

## Coordinated 2-Halo-1,3,2-dioxaphosphorinane Ligands.

### I. Syntheses and $^{13}\text{C}$ , $^{17}\text{O}$ , $^{31}\text{P}$ and $^{95}\text{Mo}$ NMR and IR Spectroscopic Characterization of some Molybdenum Pentacarbonyl Complexes of 2-Substituted-5,5-dimethyl-1,3,2-dioxaphosphorinanes

GARY M. GRAY, JAMES E. WHITTEN and JAMES W. BOX

Chemistry Department, University of Alabama in Birmingham, 219-2 University Station, Birmingham, Ala. 35294, U.S.A.

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#### Abstract

A study of the reactions of  $\text{Mo}(\text{CO})_5(\text{P}(\text{OCH}_2\text{CMe}_2\text{CH}_2\text{O})\text{X})$  ( $\text{X} = \text{Cl}, \text{Br}$ ) with a variety of nucleophiles of the type  $\text{HER}$  ( $\text{E} = \text{NH}, \text{O}, \text{S}$ ;  $\text{R} = \text{H}, \text{alkyl}, \text{aryl}$ ) is reported. The mechanism of these reactions is shown to be  $\text{S}_{\text{N}}2$ , and the significantly slower rates of reactions of *n*-propylamine with the above complexes relative to the rate of reaction of *n*-propylamine with  $\text{Mo}(\text{CO})_5(\text{Ph}_2\text{PCl})$  is discussed.

The  $^{13}\text{C}$ ,  $^{17}\text{O}$ ,  $^{31}\text{P}$  and  $^{95}\text{Mo}$  NMR data and infrared data for these complexes are presented. Good correlations between chemical shifts of the *cis* and *trans*  $\text{CO}^{13}\text{C}$  and *trans*  $\text{CO}^{17}\text{O}$  NMR resonances, CO infrared stretching force constants and the magnitudes of  $^1J_{\text{MoP}}$  and  $^2J_{\text{PC}}$  (*trans* CO) are observed and the reasons for these correlations are discussed.

The correlations between the chemical shifts of NMR-active nuclei in the  $\text{Mo}(\text{CO})_5(\text{P}(\text{OCH}_2\text{CMe}_2\text{CH}_2\text{O})\text{ER})$  complexes with the chemical shifts of similar nuclei in the  $\text{Mo}(\text{CO})_5(\text{Ph}_2\text{PER})$  complexes range from excellent to very poor. This indicates that the effects of the P-substituents on the chemical shifts of the NMR-active nuclei in these complexes are not additive.

#### Introduction

The reactions of coordinated P-donor ligands of the type  $\text{R}_2\text{PX}$  ( $\text{R} = \text{Ph}, \text{Me}$ ;  $\text{X} = \text{halogen}$ ) with N-, O- and S-nucleophiles have proven to be a versatile method for the syntheses of complexes containing unusual P-donor ligand [1–9]. In many cases these ligands are unstable in the free state and their complexes cannot be synthesized by more traditional methods. The reactions of coordinated halophosphine ligands have been used to synthesize several different unusual heteropolynuclear transition metal complexes in which the metal centers are coordinated to a flexible polydentate ligand [1, 10–12]. Several

series of metal carbonyl complexes with closely-related P-donor ligands have also been synthesized via these reactions. These complexes have been used to study the relationships between multinuclear NMR chemical spectra of the complexes and the steric and electronic properties of these ligands [13–18].

Although the reactions of coordinated P-donor ligands of the type  $\text{R}_2\text{PCl}$  ( $\text{R} = \text{Ph}, \text{Me}$ ) with a variety of N-, O- and S-nucleophiles have been studied in detail [1–9], only one preliminary study of the reactions of coordinated halophosphite ligands with these nucleophiles has been published [19]. In this study it was reported that the 2-chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane ligands (2-Cl-dmp) in  $\text{Mo}(\text{CO})_5(\text{P}(\text{OCH}_2\text{CMe}_2\text{CH}_2\text{O})\text{Cl})$  (1) reacted with refluxing alcohols to yield the 2-alkoxy compounds but did not react with amines at ambient temperature. This is in contrast to the reactions of the chlorophosphine ligand in  $\text{Mo}(\text{CO})_5(\text{Ph}_2\text{PCl})$  (2) which reacts rapidly with both alcohols and amines at ambient temperature in the presence of excess base [1, 17].

In this paper, we present the results of a study of the reactions of 2-Cl- (1) and 2-Br-dmp (3) coordinated to a  $\text{Mo}(\text{CO})_5$  group with N-, O- and S-nucleophiles. These reactions are compared to the reactions previously reported for  $\text{Ph}_2\text{PCl}$  coordinated to a  $\text{Mo}(\text{CO})_5$  group with similar nucleophiles [17]. The mechanism and rate constants for the reactions of the  $\text{Mo}(\text{CO})_5(\text{R}_2\text{PX})$  ( $\text{R}_2 = \text{Ph}_2, \text{OCH}_2\text{CMe}_2\text{CH}_2\text{O}$ ;  $\text{X} = \text{Cl}, \text{Br}$ ) complexes with *n*-propylamine have been determined in order to better understand the factors affecting the reactivity of the P-halogen bond in coordinated P-donor ligands. The mass spectra, infrared spectra and  $^{13}\text{C}$ ,  $^{17}\text{O}$ ,  $^{31}\text{P}$  and  $^{95}\text{Mo}$  NMR spectral data of the  $\text{Mo}(\text{CO})_5(2\text{-RE-dmp})$  ( $\text{R} = \text{alkyl}, \text{aryl}, \text{silyl}$ ;  $\text{E} = \text{NH}, \text{O}, \text{S}$ ; or  $\text{RE} = \text{Cl}, \text{Br}$ ) complexes are presented. Correlations between the carbonyl  $^{13}\text{C}$  and  $^{17}\text{O}$ ,  $^{31}\text{P}$  and  $^{95}\text{Mo}$  NMR chemical shifts, the magnitudes of the P–C and P–Mo NMR coupling constants, and the infrared stretching force constants of these complexes are discussed.

Correlations between the chemical shifts of the carbonyl  $^{13}\text{C}$  and  $^{17}\text{O}$ ,  $^{31}\text{P}$  and  $^{95}\text{Mo}$  NMR resonances of the  $\text{Mo}(\text{CO})_5(2\text{-RE-dmp})$  complexes and the chemical shifts of similar resonances of the  $\text{Mo}(\text{CO})_5(\text{Ph}_2\text{PER})$  complexes are also presented. These correlations provide insight into the manner in which the electronic and steric properties of these P-donor ligands affect the NMR and infrared spectra of their metal carbonyl complexes.

## Experimental

Phosphorus trichloride (Fisher) and phosphorus tribromide (Eastman) were opened under nitrogen and used as received. Molybdenum hexacarbonyl (Pressure) and 2,2-dimethyl-1,3-propanediol (Aldrich) were used as received. Liquid alcohols and amines were dried over molecular sieves prior to use while solid alcohols and amines and all thiols were used as received from the suppliers. Tetrahydrofuran (THF) and diethyl ether were distilled from calcium hydride under nitrogen before use. 2-Chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane, 2-Cl-dmp (**4**) was synthesized by the method of White *et al.* [20].  $\text{Mo}(\text{CO})_5(2\text{-Cl-dmp})$  (**1**) was synthesized by the method of Bartish *et al.* [19]. All distillations, reactions and isolation procedures were carried out under dry Ar or  $\text{N}_2$ .

