

PREPARATION AND PROPERTIES OF GROUP VI METAL CARBONYLS CONTAINING THE LIGAND BIS(DI-*o*-TOLYL)PHOSPHINOMETHANE. CRYSTAL AND MOLECULAR STRUCTURE OF DICARBONYLBIS(DI-*o*-TOLYL)PHOSPHINOMETHANECHROMIUM

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Summary

Complexes of Group VI metal carbonyls with the ligand bis(di-*o*-tolyl)phosphinomethane have been prepared and characterised by NMR spectroscopy. The crystal structure of $\text{Cr}(\text{CO})_2(\text{BDT}_o\text{M})$ has been determined by conventional X-ray diffraction techniques. The orange tabular crystals are monoclinic, space group *Cc*, *a* 24.197(1), *b* 8.162(1), *c* 16.736(1) Å, β 124.14(1)°, *V* 2735.8 Å³, *Z* = 4. Refinement by full-matrix least-squares methods employed anisotropic thermal parameters for the heavier atoms and the coordinated *o*-tolyl group. One carbonyl ligand was positioned from a 'difference' map. The final residual, *R*, is 0.078 for 1673 observed reflections.

The complex is monomeric. The BDT_oM ligand coordinates to chromium through one phenyl ring (three sites) and one phosphorus atom, with two carbonyl groups completing an octahedral 'piano stool'-like arrangement. The coordinated arene ring is planar and is in a staggered arrangement relative to the other donors. The Cr–C(arene) bonds range from 2.166(10) to 2.260(9) Å (average 2.210 Å); the distance of Cr from the plane of the ring is 1.698 Å. The *o*-methyl carbon and the non-coordinated phosphorus atom are significantly displaced from the ring plane.

Introduction

In recent years there have been studies of the reactions of sterically hindered ligand systems. The reactions have been of much interest as they quite often result in the formation of unusual and "unexpected" products, and in many cases uncommon stereochemistries and exciting bonding modes have been observed.

Probably the best example, which embraces many of the above concepts, is the reaction of tri(*o*-tolyl)phosphine with rhodium trichloride. Bennett and Longstaff

were attempting to form " $\text{RhCl}[\text{P}(o\text{-tolyl})_3]_3$ ", but one of the products obtained, $\text{RhCl}[(o\text{-tolyl})_2\text{PC}_6\text{H}_4 \cdot \text{CH}=\text{CH} \cdot \text{C}_6\text{H}_4\text{P}(o\text{-tolyl})_2]$, is formed by a coupling-dehydrogenation reaction [1]. Many diphosphines also undergo interesting reactions. For example, the long chain α,ω -diphosphines $\text{Bu}^t_2\text{P}(\text{CH}_2)_n\text{PBu}^t_2$, $n = 9, 10$ or 12 , form macrocyclic complexes with platinum metals in which the phosphorus atoms are *trans* chelated [2,3]. However, with shorter chain diphosphines mono and di proton abstraction reactions occur. In the reactions of $\text{Bu}^t_2\text{P}(\text{CH}_2)_6\text{PBu}^t_2$ with rhodium trichloride [4] and $\text{Ph}_2\text{P}(\text{CH}_2)_6\text{PPh}_2$ with bis(cycloocta-1,5-diene)- $\mu\mu'$ -dichlorodiridium(I) and bis(cycloocta-1,5-diene)- $\mu\mu'$ -dichlorodiridium(I) [5,6] the metal(I)-olefin complexes $\text{MCl}(\text{R}_2\text{PCH}_2\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}_2\text{PR}_2)$, $\text{M} = \text{Rh}$ or Ir , are formed respectively.

Up to now investigations into the reactions of tertiary phosphines containing the *o*-tolyl group have been limited to the monodentate series $\text{P}(o\text{-tolyl})_3$, $\text{P}(o\text{-tolyl})_2\text{R}$ and $\text{P}(o\text{-tolyl})\text{R}_2$. Metallation reactions occur between this series and with rhodium and platinum complexes [1,7]. During the late 1960's and early 1970's, Colton and coworkers published a series of papers which discussed the reactions of some sterically hindered ligands with the Group VI metal carbonyls. With the Group VI metal carbonyls, $\text{P}(o\text{-tolyl})_3$ forms the complexes $\text{M}(\text{CO})_3[\text{P}(o\text{-tolyl})_3]$, $\text{M} = \text{Cr}$ or Mo , in high boiling solvents. One of the *o*-tolyl groups is π -bonded while the P is uncoordinated [8]. They also discovered that bis(diphenyl)arsinomethane, $\text{Ph}_2\text{AsCH}_2\text{AsPh}_2$, formed the π -arene complexes $\text{M}(\text{CO})_2[\text{Ph}_2\text{AsCH}_2\text{AsPh}_2]$, $\text{M} = \text{Cr}$ or Mo , in which only one arsenic atom is coordinated [9].

Recently we prepared the new diphosphine ligands $(o\text{-tolyl})_2\text{P}(\text{CH}_2)_n\text{P}(o\text{-tolyl})_2$, $n = 1-4, 6$ or 8 [10] and now wish to present the results of our investigation into the reactions of one of these ligands ($n = 1$), bis(di-*o*-tolyl)phosphinomethane (BDT_0M), with the Group VI metal carbonyls. We also describe the crystal structure of $\text{Cr}(\text{CO})_2(\text{BDT}_0\text{M})$. The BDT_0M ligand is depicted in Fig. 1.

Experimental

The ^{13}C and ^{31}P NMR spectra were recorded on a JEOL FX-100 spectrometer. The ^{13}C NMR spectra were recorded using the internal lock and referenced to

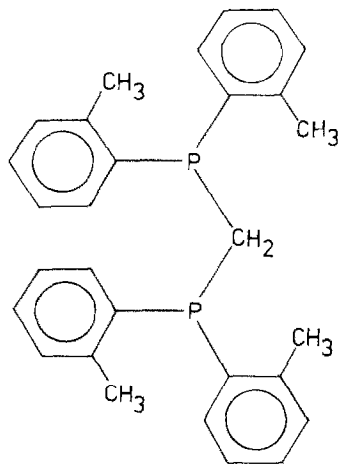


Fig. 1. The bis(di-*o*-tolyl)phosphinomethane ligand (BDT_0M).

internal TMS, while the ^{31}P spectra were recorded using the external lock and referenced to 85% H_3PO_4 . The ^1H NMR spectra were obtained on a JEOL JNM PS-100 spectrometer referenced to internal TMS. All NMR spectra were recorded on samples dissolved in CDCl_3 except for the ^{13}C NMR spectrum of $\text{Cr}(\text{CO})_2(\text{BDT}_o\text{M})$ which was recorded on a sample dissolved in C_6D_6 . The mass spectra were recorded on an AEI MS 902S instrument and the analyses were obtained from the University of Queensland Microanalytical Service and the Australian Microanalytical Service, Melbourne. The infrared spectra were recorded on Nujol mulls of the samples using a JASCO IRA-2 instrument. The ligand bis(di-*o*-tolyl)phosphinomethane was prepared as described previously [10]. Chromium, molybdenum and tungsten hexacarbonyls were purchased from Pressure Chemicals, and tetracarbonylnorbornadienechromium(0) and tetracarbonylnorbornadienemolybdenum(0) were prepared by the method outlined by Bennett, Pratt and Wilkinson [11].

