

Chromium, Molybdenum, and Tungsten Carbonyl Complexes of Phenylidibenzophosphole

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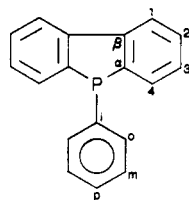
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A series of complexes of 1-phenylidibenzophosphole (DBP) of the type $(\text{DBP})_n\text{M}(\text{CO})_{6-n}$ ($\text{M} = \text{Cr}, \text{Mo}$, W ; $n = 1-3$) have been prepared and characterized by elemental analysis, physical properties, and infrared and ^1H , $^1\text{H}\{^{31}\text{P}\}$, $^{13}\text{C}\{^1\text{H}\}$, ^{17}O , $^{31}\text{P}\{^1\text{H}\}$, and ^{95}Mo NMR spectroscopy. The structures of $(\text{DBP})\text{Cr}(\text{CO})_5$ (1), *cis*- $(\text{DBP})_2\text{Cr}(\text{CO})_4$ (2), and *mer*- $(\text{DBP})_3\text{Cr}(\text{CO})_3$ (3) complexes have been determined from three-dimensional X-ray data collected by counter methods. Compound 1 crystallized in space group $P2_1/c$ with $a = 7.962$ (3) Å, $b = 23.122$ (9) Å, $c = 11.212$ (4) Å, $\beta = 95.27$ (3)°; and $Z = 4$. Compound 2 crystallizes in space group $P2_1$ with $a = 11.295$ (4) Å, $b = 13.381$ (5) Å, $c = 10.948$ (3) Å, $\beta = 103.24$ (2)°; and $Z = 2$. Compound 3 crystallizes in space group $P\bar{1}$ with $a = 10.621$ (3) Å, $b = 12.476$ (2) Å, $c = 20.489$ (4) Å, $\alpha = 92.86$ (2)°, $\beta = 101.441$ (2)°, $\gamma = 108.07$ (2)°, and $Z = 2$. The three structures were refined by least squares methods with $R = 0.070$ for 1, $R = 0.067$ for 2, and $R = 0.068$ for 3 for 2696, 2347, and 6106 unique reflections with $I/\sigma(I) \geq 3.0$ for 1, 2, and 3, respectively. Attractive interactions between two adjacent dibenzophosphole planes exist for *cis*- $(\text{DBP})_2\text{Cr}(\text{CO})_4$ and *mer*- $(\text{DBP})_3\text{Cr}(\text{CO})_3$ in the solid state. This interaction is shown by diamagnetic anisotropy effects in the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra to be present in solution as well for all the *cis*- $(\text{DBP})_2\text{M}(\text{CO})_4$ and *mer*- $(\text{DBP})_3\text{M}(\text{CO})_3$ complexes stabilizing a mutually *cis* orientation of two DBP ligands. The CO force constants for these molecules have been calculated by the Cotton-Kraihanzel method, and the Graham σ/π parameters of DBP have been evaluated to allow a comparison of the donor properties of DBP with those of other phosphorus donors. Correlations between these force constants and the chemical shifts of the various nuclei and among the chemical shifts of the various nuclei are discussed.

Introduction

In recent years there has been a lot of interest in the coordination chemistry of phospholes.²⁻⁴ Of the phospholes 1-phenylidibenzophosphole (I, DBP) is an analogue



I (DBP)
phenylidibenzophosphole ring-numbering scheme

of triphenylphosphine, but it differs from Ph_3P in two important ways. It is sterically smaller and because of the rigid dibenzophosphole ring system should be a better π -acceptor than PPh_3 . The work to date with DBP has concerned a brief comparison of its donor properties with those of PPh_3 and its potential aromaticity.⁵ DBP has been reported⁶ to be a better donor toward $\text{Ni}(\text{II})$ than is PPh_3 , and its rhodium (I) complex is a better homogeneous hydrogenation catalyst⁷ than the PPh_3 analogue. Part of

this difference in donor abilities has been attributed to the ring phosphorus conjugation in DBP.⁸ Other studies have also suggested that there exists some degree of cyclic delocalization within the dibenzophosphole ring.^{5,9}

The nitrogen analogue of the dibenzophosphole ring system, carbazole, is very well-known for its interesting photophysical properties¹⁰ which arise from electronic interactions between the π -systems of two parallel carbazole rings forming excimers. Complexes that contain two DBP ligands in a *cis* orientation could also have mutually overlapping rings that could give rise to similar electronic interactions. This type of benzophosphole ring overlap has been crystallographically observed¹¹ in pentacoordinate nickel(II) complexes.

We have prepared and characterized a series of complexes of the type $(\text{DBP})_n\text{M}(\text{CO})_{6-n}$ ($n = 1-3$; $\text{M} = \text{Cr}, \text{Mo}, \text{W}$). Three of the chromium complexes have been characterized in the solid state by X-ray crystallography, and all complexes have been characterized in solution by infrared and multinuclear (^1H , $^{31}\text{P}\{^1\text{H}\}$, $^{13}\text{C}\{^1\text{H}\}$, ^{95}Mo , ^{17}O , and $^1\text{H}\{^{31}\text{P}\}$) NMR in order to ascertain the orientation of the DBP ligands and to gain further information with regards to the donor properties of DBP.

Experimental Section

(A) Reagents and Physical Measurements. Commercially available reagents were reagent grade and were used as received

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unless otherwise indicated. Metal hexacarbonyls were obtained from Strem Chemicals. The 1-phenylidibenzophosphole was prepared by the literature method.¹² Silica gel used for column chromatography (grade 12, 28–200 mesh) was obtained from Aldrich. All preparations were carried out under a dry dinitrogen atmosphere.

Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN 37921. Melting points were determined on a Meltemp apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 599 spectrometer with a 5× abscissa expansion as CH₂Cl₂ solutions in NaCl cells. Far IR spectra were recorded on a Perkin-Elmer 1850 FT-IR as polyethylene pellets. The ³¹P{¹H} NMR spectra were obtained at 40.26 MHz on a JEOL FX-100 spectrometer in the FT mode. The ¹H, ¹³C{¹H}, ¹⁷O, and ⁹⁵Mo NMR spectra were obtained on a Bruker WH-400 at 400.13, 100.62, 54.24, and 26.08 MHz respectively. The ¹H{³¹P} NMR were recorded on a Bruker AM-400 at 400.13 MHz. Proton and carbon chemical shifts are relative to internal TMS; phosphorus chemical shifts were measured relative to PPh₃ (δ -6.0) and corrected to 85% H₃PO₄; oxygen chemical shifts were measured relative to acetone internal standards (δ 572) and corrected to H₂O (δ 0); molybdenum chemical shifts were referenced to external aqueous alkaline 2 M K₂MoO₄. A positive sign on all chemical shifts indicates a downfield position relative to the respective references. Saturated solutions for NMR were prepared by dissolving the compounds in CDCl₃ and filtering the solutions directly into the NMR sample tubes.

(B) Synthesis. Pentacarbonyl Complexes: (Phenylidibenzophosphole)pentacarbonylchromium(0). A mixture containing 1.27 g (5.8 mmol) of chromium hexacarbonyl, 1.53 g (5.8 mmol) of DBP, 0.685 g (6.2 mmol) of Me₃NO·2H₂O, and 50 mL of dichloromethane was refluxed for 2 h.¹³ The reaction mixture was allowed to cool and evaporated to dryness on a rotary evaporator, with heat. Most of the unreacted hexacarbonyl sublimed into the rotary evaporator trap. Cold methanol was added to precipitate yellow crystals, which were found to be a mixture of the pentacarbonyl and tetracarbonyl complexes. Separation of this mixture was achieved by column chromatography on silica gel with 30% dichloromethane in hexane. Recrystallization of the pentacarbonyl complex from CH₂Cl₂/methanol produced 250 mg of cream-colored crystals, mp 170–173 °C dec. Anal. Calcd for C₂₃H₁₃PCrO₅: C, 61.09; H, 2.87. Found: C, 61.01; H, 2.95. ¹H NMR (400 MHz): δ 7.34 (m, 3 H, H_{m,p}), 7.54 (m, 4 H, H_o, H₃), 7.58 (m, 2 H, H₂), 7.93 (m, J(PH) = 6.6 Hz, 2 H, H₄), 7.94 (m, J(PH) = 2.4 Hz, 2 H, H₁). ¹³C{¹H} NMR (100 MHz): δ 121.81 (d, J(PC) = 5.1 Hz, C₁), 128.75 (d, J(PC) = 10.2 Hz, C₃), 128.85 (d, J(PC) = 11.7 Hz, C_m), 130.21 (d, J(PC) = 1.0 Hz, C₂), 130.56 (d, J(PC) = 14.2 Hz, C₄), 130.64 (d, J(PC) = 11.7 Hz, C_o), 130.94 (s, C₂), 133.79 (d, J(PC) = 32.1 Hz, C₁), 139.56 (d, J(PC) = 43.3 Hz, C_o), 141.14 (d, J(PC) = 8.1 Hz, C_β), 216.14 (d, J(PC) = 13.3, cis CO's), 220.70 (d, J(PC) = 7.1 Hz, trans CO).

(Phenylidibenzophosphole)pentacarbonylmolybdenum(0). A mixture containing 1.02 g (3.9 mmol) of molybdenum hexacarbonyl, 0.97 g (3.8 mmol) of DBP, a catalytic amount of bis-(triphenylphosphine)nitrogen(1+) chloride (Strem Chemical, Inc.), and 50 mL of ethanol was refluxed for 12 h.¹⁴ On cooling, precipitation was observed. The reaction mixture was evaporated to dryness on a rotary evaporator, with heat. Separation and purification of the yellow crystalline product as above produced 450 mg of cream-colored crystals, mp 160–162 °C dec. Anal. Calcd for C₂₃H₁₃PMoO₅: C, 55.66; H, 2.64. Found: C, 55.82; H, 2.86. ¹H NMR (400 MHz): δ 7.35 (m, 2 H, H_m), 7.36 (m, 1 H, H_p), 7.49 (m, 2 H, J(PH) = 3.5 Hz, H₃), 7.53 (m, 2 H, J(PH) = 11.6 Hz, H_o), 7.58 (m, 2 H, J(PH) = 1.2 Hz, H₂), 7.86 (m, 2 H, J(PH) = 7.5 Hz, H₄), 7.97 (m, 2 H, J(PH) = 2.3 Hz, H₁). ¹³C{¹H} NMR (100 MHz): δ 121.68 (d, J(PC) = 4.9 Hz, C₁), 128.68 (d, J(PC) = 10.2 Hz, C₃), 128.80 (d, J(PC) = 10.0 Hz, C_m), 130.32 (s, C_p), 130.38 (d, J(PC) = 15.7 Hz, C₄), 130.69 (d, J(PC) = 1.5 Hz, C₂), 131.07 (d, J(PC) = 13.4 Hz, C_o), 133.82 (d, J(PC) = 30.7 Hz, C₁), 140.32 (d, J(PC) = 42.6 Hz, C_o), 141.47 (d, J(PC) = 7.9 Hz, C_β),

205.00 (d, J(PC) = 8.9 Hz, cis CO's), 209.04 (d, J(PC) = 22.0 Hz, trans CO).

(Phenylidibenzophosphole)pentacarbonyltungsten(0). A mixture containing 1.00 g (2.85 mmol) of tungsten hexacarbonyl, 0.73 g (2.82 mmol) of DBP, and 50 mL of diglyme (Aldrich Chemical Co.) was refluxed for 4 h.¹⁵ The yellow solution was evaporated to dryness on a rotary evaporator with heat. Separation and purification as above produced white crystals, mp 170–171 °C dec. Yield was approximately 47%. Anal. Calcd for C₂₃H₁₃PWO₅: C, 47.29; H, 2.24. Found: C, 47.68; H, 2.38.

