the *trans* ligand [19].

The ^1H NMR spectra of all the complexes (**1–3**) exhibit considerable downfield resonances in comparison to those of the free ligand (Table II) [7], owing to the coordination of all the donor atoms of the terdentate ligand DPBA to the metal atom. The ^1H NMR spectra of **1–3** exhibit resonances from the phenyl protons as broad multiplets around 7.3δ and resonances from the protons of the CH_2CH_2 bridges of the ligand as broad multiplets centered at around 3.3δ and 2.7δ. The multiplet at around 2.7δ may be due to the CH_2 protons attached to amine centre, whereas the peak at 3.3δ is due to the CH_2 protons bonded to the $-PPh_2$ end. Both the resonances appear as complex asymmetric multiplets possibly due to the interaction of neighbouring methylene protons followed by the coupling of ^{31}P nuclear spin. There is also a singlet at 4.5δ which is assigned to the methylene protons of the benzyl group of the ligand DPBA with a downfield shift of about 1 ppm, due to the coordination of the nitrogen donor atom.

Interaction of $M(CO)_6$ (M = Cr, Mo) with ligands DPBA and PPh_3 in 1:1:2 ratio in toluene resulted in the formation of octahedral complexes of the composition $[Cr(CO)_3(DPBA)(PPh_3)]$ (**4**) and $[Mo(CO)_2(DPBA)(PPh_3)]$ (**5**), by displacing three and four carbonyl groups, respectively. These reactions also yielded both the *mer*- and *fac*-isomers of complex **1** in the case of Cr and only the *mer*-isomer of complex **2** in the case of Mo. The presence of these products have been confirmed by ^{31}P NMR spectra. The infrared spectra in the carbonyl region display absorption frequencies at 1905, 1805 and 1795 cm^{-1} in the case of complex **4** and at 1915, 1815 and 1795 cm^{-1} in the case of **5**.

The $^{31}P\{^1H\}$ NMR spectra clearly elucidate the structure of complexes **4** and **5**. The spectrum of **4** confirms the structure as shown in **II**. The spectrum displays a high downfield doublet at 56.9 and 56.0 ppm, assigned to the coordinated P_B donor atom of the ligand DPBA, with $^2J(P_B–P_C) = 38$ Hz. There is also a doublet at 32.7 and 31.8 ppm, which is assigned to the phosphorus atom (P_C) of the monodentate triphenylphosphine. The ^{31}P NMR spectrum also suggests that the ligand DPBA which is potentially tridentate is coordinated to the metal atom through nitrogen and only one of its two phosphorus atoms, thus acting as a bidentate ligand. The spectrum shows a high field phosphorus resonance having a chemical shift of −19.4 ppm, very similar to that of the phosphorus atom of the free ligand DPBA, and the signal can therefore be assigned [16, 20, 21] to the uncoordinated phosphorus atom P_A (structure **II**) of the complex. $^2J(P–P)$ coupling values provide useful information for structural elucidation. The *cis* coupling values are usually small (20–50 Hz) whereas the values for the *trans* analogues fall in the range 50–200 Hz [19]. The $^2J(P_B–P_C)$ value of 38 Hz clearly indicates the *cis* coordinating nature of the unequivalent phosphorus atoms as shown in **II**. The presence of peaks at 56.5

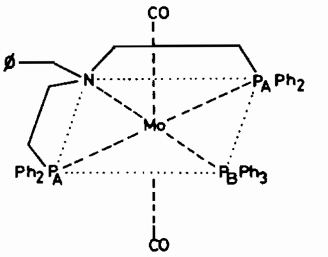


II

and 32.2 ppm indicates the presence of *mer-* and *fac*-isomers of complex **1**.

The ^{1}H NMR spectrum also confirms the bidentate nature of the ligand DPBA. The spectrum displays a well resolved multiplet at 7.3δ, owing to the presence of a large number of magnetically nonequivalent phenyl protons. The methylene protons attached to the nitrogen centre from the CH_2CH_2 bridge exhibit resonance at 2.6δ and those attached to coordinated phosphorus end at 3.0δ as multiplets. There is also a multiplet overlapping with the resonance of CH_2 attached to amine at 2.5δ, presumably due to the resonance of the CH_2 group attached to the free phosphorus end (P_A) of the ligand DPBA, and which is almost similar to that of the CH_2 resonance of the free ligand (Table II). Besides these peaks there is also a singlet at 4.4δ corresponding to the protons of the CH_2 of the benzyl group.