Preparation of $\text{Cr}(\text{CO})_2[\eta_6-(o\text{-CH}_3\text{C}_6\text{H}_4)(o\text{-CH}_3\text{C}_6\text{H}_4)\text{PCH}_2\text{P}(o\text{-CH}_3\text{C}_6\text{H}_4)_2]$

Bis(di-*o*-tolyl)phosphinomethane (0.44 g, 1.0 mmol) and chromium hexacarbonyl (0.22 g, 1.0 mmol) were refluxed in 80 ml decalin for 2 d. The solvent was then removed under reduced pressure. Approximately 50 ml of dried benzene and some decolorising charcoal were added and the solution stirred. It was then filtered, heated and isooctane added dropwise until crystallization started. The solution was cooled (-20°C), filtered and the orange crystals washed with isooctane, and dried in vacuo. The yield of $\text{Cr}(\text{CO})_2(\text{BDT}_o\text{M})$ was 0.27 g, 49%. Anal. Found: Mol.wt., 548 (M^+); C, 68.08; H, 5.59. $\text{C}_{31}\text{H}_{30}\text{CrO}_2\text{P}_2$ Calcd. mol.wt., 548; C, 67.88; H, 5.51%.

Preparation of $\text{Mo}(\text{CO})_2[\eta_6-(o\text{-CH}_3\text{C}_6\text{H}_4)(o\text{-CH}_3\text{C}_6\text{H}_4)\text{PCH}_2\text{P}(o\text{-CH}_3\text{C}_6\text{H}_4)_2]$

Bis(di-*o*-tolyl)phosphinomethane (0.44 g, 1.0 mmol) and molybdenum hexacarbonyl (0.26 g, 1.0 mmol) were refluxed in mesitylene for 2.5 d. The solution was cooled and the mesitylene removed under reduced pressure. About 40 ml of dried benzene and a small quantity of decolorising charcoal were added and the solution filtered. The complex was crystallized by heating the benzene solution and adding isooctane. The yield of the orange complex was 0.30 g (51%). Anal. Found: Mol.wt., 592 (M^+); C, 60.65; H, 4.75. $\text{C}_{31}\text{H}_{30}\text{MoO}_2\text{P}_2$ calcd. mol.wt., 592; C, 62.84; H, 5.10%.

Preparation of $\text{Cr}(\text{CO})_4[(o\text{-CH}_3\text{C}_6\text{H}_4)_2\text{PCH}_2\text{P}(o\text{-CH}_3\text{C}_6\text{H}_4)_2]$

Bis(di-*o*-tolyl)phosphinomethane (0.69 g, 1.6 mmol) and tetracarbonylnorbornadienechromium(0) (0.40 g, 1.6 mmol) were refluxed in 80 ml of isooctane for 24 h. A yellow crystalline product precipitated from solution. The solution was allowed to cool to room temperature, then filtered and the product washed with isooctane and dried in vacuo. The yield was 0.94 g (92.6%). Anal. Found: Mol.wt., 604 (M^+); C, 67.63; H, 5.85. $\text{C}_{33}\text{H}_{30}\text{CrO}_4\text{P}_2$ calcd. mol.wt., 604; C, 65.56; H, 5.00%.

Preparation of $\text{Mo}(\text{CO})_4[(o\text{-CH}_3\text{C}_6\text{H}_4)_2\text{PCH}_2\text{P}(o\text{-CH}_3\text{C}_6\text{H}_4)_2]$

Bis(di-*o*-tolyl)phosphinomethane (0.44 g, 1.0 mmol) and tetracarbonylnorbornadienemolybdenum(0) (0.30 g, 1.0 mmol) were refluxed in 40 ml of isooctane for 2 h. The product crystallized from the hot solution. The solution was then cooled, filtered and the product washed with isooctane to yield 0.53 g (81.5%). Anal. Found: mol.wt., 648 (M^+); C, 61.46; H, 4.84. $\text{C}_{33}\text{H}_{30}\text{P}_2\text{O}_4\text{Mo}$ calcd. mol.wt., 648; C, 61.12; H, 4.66%.

Preparation of $W(CO)_4 [(o-CH_3C_6H_4)_2PCH_2P(o-CH_3C_6H_4)_2]$

Bis(di-*o*-tolyl)phosphinomethane (0.44 g, 1.0 mmol) and tungsten hexacarbonyl (0.35 g, 1.0 mmol) were refluxed in 25 ml of mesitylene for 36 h resulting in a pale yellow solution plus some black precipitate. After the mesitylene was removed at reduced pressure, the compound was dissolved in chloroform and some decolorising charcoal added. The solution was filtered and the complex crystallized out with added hexane to yield 0.50 g (67.6%) of yellow crystals. Anal. Found: Mol.wt., 736 (M^+): C, 52.83; H, 4.18. $C_{33}H_{30}P_2O_4W$ calcd. mol.wt., 736; C, 53.82; H, 4.11.

X-ray experimental: $Cr(CO)_2(BDT_0M)$

Preliminary X-ray photographs of the orange crystals showed monoclinic diffraction symmetry, with systematically absent reflections ($h k l$, $h + k = 2n + 1$; $h 0 l$, $l = 2n + 1$) corresponding to space groups Cc or $C2/c$.

Subsequent structure determination and refinement has shown the correct space group to be Cc (No.9). The crystals are tabular on (1 0 0) and somewhat elongated along the b axial direction. The crystal selected for data collection was a fragment (0.30 × 0.30 × 0.14 mm) cleaved from a larger crystal. Unit cell dimensions were derived from a least-squares fit to the setting angles of twenty-five reflections on a Nonius CAD-4 diffractometer.

Crystal data. $C_{31}H_{30}CrO_2P_2$, $M = 548.53$, Monoclinic, a 24.197(1), b 8.162(1), c 16.736(1) Å, β 124.14(1)°, V 2735.8 Å³, $Z = 4$, $d_m = 1.27$ (by flotation in aqueous KI), $d_c = 1.33$, Cu- K_α radiation of λ 1.5418 Å, Ni filter, μ (Cu- K_α) 48.97 cm⁻¹.

Intensity data were collected using a variable width, variable speed $2\theta/\omega$ scan [12]. There were no non-statistical variations in the intensities of three standard reflections monitored throughout the data collection, and no reflection was sufficiently intense to warrant insertion of an attenuator into the X-ray beam. The data were corrected for Lorentz, polarization, and absorption effects, the range of transmission coefficients being approximately 0.30 to 0.53 [13]. After averaging equivalent measurements the data set consisted of 1673 unique observed reflections for which $I > 3\sigma(I)$ [14].