Tetracarbonyl Complexes: cis-Bis(phenylidibenzophosphole)tetracarbonylmolybdenum(0). A mixture containing 0.61 g (2.3 mmol) of molybdenum hexacarbonyl and 1.22 g (4.7 mmol) of DBP was refluxed in 50 mL of diglyme for 24 h. The yellow solution was evaporated to dryness on a rotary evaporator, resulting in an oily product which was found to be a mixture of the pentacarbonyl and tetracarbonyl complexes. Separation and purification as above produced bright yellow crystals, mp 214–218 °C dec. Yield was approximately 65%. Anal. Calcd for C₄₀H₂₆P₂MoO₄: C, 65.94; H, 3.60. Found: C, 66.10; H, 3.66. ¹H NMR (400 MHz): δ 7.08 (m, 4 H, J(PH) = 2.1 Hz, H₃), 7.15 (m, 4 H, J(PH) = 3.5 Hz, H_m), 7.26 (m, 4 H, H_o), 7.30 (m, 4 H, H₂), 7.38 (m, 4 H, J(PH) = 1.8 Hz, H₁), 7.39 (m, 2 H, J(PH) = 1.8 Hz, H_p), 7.48 (m, 4 H, J(PH) = 6.7 Hz, H₄). ¹³C{¹H} NMR (100 MHz): δ 121.26 (t, ³J(PC) = 4.3 Hz, C₁), 127.96 (t, ⁴J(PC) = 9.7 Hz, C₃), 128.22 (t, ⁴J(PC) = 9.4 Hz, C_m), 128.95 (s, C_p), 129.33 (s, C₂), 130.08 (5L, ²J(PC) = 11.85 Hz, ⁴J(PC) = 0.31 Hz, ²J(PP) = 19.5 Hz, C₄), 130.11 (5L, ²J(PC) = 15.99 Hz, ⁴J(PC) = -0.29 Hz, ²J(PP) = 19.5 Hz), 136.64 (5L, ¹J(PC) = 30.62 Hz, ³J(PC) = 4.38 Hz, ²J(PP) = 19.5 Hz, C₁), 138.90 (5L, ¹J(PC) = 36.26 Hz, ³J(PC) = 2.67 Hz, ²J(PP) = 19.5 Hz, C_o), 141.51 (t, ⁴J(PC) = 6.4 Hz, C_β), 209.68 (t, J(PC) = 9.6 Hz, cis CO's), 213.15 (5L, ²J(PC) = 24.34 Hz, ²J(PC) = -9.19 Hz, ²J(PP) = 19.5 Hz, ²J(PP) = 19.5 Hz, trans CO's), ³J = ¹J(PC) + ⁿ⁺²J(PC)]. The analogous cis-(DBP)₂M(CO)₄ complexes (M = Cr, W), were prepared by the same general procedure.

cis-Bis(phenylidibenzophosphole)tetracarbonylchromium(0): yellow crystals; mp 208–212 °C dec. Anal. Calcd for C₄₀H₂₆P₂CrO₄: C, 70.18; H, 3.83. Found: C, 69.85; H, 4.00.

cis-Bis(phenylidibenzophosphole)tetracarbonyltungsten(0): yellow crystals; mp 232–234 °C dec. Anal. Calcd for C₄₀H₂₆P₂WO₄: C, 58.84; H, 3.21. Found: C, 58.98; H, 3.36.

Tricarbonyl Complexes: fac-Tris(phenylidibenzophosphole)tricarbonylchromium(0). To a solution of (cycloheptatriene)tricarbonylchromium(0)¹⁶ (0.1 g, 0.4 mmol) in 20 mL of benzene¹⁷ was added 0.425 g (1.63 mmol) of DBP in 20 mL of anhydrous ether. The reaction mixture was refluxed for 4 h. Removal of solvent via a rotary evaporator produced a dark orange oily product. Crystallization with CH₂Cl₂/95% ethanol produced 0.3 g (80%) of yellow crystals, mp 160–164 °C dec. Anal. Calcd for C₅₇H₃₉P₃CrO₃·CH₃OH: C, 73.38; H, 4.53. Found: C, 73.58; H, 4.50.

fac-Tris(phenylidibenzophosphole)tricarbonylmolybdenum(0). A mixture containing 0.38 g (1.46 mmol) of molybdenum hexacarbonyl, 2.03 g (7.80 mmol) of DBP, and 50 mL of acetonitrile was refluxed for 10 days. The greenish yellow solution was evaporated to dryness, resulting in a greenish powder which was found to be a mixture of the tetracarbonyl and the tricarbonyl complexes. Separation and purification as above produced 430 mg (17%) of fine yellow crystals, mp 200–204 °C dec. Anal. Calcd for C₅₇H₃₉P₃MoO₃: C, 71.26; H, 4.09. Found: C, 70.83; H, 4.24.

fac-Tris(phenylidibenzophosphole)tricarbonyltungsten(0). A mixture containing 2.10 g (8.09 mmol) of DBP, 0.70 g (2.00 mmol) of W(CO)₆, a catalytic amount of sodium borohydride (approximately 0.30 g), and 50 mL of 95% EtOH was refluxed gently for 10 h.¹⁸ The mixture was then cooled with stirring for 12 h, after which a yellow precipitate was observed. the reaction

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Table I. Crystal and Refinement Data for 1, 2, and 3

	(DBP)Cr(CO) ₅ (1)	<i>cis</i> - (DBP) ₂ Cr- (CO) ₄ (2)	<i>mer</i> -(DBP) ₃ Cr(CO) ₃ (3)
fw	452.3	684.6	916.85
a, Å	7.962 (3)	11.295 (4)	10.621 (3)
b, Å	23.122 (9)	13.381 (5)	12.476 (2)
c, Å	11.212 (4)	10.948 (3)	20.489 (8)
α, deg			92.86 (2)
β, deg	95.27 (3)	103.24 (2)	101.44 (2)
γ, deg			108.07 (2)
V, Å ³	2056 (1)	1610.7 (9)	2511.7 (9)
space group	P2 ₁ /c	P2 ₁	P1
Z	4	2	2
no. of reflctns used to determine cell constns	15	15	15
d(calcd), g/cm ³	1.46	1.41	1.44
linear abs coeff, cm ⁻¹	6.5	4.3	4.65
cryst dimens, mm	0.07 × 0.06 × 0.37	no recorded	0.08 × 0.20 × 0.38
abs factor range	0.947–0.965		
2θ range, deg	3–45	3–50	3–45
temp, K	290	290	290
scan rate, deg/min	2–29 ^a	2–29 ^a	2–29 ^a
scan range, deg below 2θ (Kα ₁)–above 2θ (Kα ₂)	±1.1	±0.9	±0.9
no. of unique data collected	2696	2347	6107
no. of data used in refinement	1071	1048	4028
I/σ(I) > n	2.5	2.5	1.5
octants	<i>h,k,±l</i>	<i>h,k,±l</i>	<i>h,±k,±l</i>
no. of params in final cycle	271	338	376
g	0.0050	0.0	0.0005
final R _F	0.070	0.067	0.068
final R _{wF}	0.074	0.067	0.065
max on final ΔF map, e Å ⁻³	0.8	0.5	0.8

^a Backgrounds were measured at each end of the scan for 0.25 of the scan time; Mo Kα radiation; graphite monochromator; λ = 0.71069 Å.

mixture was then evaporated to dryness, producing a yellow powder which was found to contain traces of pentacarbonyl and tetracarbonyl complexes. The *fac* tricarbonyl complex was then recrystallized from CH₂Cl₂/MeOH producing yellow crystals, mp 215–218 °C dec. Yield was approximately 10%. Anal. Calcd for C₅₇H₃₉P₃WO₃·CH₃OH: C, 64.48; H, 3.98. Found: C, 64.88; H, 4.03.

***mer*-Tris(phenyldibenzophosphole)tricarbonylchromium(0).** A mixture containing 1.55 g (5.96 mmol) of DBP, 0.38 g (1.73 mmol) of chromium hexacarbonyl, and 50 mL of acetonitrile was refluxed for 14 days.¹⁹ Evaporation of the orange solution on a rotary evaporator with heat produced an orange oil that was found to be a mixture of tetracarbonyl and tricarbonyl complexes. Fractional crystallization with CH₂Cl₂/MeOH produced 0.25 g (16%) of dark orange crystals in the first fraction, mp 201–205 °C. Anal. Calcd for C₅₇H₃₉P₃CrO₃: C, 74.70; H, 4.26. Found: C, 74.50; H, 4.26.

***mer*-Tris(phenyldibenzophosphole)tricarbonyltungsten(0).** A mixture containing 0.99 g (2.83 mmol) of tungsten hexacarbonyl, 4.05 g (15.6 mmol) of DBP, and 50 mL of diglyme was refluxed for 14 days. After 24 h of reflux, 0.48 g (4.21 mmol) of Me₃NO·2H₂O was added to catalyze the reaction. The green-yellow mixture was evaporated to dryness on a rotary evaporator, with heat, producing yellow crystals which were found to be a mixture of the tetracarbonyl and the tricarbonyl complexes. Separation and purification as above produced 0.35 g (12%) of yellow crystals, mp 243–245 °C dec. Anal. Calcd for C₅₇H₃₉P₃WO₃·CH₃OH: C, 64.48; H, 3.98. Found: C, 64.73; H, 3.65.

A similar procedure was followed for the *mer*-tris(phenyldibenzophosphole)tricarbonylmolybdenum(0): yield approximately 15%; mp 220–224 °C dec. Anal. Calcd for C₅₇H₃₉P₃MoO₃·CH₂Cl₂: C, 66.64; H, 3.92. Found: C, 66.79; H, 3.87. (Note: the presence

Table II. Atom Coordinates (×10⁴) for (DBP)Cr(CO)₅ (1)

atom	x	y	z
Cr	1090 (3)	6760 (1)	7192 (2)
P(1)	-1213 (5)	6117 (2)	7225 (3)
C(1)	938 (17)	6726 (6)	5489 (14)
C(2)	-379 (20)	7421 (7)	7127 (15)
C(3)	2876 (22)	7277 (7)	7134 (13)
C(4)	1277 (18)	6794 (6)	8851 (12)
C(5)	2597 (18)	6140 (7)	7300 (14)
O(1)	845 (15)	6727 (5)	4466 (10)
O(2)	-1247 (15)	7801 (5)	7138 (11)
O(3)	3949 (15)	7604 (5)	7112 (10)
O(4)	1432 (14)	6840 (4)	9886 (8)
O(5)	3585 (12)	5766 (5)	7318 (11)
C(6)	-2744 (15)	6132 (6)	5904 (11)
C(7)	-3599 (20)	6636 (6)	5603 (14)
C(8)	-4767 (22)	6661 (6)	4612 (15)
C(9)	-5175 (20)	6198 (7)	3932 (14)
C(10)	-4373 (20)	5684 (7)	4233 (14)
C(11)	-3209 (17)	5644 (6)	5223 (12)
C(12)	-2436 (16)	6162 (6)	8503 (12)
C(13)	-3257 (17)	6632 (6)	8966 (13)
C(14)	-4093 (19)	6560 (9)	9978 (14)
C(15)	-4190 (21)	6041 (9)	10513 (15)
C(16)	-3371 (18)	5576 (7)	10093 (12)
C(17)	-2545 (15)	5609 (6)	9099 (11)
C(18)	-1525 (17)	5177 (5)	8498 (12)
C(19)	-1421 (20)	4592 (7)	8859 (14)
C(20)	-510 (21)	4228 (7)	8209 (14)
C(21)	277 (2)	4404 (7)	7232 (16)
C(22)	109 (17)	4976 (6)	6888 (13)
C(23)	-797 (16)	5353 (6)	7502 (11)

of CH₂Cl₂ and methanol in some of these compounds was proved by NMR spectroscopy.)