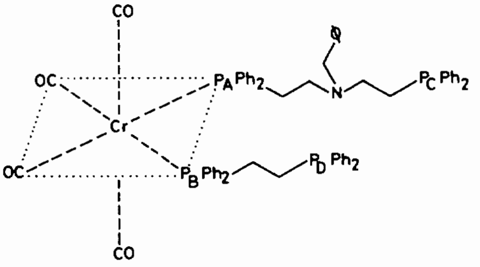
However the interaction of $Mo(CO)_6$ with DPBA and PPh_3 resulted in a complex where all the donor atoms of the ligand DPBA are coordinated to the metal atom (structure **III**). The $^{31}P\{^1H\}$ NMR spectrum of **5** displays, as envisaged, a triplet and a doublet due to the presence of unequivalent phosphorus atoms, thus confirming the assigned structure **III**. The resonance centred at 56.1 ppm is due to the *trans* disposed phosphorus atoms, P_A, of the ligand DPBA which is split into a doublet by the interaction of P_A with P_B of the PPh_3 group, with $^2J(P_A-P_B) = 27$ Hz, where as the resonance centred at 37.8 ppm which is split into a triplet due to the interaction of P_B with two equivalent *trans* disposed P_A of DPBA, can be assigned to P_B of the monodentate PPh_3 group and the $^2J(P-P)$ value also indicates the presence of P_A and P_B in the *cis* position. The decrease in intensity of the peak at 37.8 ppm on purification of the complex on a column confirms the presence of *mer*-$[Mo(CO)_3(DPBA)]$ (**2**). The ^{1}H NMR spectrum (Table II) displays downfield resonances corresponding to Ph, CH_2CH_2 and CH_2 protons.



III

The interaction of $W(CO)_6$ with PPh_3 and DPBA only yielded complex **3**, $[W(CO)_3(DPBA)]$, even after refluxing the reaction contents for 24 h in toluene. The reaction of $M(CO)_6$ (M = Cr, Mo and W) with DPBA and $P(OC_2H_5)$ or $P(OPh)_3$ also yielded complexes of the type $[M(CO)_3(DPBA)]$ (M = Cr, Mo and W).

Reaction of $Cr(CO)_6$ with DPBA and diphos in toluene for 24 h resulted in the formation of an interesting complex $[Cr(CO)_4(DPBA)(diphos)]$ (**6**), with both the ligands acting in a monodentate fashion (structure **IV**). Complexes of the type $[Cr(CO)_4(diphos)]$ and *fac*-$[Cr(CO)_3(diphos)]$ are also formed.



IV

The infrared spectrum of complex **6** displays carbonyl stretching bands at 2000, 1910, 1885 and 1870 cm^{-1}. The $^{31}P\{^1H\}$ and ^{1}H NMR spectra give valuable information for deriving the structure. The $^{31}P\{^1H\}$ NMR spectrum of **6** (Fig. 1) exhibits high field resonances at −11.8 and −19.3 ppm corresponding to the uncoordinated free phosphorus ends of the ligands diphos and DPBA, respectively, (**IV**), as these resonances are quite similar to phosphorus resonances of free ligands (Table II) [16, 7]. Based on the structure **IV** one would expect in the ^{31}P NMR spectrum two doublets for the two unequivalent phosphorus atoms P_A and P_B. If the ligand DPBA acts as a bidentate ligand by coordination of N and one of the two P ends, there should be a large chemical shift difference between P_A and P_B due to the fact that the

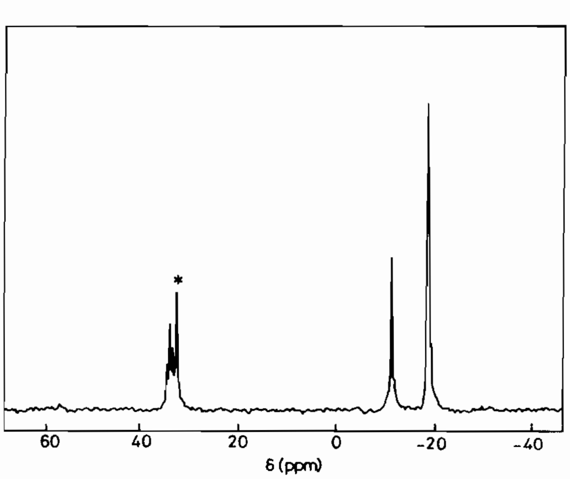
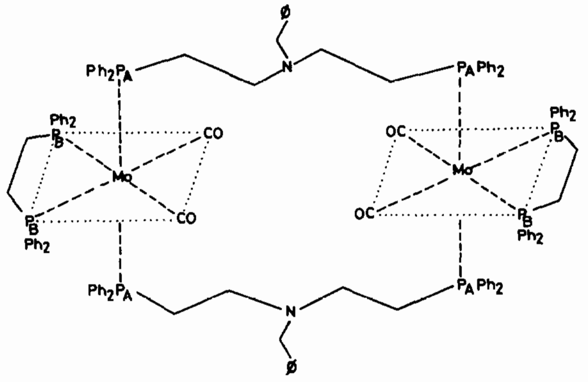


Fig. 1. $^{31}P\{^1H\}$ NMR spectrum of $[Cr(CO)_4(DPBA)(diphos)]$. The asterisk indicates the presence of $[Cr(CO)_3(DPBA)]$.