Structure determination and refinement

The structure was solved by locating the Cr and two P atoms from a Patterson function ($R = 0.29$) and the remaining non-hydrogen atoms from subsequent 'difference' electron density maps. The origin was fixed by setting the x and z coordinates of Cr at 0.0. Refinement of atomic parameters was by full-matrix least-squares minimising the function $\sum w(|F_o| - |F_c|)^2$, where $w = 4|F_o|^2/\sigma^2(F_o^2)$. During the course of the refinement one of the carbonyl groups adopted a somewhat unrealistic geometry, with a short Cr-C(1) bond (1.755 Å) and a long C(1)-O(1) bond (1.257 Å). This carbonyl group was aligned almost exactly along the b axis, with its centre of mass close to one quarter of the axial repeat distance above the chromium atom. It was considered likely that least-squares refinement of this CO group could be being adversely affected by its position relative to the Cr atom, and hence these two atoms were relocated from a 'difference' map (which gave a chemically satisfactory geometry). No attempt was made to refine them further since the precise location of the carbonyl groups was not the prime reason for undertaking the structure elucidation. Of the remaining atoms, the chromium and phosphorus atoms, the unaffected CO, and the seven carbon atoms of the coordinated *o*-tolyl

group were assigned anisotropic thermal parameters. The final residuals were $R = 0.078$ and $R_w (= \{\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2\}^{1/2}) = 0.102$.

Final atomic positions are listed in Table 1. Bond lengths, bond angles, and planes of best fit are given in Table 2, 3 and 4 respectively. The molecular geometry and atomic numbering are shown in Fig. 2. A list of thermal parameters, and tables of observed and calculated structure amplitudes are available on request from the authors (G.R.C.).

Description of the structure of Cr(CO)₂(BDT_oM)

The complex is monomeric, with an overall geometry as depicted in Fig. 2. The coordination about chromium is best described as being octahedral, with the BDT_oM moiety acting as a tetradentate ligand (the π -bound arene occupying three

(Continued on p. 212)

TABLE 1
ATOMIC POSITIONS FOR Cr(CO)₂(BDT_oM)

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Cr	0.0000	0.0871(2)	0.0000
P(1)	-0.0504(1)	-0.0370(4)	0.1485(2)
P(2)	0.0777(1)	0.0439(3)	0.1682(2)
O(1)	0.0078	0.4434	0.0273
O(2)	0.1012(4)	0.148(2)	-0.0426(6)
C(1)	0.0000	0.305	0.0137
C(2)	0.0627(6)	0.124(2)	-0.0255(8)
C(3)	-0.0703(5)	-0.035(2)	0.0254(7)
C(4)	-0.0406(5)	-0.160(2)	-0.0000(8)
C(5)	-0.0413(6)	-0.149(2)	-0.0845(7)
C(6)	-0.0710(6)	-0.014(2)	-0.1439(8)
C(7)	-0.1029(7)	0.107(2)	-0.1222(10)
C(8)	-0.1024(6)	0.099(2)	-0.0365(10)
C(9)	-0.1394(7)	0.229(2)	-0.0204(12)
C(10)	-0.0899(5)	-0.232(2)	0.1535(8)
C(11)	-0.0549(7)	-0.372(2)	0.1915(10)
C(12)	-0.0798(8)	-0.510(3)	0.2068(12)
C(13)	-0.1487(8)	-0.494(3)	0.1795(12)
C(14)	-0.1828(7)	-0.366(2)	0.1422(11)
C(15)	-0.1550(6)	-0.224(2)	0.1278(9)
C(16)	-0.1961(9)	-0.072(2)	0.0865(13)
C(17)	0.0387(5)	-0.094(1)	0.2123(7)
C(18)	0.1030(6)	0.228(2)	0.2463(8)
C(19)	0.0774(7)	0.249(2)	0.3026(9)
C(20)	0.0917(8)	0.401(2)	0.3576(11)
C(21)	0.1348(7)	0.510(2)	0.3562(11)
C(22)	0.1604(6)	0.482(2)	0.3021(10)
C(23)	0.1464(5)	0.344(2)	0.2483(8)
C(24)	0.1784(6)	0.319(2)	0.1952(9)
C(25)	0.1555(5)	-0.068(2)	0.2138(8)
C(26)	0.1567(7)	-0.153(2)	0.1401(10)
C(27)	0.2159(8)	-0.237(2)	0.1673(12)
C(28)	0.2637(8)	-0.241(3)	0.2524(13)
C(29)	0.2658(8)	-0.170(2)	0.3293(11)
C(30)	0.2108(6)	-0.078(2)	0.3104(9)
C(31)	0.2113(8)	-0.013(3)	0.3932(12)

TABLE 2
BOND LENGTHS (Å) FOR Cr(CO)₂(BDT₀M)

Cr-P(2)	2.376(2)	C(8)-C(9)	1.511(14)
Cr-C(1)	1.791	C(10)-C(11)	1.354(13)
Cr-C(2)	1.818(10)	C(10)-C(15)	1.382(12)
Cr-C(3)	2.208(8)	C(11)-C(12)	1.367(16)
Cr-C(4)	2.245(8)	C(12)-C(13)	1.466(17)
Cr-C(5)	2.260(9)	C(13)-C(14)	1.261(16)
Cr-C(6)	2.187(10)	C(14)-C(15)	1.421(14)
Cr-C(7)	2.166(10)	C(15)-C(16)	1.495(15)
Cr-C(8)	2.196(10)	C(18)-C(19)	1.397(13)
P(1)-C(3)	1.834(8)	C(18)-C(23)	1.402(12)
P(1)-C(10)	1.881(8)	C(19)-C(20)	1.468(14)
P(1)-C(17)	1.849(8)	C(20)-C(21)	1.378(16)
P(2)-C(17)	1.870(8)	C(21)-C(22)	1.374(15)
P(2)-C(18)	1.855(9)	C(22)-C(23)	1.360(14)
P(2)-C(25)	1.830(9)	C(23)-C(24)	1.484(13)
O(1)-C(1)	1.149	C(25)-C(26)	1.427(13)
O(2)-C(2)	1.134(11)	C(25)-C(30)	1.409(13)
C(3)-C(4)	1.443(12)	C(26)-C(27)	1.412(16)
C(3)-C(8)	1.402(13)	C(27)-C(28)	1.233(19)
C(4)-C(5)	1.408(11)	C(28)-C(29)	1.386(18)
C(5)-C(6)	1.383(15)	C(29)-C(30)	1.401(16)
C(6)-C(7)	1.422(18)	C(30)-C(31)	1.476(16)
C(7)-C(8)	1.430(16)		

TABLE 3
BOND ANGLES (degrees) FOR Cr(CO)₂(BDT₀M)