(C) Crystal Structure Analyses. Block-like colorless crystals of DBPCr(CO)₅ (1), yellow crystals of *cis*-(DBP)₂Cr(CO)₄ (2), and red crystals of *mer*-(DBP)₃Cr(CO)₃ (3) were isolated from dichloromethane/methanol solutions. Crystal data and additional details of data collection and refinement are given in Table I. Intensity data were taken with a Syntex P2₁ diffractometer in the θ–2θ mode and corrected for Lorentz and polarization. An absorption correction was applied to 1, by the Gaussian method, but in view of the minimal correction, this was not carried out for 2 or 3. Systemic absences (*h*0*l*, *l* ≠ 2*n*; 0*k*0, *k* ≠ 2*n*) indicated space group P2₁/c for 1; 0*k*0, *k* ≠ 2*n*, indicated P2₁ or P2₁/*m* for 2, and no systematic absences were found for 3. For 1 the heavy atoms were located by Patterson techniques, and the light atoms were then found on successive Fourier syntheses. For 2 an initial Patterson synthesis in space group P2₁/*m* revealed a possible Cr position, but no other atoms could be located. Using P2₁ one Cr and two P positions were found by the Patterson interpretation section of SHELXTL, and the remaining atoms were located by Fourier techniques. Because of the weak scattering from the crystal, no attempt was made to define the hand of the individual crystal examined. Anisotropic thermal parameters were used for all non-hydrogen atoms in 1 and for all but some C atoms in 2. Hydrogen atoms were inserted at calculated positions with fixed isotropic temperature factors and were not refined. Final refinement was by least-squares methods (minimizing ∑w(F_o – F_c)²) in cascaded large blocks. Weighting schemes of the form 1/(σ²(F) + gF²) were shown to be satisfactory by weight analyses. For 3 after a number of attempts to solve the structure by direct methods had failed, it was noticed that several of the false solutions could be interpreted as a double image of the T-shaped CrP₃ unit, in which the middle P atom of one image was superimposed upon the Cr atom of the other, and the second image was shifted from the first by the corresponding Cr–P vector. In such cases²⁰ the correct solution is often exactly halfway between the two images, and that also proved to be the case here. The structure was refined with anisotropic Cr, P, carbonyls, and disordered solvent (two molecules of dichloromethane, each with

(19) Chatt, J.; Leigh, G. J.; Thankarajan, N. J. *Organomet. Chem.* 1971, 29, 105.

(20) Caira, M. R.; Giles, R. G. F.; Nassimbeni, L. R.; Sheldrick, G. M.; Hazell, R. G. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* 1976, B32, 1467.

Table III. Atom Coordinates ($\times 10^4$) for $(\text{DBP})_2\text{Cr}(\text{CO})_4$ (2)

atom	x	y	z
Cr	988 (3)	5000	7322 (3)
P(1)	2683 (5)	5905 (5)	8511 (4)
P(2)	2139 (5)	4233 (5)	6027 (5)
O(1)	297 (16)	6729 (14)	5490 (15)
O(2)	1551 (14)	3371 (12)	9259 (13)
O(3)	-663 (14)	5800 (15)	8866 (15)
O(4)	-1236 (12)	3864 (14)	5993 (13)
C(1)	559 (18)	6115 (17)	6178 (18)
C(2)	1404 (18)	3996 (16)	8514 (19)
C(3)	-7 (16)	5516 (15)	8289 (17)
C(4)	-377 (16)	4247 (18)	6505 (16)
C(11)	2402 (16)	6347 (14)	10005 (15)
C(12)	1961 (17)	7249 (16)	10151 (18)
C(13)	1648 (21)	7520 (18)	11283 (19)
C(14)	1809 (20)	6816 (17)	12279 (17)
C(15)	2269 (16)	5909 (17)	12123 (18)
C(16)	2625 (18)	5631 (16)	11010 (16)
C(17)	3253 (15)	7020 (14)	7890 (15)
C(18)	2699 (22)	7834 (15)	7252 (19)
C(19)	3316 (19)	8603 (17)	6844 (19)
C(110)	4543 (19)	8538 (19)	7081 (19)
C(111)	5146 (19)	7754 (16)	7710 (19)
C(112)	4547 (16)	6999 (15)	8168 (17)
C(113)	5092 (18)	6020 (17)	8753 (18)
C(114)	6326 (15)	5803 (16)	9111 (16)
C(115)	6591 (17)	4862 (17)	9624 (17)
C(116)	5764 (16)	4227 (17)	9809 (17)
C(117)	4539 (20)	4421 (17)	9486 (16)
C(118)	4244 (15)	5375 (14)	8986 (16)
C(21)	1411 (17)	4014 (15)	4378 (17)
C(22)	1907 (21)	3319 (18)	3649 (21)
C(23)	1411 (22)	3187 (21)	2409 (24)
C(24)	458 (19)	3740 (25)	1821 (21)
C(25)	-85 (17)	4392 (21)	2457 (19)
C(26)	434 (18)	4549 (19)	3789 (17)
C(27)	2800 (17)	3060 (18)	6608 (19)
C(28)	2297 (19)	2241 (16)	6922 (18)
C(29)	2873 (26)	1434 (21)	7464 (22)
C(210)	4187 (29)	1488 (19)	7632 (22)
C(211)	4782 (22)	2288 (17)	7366 (18)
C(212)	4057 (18)	3089 (17)	6782 (17)
C(213)	4505 (17)	4046 (15)	6313 (17)
C(214)	5753 (20)	4264 (19)	6346 (19)
C(215)	5944 (21)	5206 (19)	5852 (19)
C(216)	5094 (18)	5873 (19)	5432 (18)
C(217)	3830 (19)	5643 (15)	5442 (16)
C(218)	3616 (18)	4732 (16)	5873 (19)

one Cl distributed over two sites; occupation factors refined to 0.268 (4) for Cl_2' and 0.103 (10) for Cl_4' . Complex neutral atom scattering factors²¹ were employed. Computing was done with the SHELXTL system²² on a Data General NOVA 3, following initial processing on a Burroughs B6800. Scattering factors were taken from ref 21. Three standard reflections were monitored every 200 reflections and showed slight changes during data collection for 1, 2, and 3. The data were rescaled to correct for this. Final atom coordinates for 1, 2, and 3 are given in Tables II, III, and IV and selected bond lengths and angles in Tables V, VI, and VII, respectively.

Results and Discussion

The general preparation of the $(\text{DBP})_n\text{M}(\text{CO})_{6-n}$ complexes involves heating the reactants in a solvent at the reflux temperature until all or most of the hexacarbonyl is consumed. The degree of substitution depends upon the reaction stoichiometry, temperature, and time, increasing with increasing temperature and time. The $(\text{DBP})_2\text{M}(\text{CO})_4$ complexes appear to be the thermodynamically most stable species and were formed in varying amounts in all prep-

Table IV. Atom Coordinates ($\times 10^4$) for $\text{mer}-(\text{DBP})_3\text{Cr}(\text{CO})_3$ (3)

atom	x	y	z
Cr	2992 (1)	2431 (1)	7950 (1)
P(1)	2346 (2)	454 (1)	7816 (1)
P(2)	3853 (2)	4421 (1)	8119 (1)
P(3)	1394 (2)	2504 (1)	6970 (1)
C(11)	3587 (6)	-167 (5)	8259 (3)
C(12)	4551 (7)	-386 (6)	7965 (4)
C(13)	5447 (8)	-887 (6)	8290 (4)
C(14)	5416 (8)	-1150 (6)	8919 (4)
C(15)	4498 (8)	-942 (6)	9234 (4)
C(16)	3576 (7)	-431 (6)	8904 (4)
C(21)	772 (6)	-464 (5)	8008 (3)
C(22)	303 (7)	-387 (6)	8582 (4)
C(23)	-933 (7)	-1175 (6)	8637 (4)
C(24)	-1644 (8)	-2016 (6)	8114 (4)
C(25)	-1209 (7)	-2083 (6)	7542 (4)
C(26)	20 (7)	-1303 (5)	7476 (3)
C(31)	1895 (7)	-374 (5)	6988 (3)
C(32)	2595 (7)	-219 (6)	6487 (3)
C(33)	2088 (8)	-956 (6)	5892 (4)
C(34)	863 (8)	-1792 (7)	5806 (4)
C(35)	150 (8)	-1947 (6)	6290 (4)
C(36)	647 (7)	-1250 (5)	6904 (3)
C(41)	5499 (6)	5078 (5)	8696 (3)
C(42)	6572 (7)	4721 (6)	8623 (4)
C(43)	7879 (8)	5243 (7)	9026 (4)
C(44)	8088 (8)	6109 (6)	9513 (4)
C(45)	7052 (8)	6456 (6)	9608 (4)
C(46)	5737 (7)	5951 (6)	9201 (3)
C(51)	2864 (4)	5251 (5)	8380 (3)
C(52)	2278 (7)	5162 (5)	8918 (3)
C(53)	1550 (7)	5891 (6)	9044 (4)
C(54)	1412 (7)	6654 (6)	8600 (4)
C(55)	1984 (7)	6755 (6)	8061 (4)
C(56)	2734 (6)	6071 (5)	7934 (3)
C(61)	4140 (7)	5291 (5)	7437 (3)
C(62)	4924 (7)	5210 (6)	6979 (4)
C(63)	5052 (8)	5986 (7)	6498 (4)
C(64)	4388 (8)	6761 (7)	6490 (4)
C(65)	3610 (8)	6848 (6)	6920 (4)
C(66)	3467 (7)	6086 (5)	7418 (3)
C(71)	-119 (6)	1249 (5)	6617 (3)
C(72)	-402 (7)	737 (6)	5962 (4)
C(73)	-1594 (7)	-170 (6)	5721 (4)
C(74)	-2494 (8)	-551 (6)	6124 (4)
C(75)	-2237 (7)	-43 (6)	6760 (4)
C(76)	-1033 (7)	856 (6)	7018 (4)
C(81)	1945 (6)	3021 (5)	6223 (4)
C(82)	2756 (7)	2657 (6)	5871 (3)
C(83)	3089 (7)	3175 (6)	5310 (4)
C(84)	2609 (7)	4032 (6)	5125 (4)
C(85)	1788 (7)	4404 (6)	5462 (4)
C(86)	1445 (7)	3893 (5)	6022 (3)
C(91)	499 (6)	3545 (5)	6981 (3)
C(92)	-274 (7)	3699 (5)	7427 (3)
C(93)	-943 (7)	4499 (6)	7321 (4)
C(94)	-822 (8)	5117 (6)	6790 (4)
C(95)	-30 (7)	4992 (6)	6359 (4)
C(96)	627 (7)	4184 (5)	6441 (3)
C(1)	1686 (7)	2403 (6)	8446 (4)
O(1)	942 (5)	2372 (4)	8784 (3)
C(2)	4112 (7)	2427 (5)	8758 (3)
O(2)	4753 (5)	2417 (4)	9283 (2)
C(3)	4328 (7)	2422 (5)	7487 (4)
O(3)	5209 (5)	2424 (4)	7229 (3)
C(4)	2618 (11)	8212 (9)	700 (5)
Cl(1)	1413 (3)	8688 (3)	215 (1)
Cl(2)	2348 (5)	7906 (6)	1500 (3)
Cl(2')	1797 (16)	7168 (16)	958 (14)
C(5)	3244 (9)	7750 (7)	4066 (4)
Cl(3)	4724 (3)	8901 (2)	4362 (2)
Cl(4)	2955 (5)	6950 (3)	4716 (2)
Cl(4')	3529 (37)	6521 (30)	4253 (24)

arations. Direct displacement of three carbon monoxide groups by DBP is difficult, and preparation of $\text{mer}-(\text{DBP})_3\text{M}(\text{CO})_3$ ($\text{M} = \text{Mo}, \text{W}$) required the use of tri-

(21) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

(22) Sheldrick, G. M. SHELXTL User Manual; Nicolet: Madison, WI, 1981.