### *2-Br-5,5-dimethyl-1,3,2-dioxaphosphorinane, 2-Br-dmp (5)*

A solution of 36.16 g (0.3472 mol) of 2,2-dimethyl-1,3-propanediol and 56.17 ml (0.6945 mol) of pyridine in 150 ml of diethyl ether and a solution of 34.72 ml (0.3472 mol) of phosphorus tribromide in 200 ml of diethyl ether were simultaneously added in a dropwise fashion over a 1 h period to 200 ml of stirred diethyl ether at  $5^\circ\text{C}$ . When the addition was completed, the ice was removed, and the mixture was stirred for one hour before being vacuum filtered to remove the pyridine hydrobromide. The filtrate was evaporated to dryness and the residue distilled at  $92\text{--}100^\circ\text{C}$  under water aspirator vacuum to yield 50.55 g (68.4%) of 2-Br-dmp (**5**) as a colorless liquid.

### *(2-Bromo-5,5-dimethyl-1,3,2-dioxaphosphorinane)pentacarbonylmolybdenum(0), Mo(CO)<sub>5</sub>(2-Br-dmp) (3)*

A solution of 26.4 g (0.100 mol) of molybdenum hexacarbonyl and 13.7 ml (0.100 mol) of 2-Br-dmp (**5**) in 125 ml of methylcyclohexane was heated at reflux for three hours during which time 2.4 l of gas was evolved. The solution was then evaporated to dryness and the residue was recrystallized from hexanes to yield 33.65 g (75.1%) of  $\text{Mo}(\text{CO})_5(2\text{-Br-dmp})$  (**3**).

### *(2-Alkoxy-5,5-dimethyl-1,3,2-dioxaphosphorinane)pentacarbonylmolybdenum(0), Mo(CO)<sub>5</sub>(2-RO-dmp) (R = n-Pr, i-Pr) (6) and (7)*

A solution of 5.56 mmol of 1-propanol or 2-propanol in 20 ml of THF was stirred at ambient temperature as 3.25 ml of a 1.6 M solution of *n*-butyllithium in hexanes was added from a syringe. This mixture was stirred for 10 min before 1.50 g (3.71 mmol) of  $\text{Mo}(\text{CO})_5(2\text{-Cl-dmp})$  (**1**) was added. This mixture was stirred at ambient temperature for 66 h. The reaction mixture was then evaporated to dryness and the residue treated with 30 ml of dichloromethane and 50 ml of a 5% aqueous sodium bicarbonate solution. The layers were shaken together and then separated. The organic layer was dried over magnesium sulfate and then filtered. The filtrate was evaporated to dryness to yield 1.43 g (90.0%) of  $\text{Mo}(\text{CO})_5(2\text{-n-PrO-dmp})$  (**6**), or 1.33 g (84.2%) of  $\text{Mo}(\text{CO})_5(2\text{-i-PrO-dmp})$  (**7**) as colorless oils which crystallized on standing in the refrigerator.

### *(2-Alkylthio-5,5-dimethyl-1,3,2-dioxaphosphorinane)pentacarbonylmolybdenum(0), Mo(CO)<sub>5</sub>(2-RS-dmp) (R = n-Pr, i-Pr) (8) and (9)*

A solution of 5.56 ml of *n*-propylmercaptan or *i*-propylmercaptan in 20 ml of THF was stirred at ambient temperature as 3.25 ml of a 1.6 M solution of *n*-butyllithium in hexanes was added from a syringe. This mixture was stirred for five minutes before 1.50 g of  $\text{Mo}(\text{CO})_5(2\text{-Cl-dmp})$  (**1**) was added. The reaction mixture was then stirred at ambient temperature overnight before being evaporated to dryness. The residue was treated with 40 ml of dichloromethane and 50 ml of a 5% aqueous sodium bicarbonate solution, and the layers were shaken and allowed to separate. The organic phase was then dried over magnesium sulfate, filtered and the filtrate evaporated to dryness. The brown residue was taken up in hexanes, and this solution was filtered through a 1 cm column of chromatography grade neutral alumina in a  $15\text{ cm}^3$  medium sintered glass funnel. The filtrate was evaporated to dryness to yield 1.57 g (95.2%) of  $\text{Mo}(\text{CO})_5(2\text{-n-PrS-dmp})$  (**8**), or 1.63 g (98.9%) of  $\text{Mo}(\text{CO})_5(2\text{-i-PrS-dmp})$  (**9**).

### *(2-n-Propylamino-5,5-dimethyl-1,3,2-dioxaphosphorinane)pentacarbonylmolybdenum(0), Mo(CO)<sub>5</sub>(2-n-PrNH-dmp) (10)*

A solution of 1.50 g (3.71 mmol) of  $\text{Mo}(\text{CO})_5(2\text{-Cl-dmp})$  (**1**) and 5.0 ml (60.9 mmol) of 1-propylamine in 20 ml of THF was heated at reflux for 4 h. The solution was then evaporated to dryness, and the residue washed with three 20 ml portions of hexanes. The washes were combined and filtered through a 1 cm column of chromatography grade neutral alumina in a  $15\text{ cm}^3$  medium sintered glass funnel. The filtrate was evaporated to dryness and the resi-

due was cooled to  $-5^\circ\text{C}$ . After several hours, 1.37 g (86.5%) of off-white solid  $\text{Mo}(\text{CO})_5(2\text{-n-PrNH-dmp})$  (**10**) was collected.

*(2-i-Propylamino-5,5-dimethyl-1,3,2-dioxaphosphorinane)pentacarbonylmolybdenum(0)*,  $\text{Mo}(\text{CO})_5(2\text{-i-PrNH-dmp})$  (**11**)

A solution of 1.45 g (3.20 mmol) of  $\text{Mo}(\text{CO})_5(2\text{-Br-dmp})$  (**3**) in 10 ml of 2-propylamine was stirred at ambient temperature for 66 h after which the solution was evaporated to dryness. The residue was treated with 40 ml of diethyl ether, and this mixture was filtered to remove the 2-propylammonium bromide. The filtrate was evaporated to dryness, and the residue was cooled to  $-5^\circ\text{C}$ . After several hours the residue had crystallized and 1.26 g (92.0%) of  $\text{Mo}(\text{CO})_5(2\text{-i-PrNH-dmp})$  (**11**) was collected.

*(2-p-Tolylloxy-5,5-dimethyl-1,3,2-dioxaphosphorinane)pentacarbonyl-molybdenum(0)*,  $\text{Mo}(\text{CO})_5(2\text{-p-tolylO-dmp})$  (**12**)

A solution of 0.65 ml (6.02 mmol) of p-cresol in 20 ml of THF was stirred at ambient temperature as 3.60 ml of a 1.6 M solution of n-butyllithium in hexanes was added from a syringe. After 5 min, 1.50 g (3.71 mmol) of  $\text{Mo}(\text{CO})_5(2\text{-Cl-dmp})$  (**1**) was added. The reaction mixture was then stirred at ambient temperature for 66 h before being evaporated to dryness. The residue was treated with 50 ml of diethyl ether and 50 ml of a 5% aqueous potassium carbonate solution, and the layers shaken together before being separated. The organic layer was washed with 50 ml of water and then dried over magnesium sulfate. This mixture was filtered, and the filtrate was evaporated to dryness. The residue was recrystallized from dichloromethane–hexanes to yield 1.14 g (64.6%) of white crystalline  $\text{Mo}(\text{CO})_5(2\text{-p-tolylO-dmp})$  (**12**).