P(2)-Cr-C(1)	93.0	C(11)-C(12)-C(13)	114.3(12)
P(2)-Cr-C(2)	95.3(3)	C(12)-C(13)-C(14)	122.9(13)
C(1)-Cr-C(2)	85.6	C(13)-C(14)-C(15)	121.2(11)
C(3)-P(1)-C(10)	103.8(4)	C(10)-C(15)-C(14)	118.5(8)
C(3)-P(1)-C(17)	97.9(3)	C(10)-C(15)-C(16)	121.7(9)
C(10)-P(1)-C(17)	102.5(4)	C(14)-C(15)-C(16)	119.8(9)
Cr-P(2)-C(17)	108.5(3)	P(1)-C(17)-P(2)	107.6(4)
Cr-P(2)-C(18)	116.3(3)	P(2)-C(18)-C(19)	118.6(7)
Cr-P(2)-C(25)	120.9(3)	P(2)-C(18)-C(23)	120.6(7)
C(17)-P(2)-C(18)	104.5(4)	C(19)-C(18)-C(23)	120.8(9)
C(17)-P(2)-C(25)	99.4(4)	C(18)-C(19)-C(20)	119.2(9)
C(18)-P(2)-C(25)	104.9(4)	C(19)-C(20)-C(21)	116.7(10)
Cr-C(1)-O(1)	172.1	C(20)-C(21)-C(22)	121.8(11)
Cr-C(2)-O(2)	179.2(10)	C(21)-C(22)-C(23)	122.7(10)
P(1)-C(3)-C(4)	117.7(6)	C(18)-C(23)-C(22)	118.6(8)
P(1)-C(3)-C(8)	121.6(7)	C(18)-C(23)-C(24)	121.9(8)
C(4)-C(3)-C(8)	119.7(8)	C(22)-C(23)-C(24)	119.5(9)
C(3)-C(4)-C(5)	121.3(8)	P(2)-C(25)-C(26)	113.4(7)
C(4)-C(5)-C(6)	119.0(9)	P(2)-C(25)-C(30)	126.7(7)
C(5)-C(6)-C(7)	120.5(9)	C(26)-C(25)-C(30)	119.9(9)
C(6)-C(7)-C(8)	121.5(9)	C(25)-C(26)-C(27)	117.7(10)
C(3)-C(8)-C(7)	118.0(9)	C(26)-C(27)-C(28)	120.6(13)
C(3)-C(8)-C(9)	123.8(10)	C(27)-C(28)-C(29)	125.6(14)
C(7)-C(8)-C(9)	118.2(10)	C(28)-C(29)-C(30)	118.7(13)
P(1)-C(10)-C(11)	122.5(7)	C(25)-C(30)-C(29)	117.2(10)
P(1)-C(10)-C(15)	118.0(7)	C(25)-C(30)-C(31)	124.1(10)
C(11)-C(10)-C(15)	119.1(9)	C(29)-C(30)-C(31)	118.3(10)
C(10)-C(11)-C(12)	124.1(11)		

TABLE 4
LEAST-SQUARES PLANES FOR $\text{Cr}(\text{CO})_2(\text{BDT}_0\text{M})$

The equations of the planes are of the form $AX + BY + CZ - D = 0$, where X , Y , and Z are orthogonalized axes					
Plane No.	A	B	C	D	ψ^2
1	-0.6998	-0.5049	-0.5053	1.339	4
2	0.2282	-0.3281	-0.9167	-2.150	1
3	-0.4230	0.4579	-0.7819	-1.911	7
4	0.5476	0.8256	-0.1357	0.085	4

Plane No.	Atoms in plane		Other atoms			
1	C(3)	-0.015	C(4)	0.009	Cr	-1.698
	C(5)	0.008	C(6)	-0.019	C(9)	0.086
	C(7)	0.013	C(8)	0.004	P(1)	-0.397
2	C(10)	-0.004	C(11)	0.001	P(1)	-0.232
	C(12)	0.006	C(13)	-0.012	C(16)	-0.023
	C(14)	0.010	C(15)	-0.002		
3	C(18)	0.020	C(19)	-0.026	P(2)	0.126
	C(20)	0.019	C(21)	-0.006	C(24)	-0.063
	C(22)	-0.002	C(23)	-0.005		
4	C(25)	0.015	C(26)	-0.020	P(2)	0.060
	C(27)	0.006	C(28)	0.015	C(31)	-0.133
	C(29)	-0.020	C(30)	0.005		

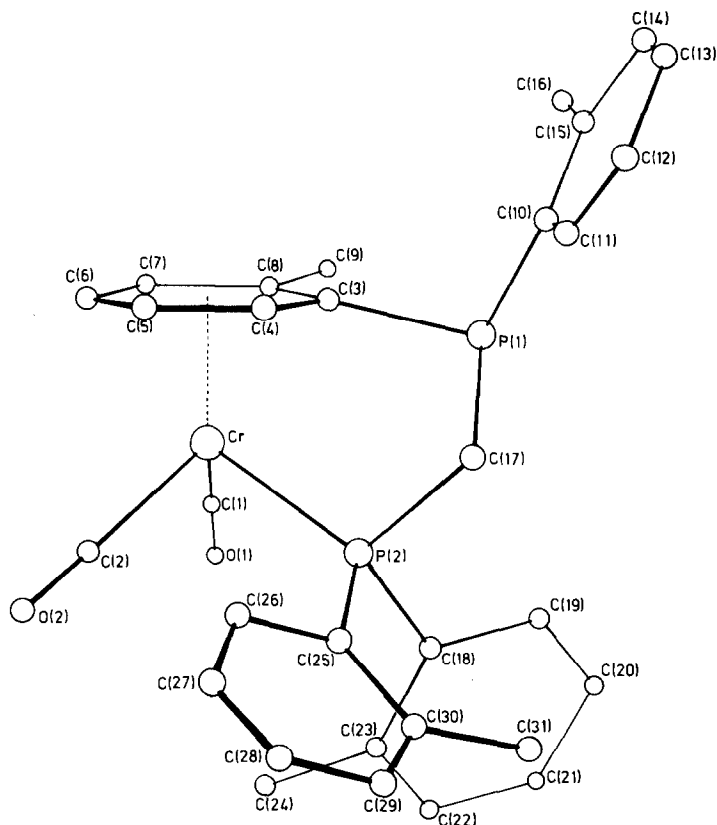


Fig. 2. The molecular geometry and atomic numbering scheme for $\text{Cr}(\text{CO})_2(\text{BDT}_0\text{M})$.

coordination sites, the phosphine the fourth). Two carbonyl groups comprise the fifth and sixth donors. The geometry is adequately described as being a variant of the 'piano stool' arrangement, even though the three 'legs' are not all carbonyl groups.

The Cr-CO bonding. In describing the chromium-carbonyl bonding it must be remembered that positions for C(1) and O(1) are only approximate. It is therefore appropriate to consider only the Cr-C(2)-O(2) geometry, for which Cr-C(2) is 1.818(10) Å, C(2)-O(2) is 1.134(11) Å, and Cr-C(2)-O(2) is 179.2(10)°. These are normal values. The Cr-CO bond compares closely with the corresponding averages of 1.841, 1.824, 1.823 and 1.83 Å in the structurally similar complexes Cr(CO)₃(π -benzene) [15], Cr(CO)₃(π -toluene) [16], Cr(CO)₂(PPh₃)(C₆H₅COOCH₃) [17], and $\{(\pi\text{-C}_6\text{H}_5)(\text{C}_6\text{H}_5)\text{AsCH}_2\text{As}(\text{C}_6\text{H}_5)_2\}\text{Cr}(\text{CO})_2$ [9] respectively. These bonds are all slightly shorter than those found in complexes containing a greater number of carbonyl groups, e.g. 1.909 in Cr(CO)₆ [18], 1.880 in Cr(CO)₅PPh₃ [19] and 1.884 Å in Cr(CO)₄(Ph₂PCH₂CH₂PPh₂) [20], where there is greater competition for back-donated electron density from the metal centre.

The Cr-BDT_oM bonding. The particular configuration adopted by the coordinated BDT_oM ligand and the relative orientations of the *o*-tolyl substituents are clearly seen in Fig. 2. The bond lengths and angles (Tables 2 and 3) show evidence of considerable strain, and we note in particular the asymmetry of bond angles at P(1) (range 97.9–103.8°) and P(2) (range 99.4–120.9°), and the substantial bend at C(3) (P(1) is 0.397 Å from the plane of the coordinated aromatic ring C(3)-C(8), a much greater displacement of phosphorus than that which occurs from the other three phenyl rings (Table 4)).