Table V. Selected Bond Distances and Angles for (DBP)Cr(CO)₅ (1)

Bond Lengths (Å)			
Cr-P(1)	2.364 (4)	Cr-C(1)	1.903 (15)
Cr-C(2)	1.922 (16)	Cr-C(3)	1.863 (17)
Cr-C(4)	1.854 (14)	Cr-C(5)	1.866 (15)
P(1)-C(6)	1.844 (12)	P(1)-C(12)	1.808 (14)
P(1)C(23)	1.820 (14)	C(1)-O(1)	1.142 (19)
C(2)-O(2)	1.118 (20)	C(3)-O(3)	1.143 (21)
C(4)-O(4)	1.161 (17)	C(5)-O(5)	1.168 (18)
C(6)-C(7)	1.364 (19)	C(6)-C(11)	1.389 (19)
C(12)-C(17)	1.450 (18)	C(18)-C(23)	1.366 (19)
C(17)-C(18)	1.487 (18)		
Bond Angles (deg)			
P(1)-Cr-C(1)	90.7 (4)	P(1)-Cr-C(2)	91.7 (5)
P(1)-Cr-C(3)	178.5 (5)	P(1)-Cr-C(4)	90.1 (5)
P(1)-Cr-C(5)	90.6 (5)	C(1)-Cr-C(4)	179.1 (6)
C(2)-Cr-C(5)	177.2 (6)	C(1)-Cr-C(5)	90.8 (6)
Cr-P(1)-C(6)	116.2 (4)	Cr-P(1)-C(12)	116.8 (4)
Cr-P(1)-C(23)	118.9 (4)	C(12)-P(1)-C(23)	91.3 (6)
P(1)-C(12)-C(17)	112.0 (9)	P(1)-C(23)-C(18)	110.1 (10)
C(6)-P(1)-C(12)	105.3 (6)	C(6)-P(1)-C(23)	104.7 (6)

Table VI. Selected Bond Distances and Angles for cis-(DBP)₂Cr(CO)₄ (2)

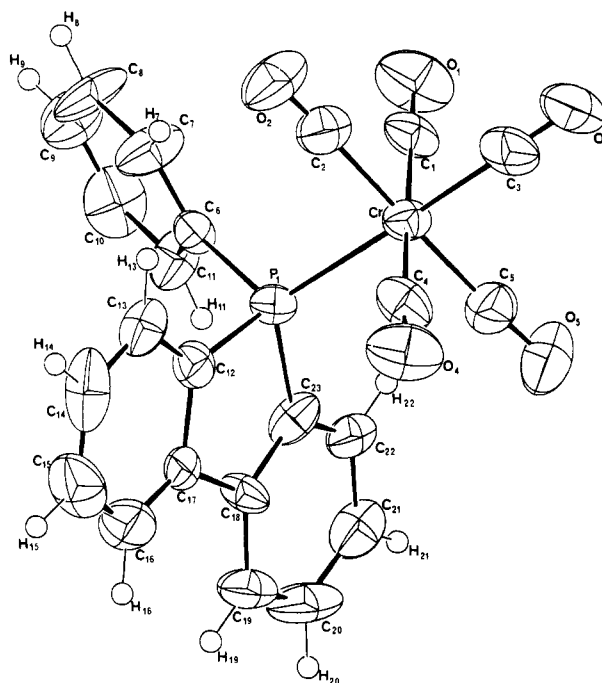
Bond Lengths (Å)			
Cr-P(1)	2.385 (6)	Cr-P(2)	2.366 (7)
Cr-C(1)	1.937 (21)	Cr-C(2)	1.857 (21)
Cr-C(3)	1.846 (21)	Cr-C(4)	1.887 (19)
P(1)-C(11)	1.834 (18)	P(1)-C(17)	1.817 (19)
P(1)-C(118)	1.861 (18)	P(2)-C(21)	1.828 (18)
P(2)-C(27)	1.791 (23)	P(2)-C(218)	1.839 (22)
C(1)-O(1)	1.107 (27)	C(2)-O(2)	1.154 (26)
C(3)-O(3)	1.143 (27)	C(4)-O(4)	1.127 (23)
C(17)-C(112)	1.423 (24)	C(112)-C(113)	1.524 (29)
C(113)-C(118)	1.357 (29)	C(27)-C(212)	1.390 (28)
C(212)-C(213)	1.510 (31)	C(213)-C(218)	1.364 (28)
Bond Angles (deg)			
P(1)-Cr-C(4)	175.4 (6)	P(1)-Cr-C(3)	90.9 (6)
P(1)-Cr-C(1)	90.7 (6)	P(2)-Cr-C(2)	91.2 (7)
C(1)-Cr-C(2)	175.8 (9)	C(3)-Cr-C(4)	86.1 (8)
P(1)-Cr-P(2)	93.7 (2)	Cr-P(1)-C(11)	111.7 (6)
Cr-P(2)-C(21)	118.5 (7)	C(17)-P(1)-C(118)	91.3 (8)
C(27)-P(2)-C(218)	92.2 (10)	P(1)-C(17)-C(112)	109.8 (13)
P(1)-C(118)-C(113)	111.7 (14)	C(112)-C(113)-C(118)	113.0 (17)
C(17)-C(112)-C(113)	113.8 (17)	P(2)-C(27)-C(212)	110.7 (17)
P(2)-C(218)-C(213)	109.5 (16)	C(27)-C(212)-C(213)	112.8 (18)
C(212)-C(213)-C(218)	114.4 (18)		

methylamine oxide. This reagent irreversibly and stoichiometrically converts coordinated CO to CO₂.²³ The *fac*-(DBP)₃Cr(CO)₃ complex was prepared by displacement of cycloheptatriene from C₇H₈Cr(CO)₃, a general synthesis developed by Wilkinson et al.²⁴ In spite of careful attempts to control the reaction conditions, a mixture of complexes was usually obtained. Their separation was accomplished by column chromatography on silica gel with a dichloromethane/hexane (30/70) eluant. The most soluble complex elutes first from the column and for each metal the solubility decreases in the order (DBP)₃M(CO)₃ > *cis*-(DBP)₂M(CO)₄ > *fac*-(DBP)₃M(CO)₃ > *mer*-(DBP)₃M(CO)₃. Column chromatography was conveniently monitored by infrared spectroscopy in the carbonyl region.

One note of interest is that the (DBP)₂M(CO)₄ complexes are exclusively *cis*. Only for (DBP)₂W(CO)₄ could a trace of the *trans* isomer be detected by ³¹P NMR (δ 15.76 ($J_{WP} = 277.7$ Hz)), but it could not be isolated. For the (DBP)₃M(CO)₃ complexes the facial isomer is the kinetic product and it undergoes thermally induced geometrical isomerization to the meridional isomer. This

Table VII. Selected Bond Distances and Angles for mer-(DBP)₃Cr(CO)₃ (3)

Bond Lengths (Å)			
Cr-P(1)	2.332 (3)	Cr-P(2)	2.345 (3)
Cr-P(3)	2.384 (3)	Cr-C(1)	1.869 (9)
Cr-C(2)	1.838 (7)	Cr-C(3)	1.859 (9)
C(1)-O(1)	1.142 (11)	C(2)-O(2)	1.156 (8)
C(3)-O(3)	1.162 (11)	P(1)-C(11)	1.842 (7)
P(1)-C(21)	1.838 (7)	P(1)-C(31)	1.836 (7)
P(2)-C(41)	1.823 (6)	P(2)-C(51)	1.817 (8)
P(2)-C(61)	1.827 (7)	P(3)-C(71)	1.850 (6)
P(3)-C(81)	1.821 (7)	P(3)-C(91)	1.834 (8)
C(21)-C(26)	1.395 (8)	C(31)-C(36)	1.405 (8)
C(26)-C(36)	1.452 (11)	C(51)-C(56)	1.425 (9)
C(56)-C(66)	1.428 (11)	C(61)-C(66)	1.389 (11)
C(81)-C(86)	1.397 (11)	C(86)-C(96)	1.444 (11)
C(91)-C(96)	1.399 (9)		
Bond Angles (deg)			
P(1)-Cr-P(2)	174.6 (1)	P(1)-Cr-P(3)	94.1 (1)
P(2)-Cr-P(3)	90.1 (1)	P(3)-Cr-C(2)	173.9 (3)
P(3)-Cr-C(1)	88.6 (2)	P(3)-Cr-C(3)	93.9 (2)
P(1)-Cr-C(2)	88.1 (2)	P(2)-Cr-C(2)	88.0 (2)
C(1)-Cr-C(3)	177.2 (3)	Cr-P(1)-C(11)	116.2 (2)
Cr-P(1)-C(21)	123.0 (3)	Cr-P(1)-C(31)	122.1 (2)
Cr-P(2)-C(41)	117.4 (2)	Cr-P(2)-C(51)	121.1 (2)
C(21)-P(1)-C(31)	89.9 (3)	C(51)-P(2)-C(61)	89.5 (3)
C(81)-P(3)-C(91)	89.9 (3)	C(11)-P(1)-C(21)	100.6 (3)
C(11)-P(1)-C(31)	99.4 (3)	C(41)-P(2)-C(51)	101.7 (3)
C(41)-P(2)-C(61)	98.5 (3)	C(71)-P(3)-C(81)	102.7 (3)
C(71)-P(3)-C(91)	97.1 (3)		

**Figure 1.** ORTEP plot of the structure of (phenyldibenzophosphole)chromium pentacarbonyl (1) showing the atom-labeling scheme (50% probability ellipsoids).

isomerization proceeds more cleanly in the presence of excess DBP and is easily visually detected by a change in the solution color from bright yellow to a deep yellow or orange. On the basis of electronic effects and the trans influence theory, the facial isomer would be expected to be the thermodynamically more stable form. Hence, steric effects (*vide infra*) may be the determining influence in the formation of the meridional isomer.²⁵

The exclusive formation of the *cis* isomer of (DBP)₂M(CO)₄ indicates that there is a strong stabilizing electronic

(23) Luh, T. Y. *Coord. Chem. Rev.* 1984, 60, 255.(24) Abel, E. W.; Bennet, M. A.; Wilkinson, G. *J. Chem. Soc.* 1959, 2323.(25) Bond, A. M.; Cotton, R.; Kevecodes, J. E. *Inorg. Chem.* 1986, 25, 749.