*(2-p-Tolylthio-5,5-dimethyl-1,3,2-dioxaphosphorinane)pentacarbonylmolybdenum(0)*,  $\text{Mo}(\text{CO})_5(2\text{-p-tolylS-dmp})$  (**13**)

A solution of 0.50 g (4.00 mmol) of p-methylthiophenol in 20 ml of THF was stirred at ambient temperature as 2.4 ml of a 1.6 M solution of n-butyllithium in hexanes was added from a syringe. After 5 min, 1.50 g (3.71 mmol) of  $\text{Mo}(\text{CO})_5(2\text{-Cl-dmp})$  (**1**) was added and the reaction mixture was stirred for 18 h. The reaction mixture was then evaporated to dryness and the residue was treated with 40 ml of a 1:1 dichloromethane–hexanes mixture and 50 ml of a 5% aqueous potassium carbonate solution. The layers were shaken together, separated, and then the organic layer was dried over magnesium sulfate before being filtered. The filtrate was treated with 20 ml of hexanes and heated under a stream of nitrogen until its volume reached 20 ml.

This solution was cooled to  $-5^\circ\text{C}$  for several hours and was then filtered to yield 1.24 g (67.9%) of  $\text{Mo}(\text{CO})_5(2\text{-p-tolylS-dmp})$  (**13**) as white needle-like crystals.

*(2-p-Tolylamino-5,5-dimethyl-1,3,2-dioxaphosphorinane)pentacarbonylmolybdenum(0)*,  $\text{Mo}(\text{CO})_5(2\text{-p-tolylNH-dmp})$  (**14**)

A solution of 1.35 g (3.00 mmol) of  $\text{Mo}(\text{CO})_5(2\text{-Br-dmp})$  (**3**), 0.32 g (3.00 mmol) of p-toluidine and 0.84 ml (6.00 mmol) of triethylamine in 40 ml of THF was heated at reflux for 3 h and was then evaporated to dryness. The residue was treated with 40 ml of diethyl ether and filtered to remove the triethylammonium bromide by-product. The filtrate was evaporated to dryness, and the residue recrystallized from dichloromethane–hexanes to yield 0.81 g (57%) of  $\text{Mo}(\text{CO})_5(2\text{-p-tolylNH-dmp})$  (**14**) as off-white crystals.

*Triethylammonium (2-oxy-5,5-dimethyl-1,3,2-dioxaphosphorinane)pentacarbonyl-molybdenum(0)*,  $[\text{Et}_3\text{-NH}][\text{Mo}(\text{CO})_5(2\text{-O}^-\text{-dmp})]$  (**15**)

A solution of 5.00 g (11.1 mmol) of  $\text{Mo}(\text{CO})_5(2\text{-Br-dmp})$  (**5**), 5.0 ml of deionized water, 5.0 ml of triethylamine and 50 ml of acetonitrile was stirred at ambient temperature for 4 h before being evaporated to dryness. The residue was washed with four, 50 ml portions of water, and then the insoluble portion was recrystallized from a diethyl ether–hexanes mixture to yield 2.40 g (44.2%) of  $[\text{Et}_3\text{-NH}][\text{Mo}(\text{CO})_5(2\text{-O}^-\text{-dmp})]$  (**15**) as a white crystalline solid.

*(2-Trimethylsilyloxy-5,5-dimethyl-1,3,2-dioxaphosphorinane)pentacarbonylmolybdenum(0)*,  $\text{Mo}(\text{CO})_5(2\text{-Me}_3\text{SiO-dmp})$  (**16**)

A solution of 0.80 g (1.64 mmol) of  $[\text{Et}_3\text{NH}][\text{Mo}(\text{CO})_5(2\text{-O}^-\text{-dmp})]$  (**15**) in 20 ml of THF was stirred as 0.21 ml (1.64 mmol) of chlorotrimethylsilane was added. After 1 h the mixture was evaporated to dryness and the residue treated with 40 ml of diethyl ether. This mixture was filtered through a 1 cm layer of alumina in a 15 cm<sup>3</sup> medium sintered glass funnel, and the filtrate was evaporated to dryness to yield 0.68 g (90%) of  $\text{Mo}(\text{CO})_5(2\text{-Me}_3\text{-SiO-dmp})$  (**16**) as a colorless oil which crystallized upon standing at  $-5^\circ\text{C}$ .

The 2-X-dmp ( $\text{X} = \text{Cl}$  (**4**) and  $\text{Br}$  (**5**)) ligands were characterized by comparison of their boiling ranges and <sup>1</sup>H NMR spectra with literature values [20].

All of the complexes were characterized by <sup>13</sup>C, <sup>17</sup>O, <sup>31</sup>P and <sup>95</sup>Mo NMR, and the NMR spectra data for the complexes are summarized in Table I. The multinuclear NMR spectra of 0.50 M d<sub>1</sub>-chloroform solutions of the complexes in nitrogen-filled 10 mm NMR tubes were run on a JEOL FX90Q NMR

TABLE I. Carbonyl  $^{13}\text{C}$  and  $^{17}\text{O}$ ,  $^{31}\text{P}$  and  $^{95}\text{Mo}$  NMR Data for the  $\text{Mo}(\text{CO})_5(2\text{-RE-dmp})$  Complexes ( $\delta$  in ppm, and  $J$  in Hz)<sup>a</sup>

RE	<i>trans</i> CO			<i>cis</i> CO			P $\delta(^{31}\text{P})^c$	Mo		
	$\delta(^{13}\text{C})^b$	$ ^2J_{\text{PC}} $	$\delta(^{17}\text{O})^c$	$\delta(^{13}\text{C})^b$	$ ^2J_{\text{PC}} $	$\delta(^{17}\text{O})^c$		$\delta(^{95}\text{Mo})^c$	$ ^1J_{\text{PC}} $	$\Delta\nu_{1/2}$
Cl (1)	207.84	52.7	372.9	203.04	13.9	361.3	160.48	-1756.8	242	16
Br (3)	207.92	55.0	374.5	203.09	13.2	361.3	157.45	-1766.9	244	22
O-n-Pr (6)	208.46	41.0	366.5	204.41	13.9	360.9	152.06	-1856.5	221	7
O-i-Pr (7)	208.59	41.0	366.1	204.49	13.2	360.9	150.88	-1849.1	219	7
S-n-Pr (8)	209.19	43.2	370.1	204.20	13.2	360.9	184.70	-1771.7	213	23
S-i-Pr (9)	209.25	43.2	370.5	204.21	12.4	360.9	185.11	-1769.8	213	20
NH-n-Pr (10)	209.01	35.2	366.5	205.12	12.5	361.3	155.39	-1844.7	200	6
NH-i-Pr (11)	209.06	34.4	365.7	205.19	12.5	361.3	153.81	-1841.7	200	6
O-p-tolyl (12)	208.00	44.0	366.1	203.73	13.9	360.9	149.57	-1838.6	229	13
S-p-tolyl (13)	208.98	45.4	369.7	203.63	12.4	360.5	180.90	-1766.9	218	30
NH-p-tolyl (14)	208.80	40.3	366.9	204.36	13.2	360.5	149.88	-1828.3	215	11
$\text{O}^-\text{Et}_3\text{NH}^+$ (15)	212.33	31.0	362.9	207.22	15.0	357.7	126.26	-1828.9	199	4
$\text{OSiMe}_3$ (16)	208.91	42.5	366.1	204.65	14.7	359.7	131.81	-1830.9	226	6

<sup>a</sup>Spectra run on 0.50 M  $\text{d}_1$ -chloroform solutions. <sup>b</sup>Doublet. <sup>c</sup>Singlet.

spectrometer equipped with either a broad band or a low frequency probe insert. The instrumental parameters for data acquisition and work up and the standards used have been previously reported [17].