The Cr-P(2) distance of 2.376(2) Å falls within the normal range of 2.360–2.422 Å [17] for chromium complexes where a phosphine ligand is situated *trans* to CO ligands. By contrast, the Cr-P distance in Cr(CO)₂(PPh₃)(C₆H₅COOCH₃) is only 2.337 Å, which has been attributed to the fact that the phosphine occupied a coordination site *trans* to methylbenzoate which exhibits a weaker structural *trans* influence than CO [17]. It is difficult to estimate the magnitude of a *trans* influence of the arene component of the BDT_oM ligand, but it can be noted that the Cr-CO distances are, if anything, shorter than those in Cr(CO)₂(PPh₃)(C₆H₅COOCH₃), and it is therefore likely that the reason for the greater Cr-P distance in the present compound is a direct manifestation of intraligand strain within the coordinated BDT_oM ligand.

The Cr-arene bonding is normal, with Cr-C values ranging from 2.166(10) to 2.260(9) Å (average 2.210 Å), and the perpendicular distance from Cr to the arene plane defined by C(3) to C(8) is 1.698 Å (Table 4). The corresponding average Cr-C(arene) distances in Cr(CO)₃(π -benzene), Cr(CO)₃(π -toluene) and Cr(CO)₂(PPh₃)(C₆H₅COOCH₃) are 2.230, 2.22, and 2.198 Å respectively [15–17]. The aromatic ring itself is planar to within the least-squares estimated uncertainties in the atom positions (maximum displacement 0.019 Å), but the substituents are not coplanar, the methyl carbon C(9) being displaced 0.086 Å in a direction away from Cr, while P(1) is displaced 0.397 Å towards Cr. The direction of the C(9) displacement is in the opposite sense to the situation observed in Cr(CO)₃(C₆H₆) where the six hydrogen atoms are all angled towards the chromium atom [15], and the magnitude of the displacement is surprising in view of the finding that in Cr(CO)₃(π -toluene) the methyl substituent is coplanar with the aromatic ring [16].

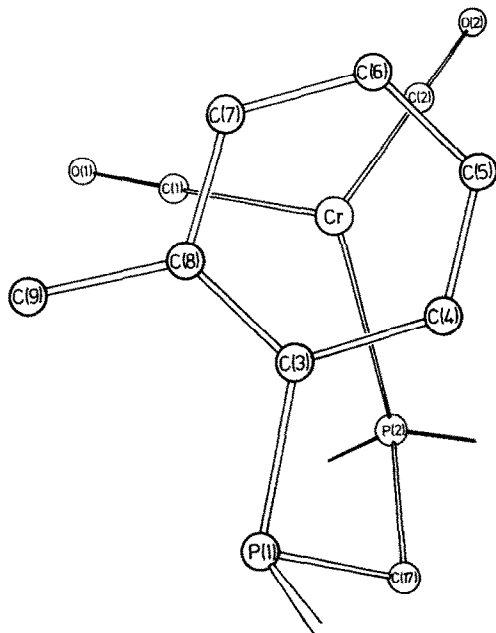


Fig. 3. A projection of the molecule of $\text{Cr}(\text{CO})_2(\text{BDT}_0\text{M})$ onto the plane of the coordinated arene ring.

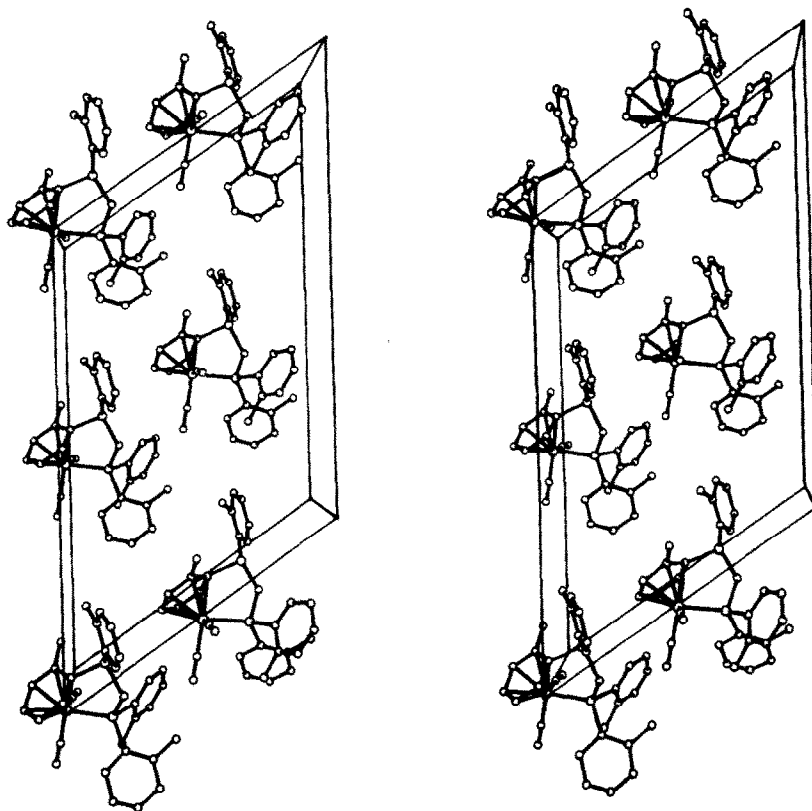


Fig. 4. Stereoview of the molecular packing in $\text{Cr}(\text{CO})_2(\text{BDT}_0\text{M})$.

In order to assess whether the displacement of C(9) arises from otherwise untenable intermolecular contacts, the stereopair diagrams of Fig. 4 were plotted, but there appears to be no evidence for particularly close approaches. The shortest intermolecular contact calculates for O(1) \cdots C(4) (3.39 Å) with no other approaches being shorter than 3.5 Å. The Cr–CO and Cr–P bonds are seen to be in a staggered configuration with respect to the Cr–C bonds to the coordinated arene ring (Fig. 3). It has been noted previously that where a coordinated arene contains an electronegative substituent an eclipsed configuration is preferred, otherwise a staggered configuration is likely [17]. However, the bonds are eclipsed in (1,3,5-trimethylbenzene)-(CO)₃Mo yet staggered in (hexamethylbenzene)(CO)₃Mo [21], and it is clearly difficult to predict with certainty which configuration will be adopted. This difficulty is compounded for BDT_oM where twisting of the arene is likely to be hindered by the chelating nature of this ligand.

Another aspect of the geometry of a coordinated arene which has attracted much interest in recent years is whether the arene geometry is significantly altered upon π -complexation. Such a change in symmetry has been observed for Cr(CO)₃(C₆H₆) [15], but the standard deviations in the C–C bond lengths in the present compound do not allow similarly definitive conclusions to be drawn.