Table VIII. Comparison of Bond Distances for Compounds of the Type $\text{LCr}(\text{CO})_5$

ligand	Cr-P, Å	Cr-C(trans), Å	C-O(trans), Å	Cr-C(cis), Å	C-O(cis), Å	ref
Ph_3P	2.422 (1)	1.844 (4)	1.154 (5)	1.880 (4)	1.147 (6)	59
$\text{P}(\text{OPh})_3$	2.309 (1)	1.861 (4)	1.136 (6)	1.896 (4)	1.131 (6)	59
$\text{P}(\text{C}\equiv\text{CPh})_3$	2.322 (1)	1.856 (4)	1.143 (7)	1.897 (7)	1.126 (9)	60
$\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3$	2.364 (1)	1.876 (4)	1.136 (4)	1.891 (4)	1.138 (4)	61
DBP	2.364 (4)	1.86 (2)	1.14 (2)	1.89 (2)	1.15 (2)	this work

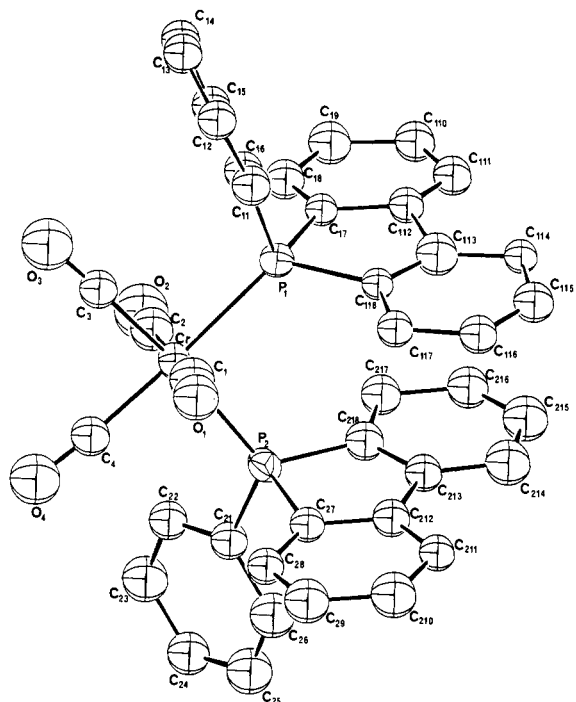


Figure 2. ORTEP plot of the structure of *cis*-bis(phenylidibenzophosphole)chromium tetracarbonyl (2) showing the atom-labeling scheme (50% probability ellipsoids).

interaction in the *cis* isomer since for ligands with steric bulk similar to DBP, the *trans* isomer is thermodynamically preferred.²⁶ The nature of this interaction is clearly revealed by X-ray crystallography. The crystal structures of $(\text{DBP})\text{Cr}(\text{CO})_5$ (1), *cis*- $(\text{DBP})_2\text{Cr}(\text{CO})_4$ (2), and *mer*- $(\text{DBP})_3\text{Cr}(\text{CO})_3$ (3) are shown in Figures 1, 2, and 3, respectively. Each complex crystallizes as discrete molecules with no unusually close intermolecular contacts. In all three structures the dibenzophosphole rings are planar and in *cis*- $(\text{DBP})_2\text{Cr}(\text{CO})_4$ and *mer*- $(\text{DBP})_3\text{Cr}(\text{CO})_3$ lie above one another such that there is a mutual overlap of these ring systems. The distances between these planes, ~ 3.4 Å in 2 and ~ 3.3 Å in 3, compare with the sum of carbons' van der Waals radii (3.30–3.40 Å), attesting to the closeness of approach of these rings. For *mer*- $(\text{DBP})_3\text{Cr}(\text{CO})_3$ there is an additional interaction between a phenyl ring and a dibenzophosphole ring separated by ~ 3.45 Å. The mutual overlap of the aromatic rings is maintained in solution for all the $(\text{DBP})_2\text{M}(\text{CO})_4$ and *mer*- $(\text{DBP})_3\text{M}(\text{CO})_3$ complexes, giving rise to diamagnetic anisotropy effects in their ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra which will be discussed later.

The crystallographic results also allow an evaluation of the donor properties of DBP in relation to other phosphorus donors. Selected bond distances and angles for $(\text{DBP})\text{Cr}(\text{CO})_5$, *cis*- $(\text{DBP})_2\text{Cr}(\text{CO})_4$, and *mer*- $(\text{DBP})_3\text{Cr}(\text{CO})_3$ are given in Tables V, VI, and VII, respectively. In each of these complexes the chromium atom is situated in a nearly regular octahedron. $(\text{DBP})\text{Cr}(\text{CO})_5$ has an

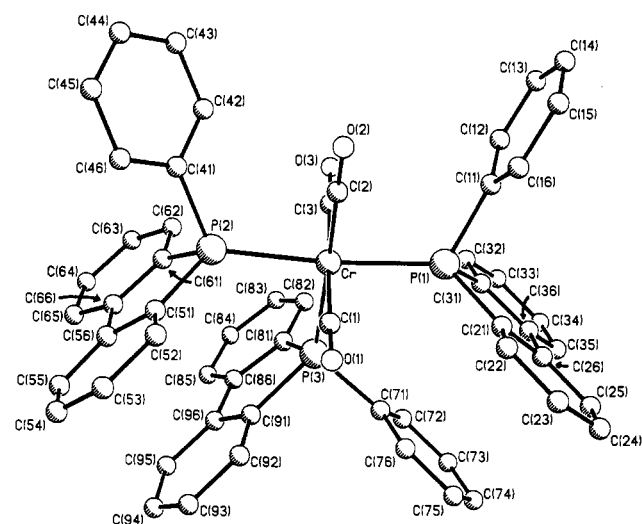


Figure 3. View of the structure of *mer*-tris(phenylidibenzophosphole)chromium tricarbonyl (3) showing the atom-labeling scheme (radii arbitrary).

average C–M–C angle of 89.6° and average P–M–C angles of 91.2° . For *cis*- $(\text{DBP})_2\text{Cr}(\text{CO})_4$ the C–M–C, P–M–C, and P–M–P angles average 89.1° , 90.1° , and 93.7° , respectively. The C–M–C, P–M–C, and P–M–P angles average 88.8° , 89.9° , and 92.1° , respectively, for *mer*- $(\text{DBP})_3\text{Cr}(\text{CO})_3$. In all three complexes there are two different Cr–C distances, with the distance to the carbon *trans* to DBP being shorter than that of the carbon *trans* to CO. For all three complexes these distances average 1.849 (2) and 1.886 (2) Å, respectively. An opposite trend is observed for the CO bond lengths where for $(\text{DBP})\text{Cr}(\text{CO})_5$ these are 1.143 (2) and 1.147 (2) Å, for $(\text{DBP})_2\text{Cr}(\text{CO})_4$ these are 1.122 (5) and 1.153 Å, and for $(\text{DBP})_3\text{Cr}(\text{CO})_3$ these are 1.152 (7) and 1.156 (9) Å. The Cr–C distance decreases and the CO distance increases in the sequence $(\text{DBP})\text{Cr}(\text{CO})_5$, $(\text{DBP})_2\text{Cr}(\text{CO})_4$, $(\text{DBP})_3\text{Cr}(\text{CO})_3$. All these trends are consistent with CO being a better π -acceptor than DBP. Since there are only three d orbitals with π -symmetry in an octahedral environment, the maximum Cr–CO π -back-bonding should result for *fac*- $(\text{DBP})_3\text{Cr}(\text{CO})_3$.

The structural data for other $\text{R}_3\text{PCr}(\text{CO})_5$ complexes is compared with that of $(\text{DBP})\text{Cr}(\text{CO})_5$ in Table VIII. From these data, particularly the Cr–P distances, we may conclude that the donor ability of these ligands toward Cr(0) follows the sequence $\text{P}(\text{OPh})_3 > \text{P}(\text{C}\equiv\text{CPh})_3 > \text{P}(\text{CH}_2\text{CH}_2\text{CN})_3 \approx \text{DBP} > \text{PPh}_3$.

Infrared Spectroscopy. The $(\text{DBP})_n\text{M}(\text{CO})_{6-n}$ complexes are easily differentiated by the number and frequency of their ν_{CO} vibrations. Due to solubility limitations all spectra were recorded in CH_2Cl_2 and the data are given in Table IX. The frequency of the CO vibrations could be used as an indicator of the CO bond strengths²⁷ and hence as an indirect measure of the DBP donor properties. A better approach is to consider the CO force constants (Table IX) evaluated by the Cotton–Kraihanzel²⁸ calcu-

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Table IX. Infrared Spectral Data (in CH₂Cl₂ Solutions) in the ν_{CO} Region and Force Constants for (DBP)_nM(CO)_{6-n} Derivatives

(DBP) _n M(CO) _{6-n}	$\nu_{\text{CO}}, \text{cm}^{-1}$				k_1	k_2	k_3
	A ₁ ⁽¹⁾	B ₁	A ₁ ⁽²⁾	E			
(DBP)Cr(CO) ₅	2066	1990 (sh)	1946	1946	15.52	15.99	0.349
(DBP)Mo(CO) ₅	2073	1993 (sh)	1952	1952	15.60	16.04	0.326
(DBP)W(CO) ₅	2072	1986 (sh)	1940	1943	15.47	15.93	0.342
(DBP) ₂ M(CO) ₄	$\nu_{\text{CO}}, \text{cm}^{-1}$				k_1	k_2	k_3
	A ₁ ⁽¹⁾	A ₁ ⁽²⁾	B ₁	B ₂			
(DBP) ₂ Cr(CO) ₄	2007	1923 (sh)	1897	1897	14.80	15.47	0.272
(DBP) ₂ Mo(CO) ₄	2019	1930 (sh)	1908	1908	14.99	15.61	0.287
(DBP) ₂ W(CO) ₄	2016	1925 (sh)	1899	1899	14.85	15.55	0.295
(DBP) ₃ M(CO) ₃	$\nu_{\text{CO}}, \text{cm}^{-1}$		k	k_i			
	A ₁	E					
	<i>fac</i> -(DBP) ₃ Cr(CO) ₃	1935	1845	14.20	0.458		
	<i>fac</i> -(DBP) ₃ Mo(CO) ₃	1947	1853	14.35	0.481		
<i>fac</i> -(DBP) ₃ W(CO) ₃	1943	1848	14.28	0.485			
(DBP) ₃ M(CO) ₃	$\nu_{\text{CO}}, \text{cm}^{-1}$						
	A ₁ ⁽¹⁾	A ₁ ⁽²⁾	B ₁	k_1	k_2	k_i	
	<i>mer</i> -(DBP) ₃ Cr(CO) ₃	1953	1862 (sh)	1845	14.20	14.47	0.360
	<i>mer</i> -(DBP) ₃ Mo(CO) ₃	1972	1863 (sh)	1863	14.14	14.80	0.390
<i>mer</i> -(DBP) ₃ W(CO) ₃	1965	1869 (sh)	1852	14.33	14.61	0.378	

^aData believed to be accurate to $\pm 1 \text{ cm}^{-1}$.