Infrared spectra of dilute n-hexanes solutions of the complexes in a 0.20 mm NaCl solution cell with pure hexanes in a matched reference cell were run from 2100 to 1800  $\text{cm}^{-1}$  using a Perkin-Elmer 283B infrared spectrometer. The assignment of the frequencies due to the  $A_1^2$  and E stretching modes was carried out in the following manner. Approximate infrared stretching force constants were calculated from the  $A_1^1$ ,  $A_1^2$  and E absorption frequencies using the Cotton-Kraihanzel approximation [21] for both possible assignments of the  $A_1^2$  and E absorptions. The two sets of force constants were then used to calculate the frequency for the  $B_1$  absorption. The assignments for the  $A_1^2$  and E absorptions which gave the best fit between the calculated and observed  $B_1$  frequency were assumed to be the correct assignments. The frequencies assigned to the four stretching absorptions using this method, the stretching force constants and the calculated  $B_1$  frequency are given in Table II.

Mass spectra of all of the complexes, except for 15 which is ionic, were obtained on a Hewlett Packard 5993/95 GS/MS using the solids inlet probe. Parent ions were observed for all of the complexes. The masses of the major ions are available, see 'Supplementary Material'.

The kinetics experiments were run on a Nicolet 300 MHz wide-bore multinuclear NMR spectrometer at 24 °C. The halo-P-donor ligand complex and the 1-propylamine were added to a 2.00 ml volumetric flask and then  $\text{d}_1$ -chloroform was added to volume. This solution was transferred to a 10 mm NMR

tube which was fitted with a vortex plug and then placed in the magnet.  $^{31}\text{P}$  NMR spectra were taken at regular intervals, depending on the rate of the reaction being observed. The relative concentrations of the reactant and product complexes were determined by integrating the  $^{31}\text{P}$  resonances of the reactant and product. The exact concentrations of the reactant and product were then calculated from the initial concentrations of the complexes. Each reaction was studied using at least three different sets of amine/complex concentrations. Both initial reaction rates and rate constants were calculated from the  $^{31}\text{P}$  NMR data and are summarized in Table III.

The correlations between the various NMR chemical shifts and coupling constants and the infrared carbonyl stretching force constants were run using the ABSTAT<sup>TM</sup> release 4 program of Anderson-Bell. Linear regression analyses were run for all of the correlations and the level of confidence determined by an analysis of variance of the regression using the  $F$  test. All levels of confidence reported in this paper are measures of the likelihood that the correlation in question is valid.

## Results

### Synthetic Methods

The literature procedure for the synthesis of 2-Br-dmp (5) gives a low yield (~30%) of the product [20]. However, simultaneous addition of an ether solution of  $\text{PBr}_3$  and an ether solution of a mixture of pyridine and the diol to a vigorously stirred ether solution at 5 °C gave higher yields of 5. The exact yield obtained appears to be dependent upon the simultaneity of the addition of the two solutions.

TABLE II. Infrared Stretching Frequencies and Approximate Stretching Force Constants For the  $\text{Mo}(\text{CO})_5(2\text{-RE-dmp})$  Complexes

RE	$A_1^1$ <sup>a</sup> ( $\text{cm}^{-1}$ )	$B_1$ <sup>b</sup> ( $\text{cm}^{-1}$ )	$A_1^2$ <sup>c</sup> ( $\text{cm}^{-1}$ )	$E^c$ ( $\text{cm}^{-1}$ )	$k_1$ mdyne/A	$k_2$ mdyne/A	$k_i$ mdyne/A	$B_1$ calc. ( $\text{cm}^{-1}$ )
Cl (1)	2088	2006	1982	1974	16.07	16.30	0.28	2009
Br (3)	2089	2008	1983	1975	16.09	16.32	0.28	2010
O-n-Pr (6)	2082	1998	1972	1959	15.94	16.10	0.30	1996
O-i-Pr (7)	2081	1999	1971	1958	15.92	16.08	0.30	1995
S-n-Pr (8)	2082	2001	1971	1963	15.90	16.15	0.29	1999
S-i-Pr (9)	2081	2000	1971	1963	15.90	16.14	0.29	1999
NH-n-Pr (10)	2077	1987	1964	1952	15.82	15.95	0.31	1987
NH-i-Pr (11)	2076	1987	1964	1953 1942	15.82	15.96	0.31	1987
O-p-tolyl (12)	2083	1999	1972	1967	15.91	16.20	0.28	2002
S-p-tolyl (13)	2081	<sup>d</sup>	1971	1963	15.90	16.14	0.29	1999
NH-p-tolyl (14)	2080	1997	1966	1963	15.81	16.14	0.29	1999
OSiMe <sub>3</sub> (16)	2081	1997	1968	1962 1954	15.87	16.09	0.30	1995

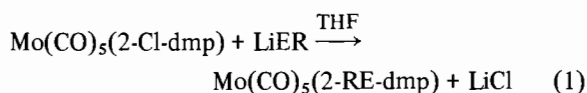
<sup>a</sup>Medium. <sup>b</sup>Very weak. <sup>c</sup>Strong. <sup>d</sup>Not observed.

TABLE III. Rate Data for the  $\text{Mo}(\text{CO})_5(\text{R}_2\text{PX})$  Complexes

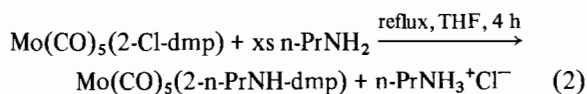
$\text{R}_2$	X	Complex (mol/l)	1-Propylamine (mol/l)	Initial rate ( $\text{mol l}^{-1} \text{s}^{-1}$ )	$k$ ( $\text{l mol}^{-1} \text{s}^{-1}$ )
$\text{Ph}_2$	Cl (2)	0.200	0.400	$3.25 \times 10^{-3}$	$4.05 \times 10^{-2}$
		0.100	0.200	$8.10 \times 10^{-4}$	$4.05 \times 10^{-2}$
		0.050	0.200	$4.27 \times 10^{-4}$	$4.27 \times 10^{-2}$
$\text{OCH}_2\text{CMe}_2\text{CH}_2\text{O}$	Br (3)	0.400	0.800	$1.03 \times 10^{-4}$	$3.20 \times 10^{-4}$
		0.200	0.800	$4.78 \times 10^{-5}$	$2.98 \times 10^{-4}$
		0.200	0.400	$2.45 \times 10^{-5}$	$3.07 \times 10^{-4}$
$\text{OCH}_2\text{CMe}_2\text{CH}_2\text{O}$	Cl (1)	0.800	1.600	$1.76 \times 10^{-5}$	$1.37 \times 10^{-5}$
		0.400	1.600	$8.50 \times 10^{-6}$	$1.33 \times 10^{-5}$
		0.400	0.800	$2.21 \times 10^{-6}$	$6.90 \times 10^{-6}$
		0.200	0.800	$1.10 \times 10^{-6}$	$6.88 \times 10^{-6}$

$\text{Mo}(\text{CO})_5(2\text{-Br-dmp})$  (3) was synthesized by the thermal reaction of  $\text{Mo}(\text{CO})_6$  and 2-Br-dmp (5) in refluxing methylcyclohexane in 75% yield. This procedure is similar to that used by Bartish and Kraihanzel [19] for the synthesis of  $\text{Mo}(\text{CO})_5(2\text{-Cl-dmp})$  (1).