Discussion

The reaction of bis(*di-o*-tolyl)phosphinomethane (BDT_oM) with the Group VI metal carbonyls results in two series of complexes being formed. These are M(CO)₄(BDT_oM), M = Cr, Mo or W, and M(CO)₂(BDT_oM), M = Cr or Mo. In low boiling solvents (e.g. isooctane), the tetracarbonyl series is formed, but these are more conveniently formed by the simple substitution reaction of M(CO)₄(C₇H₈), M = Cr or Mo, and C₇H₈ = norbornadiene. In high boiling solvents (e.g. decalin or mesitylene), the dicarbonyl series is formed. Only the tetracarbonyl compound of tungsten could be formed in a high boiling solvent and this characteristic parallels the reactions of tri(*o*-tolyl)phosphine and bis(diphenyl)arsinomethane with the Group VI carbonyls [8,9]. All the compounds are stable in the solid state and in solution except for Cr(CO)₂(BDT_oM) which decomposes slowly in chloroform. For the compounds M(CO)₄(BDT_oM) and M(CO)₂(BDT_oM) there are four and two strong carbonyl absorbances in the infrared spectrum respectively (see Table 5), and these are very similar to the absorbances observed for the series M(CO)₄[bis-(diphenyl)arsinomethane] and M(CO)₂[bis(diphenyl)arsinomethane] [9,22].

TABLE 5
CARBONYL STRETCHING FREQUENCIES (cm⁻¹)^a

Compound					
Cr(CO) ₄ (BDT _o M)	2010s	1927s	1890s	1860s	
Mo(CO) ₄ (BDT _o M)	2025s	1924s	1915sh	1895s	1856s
W(CO) ₄ (BDT _o M)	2015m	1932s	1905sh	1888s	1852s
Cr(CO) ₂ (BDT _o M)	1889s	1840s			
Mo(CO) ₂ (BDT _o M)	1902s	1854s			

^a s = strong; m = medium; sh = shoulder.

NMR spectral results for the compounds $M(\text{CO})_4(\text{BDT}_o\text{M})$, $M = \text{Cr}, \text{Mo}$ or W

The NMR spectra for the series $M(\text{CO})_4(\text{BDT}_o\text{M})$ are reasonably simple to interpret. For the ligand, BDT_oM , the ^{31}P spectrum consists of a singlet at 44.05 ppm and for $\text{W}(\text{CO})_4(\text{BDT}_o\text{M})$ the resonance is found at 21.4 ppm and tungsten satellites are observed with $J(^{181}\text{W}-^{31}\text{P})$ of 196.5 Hz. In the ^1H NMR spectrum (Table 6), the ligand consists of three resonances at 7.4–7.0 (m), 2.63 (t) and 2.26 (s) for the phenyl methylene and methyl protons respectively. For the complexes, $M(\text{CO})_4(\text{BDT}_o\text{M})$, the ^1H NMR remains trivial. The methyl resonance has been shifted slightly upfield ($\Delta\delta \approx 0.2$ ppm) and remains a singlet, while the methylene resonance has been shifted considerably downfield ($\Delta\delta \approx 1.8$ –2.2 ppm) and remains a triplet. The $^{31}\text{P}-^1\text{H}$ coupling constant has increased from 3 in the ligand to 8 Hz in the complexes. In the ^{13}C NMR spectra of the compounds $M(\text{CO})_4(\text{BDT}_o\text{M})$ (Table 7), four series of resonances occur corresponding to the carbonyl carbons, the aromatic carbons, the methylene and the methyl carbons. The carbonyl resonance at lower field is an ill defined triplet and is assigned to the carbonyls *trans* to the P atoms, while the carbonyl resonance at higher field is a sharp triplet and is assigned to the carbonyls *cis* to the P atoms. These assignments are in accord with the previous assignments of similar compounds [23]. The aromatic carbons have been assigned according to the chemical shift and coupling constants as discussed earlier [10,24]. While the methylene carbon has been shifted downfield as would be expected, the methyl carbon has remained almost stationary compared to the free ligand. The triplet nature which occurs in the above proton and carbon resonances originates from the virtual coupling of the two magnetically equivalent P atoms. All the above physical information is consistent with the tetracarbonyl compounds having an octahedral structure with the bis(*di-o-tolyl*)phosphinomethane acting as a bidentate ligand.

NMR spectral results for the compounds $M(\text{CO})_2(\text{BDT}_o\text{M})$, $M = \text{Cr}$ or Mo

The NMR spectra for the dicarbonyl compounds are far more complex than for

TABLE 6

^1H NMR SPECTRAL DATA FOR THE COMPOUNDS $M(\text{CO})_4(\text{BDT}_o\text{M})$ AND $M(\text{CO})_2(\text{BDT}_o\text{M})$ ^{a,c}

Compound	$\delta(\text{phenyl})$	$\delta(\text{CH}_2)$	$\delta(\text{CH}_3)$	$J(\text{P-H})$ of CH_2	$J(\text{H-H})$ of CH_2
BDT_oM	7.4–7.0(m)	2.63(t)	2.26(s)	3.0	–
$\text{Cr}(\text{CO})_4(\text{BDT}_o\text{M})$	7.9–7.2(m)	4.44(t)	2.06(s)	8.0	–
$\text{Mo}(\text{CO})_4(\text{BDT}_o\text{M})$	7.8–7.0(m)	4.46(t)	2.08(s)	8.0	–
$\text{W}(\text{CO})_4(\text{BDT}_o\text{M})$	7.8–7.0(m)	4.89(t)	2.02(s)	8.0	–
$\text{Cr}(\text{CO})_2(\text{BDT}_o\text{M})$	8.3–7.0(m) and 5.0(qt) ^b	4.12(sep) and 3.20(q)	2.53(s) 2.04(s) 1.84(s)	27.0 and 12.0 5.0	14.0
$\text{Mo}(\text{CO})_2(\text{BDT}_o\text{M})$	8.3–7.0(m) and 5.2(qt) ^b	4.10(o) and 3.30(q)	2.52(s) 2.48(s) 2.05(s) 2.01(s)	27.0 and 12.0 5.5	14.0

^a s = singlet; t = triplet; q = quartet; sep = septet; o = octet; m = multiplet; qt = quartet of triplets. ^b π -Bonded aromatics centered at the chemical shift. ^c δ in ppm referenced to internal TMS (δ 0 ppm). J in Hz.