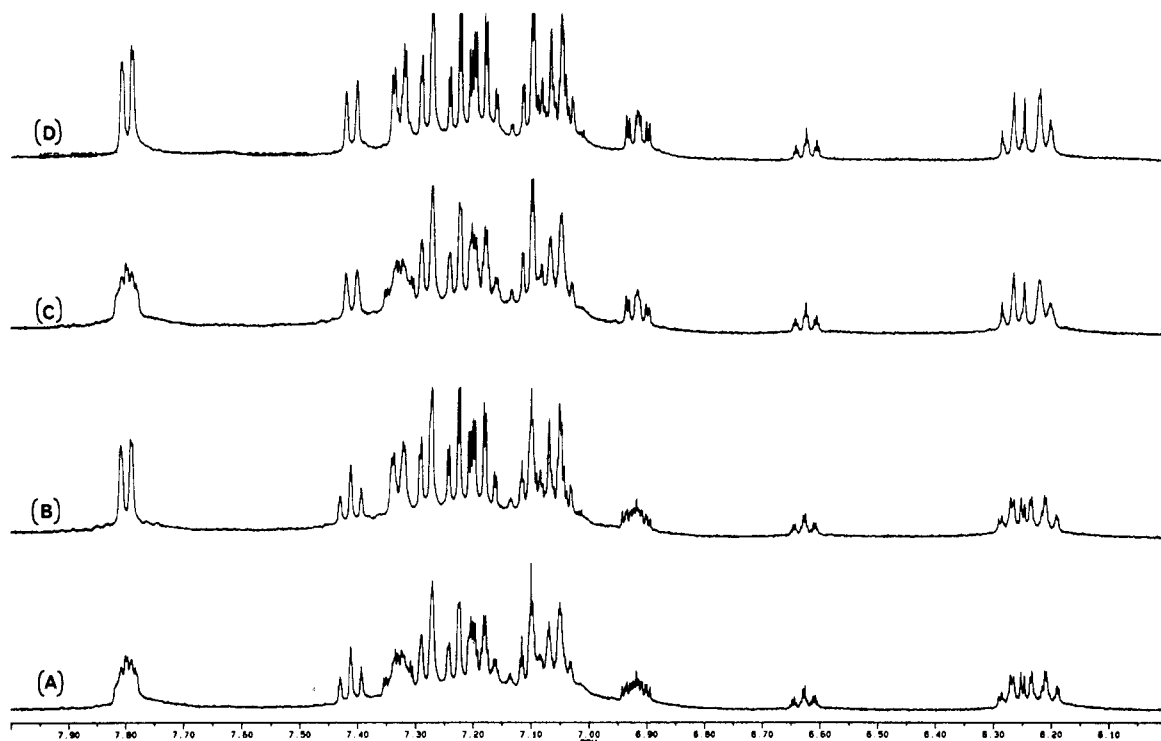


Figure 4. 400-MHz ¹H (A), ¹H{³¹P} selective, P₁, P₂ irradiated (B) ¹H{³¹P} selective, P₃ irradiated (C), and ¹H{³¹P} broad-band decoupled (D) NMR spectra of *mer*-(DBP)₃Mo(CO)₃ in CDCl₃ at 298 °C.

lations and analyzed by using Graham's²⁹ approximations to obtain σ - and π -bonding parameters (Table X). On the basis of these parameters for R₃PMo(CO)₅ complexes, we conclude that the sequence of σ -donor abilities towards Mo(0) is P(CH₂CH₂CN)₃ > P(*n*-C₄H₉)₃ > DMPP > PPh₃ > P(OPh)₃ > DBP > P(C≡CPh)₃ and the π -acceptor abilities follow the sequence P(CH₂CH₂CN)₃ > P(*n*-C₄H₉)₃ \approx P(OPh)₃ > DMPP > DBP > PPh₃ > P(C≡CPh)₃. This π -acceptor ordering is not intuitively in keeping with expectations based upon the electronegativity of the groups

on phosphorus. In theory Graham's method is simple and quite reasonable. But, because it is based upon small differences in large numbers, in practice the results are often not reasonable.

¹H NMR Spectroscopy. The proton NMR spectra of the (DBP)_nM(CO)₅ complexes were assigned by previously described techniques⁸ and were used to aid in the assignments of the second-order spectra observed for (DBP)₂M(CO)₄ and (DBP)₃M(CO)₃ (Table XI, supplementary material). The values of the H-H coupling constants for all these molecules are essentially the same as for the free ligand itself.⁸ Several of the PH coupling constants increase, in some cases substantially, upon coordination. This is particularly true for ⁴J(PH₁), ⁴J(PH₄), ³J(PH₆), and

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Table X. σ - and π -Bonding Parameters for Pentacarbonyl Molybdenum Complexes^a

L in LMo(CO) ₅	force constants, mdyn/Å			$\Delta\sigma$, mdyn/Å	$\Delta\pi$ mdyn/Å
	k_1	k_2	k_3		
PPh ₃ ^b	15.49	15.96	0.30	-0.15	0.27
P(OC ₆ H ₅) ₃ ^b	15.93	16.19	0.29	-0.13	0.48
P(<i>n</i> -C ₄ H ₉) ₃ ^b	15.58	15.84	0.30	-0.48	0.48
P(C≡CPh) ₃ ^c	15.18	16.09	0.29	0.42	-0.17
P(CH ₂ CH ₂ CN) ₃ ^d	15.36	15.59	0.10	-0.85	0.51
DMPP ^e	15.62	16.01	0.29	-0.18	0.35
DBP	15.58	16.02	0.29	-0.12	0.30

^aData are based on measurements taken in hexane solutions except where noted. ^bReference 29. ^cCalculated from frequencies measured in cyclohexane solution ref 30. ^dCalculated from frequencies measured in dichloromethane solution ref 59. ^eDMPP = 1-phenyl-3,4-dimethylphosphole.

⁴J(PH_m). Such increases are normal.³⁰ Complete assignment of the (DBP)₃M(CO)₃ spectra required selective ¹H{³¹P} experiments, and a typical example is illustrated in Figure 4. In comparing the ¹H chemical shifts of free and coordinated DBP in (DBP)₃M(CO)₅, we observe that there is a downfield shift of all proton resonances upon coordination as is anticipated from previous observations.^{8,30} This downfield shift is not as large as that observed for DBP=O for the phenyl protons. The phenyl protons subtend the magnetically anisotropic^{31,32} CO's, and hence the diamagnetic shielding of the CO groups offsets the expected downfield shift due to coordination. This upfield shift is even more obvious for (DBP)₂M(CO)₄ and (DBP)₃M(CO)₃. For these complexes all of the proton resonances of the DBP rings occur upfield of those of the free ligand. We attribute the upfield shift to the diamagnetic anisotropy³³ of the dibenzophosphole rings. For the *cis*-(DBP)₂M(CO)₄ complexes, the shift increase probably results from the mutual overlap of the dibenzophosphole rings as observed in the crystal structure of *cis*-(DBP)₂Cr(CO)₄.

If these rings were frozen in a partially overlapped structure as they are in the solid state, the two halves of the dibenzophosphole rings would be symmetry distinct. In this case two sets of DBP resonances would result, but only one set of ring proton resonances is observed for each (DBP)₂M(CO)₄ complex. Hence, the DBP groups are undergoing a scissor-type librational motion rendering the two dibenzophosphole rings fully eclipsed and symmetry-related on average. The chemical shifts of the phenyl protons are essentially the same as those of the free ligand. This is due to the counterbalancing effects of a downfield shift due to coordination and an upfield shift due to the adjacent magnetically anisotropic CO's. The chemical shift of H_p is downfield of the free ligand because it is remote from the CO's.

There is also only one set of resonances for the *fac*-(DBP)₃M(CO)₃ complexes, but here the spin system is much more complicated, the lines are somewhat broadened, and P-H coupling is only observed for a few of the protons. Hence, for these molecules, there is probably intermediate rate ligand rotation and/or exchange.

The ¹H NMR spectra of the *mer*-(DBP)₃M(CO)₃ complexes show two sets of resonances for each proton with 2:1 intensity ratios (Figure 4). These have line shapes typical of isolated [AX]₂ and AX spin systems and as a

result can be analyzed individually. The large difference in the chemical shifts for each proton type results from the magnetic anisotropy effects discussed above and suggests that the solution structure like that in the solid state contains overlapping dibenzophosphole and phenyl rings.

¹³C{¹H} NMR Spectroscopy. The 100-MHz ¹³C{¹H} NMR assignments (Table XII, supplementary material) were made by the previously described techniques.⁸ Several trends in the data can be seen. The same diamagnetic anisotropy effects that were evident in the ¹H NMR data are also found in the ¹³C NMR data but are less pronounced. Hence, the ¹³C data support the arguments based upon the ¹H NMR data that in the (DBP)₂M(CO)₄ and (DBP)₃M(CO)₃ complexes the orientations of the DBP planes are essentially the same in solution and in the solid state.

Analysis of the carbonyl chemical shifts reveals that the carbonyl resonances of (DBP)_nM(CO)_{6-n} are at lower field than those of the M(CO)₆ parents. This is contrary to expectations if we simply consider variations in the ¹³C carbonyl chemical shift as being dominated by contributions from local diamagnetic shielding or the dependence of paramagnetic shielding upon electron density.³⁴ We would have expected a deshielding of the carbonyl resonance since DBP like other phosphines has a high σ -donor/ π -acceptor ratio relative to CO.³⁵ The best explanation for this behavior³⁶ is that increased π -back-bonding increases the electron density on oxygen and decreases the electron density on carbon. The metal CO π -back-bonding should increase M(CO)₆ < DBPM(CO)₅ < (DBP)₂M(CO)₄ < (DBP)₃M(CO)₃, and the trends in the CO chemical shifts support this explanation.

There is also an increase in these chemical shifts with a decrease in the size of the metal in line with more effective overlap between metal d and carbon p orbitals. The chemical shifts of the carbonyl carbons trans to DBP are always downfield of those cis to DBP, reflecting greater metal CO π -back-bonding for the trans CO's. Since there is an apparent deshielding of the carbonyl resonance with increasing metal-carbon π -back-bonding, the carbonyl chemical shifts should give an indication of the donor/acceptor ratio of phosphorus ligands. For a series of R₃PCr(CO)₅ complexes the ratio obtained increases in the order^{34,37,38} P(OPh)₃ < P(OMe)₃ < PH₃ < DBP < PPh₃ < PEt₃ < PR₃ (R = butyl, pentyl, hexyl). From this we conclude that DBP is a weaker σ -donor and/or a stronger π -acceptor than PPh₃ which is consistent with the structural and infrared data.

The magnitudes of ²J(PMC) to the trans CO's are always larger than to those to the cis CO's except for (DBP)Cr(CO)₅. This behavior has been observed for several other ligands.^{34,37,39} The larger magnitude of the trans coupling has been attributed³⁹ to the larger mutual polarizability when a phosphine is trans to CO. Double-resonance experiments⁴⁰ indicate that the signs of ²J(PWC) in tungsten carbonyl complexes are positive for trans couplings and negative for cis couplings, and such is probably the case for (DBP)W(CO)₅.