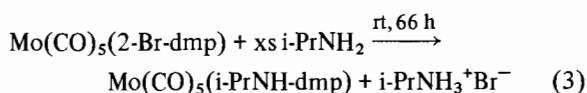
Displacement of the Cl groups in  $\text{Mo}(\text{CO})_5(\text{Ph}_2\text{Cl})$  (2) by alcohols, thiols and amines is complete in 30 min at 25 °C in the presence of base [1, 17]. In contrast, the Cl groups in (1) are not displaced under these conditions, and it is necessary to use substantially longer reaction times and either higher temperatures or stronger nucleophiles for these displacements to occur. These reactions are shown in eqns. (1) and (2). When poor nucleophiles such as water, 2-propylamine and p-toluidene are used, it is not possible to cleanly displace the Cl group from 1. However, it is possible to displace the Br from 3



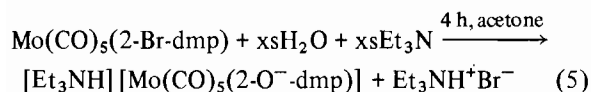
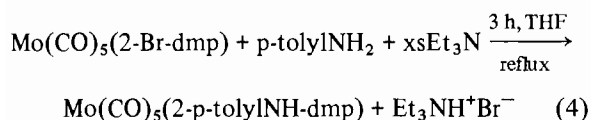
(E = O, S; R = n-Pr, i-Pr, p-tolyl)



(xs, excess)

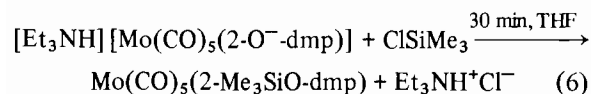


to yield the desired products as shown in eqns. (3)–(5). These reactions are still much slower than are the



corresponding reactions of 2, although Br is a much better leaving group than Cl.

In contrast to the above reactions, the reaction of  $[\text{Et}_3\text{NH}][\text{Mo}(\text{CO})_5(2\text{-O}^-\text{-dmp})]$  (14) with chlorotrimethylsilane, shown in eqn. (6), is quite rapid.



This is not surprising since the reaction involves a nucleophilic attack on Si rather than P.

The reasons for the surprising differences in reactivity of the P-halogen bonds in 1, 2 and 3 are not obvious. In order to better understand these reactions, we have followed the reactions of these complexes with 1-propylamine by  $^{31}\text{P}$  NMR spectroscopy. This particular nucleophile was chosen because all of the reactants and products are soluble in  $d_1$ -chloroform. The initial concentrations of amine and complex used and the initial rates and rate constants calculated from the NMR data are given in Table I. The initial rates indicate that, as expected, all of the reaction proceed by  $\text{S}_{\text{N}}2$  mechanisms. The rate constants observed for the reactions are consistent with the qualitative results observed during the syntheses of the complexes with  $k(\text{Ph}_2\text{PCl}) \gg k(2\text{-Br-dmp}) \gg k(2\text{-Cl-dmp})$ . The rates exhibit some dependence on the polarity of the reaction medium as high concentrations of the amine (1.6 M) result in increased reaction rates.

#### Carbonyl $^{13}\text{C}$ and $^{17}\text{O}$ NMR Spectra

The  $^{13}\text{C}\{^1\text{H}\}$  and  $^{17}\text{O}$  NMR data for the *cis* and *trans* carbonyls of the  $\text{Mo}(\text{CO})_5(2\text{-RE-dmp})$  complexes are reported in Table I. The *cis* and *trans* carbonyl  $^{13}\text{C}$  resonances are found upfield of those in  $\text{Mo}(\text{CO})_5(\text{Ph}_2\text{PER})$  complexes while the *cis* and *trans*  $^{17}\text{O}$  resonances are found downfield of those in  $\text{Mo}(\text{CO})_5(\text{Ph}_2\text{PER})$  complexes [17]. According to the Bodner-Todd theory of carbonyl chemical shifts, this indicates that the 2-RE-dmp ligands are better  $\pi$ -acceptors than are the  $\text{Ph}_2\text{PER}$  ligands [22, 23].

The magnitudes of the  $^2J_{\text{PC}}$  values of the *cis* and *trans* carbonyls of the  $\text{Mo}(\text{CO})_5(2\text{-RE-dmp})$  complexes (12.4–15.0 Hz and 31.0–55.0 Hz, respectively) are significantly larger than those of the *cis* and *trans* carbonyl resonances of the  $\text{Mo}(\text{CO})_5$ -

$(\text{Ph}_2\text{PER})$  complexes (9–10 Hz and 23–32 Hz respectively) [17]. The relative magnitudes of the  $^2J_{\text{PC}}$  values in the two series of complexes are consistent with the smaller cone angles and the greater electronegativities of the 2-RE-dmp ligands relative to the  $\text{Ph}_2\text{PER}$  ligands [24].

#### $^{31}\text{P}\{^1\text{H}\}$ NMR Spectra

The  $^{31}\text{P}\{^1\text{H}\}$  NMR resonances of the  $\text{Mo}(\text{CO})_5(2\text{-RE-dmp})$  complexes, whose chemical shifts are summarized in Table I, are singlets. The chemical shift of the  $^{31}\text{P}$  resonance is extremely sensitive to the nature of the E group, however the downfield shift does not parallel the electronegativity of the E group as is the case for the  $^{31}\text{P}$  chemical shifts of the  $\text{Mo}(\text{CO})_5(\text{Ph}_2\text{PER})$  complexes [15, 17]. Instead the  $^{31}\text{P}$  chemical shifts of the E = S complexes, in which E is the least electronegative, are found farthest downfield. These results are consistent with previous theoretical and experimental studies in which the  $^{31}\text{P}$  chemical shift has been shown to be extremely sensitive to the nature of the groups directly bonded to the P [24, 25].

#### $^{95}\text{Mo}$ NMR Spectra

The  $^{95}\text{Mo}$  NMR spectra of the  $\text{Mo}(\text{CO})_5(2\text{-RE-dmp})$  complexes consist of doublets which are found 1756.8 to 1856.5 ppm upfield of the resonance of 2 M  $\text{Na}_2\text{MoO}_4$  and have  $|^1J_{\text{MoP}}|$  values of 199 to 244 Hz (Table I). These  $^{95}\text{Mo}$  chemical shifts and  $|^1J_{\text{MoP}}|$  values are similar to those previously reported for other P-donor ligand-substituted molybdenum carbonyl complexes [14–17, 26]. The magnitudes of  $^1J_{\text{MoP}}$  are larger than are those reported for  $^1J_{\text{MoP}}$  in the  $\text{Mo}(\text{CO})_5(\text{Ph}_2\text{PER})$  complexes (142 to 165 Hz) [17] and are consistent with the larger  $^2J_{\text{PC}}$  values which are observed for the 2-RE-dmp complexes. The chemical shifts of the  $^{95}\text{Mo}$  resonance are sensitive to the nature of the E group, with the resonance moving downfield in the order  $\text{O} > \text{N} \gg \text{S} > \text{Br} > \text{Cl}$ . This behavior is similar to that reported for the chemical shifts of the  $^{95}\text{Mo}$  resonance of the  $\text{Mo}(\text{CO})_5(\text{Ph}_2\text{PER})$  complexes, but the resonances of the 2-RE-dmp complexes are found 50 to 80 ppm farther upfield [17].