TABLE 7

¹³C NMR SPECTRAL DATA FOR THE COMPOUNDS M(CO)₄(BDT_OM) AND M(CO)₂(BDT_OM)^{a,b}

Compound	δ(CO)		α		β		δ(phenyl)		γ'	δ	δ(CH ₂)	δ(CH ₃)
					β'	γ						
BDT _O M	-	-	142.3(t)	129.9(t)	137.4(t)	131.2(s)	128.4(s)	125.9(s)	26.5(t)	21.2(t)		
Cr(CO) ₄ (BDT _O M)	e	e	140.8(s)	132.8(t)	133.0(s)	131.5(s)	125.7(t)	130.5(s)	41.6(t)	21.5(s)		
Mo(CO) ₄ (BDT _O M)	219.1(l) ^c	210.0(t) ^d	141.0(s)	132.4(t)	133.0(t)	131.5(s)	125.8(t)	130.5(s)	41.0(t)	21.5(s)		
W(CO) ₄ (BDT _O M)	210.6(t) ^c	203.0(t) ^d	140.7(t)	131.4(t)	133.3(t)	131.7(t)	125.8(t)	130.8(s)	44.4(t)	21.5(t)		
Cr(CO) ₂ (BDT _O M)	241.1(d)	238.3(d)			143 - 126(m)				40.0(q)	22.3(d)		
			115.8(d)	85.3(d)	92.6(d)	92.6(s)	85.2(s)	90.1(s) ^f	21.9(d)			
Mo(CO) ₂ (BDT _O M)	227.8(d)	226.3(d)			143 - 126(m)				41.1(q)	22.2(d)		
			115.4(d)	85.0(t)	96.0(d)	92.0(d)	82.0(d)	91.6(s) ^f	21.8(d)			
										21.5(d)		
											20.4(d)	
												20.4(d)
Compound	J(P-CO)	J(P-CO)	J(P-C _α)	J(P-C _β)	J(P-C _{β1})	J(P-C _γ)	J(P-C _{γ1})	J(P-C _δ)	J(P-CH ₂)	J(P-CH ₃)		
BDT _O M			13.7	2.4	4.3	0	0	0	22.9	11.9		
Cr(CO) ₄ (BDT _O M)			g	6.8	g	g	8.7	0	16.6	g		
Mo(CO) ₄ (BDT _O M)	g	g	g	17.1	9.8	g	6.1	0	17.4	g		
W(CO) ₄ (BDT _O M)	7.8 ^c	6.8 ^d	2.9	19.5	9.8	2.9	5.9	0	22.0	3.9		
Cr(CO) ₂ (BDT _O M)	17.6	15.6	33.2 ^f	5.9 ^f	5.9 ^f	g ^f	0 ^f	0 ^f	20.5	5.5		
										8.8	7.3	
											6.1	
												22.6
Mo(CO) ₂ (BDT _O M)	11.7	10.2	33.0 ^f	4.0 ^f	12.5 ^f	4.4 ^f	3.7 ^f	0 ^f	22.4	5.1		
				and 4.0 ^f						14.3	7.3	
											8.1	
												22.7

^a s = singlet; d = doublet; t = triplet; m = multiplet.^b δ measured in ppm (±0.1 ppm) referenced to internal TMS (δ = 0 ppm) J measured in Hz (±0.1 Hz).^c *trans* carbonyls.^d *cis* carbonyls.^e not observed.^f π-bonded aromatics^g not resolved.

the tetracarbonyl compounds, and this in effect represents the complexity of the bonding in these compounds.

In the ³¹P spectra of Cr(CO)₂(BDT_OM), there are two resonances occurring at 34.7 ppm and at -85.4 ppm in the form of an AB quartet with a ³¹P-³¹P coupling constant of 39.1 Hz. An important feature of the ³¹P spectrum is that the intensity of the resonance at lower field is only about one third of the intensity of the resonance at higher field.

The ^1H NMR spectra for the dicarbonyl series are quite complex. For the complex $\text{Cr}(\text{CO})_2(\text{BDT}_0\text{M})$, the ^1H NMR spectrum consists of an aromatic region at 8.3–7.0 ppm (12 protons), a coordinated aromatic region centered at 5.0 ppm (4 protons), a complex methylene region from 3.0 to 4.5 ppm (2 protons) and a methyl region at 1.8 to 2.5 ppm (12 protons). The coordinated aromatic region is a 12 line multiplet resolved into a quartet of triplets. The methylene protons form an AB quartet with $J(\text{H-H})$ of 14 Hz further complicated by ^{31}P coupling. The high field part of the AB quartet at 3.20 ppm is further coupled by one phosphorus atom with a phosphorus-proton coupling of 5.0 Hz resulting in a fourline spectrum. The lowfield part of the AB quartet at 4.12 ppm is coupled by both phosphorus atoms with phosphorus-proton couplings of 12.0 and 27.0 Hz respectively resulting in a seven line (1/1/1/2/1/1/1) spectrum. There are three methyl resonances in the ratio of 2/1/1 at 2.53, 2.04 and 1.84 ppm respectively. The peak at 2.53 obviously consists of two methyl resonances which are accidentally magnetically equivalent. The ^1H NMR spectrum for $\text{Mo}(\text{CO})_2(\text{BDT}_0\text{M})$ (Fig. 5) is similar to that of $\text{Cr}(\text{CO})_2(\text{BDT}_0\text{M})$ with some important qualifying differences. The resonances for the coordinated aromatics centered around 5.2 ppm are not as well resolved, while both parts of the AB quartet for the methylene protons are fully resolved into an

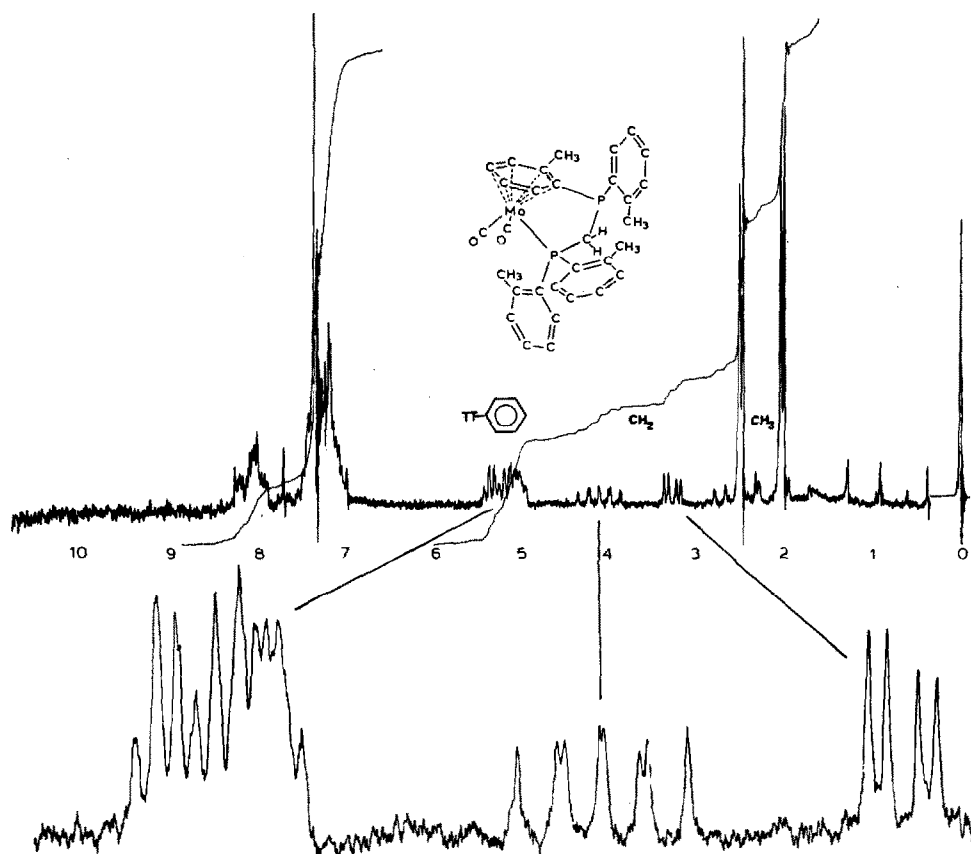


Fig. 5. ^1H NMR spectrum of $\text{Mo}(\text{CO})_2(\text{BDT}_0\text{M})$.

octet for the lowfield part and a quartet for the highfield part. The methyl resonances for $\text{Mo}(\text{CO})_2(\text{BDT}_o\text{M})$ are also resolved into four singlets.