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Table XIII. ^{31}P NMR Data for the Complexes $(\text{DBP})_n\text{M}(\text{CO})_{6-n}$

compd	$\delta(^{31}\text{P})$	$\Delta\delta(^{31}\text{P})$		$\Delta\Delta\delta(^{31}\text{P})(\text{obsd} - \text{calcd})$ (% diff)
		obsd	calcd	
DBP	-10.66			
$(\text{DBP})\text{Cr}(\text{CO})_5$	49.05	59.71	62.01	-2.3 (3.7)
$(\text{DBP})\text{Mo}(\text{CO})_5$	29.25	39.91	41.70	-1.79 (4.3)
$(\text{DBP})\text{W}(\text{CO})_5$	9.26 ($J_{\text{WP}} = 232$ Hz)	19.92	22.78	-2.86 (12.6)
$(\text{DBP})_2\text{Cr}(\text{CO})_4$	48.32	58.98	60.01	-1.03 (1.7)
$(\text{DBP})_2\text{Mo}(\text{CO})_4$	30.43	41.09	45.35	-4.26 (9.4)
$(\text{DBP})_2\text{W}(\text{CO})_4$	9.51 ($J_{\text{WP}} = 232$ Hz)	20.17	20.82	-0.65 (3.1)
<i>fac</i> - $(\text{DBP})_3\text{Cr}(\text{CO})_3$	48.32	58.98	66.90	-7.92 (11.8)
<i>fac</i> - $(\text{DBP})_3\text{Mo}(\text{CO})_3$	26.58	37.24	37.61	-0.37 (1.0)
<i>fac</i> - $(\text{DBP})_3\text{W}(\text{CO})_3$	8.48 ($J_{\text{WP}} = 219.7$ Hz)	19.14	18.69	0.45 (2.4)
<i>mer</i> - $(\text{DBP})_3\text{Cr}(\text{CO})_3$	62.20 (d), 35; 48.35 (t), 35	72.86, 59.01	74.22, 62.84	-1.36 (1.8), -3.83 (6.1)
<i>mer</i> - $(\text{DBP})_3\text{Mo}(\text{CO})_3$	40.08 (d), 17.3; 29.7 (t), 17.3	50.74, 40.45	49.26, 36.93	1.48 (3.0), 3.52 (9.5)
<i>mer</i> - $(\text{DBP})_3\text{W}(\text{CO})_3$	13.92 (d, $J_{\text{WP}} = 268.6$ Hz), 9.8; 8.84 (t), 9.8	24.58, 19.14	23.42, 18.49	1.16 (5.0), 0.65 (3.5)

^{31}P NMR Spectroscopy. All complexes except for *mer*- $(\text{DBP})_3\text{M}(\text{CO})_3$ exhibit a single ^{31}P resonance (Table XIII). The coordination chemical shift ($\Delta\delta(^{31}\text{P}) = \delta(^{31}\text{P})_{\text{complex}} - \Delta\delta(^{31}\text{P})_{\text{ligand}}$) might be expected to be a measure of the σ -donor ability of the ligand. On the basis of the magnitude of $\Delta\delta(^{31}\text{P})$, DBP appears to be a slightly poorer donor than PPh_3 ,⁴¹ though the small $\Delta\delta$ may simply be a reflection of the DBP ligand's inability to change its C-P-C angles as readily as PPh_3 . For a given metal the coordination chemical shift is essentially independent of the number of DBP ligands that are coordinated as long as the trans ligand is a carbonyl. Coordination trans to DBP as in *mer*- $(\text{DBP})_3\text{M}(\text{CO})_3$ brings about a much larger coordination chemical shift as a result of the lower trans influence of DBP than of CO. The value of $^1J_{\text{WP}}$ is the same for $(\text{DBP})\text{W}(\text{CO})_5$ and *cis*- $(\text{DBP})_2\text{W}(\text{CO})_4$ (232 Hz) but decreases to 220 Hz in *fac*- $(\text{DBP})_3\text{W}(\text{CO})_3$ and increases to 269 Hz for the mutually trans phosphorus nuclei in *mer*- $(\text{DBP})_3\text{W}(\text{CO})_3$. Grim⁴² has observed a larger value of $^1J_{\text{WP}}$ for *trans*- $(\text{Bu}_3\text{P})_2\text{W}(\text{CO})_4$ (280 Hz) than for $(\text{Ph}_3\text{P})\text{W}(\text{CO})_5$ (265 Hz). The value of $^2J_{\text{PP}}$ for *mer*- $(\text{DBP})_3\text{M}(\text{CO})_3$ decreases with increasing size of the metal as is commonly observed in transition-metal phosphine complexes.⁴³

Previous authors⁴⁴ have demonstrated that there is a good correlation between $\Delta\delta(^{31}\text{P})$ and the free ligand chemical shift of the form $\Delta\delta(^{31}\text{P}) = A\delta_{\text{ligand}} + B$. The A value⁴⁴ in this equation reflects the phosphorus substituent effects and polarizability while the B value approximates the average coordination chemical shift. We have collected all the available ^{31}P data for complexes of the type $\text{L}_n\text{M}(\text{CO})_{6-n}$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}; n = 1-3$) and determined new correlation equations therefrom (Table XIV). The calculated $\Delta\delta(^{31}\text{P})$ values (Table XIII) were determined by using these equations and agree well with the experimental values. On this basis we conclude that the donor properties of DBP are those of a typical phosphine.

The one-bond tungsten-phosphorus coupling constant is also anticipated to be a measure of the phosphorus-tungsten bond strength. On the basis of this coupling constant for $\text{R}_3\text{PW}(\text{CO})_5$ complexes⁴⁵ the following order

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Table XIV. Values of A and B in the Equation $\Delta\delta_{\text{calcd}} = A\delta_{\text{free}} + B$ for a Variety of Complexes of the Type $\text{L}_n\text{M}(\text{CO})_{6-n}$ ($n = 1-3$; $\text{L} = \text{Phosphines}$)^a

$\text{LM}(\text{CO})_5$	A	B	r^2	n
Cr	-0.153	60.38	0.775	24
Mo	-0.142	40.19	0.944	20
W	-0.128	21.42	0.614	19
<i>cis</i> - $\text{L}_2\text{M}(\text{CO})_4$	A	B	r^2	n
Cr	-0.196	57.92	0.765	9
Mo	-0.136	43.90	0.809	11
W	-0.138	19.35	0.879	13
<i>fac</i> - $\text{L}_3\text{M}(\text{CO})_3$	A	B	r^2	n
Cr	-0.216	64.60	0.885	4
Mo	-0.105	36.49	0.648	7
W	-0.094	17.69	0.998	3
<i>mer</i> - $\text{L}_3\text{M}(\text{CO})_3$ ^b	A	B	r^2	n
Cr	-0.111	61.66	0.955	3
	-0.142	72.71	0.993	3
Mo	-0.093	35.94	0.582	5
	-0.091	48.29	0.838	5
W	-0.109	17.33	0.997	3
	-0.102	22.33	0.991	3

^aThe correlation coefficients r^2 and the numbers of compounds of each type examined (n) are also given. ^bThe first entry corresponds to the pair of mutually trans phosphines.

Table XV. ^{17}O NMR Chemical Shift for $(\text{DBP})_n\text{M}(\text{CO})_{6-n}$ Complexes

compd	$\delta(^{17}\text{O})$		$\Delta\delta(^{17}\text{O})$ ^c	
	<i>cis</i> ^b	<i>trans</i>	<i>cis</i>	<i>trans</i>
$\text{Cr}(\text{CO})_6$ ^a	375.3			
$(\text{DBP})\text{Cr}(\text{CO})_5$	370.4	not obsd	-4.9	...
$(\text{DBP})_2\text{Cr}(\text{CO})_4$	375.0	377.5	-0.3	2.2
<i>fac</i> - $(\text{DBP})_3\text{Cr}(\text{CO})_3$	354.4		-20.9	
<i>mer</i> - $(\text{DBP})_3\text{Cr}(\text{CO})_3$	376.2	not obsd	+0.9	...
$\text{Mo}(\text{CO})_6$ ^a	364.9			
$(\text{DBP})\text{Mo}(\text{CO})_5$	370.4	372.0	5.5	7.1
$(\text{DBP})_2\text{Mo}(\text{CO})_4$	366.9	369.0	2.0	4.1
<i>fac</i> - $(\text{DBP})_3\text{Mo}(\text{CO})_3$	345.1		-19.8	
<i>mer</i> - $(\text{DBP})_3\text{Mo}(\text{CO})_3$	378.4	not obsd	13.5	...
$\text{W}(\text{CO})_6$ ^a	355.5			
$(\text{DBP})\text{W}(\text{CO})_5$	352.2	354.4	-3.3	-1.1
$(\text{DBP})_2\text{W}(\text{CO})_4$	357.5	359.5	2.0	4.0
<i>fac</i> - $(\text{DBP})_3\text{W}(\text{CO})_3$	333.9		-21.6	
<i>mer</i> - $(\text{DBP})_3\text{W}(\text{CO})_3$	356.2	not obsd	0.7	...

^aValues taken from ref 38. ^b*Cis* indicates oxygens that are *cis* to phosphorus. ^c $\delta\Delta(^{17}\text{O}) = \delta(^{17}\text{O})_{\text{L}_n\text{M}(\text{CO})_{6-n}} - \delta(^{17}\text{O})_{\text{M}(\text{CO})_6}$.

of phosphorus donor abilities obtains: $\text{P}(\text{n-Bu})_3$ (227 Hz) < PMe_2Ph (230) < DBP (232) < PBu_2Ph (235) < PMePh_2 (245) = PPh_3 (245)⁴⁶ < PBuPh_2 (250) < $\text{P}(\text{NMe}_2)_3$ (297) < $\text{P}(\text{OMe})_3$ (398).

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Table XVI. ^{95}Mo NMR Data^a for $(\text{DBP})_n\text{Mo}(\text{CO})_{6-n}$ ($n = 1-3$)

complex	δ (mult, J (Hz))	$\Delta\delta(^{95}\text{Mo})^c$	$w_{1/2}$, Hz
$\text{Mo}(\text{CO})_6^b$	-1857	0	4
$(\text{DBP})\text{Mo}(\text{CO})_5$	-1795 (d, 132)	62	38
$(\text{DBP})_2\text{Mo}(\text{CO})_4$	-1714 (t, 134)	143	58
<i>fac</i> -(DBP) $_3\text{Mo}(\text{CO})_3$	-1494 (q, 126)	363	15

^a In CDCl_3 at 297 K. Abbreviations d, doublet; t, triplet; q, quartet. ^b Reference 47. ^c $\Delta\delta = \delta_{\text{complex}} - \delta_{\text{Mo}(\text{CO})_6}$.

^{17}O NMR Spectroscopy. The ^{17}O chemical shifts of the $(\text{DBP})_n\text{M}(\text{CO})_{6-n}$ complexes (Table XV) range from 350 to 380 ppm and have varying half-widths (16–110 Hz). Due to the low natural abundance of ^{17}O and solubility limitations the resonances of the carbonyl oxygens trans to DBP were often not observed. The ^{17}O resonance generally moves upfield as π -back-bonding to CO increases. Note in particular the difference in chemical shifts between $\text{M}(\text{CO})_6$ and the corresponding *fac*-(DBP) $_3\text{M}(\text{CO})_3$ complexes and that the change is nearly independent of the nature of the metal. This is opposite to the trend observed for the carbonyl carbon chemical shifts and has been interpreted by Todd and co-workers.³⁶ They suggested that an increase in π -back-donation from the metal to the carbonyl increases the oxygen and decreases the carbon electron density.

^{95}Mo NMR Spectroscopy. The ^{95}Mo NMR data (Table XVI) were readily obtained for three of the molybdenum complexes due to the relatively narrow (<60 Hz) line widths of their resonances. In contrast, numerous attempts to record the ^{95}Mo NMR spectrum for solutions of *mer*-(DBP) $_3\text{Mo}(\text{CO})_3$ were unsuccessful. We attribute this to the low solubility of this complex and the expectedly wider line width of the anticipated multiplet. The $^1J_{\text{MoP}}$ observed for the three complexes was clearly resolved and did not differ significantly with the degree of carbonyl substitution, as observed for a wide variety of phosphine ligands.^{47,48} As with $^1J_{\text{WP}}$, $^1J_{\text{MoP}}$ is less than the $^1J_{\text{MoP}}$ values observed for the analogous Ph_3P complexes.⁴⁷ Similarly, relatively lower coupling constants are known for some comparable platinum and mercury complexes,⁴⁹ suggesting the general conclusion that DBP has lower bond strengths than Ph_3P toward metal ions. The magnitude of $^1J_{\text{MoP}}$ for a series of $\text{R}_3\text{PMo}(\text{CO})_5$ complexes, which is expected⁵⁰ to be influenced by the same effects as is the $^1J_{\text{WP}}$ coupling constant (vide supra), suggests the following order of donor ability: $\text{P}(n\text{-Bu})_3$ (129 Hz) < DBP (132) < Ph_2PEt (137) < PPh_3 (139) < $\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3$ (140) < $\text{P}(\text{OMe})_3$ (216).