#### Carbonyl Infrared Spectra (2100–1900 $\text{cm}^{-1}$ )

The infrared spectra of the  $\text{Mo}(\text{CO})_5$  group should consist of four absorptions, two of  $\text{A}_1$  symmetry, one of  $\text{B}_1$  symmetry and one of E symmetry [21]. As shown in Table III, these absorptions are observed for most of the  $\text{Mo}(\text{CO})_5(2\text{-RE-dmp})$  complexes in this study. However, several of the complexes appear to exhibit a split E absorption band which is highly unusual. This does not appear to be due to impurities since the mass spectra,  $^{31}\text{P}$  NMR spectra and both thin layer and column chromatography of the complexes on silica gel confirm the purity of

the complexes in question. The additional IR absorption may be due to the presence of the unsymmetrical 2-RE-dmp ligand which would lower the symmetry of the metal center and cause the E band to split. However, this does not explain why this effect is observed in only three of the complexes and is not observed at all in the  $\text{Ph}_2\text{PER}$  complexes which contain equally unsymmetric ligands. An alternate explanation may be that two different conformations of the phosphorinane ring are present in these complexes such as have been observed for other 1,3,2-dioxaphosphorinanes [27–32], but, if this were the case, all four bands might be expected to be split.

Infrared stretching force constants for all the complexes in this study were calculated using the Cotton–Kraihanzel approximation [21] and are given in Table III. This approximation gives four equations with three unknowns, and thus, only three of the four carbonyl infrared absorptions need to be used. The  $A_1^1$ ,  $A_1^2$  and E absorptions are used for these calculations since these are the strongest absorptions. The absorptions for the  $A_1^2$  and E stretching modes are overlapped, and the assignment of symmetry mode of these absorptions was made by using the stretching force constants to calculate the frequency of the  $B_1$  absorption. The assignments which are given in Table III are those which give the best fit between the calculated and measured values. For those complexes in which the E absorption was split, the average of the two frequencies was used.

The approximate infrared stretching force constants for the 2-RE-dmp complexes are larger than those reported for the  $\text{Ph}_2\text{PER}$  complexes [1]. This indicates that the 2-RE-dmp ligands are better  $\pi$ -acceptors than are the  $\text{Ph}_2\text{PER}$  ligands because less electron density is being donated from the metal d orbitals into the CO  $\pi^*$  antibonding orbitals. The same conclusion is also obtained upon examination of the CO  $^{13}\text{C}$  and  $^{17}\text{O}$  chemical shifts.

## Discussion

### Nucleophilic Displacement of Halogens From P-Donor Ligands

The rate data for the reactions of the  $\text{Mo}(\text{CO})_5(\text{R}_2\text{PX})$  ( $\text{R}_2 = \text{OCH}_2\text{CMe}_2\text{CH}_2\text{O}$  and  $\text{X} = \text{Cl}$  (1) or  $\text{Br}$  (3); or  $\text{R}_2 = \text{Ph}_2$  and  $\text{X} = \text{Cl}$  (2)) complexes with n-propylamine, given in Table III, indicate that the mechanism of this reaction is an  $\text{S}_{\text{N}}2$  displacement of the halide from the P by the amine. The relative reaction rates,  $2 \gg 3 \gg 1$ , are surprising in view of the greater electronegativity and smaller size of the phosphorinane group relative to the Ph groups since both of these factors should cause the halide to be more rapidly displaced from 1 and 3 than from 2.

The relative rates of nucleophilic halide substitution of the  $\text{Mo}(\text{CO})_5(\text{R}_2\text{PX})$  ( $\text{R}_2 = \text{OCH}_2\text{CMe}_2\text{CH}_2\text{O}$  and  $\text{X} = \text{Cl}$  (1) or  $\text{Br}$  (3); or  $\text{R}_2 = \text{Ph}_2$  and  $\text{X} = \text{Cl}$  (2)) complexes are consistent with literature reports. For compounds of the type  $\text{R}_2\text{P}(\text{O})\text{Cl}$ , the  $\text{R} =$  alkyl compounds were observed to react much more rapidly with water and alcohols than were the  $\text{R} =$  alkoxy compounds [33]. Thus, it would appear that halides on P which is bonded to carbons are more rapidly displaced than are halides on P which are bonded to oxygens.

The rationalization given for the relative rates of nucleophilic displacement of the halides from the  $\text{R}_2\text{P}(\text{O})\text{Cl}$  compounds was that  $d\pi\text{--}p\pi$  bonding between the alkoxy oxygens and the P caused an increase in the electron density at the P and that this reduced the rate of the reaction [33]. If this is also the case for the  $\text{Mo}(\text{CO})_5(\text{R}_2\text{PX})$  ( $\text{R}_2 = \text{OCH}_2\text{CMe}_2\text{CH}_2\text{O}$  and  $\text{X} = \text{Cl}$  (1) or  $\text{Br}$  (3); or  $\text{R}_2 = \text{Ph}_2$  and  $\text{X} = \text{Cl}$  (2)) complexes, then the 2-halo-dmp ligands should be poorer  $\pi$ -acceptors than the  $\text{Ph}_2\text{P}(\text{O})\text{Cl}$  ligands. However, both the chemical shifts of the carbonyl  $^{13}\text{C}$  and  $^{17}\text{O}$  NMR resonances and the infrared carbonyl stretching force constants of complexes 1, 2 and 3 indicate that the 2-halo-dmp ligands are better  $\pi$ -electron acceptors than is the  $\text{Ph}_2\text{P}(\text{O})\text{Cl}$  ligand. Thus, an alternative explanation for the rates of nucleophilic displacement of the halide groups in these complexes must be found. The results of a study of the nucleophilic displacement of chlorides from Group 6 pentacarbonyl complexes of 2-chloro-4-methyl-1,3,2-dioxaphosphorinanes which provides significant insight into the factors affecting these rates will be reported in a subsequent paper.