The ^{13}C NMR spectra (Fig. 6) for the complexes $\text{M}(\text{CO})_2(\text{BDT}_o\text{M})$ are complicated due to the lack of symmetry in the molecule. Because of this, there are 31 magnetically non-equivalent carbon atoms further complicated by possible coupling to two non-equivalent phosphorus atoms. The carbonyl resonances occur at 241.1 and 238.3 ppm for $\text{M} = \text{Cr}$ and at 227.8 and 226.3 ppm for $\text{M} = \text{Mo}$. These carbonyl resonances are downfield compared to π -arene carbonyl complexes. For example, in $(\pi\text{-toluene})\text{Cr}(\text{CO})_3$ and $(\pi\text{-mesitylene})\text{Cr}(\text{CO})_3$, the carbonyl resonance occurs at 233.5 [25] and 235.1 ppm [26,27] respectively; and in $(\pi\text{-}m\text{-xylene})\text{Mo}(\text{CO})_3$ and $(\pi\text{-mesitylene})\text{Mo}(\text{CO})_3$, the carbonyl resonance occurs at 223.1 [28] and 223.7 ppm

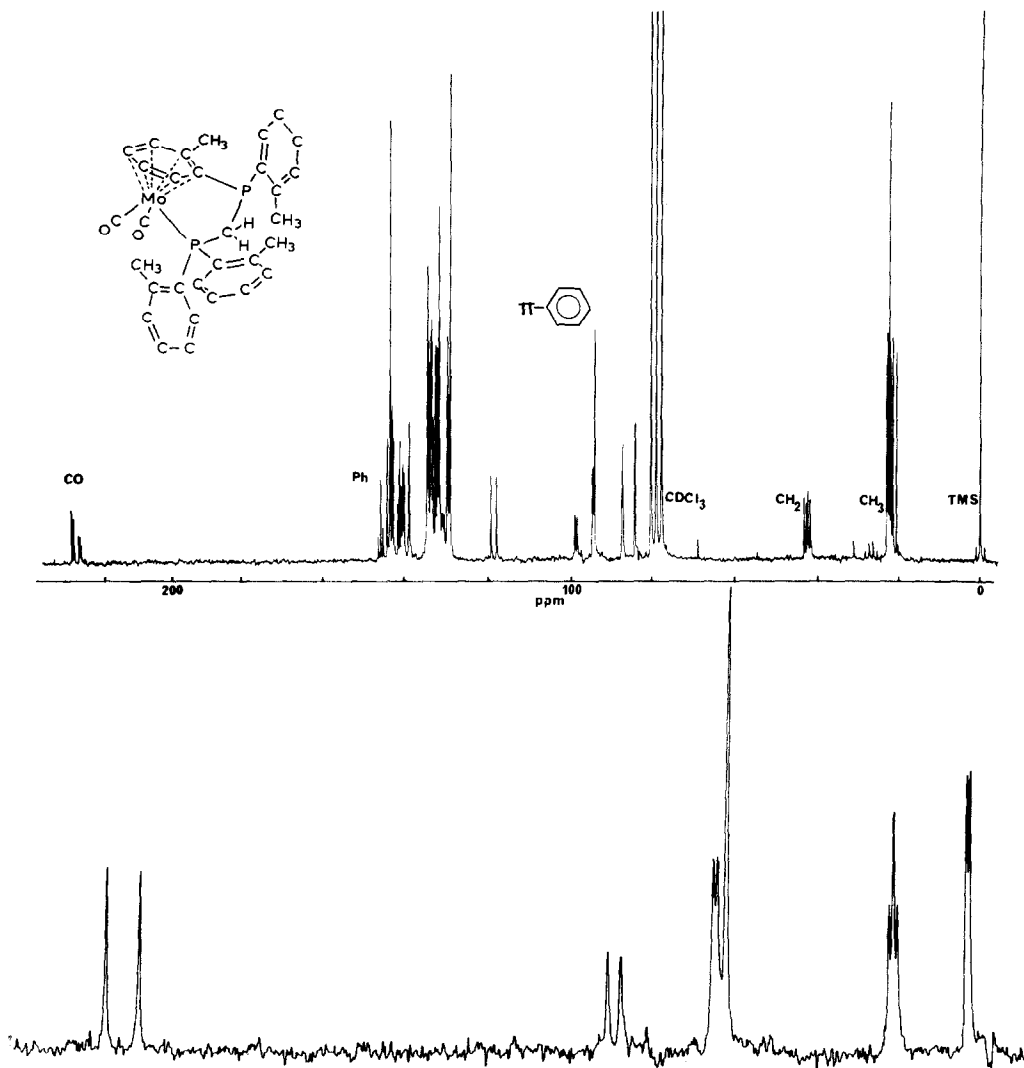


Fig. 6. ^{13}C NMR spectrum of $\text{Mo}(\text{CO})_2(\text{BDT}_o\text{M})$.

[26,27], respectively. Due to the chelate effect of our ligand, increased bonding to the arene ring would be expected, which would increase the π -back bonding and decrease the M-C(carbonyl) bond length. Indeed, the Cr-C(carbonyl) bond lengths of 1.79 and 1.81 Å are relatively short. This correlation parallels that found for the series of chromium carbonyl complexes studied by Bodner and Todd [29]. The π -bonded arene carbons are shifted well upfield compared to non-bonded arene carbons. The shift upfield is between 27–47 ppm depending on the individual carbon atom. Whilst the π -bonded arene carbons are well separated, they could not be assigned unequivocally. It is interesting to note that one carbon C_β (coordinated) of the molybdenum compound is coupled to both phosphorus atoms indicating that coupling is occurring through the π -system of the molecule. The methylene carbon is shifted downfield compared to that of the free ligand and is a quartet showing two distinct coupling constants. There are four methyl resonances each a doublet coupled to a phosphorus atom. In the chromium compound they are resolved into an eight line spectrum, but in the molybdenum complex two resonances overlap resulting in a seven line 1/1/1/2/1/1/1 spectrum. The methyl resonance most upfield with a coupling constant of 22.6 and 22.7 Hz for $\text{Cr}(\text{CO})_2(\text{BDT}_o\text{M})$ and $\text{Mo}(\text{CO})_2(\text{BDT}_o\text{M})$ respectively, obviously belongs to the methyl resonance of the non-coordinated *o*-tolyl group of the non-coordinated phosphorus atom. The other resonances, with the present information, cannot be unequivocally assigned.

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- 12 The omega scan angle is given by $\omega = A + B \tan\theta$, where *A* is a constant dependent on the crystal mosaicity and beam divergence, and the *B*tan θ term allows for reflection widening at high theta. Values used were *A* = 0.60, *B* = 0.142. The scans were automatically extended by 25% at each side of the peak to afford a background measurement. After a rapid prescan, observed reflections were counted for either 99 s or else for sufficient time for $\sigma(I)/I$ to be less than 0.02.
- 13 All computing was carried out using the SDP suite of programs on a PDP-11 computer.
- 14 $\sigma(I) = \frac{20.1166}{NPI} \sqrt{C + 4B}$, where the constant term is the maximum possible scan rate, *NPI* is the ratio of the maximum possible scan rate to the scan rate for the measurement, *C* = total counts, *B* = total background.
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