The differing coordination ability of DBP as compared to PPh_3 is more dramatically and accurately shown by the ^{95}Mo NMR chemical shift data. It is well established^{47,48} that chemical shifts for this quadrupolar nucleus ($I = 5/2$, 15.7% natural abundance) are explicable in terms of the Ramsey expression for paramagnetic shielding. The dominance of the ΔE term, involving the HOMO – LUMO energy gap, for a given series such as $\text{LMo}(\text{CO})_5$ or $\text{L}_2\text{Mo}(\text{CO})_4$, results in $\delta(^{95}\text{Mo})$ being a sensitive probe of the position of a ligand L in the spectrochemical series. Comparing $\delta(^{95}\text{Mo})$ values⁴⁷ for some $\text{LMo}(\text{CO})_5$ complexes [$\text{P}(n\text{-Bu})_3$ (-1843), $\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3$ (-1795), DBP (-1795), Ph_2PEt (-1789), PPh_3 (-1743)] or for some *cis*- $\text{L}_2\text{Mo}(\text{CO})_4$

Table XVII. Correlation Coefficients (r^2) Calculated between ν_{CO} Stretching Force Constants and Various Chemical Shifts for the $(\text{DBP})\text{M}(\text{CO})_5$ Complexes ($\text{M} = \text{Cr, Mo, W}$)

	$\delta(^{13}\text{C}_{\text{trans}})$	$\delta(^{13}\text{C}_{\text{cis}})$	$\delta(^{17}\text{O}_{\text{cis}})$	$\delta(^{31}\text{P})$
k_2	0.129			0.147
k_1		0.238	0.794 ^a	0.659
$\delta(^{13}\text{C}_{\text{trans}})$				0.999 ^b
$\delta(^{13}\text{C}_{\text{cis}})$			0.690	0.996 ^c
$\delta(^{17}\text{O}_{\text{cis}})$				0.867 ^d

^a $\delta(^{17}\text{O}) = 170.0k_1 - 2353$. ^b $\delta(^{31}\text{P}) = 1.784\delta(^{13}\text{C}_{\text{trans}}) - 34.5$; $\delta(^{13}\text{C})$ 220.7 (Cr), 209.0 (Mo), 198.4 (W). ^c $\delta(^{31}\text{P}) = 1.992\delta(^{13}\text{C}_{\text{cis}}) - 380.5$; $\delta(^{13}\text{C})$ 216.1 (Cr), 205.0 (Mo), 196.2 (W). ^d $\delta(^{31}\text{P}) = 1.642\delta(^{17}\text{O}_{\text{cis}}) - 569.2$.

Table XVIII. Correlation Coefficients (r^2) Calculated between ν_{CO} Stretching Force Constants and Various Chemical Shifts for the $(\text{DBP})_2\text{M}(\text{CO})_4$ Complexes ($\text{M} = \text{Cr, Mo, W}$)

	$\delta(^{13}\text{C}_{\text{trans}})$	$\delta(^{13}\text{C}_{\text{cis}})$	$\delta(^{17}\text{O}_{\text{trans}})$	$\delta(^{17}\text{O}_{\text{cis}})$	$\delta(^{31}\text{P})$
k_2	0.089		0.050		0.044
k_1		0.422		0.285	0.283
$\delta(^{13}\text{C}_{\text{trans}})$			0.993 ^a		0.994 ^b
$\delta(^{13}\text{C}_{\text{cis}})$				0.985 ^c	0.979 ^d
$\delta(^{17}\text{O}_{\text{trans}})$					1.000 ^e
$\delta(^{17}\text{O}_{\text{cis}})$					1.000 ^f

^a $\delta(^{17}\text{O}_{\text{trans}}) = 0.857\delta(^{13}\text{C}_{\text{trans}}) + 185.4$; $\delta(^{13}\text{C})$ 224.5 (Cr), 213.2 (Mo), 203.5 (W). ^b $\delta(^{31}\text{P}) = 1.853\delta(^{13}\text{C}_{\text{trans}}) - 336.8$. ^c $\delta(^{17}\text{O}_{\text{cis}}) = 0.858\delta(^{13}\text{C}_{\text{cis}}) + 185.8$; $\delta(^{13}\text{C})$ 221.2 (Cr), 209.7 (Mo), 201.6 (W). ^d $\delta(^{31}\text{P}) = 1.958\delta(^{13}\text{C}_{\text{cis}}) - 383.2$. ^e $\delta(^{31}\text{P}) = 2.157\delta(^{17}\text{O}_{\text{trans}}) - 765.8$. ^f $\delta(^{31}\text{P}) = 2.218\delta(^{17}\text{O}_{\text{cis}}) - 783.4$.

Table XIX. Correlation Coefficients (r^2) Calculated between ν_{CO} Force Constants and Various Chemical Shifts for the *fac*-(DBP) $_3\text{M}(\text{CO})_3$ Complexes ($\text{M} = \text{Cr, Mo, W}$)

	$\delta(^{13}\text{C})$	$\delta(^{17}\text{O})$	$\delta(^{31}\text{P})$
k	0.073	0.237	0.333
$\delta(^{13}\text{C})$		0.946 ^a	0.888 ^b
$\delta(^{17}\text{O})$			0.696

^a $\delta(^{17}\text{O}) = 1.687\delta(^{13}\text{C}) - 19.16$; $\delta(^{13}\text{C})$ 220.2 (Cr), 217.4 (Mo), 208.9 (W). ^b $\delta(^{31}\text{P}) = 3.18\delta(^{17}\text{O}) - 656.9$.

complexes [$\text{P}(n\text{-Bu})_3$ (-1743), $\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3$ (-1737), DBP (-1714), Ph_2PEt (-1657), PPh_3 (-1556)] leads to the same conclusion. The lower σ -donor ability of DBP relative to that of PPh_3 is more than compensated for by the greater π -acceptor character of the phosphole. The similarity of DBP and $\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3$ as ligands, as judged by the $\delta(^{95}\text{Mo})$ data, is especially noteworthy and strongly corroborates our conclusions based on structural and infrared comparisons.

Correlations among NMR Data. It has been demonstrated that a systematic variation in the steric and electron properties of donor ligands would lead to corresponding changes in the chemical shifts and coupling constants of the NMR-active nuclei in their metal carbonyl complexes.^{51,52} Numerous workers have reported good correlations between ^{13}C and ^{17}O chemical shifts,^{53,54} between aromatic C(1) and ^{95}Mo ,⁵¹ and between ^{13}C and ^{31}P chemical shifts.⁵⁵ Good to excellent correlations have also been found between carbonyl ^{13}C chemical shifts and infrared CO stretching force constants,^{34,35,53,56} between

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Table XX. Correlation Coefficients (r^2) Calculated between ν_{CO} Stretching Force Constants and Various Chemical Shifts for the *mer*-(DBP)₃M(CO)₃ Complexes (M = Cr, Mo, W)

	$\delta(^{13}\text{C}_{\text{trans}})$	$\delta(^{13}\text{C}_{\text{cis}})$	$\delta(^{17}\text{O}_{\text{cis}})$	$\delta(^{31}\text{P}_1)^a$	$\delta(^{31}\text{P}_2)^a$
k_2	0.376			0.488	0.496
k_1		0.288	0.031	0.149	0.143
$\delta(^{13}\text{C}_{\text{trans}})^b$				0.987 ^d	0.985 ^e
$\delta(^{13}\text{C}_{\text{cis}})^b$			0.542	0.971 ^f	0.969 ^g
$\delta(^{17}\text{O}_{\text{cis}})^c$				0.705	0.713

^aP₁ = phosphorus trans to CO; P₂ = phosphorus trans to P.
^bC_{trans} = carbon trans to P₁; C_{cis} = carbon cis to all P. ^cO_{cis} = oxygen on CO group cis to all phosphorus. ^d $\delta(^{31}\text{P}_1) = 1.860\delta(^{13}\text{C}_{\text{trans}}) - 378.1$; $\delta(^{13}\text{C})$ 229.9 (Cr), 217.9 (Mo), 208.6 (W). ^e $\delta(^{31}\text{P}_2) = 2.251\delta(^{13}\text{C}_{\text{trans}}) - 453.8$. ^f $\delta(^{31}\text{P}_1) = 1.954\delta(^{13}\text{C}_{\text{cis}}) - 393.5$; $\delta(^{13}\text{C})$ 226.9 (Cr), 214.7 (Mo), 206.9 (W). ^g $\delta(^{31}\text{P}_2) = 2.370\delta(^{13}\text{C}_{\text{cis}}) - 473.8$.

carbonyl ¹⁷O chemical shifts and CO stretching force constants,^{51,54} and between ¹J(¹⁸³W³¹P) and the frequency of the strongest ν_{CO} band.⁵⁷

In this work we have sought to determine the degree of correlation between the chemical shifts of various nuclei and between some of the chemical shifts and the carbonyl stretching force constants of the (DBP)_nM(CO)_{6-n} complexes. The results are summarized in Tables XVI-XX. Generally, there seems to be no correlation between stretching force constants and the chemical shifts of any of the nuclei. This behavior is surprising since the only variation in these complexes is the metal center. For the (DBP)M(CO)₅ complexes, the only good correlation observed is between $\delta(^{13}\text{C})$ (both cis and trans carbonyls) and $\delta(^{31}\text{P})$, and this same correlation exists for all other complexes as well. For the (DBP)₂M(CO)₄ complexes, good

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correlations are observed between the chemical shifts of several of the nuclei, especially between $\delta(^{17}\text{O})$ and $\delta(^{31}\text{P})$. This is also surprising because very few literature reports have noted such a correlation.

The NMR chemical shifts measure electron density at the various nuclei, and it might be anticipated that these chemical shifts would correlate with the redox potentials of these complexes. Such correlations are discussed in the following paper.⁵⁸

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Registry No. 1, 114860-43-4; 2, 114860-44-5; 3-2CH₂Cl₂, 114860-46-7; (DBP)Mo(CO)₅, 111267-08-4; *cis*-(DBP)₂Mo(CO)₄, 114860-47-8; *mer*-(DBP)₃Mo(CO)₃, 114860-48-9; (DBP)W(CO)₅, 71248-95-8; *cis*-(DBP)₂W(CO)₄, 114860-49-0; *mer*-(DBP)₃W(CO)₃, 114860-50-3; *fac*-(DBP)₃Cr(CO)₃, 114925-26-7; *fac*-(DBP)₃Mo(CO)₃, 114925-27-8; *fac*-(DBP)₃W(CO)₃, 114925-28-9; Cr(CO)₆, 13007-92-6; Mo(CO)₆, 13939-06-5; W(CO)₆, 14040-11-0; C₇H₈Cr(CO)₃, 12125-72-3; ⁹⁶Mo, 14392-17-7.

Supplementary Material Available: Table XI, ¹H NMR data, Table XII, ¹³C{¹H} NMR data, and listings of thermal parameters and hydrogen atom coordinates (14 pages); listings of observed and calculated structure factors (50 pages). Ordering information is given on any current masthead page.

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