### NMR Chemical Shift, NMR Coupling Constant and IR Stretching Force Constant Correlations in the $\text{Mo}(\text{CO})_5(2\text{-RE-dmp})$ Complexes

The shieldings of all nuclei heavier than Li are dominated by the paramagnetic term,  $\sigma_{\text{p}}$ . For polyatomic ions and molecules,  $\sigma_{\text{p}}$  is usually described by the Jameson and Gutowsky equation [34], shown in eqn. 7, where  $\Delta E$  represents the average excitation

$$\sigma_{\text{p}} = \frac{2e^2h^2}{3m^2c^2} \frac{1}{\Delta E} [\langle r^{-3} \rangle_{\text{p}} P_{\text{u}} + \langle r^{-3} \rangle_{\text{d}} D_{\text{u}}] \quad (7)$$

energy.  $\langle r^{-3} \rangle_{\text{p}}$  or  $\text{d}$  represents the average value of  $r^{-3}$  over the p or d wavefunctions, and  $P_{\text{u}}$  and  $D_{\text{u}}$  represent the 'imbalance' in the valence electrons in the p and d orbitals, respectively. This means that the chemical shifts of the heavy nuclei will be affected by changes in bond overlap and hybridization (via the  $P_{\text{u}}$  and  $D_{\text{u}}$  terms) and changes in atomic charges (via the  $\langle r^{-3} \rangle$  terms and  $\Delta E$ ) [25]. Simultaneous variations in both the steric and electron donor/acceptor properties of the R-substituents of a  $\text{PRR}'\text{R}''$  ligand of a transition metal complex may affect all three of these parameters,

and thus, if these effects are of similar magnitude, linear correlations between the chemical shifts of the various NMR active nuclei in the complexes and between these chemical shifts and other parameters, such as infrared stretching force constants, may not be observed. For metal carbonyl complexes of P-donor ligands, the best correlations which are observed are between the  $^{13}\text{C}$  chemical shifts and infrared stretching force constants of CO ligands [13, 35–43], between the  $^{13}\text{C}$  and  $^{17}\text{O}$  chemical shifts of the CO ligands [13, 23] and between the  $^{13}\text{C}$  chemical shifts and the  $E^\circ$  value [44]. All of these correlations involve the chemical shifts of the CO ligands which are relatively distant from the P ligand(s), and thus, the least affected by changes in the properties of the P-substituents.

Based on the literature results described above, the best linear chemical shift correlations should be observed between the chemical shifts of the *trans* CO  $^{13}\text{C}$  and  $^{17}\text{O}$  and *cis* CO  $^{13}\text{C}$  resonances and between these resonances and the *cis* and *trans* CO stretching force constants of the  $\text{Mo}(\text{CO})_5(2\text{-RE-dmp})$  ( $E = \text{NH}, \text{O}, \text{S}; \text{R} = \text{alkyl, aryl, silyl}; \text{or RE} = \text{Cl, Br}$ ) complexes. Correlations with the chemical shifts or the *cis* CO  $^{17}\text{O}$  resonance are not considered since the chemical shift of this resonance with changes in the RE group is small relative to the measurement error. Good correlations (levels of confidence  $\geq 99.8\%$ ) are observed between the chemical shifts of the *cis* CO  $^{13}\text{C}$  and the *trans* CO  $^{17}\text{O}$  resonances ( $r = -0.8020$ ), between the chemical shift of the *cis* CO  $^{13}\text{C}$  resonance and  $k_1$  ( $r = -0.8478$ ) and  $k_2$  ( $r = -0.9597$ ) and between the chemical shift of the *trans* CO  $^{17}\text{O}$  resonance and  $k_1$  ( $r = 0.7974$ ). In contrast, all correlations involving the chemical shift of the *trans* CO  $^{13}\text{C}$  resonance are poor. However, if the data for the  $E = \text{S}$  complexes is dropped from the calculations, the correlations improve significantly with good correlations observed between the chemical shift of the *trans* CO  $^{13}\text{C}$  resonance and the chemical shift of the *cis* CO  $^{13}\text{C}$  resonance ( $r = 0.9580$ ),  $k_1$  ( $r = -0.8841$ ) and  $k_2$  ( $r = -0.9149$ ). This suggests that there is some type of through space interaction, either steric or electronic, between the *trans* CO carbon and the sulfur which does not occur in the other complexes and that this results in the poor correlations which are observed when the data for the  $E = \text{S}$  complexes are included in the calculations. This is shown in the plots of the  $^{13}\text{C}$  chemical shifts of the *cis* and *trans* CO versus the  $k_2$  values of the *cis* COs which are shown in Figs. 1 and 2, respectively.

An excellent linear correlation (level of confidence  $\geq 99.9\%$ ) is observed between  $|^2J_{\text{PC}}|$  for the *trans* CO and  $|^1J_{\text{MoP}}|$  ( $r = 0.9224$ ). In addition, good correlations are observed between both  $|^2J_{\text{PC}}|$  for the *trans* CO and  $|^1J_{\text{MoP}}|$  and the chemical shifts of the *cis*  $^{13}\text{C}$  resonance ( $r = -0.9554$  and  $-0.8680$ ,

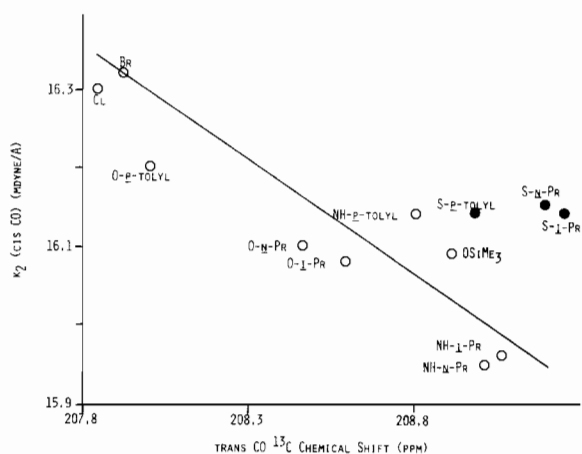


Fig. 1. Plot of  $k_2$  (*cis* CO) vs. the  $^{13}\text{C}$  (*trans* CO) chemical shift for the  $\text{Mo}(\text{CO})_5(2\text{-RE-dmp})$  ( $\text{R} = \text{alkyl, aryl silyl}; \text{E} = \text{O, S, NH}$ ) complexes.

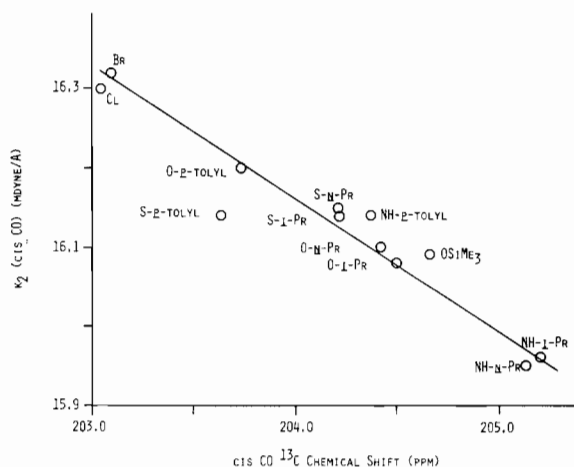


Fig. 2. Plot of  $k_2$  (*cis* CO) vs.  $^{13}\text{C}$  (*cis* CO) chemical shift for the  $\text{Mo}(\text{CO})_5(2\text{-RE-dmp})$  ( $\text{R} = \text{alkyl, aryl silyl}; \text{E} = \text{O, S, NH}$ ) complexes.

respectively), the *trans* CO  $^{13}\text{C}$  resonance ( $E \neq \text{S}$ ) ( $r = -0.8824$  and  $-0.8848$ , respectively),  $k_1$  ( $r = 0.9151$  and  $0.8775$ , respectively) and  $k_2$  ( $r = 0.9583$  and  $0.9088$ , respectively). Plots of  $|^2J_{\text{PC}}|$  for the *trans* CO versus the chemical shifts of the *cis* and *trans* CO  $^{13}\text{C}$  resonances are shown in Figs. 3 and 4, respectively. The magnitudes of one-bond P–metal coupling constants have been demonstrated to be a function both of the amount of s-character in the bonds through which the coupling is transmitted and of the electronegativity of the P-substituents [24]. Thus, it seems likely that the  $^{13}\text{C}$  chemical shifts and stretching force constants of the CO ligands in these complexes are also sensitive to changes in one of these factors. The correlations between the chemical shifts and stretching force constants with the  $|^2J_{\text{PC}}|$  values of the *cis* COs were not examined because the variation in the magnitudes