ligand DPBA on coordination would form a five-membered chelate ring and in turn would shift the ^{31}P resonance to a more downfield value than to that of a monodentate ligand. However, unusually the spectrum exhibits a triplet centred at 33.9 ppm with the center peak having higher intensity than the other two peaks. The higher intensity of the middle peak is probably due to the very close chemical shift (δ) values thus merging the inner two peaks of the two doublets which are expected for the complex **6**. These unusual close chemical shift values resulting in a triplet instead of two doublets can possibly be due to the fact that both the potential tridentate and bidentate ligands (DPBA and diphos) coordinate to the metal atom through only one of its donor atoms in a monodentate manner with the other donor ends free, and both the coordinated groups are also *trans* disposed to the carbonyl groups, thus making both the phosphorus atoms (P_A and P_B) of the two different ligands almost magnetically equivalent. The $^2J(P_A-P_B)$ value of 30.1 Hz also indicates the *cis* coordination of P_A and P_B confirming the assigned structure **IV**. The ^{31}P NMR spectrum also exhibits peaks at 80.3 and 32.5 ppm indicating the formation of $[Cr(CO)_4(diphos)]$ [16] and *fac*-$[Cr(CO)_3(DPBA)]$, respectively. The ^1H NMR spectrum also indicates the monodentate coordination of both the ligands DPBA and diphos. The spectrum displays a singlet at 3.5δ due to CH_2 protons of the benzyl group of the ligand DPBA, which is similar to the value of CH_2 resonance of the free DPBA. If the N donor atom coordinates to the metal atom there would be an almost 1 ppm downfield shift of the resonance as evidenced earlier. The methylene protons of the CH_2CH_2 bridge of the free end of the ligand also exhibit resonances close to that of the free ligand (Table II). However, the methylene protons of the CH_2CH_2 bridge attached to the coordinated P end are displayed at 3.0δ as a broad multiplet and the multiplet of the CH_2 group attached to the N end might have been merged with the other CH_2 resonances. The ^1H NMR spectrum also exhibits a broad resonance at 2.2δ corresponding to the methylene protons of the CH_2 attached to the free P end of the diphos. Apart from these resonances the spectrum also displays peaks due to the phenyl protons (Table II). The above NMR data clearly support the assigned structure **IV** to complex **6**, where the ligand DPBA acts in a monoligate monometallic manner.

A unique binuclear complex $[Mo(CO)_2(DPBA)(diphos)]_2$ (**7**), resulted on interaction of $Mo(CO)_6$, DPBA and diphos in refluxing xylene for 24 h, with the ligand DPBA acting as a bidentate bridging ligand between the two mononuclear moieties. The reaction also resulted in the formation of *fac*-$[Mo(CO)_3(DPBA)]$. The infrared spectrum displays carbonyl stretching modes at 1915, 1850 and 1780 cm^{-1}. The $^{31}P\{^1H\}$ and ^1H NMR spectra give valuable information in deriving the structure of complex **7** as shown in structure **V**. The $^{31}P\{^1H\}$ NMR spectrum of **7** displays two triplets centred at 65.7 and 45.4 ppm. One would expect a similar type of spectrum for a mononuclear complex of the type $[Mo(CO)(DPBA)(diphos)]$ where all the donor atoms of both the ligands coordinate to the metal atom by displacing five carbonyl groups but this structure can be excluded on the fact that the phosphine ligands would at the most displace not more than four carbonyl groups [11]. A complex of the type $[Mo(CO)_2(DPBA)(diphos)]$ where the diphos acts as a bidentate ligand and DPBA also acts as a bidentate ligand with both the phosphorus ends coordinating with the nitrogen end free, thus forming a 8-membered chelate ring, can also be excluded based on the chemical shift values as large chelate rings would shift the values to less downfield when compared to a 5-membered chelate ring [16]. Thus the resonance signal at 65.7 ppm can be assigned to the phosphorus atoms (P_B) of the diphos (structure **V**) which is split into a triplet by equivalent phosphorus atoms (P_A) of the ligand DPBA, and the triplet at 45.4 ppm is assigned to P_A of DPBA. The more downfield resonance of P_B might be due to the formation of a 5-membered chelate ring on coordination. The $^2J(P_A-P_B)$ value of 12.7 Hz also indicates the *cis* coordination of P_A and P_B.



V

The ^1H NMR spectrum of **7** also clearly corroborates the above assigned structure. The spectrum displays a singlet at 3.5δ due to the CH_2 protons of the benzyl group of DPBA confirming the free N donor atom. Apart from this resonance the spectrum also displays broadened signals due to the methylene protons of both the ligands and phenyl protons (Table II). Based on the NMR spectral data a binuclear complex with two DPBA ligands acting as a bridge with the two P ends coordinating to two different Mo atoms and the amine being free in a biligate bimetallic manner can be proposed as shown in **V**.

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