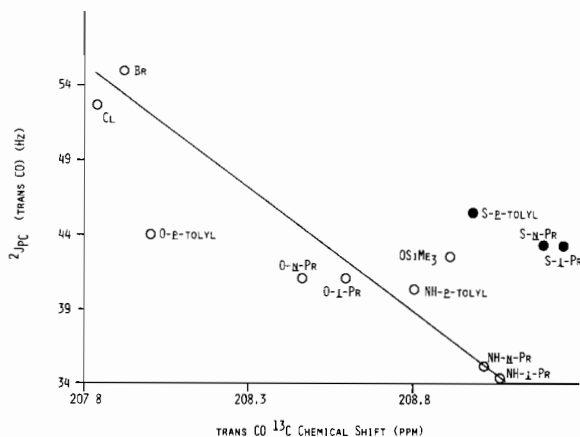


Fig. 3. Plot of  $^2J_{\text{PC}}$  (*trans* CO) vs  $^{13}\text{C}$  (*trans* CO) chemical shift for the  $\text{Mo}(\text{CO})_5(2\text{-RE-dmp})$  ( $\text{R} = \text{alkyl, aryl silyl}$ ,  $\text{E} = \text{O, S, NH}$ ) complexes

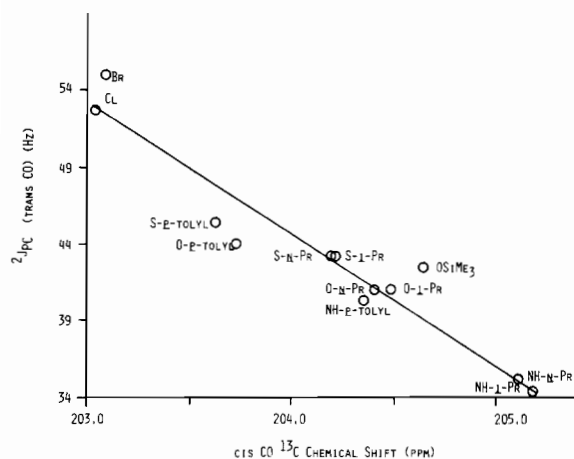


Fig. 4. Plot of  $^2J_{\text{PC}}$  (*trans* CO) vs  $^{13}\text{C}$  (*cis* CO) chemical shift for the  $\text{Mo}(\text{CO})_5(2\text{-RE-dmp})$  ( $\text{R} = \text{alkyl, aryl silyl}$ ,  $\text{E} = \text{O, S, NH}$ ) complexes.

of these coupling constants as the RE group is varied is small relative to the measurement error.

Studies by Grim *et al.* [45, 46] and Bodner [39], among others, suggest that the effects of the three P substituents on the NMR chemical shifts of many of the NMR active nuclei in their compounds are additive. If this is true for the  $\text{Mo}(\text{CO})_5(\text{R}'_2\text{PER})$  complexes, the *cis* and *trans* CO  $^{13}\text{C}$ , the *trans* CO  $^{17}\text{O}$ , the  $^{31}\text{P}$  and the  $^{95}\text{Mo}$  resonances of the  $\text{Ph}_2\text{PER}$  complexes should be shifted from similar resonances in the 2-RE-dmp by a constant amount regardless of the nature of the ER group. This would result in good linear correlations between the similar chemical shifts in the two sets of complexes as the ER group is varied. However, good linear correlations are not observed between the chemical shifts of all of the similar resonances in the two sets of complexes. The linear correlations between the chemical shifts of the *trans* CO  $^{13}\text{C}$  resonances ( $r = 0.9666$ ), the *cis*

CO  $^{13}\text{C}$  resonances ( $r = 0.8478$ ) and the  $^{95}\text{Mo}$  resonances ( $r = 0.9250$ ) are excellent (level of confidence  $\geq 99.9\%$ ). In contrast, the correlations between the chemical shifts of the *trans* CO  $^{17}\text{O}$  resonances ( $r = 0.4861$ ) and the  $^{31}\text{P}$  resonances ( $r = -0.6649$ ) are extremely poor. The variation in the degree of correlation suggests that the effects of the P substituents on the various NMR chemical shifts are not always independent of one another, and that additivity relationships for the calculation of NMR chemical shifts, such as those described above, may be of limited utility.

## Conclusions

Nucleophilic displacement of the halide ligands from the  $\text{Mo}(\text{CO})_5(2\text{-X-dmp})$  ( $\text{X} = \text{Cl}$  (1),  $\text{Br}$  (3)) complexes occurs much less readily than does displacement of the chloride from  $\text{Mo}(\text{CO})_5(\text{Ph}_2\text{PCl})$ . This displacement occurs via an  $\text{S}_{\text{N}}2$  mechanism, and when the nucleophile is 1-propylamine, the difference in reaction rates between 1 and 2 is nearly four orders of magnitude. Similar differences in the rates of chloride displacement from the related  $\text{OPR}_2\text{Cl}$  ( $\text{R} = \text{alkyl, alkoxy}$ ) compounds has been postulated to be due to  $d\pi-p\pi$  bonding between the P and O. However, this explanation is inconsistent with both the  $^{13}\text{C}$  and  $^{17}\text{O}$  NMR chemical shifts and the infrared stretching force constants of the CO ligands of 1, 2 and 3 which indicate that the 2-X-dmp ligands in 1 and 3 are better  $\pi$ -acceptors than  $\text{Ph}_2\text{PCl}$ .

The good linear correlations (level of confidence  $\geq 99.8\%$ ) which exist between the chemical shifts of *cis* and *trans* ( $\text{E} \neq \text{S}$ )  $^{13}\text{C}$  and *trans*  $^{17}\text{O}$  CO resonances and the infrared stretching force constants of the  $\text{Mo}(\text{CO})_5(2\text{-RE-dmp})$  complexes are consistent with previous literature reports. Good linear correlations are also observed between these chemical shifts and force constants and the magnitudes of both  $^1J_{\text{MoP}}$  and  $^2J_{\text{PC}}$  (*trans* CO). These correlations suggest that both the CO chemical shifts and stretching force constants and the magnitudes of the coupling constants are responding either to changes in the hybridization of the 2-RE-dmp ligands induced by changes in the steric bulk of the RE groups or to changes in the electron donor ability of the 2-RE-dmp ligands induced by changes in the electronegativity of the E groups.

Surprisingly, the degree of linear correlation between the chemical shifts of the *cis* and *trans*  $^{13}\text{C}$  and *trans*  $^{17}\text{O}$  CO resonances, the  $^{31}\text{P}$  resonances and the  $^{95}\text{Mo}$  resonances of the  $\text{Mo}(\text{CO})_5(2\text{-RE-dmp})$  complexes and the chemical shifts of similar resonances of the  $\text{Mo}(\text{CO})_5(\text{Ph}_2\text{PER})$  complexes varies from excellent to extremely poor. This indicates

that the effects of the three phosphorus substituents on the chemical shifts of the various nuclei are not independent as has been previously suggested.

### Supplementary Material

Mass spectral data for the complexes **1**, **3**, **6–14**, and **16** (1 page), are available from the authors on request.

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