Coordinated 2-Halo-1,3,2-dioxaphosphorinane Ligands.
II. Syntheses and ^{13}C, ^{31}P and ^{95}Mo NMR and IR Spectroscopic Characterization of some Cr and Mo Pentacarbonyl Complexes of 2-Substituted-4-methyl-1,3,2-dioxaphosphorinanes

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(Received March 17, 1986; revised May 12, 1986)

Abstract

A study of the reactions of $M(CO)_5(P(OCH_2CH_2CH(Me)O)Cl)$ (M = Cr, Mo) with a variety of nucleophiles of the type HER (E = NH, O, S; R = H, alkyl, aryl) is reported. The ^{13}C, ^{31}P and ^{95}Mo NMR and IR spectral data for the $M(CO)_5(P(OCH_2CH_2CH(Me)O)ER)$ complexes is presented and compared to that previously reported for some $Mo(CO)_5(P(OCH_2CMe_2CH_2O)ER)$ complexes. This comparison provides insight into the manner in which variations in the metal and in the substitution on the 1,3,2-dioxaphosphorinane ring affect the electron density distribution within these complexes.

The results from a study of the rates of chloride substitution by n-propylamine in the $M(CO)_5(P(OCH_2CH_2CH(Me)O)Cl)$ complexes are also presented. These rates are compared with those previously reported for chloride substitution by n-propylamine in the $Mo(CO)_5(P(OCH_2CMe_2CH_2O)Cl)$ and $Mo(CO)_5(Ph_2PCl)$ complexes. These comparisons, in conjunction with the NMR and IR studies, suggest that both the position of the Me groups on the phosphorinane ring and the amount of electron density on the P have significant effects upon the rate of chloride substitution in these complexes.

Introduction

The nucleophilic displacement of chloride from chlorophosphine ligands coordinated to transition metal complexes has been studied in detail [1–10]. In contrast, only two studies of the nucleophilic displacement of chloride from coordinated chlorophosphite ligands have been reported [11, 12]. These studies demonstrated that the rate of nucleophilic displacement of the chloride from $Mo(CO)_5$-(R_2PCl) complexes by n-propylamine is four orders

of magnitude less for $R_2 = OCH_2CMe_2CH_2O$ (2-Cl-5,5-dmp) ligands than for $R_2 = Ph_2$ (Ph_2PCl) ligands [12]. The reasons for the large difference in the rates of nucleophilic displacement of chloride from the R_2PCl complexes are not known [12]. In order to better understand the factors affecting these rates, we have carried out a study of the nucleophilic displacement of chloride from both $Mo(CO)_5$ and Cr-$(CO)_5$ complexes of $ClP(OCH_2CH_2CH(Me)O)$ (2-Cl-4-mp) by a variety of nucleophiles of the type HER' E = NH, O, S; R' = alkyl, aryl). The rate constants for the reactions of these complexes with n-propylamine are reported, and the factors which affect the rates of nucleophilic displacement of chloride from these R_2PCl ligands are discussed.

The multinuclear NMR and infrared data of the $M(CO)_5(2$-RE-4-mp) (M = Cr, Mo; R = NH, O, S; R = n-Pr, p-tolyl or RE = Cl) complexes are also presented. The data provide significant insight into the manner in which variations in the steric and electronic effects of the P-substituents affect the electron density distributions in these complexes. Comparison of the spectroscopic data with that which has previously been reported for other $M(CO)_5$ complexes of P-donor ligands [10, 12, 13–21] provides additional insight into the factors which may affect the electron density distributions, and thus, the rates of nucleophilic displacement of chloride in these complexes.

Experimental

Phosphorus trichloride (Fisher), 1,3-butanediol (Aldrich) and molybdenum and chromium hexacarbonyls (Pressure) were used as received. Liquid alcohols and amines were dried over molecular sieves prior to use, while solid alcohols and all thiols were used as received. Tetrahydrofuran (THF) was distilled from calcium hydride under nitrogen before use, while diethyl ether was distilled from sodium and benzophenone prior to use. Literature proce-

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dures were used for the synthesis of Cr(CO)$_5$(MeCN) [22] while the procedure used for the synthesis of 2-Cl-4-mp is similar to those previously reported for the syntheses of other 1,3,2-dioxaphosphorinanes [12, 23]; All reactions and purifications were run under an inert atmosphere of either argon or nitrogen.

2-Cl-4-methyl-1,3,2-dioxaphosphorinane, 2-Cl-4-mp (1)

A solution of 50.00 g (0.3640 mol) of phosphorus trichloride in 200 ml of diethyl ether and a solution of 32.80 g (0.3640 mol) of 1,3-butanediol and 57.59 g (0.7281 mol) of pyridine in 200 ml of diethyl ether were simultaneously added in a dropwise fashion over a 45 min period to 200 ml of stirred diethyl ether at 5 °C. Once the addition was finished, the ice bath was removed, and the mixture was stirred for 30 min. The mixture was then vacuum filtered to remove the pyridine hydrochloride, and the filtrate was rotary evaporated to dryness. The residue distilled at 90 °C under water aspirator to yield 29.38 g (52.23%) of 1 as a colorless liquid.

(2-Chloro-4-methyl-1,3,2-dioxaphosphorinane)pentacarbonylmolybdenum(0), Mo(CO)$_5$(2-Cl-4-mp) (2)

A solution of 5.00 g (18.9 mmol) of molybdenum hexacarbonyl and 2.93 g (18.9 mmol) of 2-Cl-4-mp (1) in 40 ml of methylcyclohexane was heated at reflux for 9 h during which time 585 ml of gas was evolved. The mixture was then evaporated to dryness and the residue was recrystallized from hexanes to yield 4.65 g (62.8%) of white crystalline 2.

(2-n-Propyloxy-4-methyl-1,3,2-dioxaphosphorinane)pentacarbonylmolybdenum(0), Mo(CO)$_5$(2-n-PrO-4-mp) (3)

A mixture of 5.0 ml (65 mmol) of 1-propanol and 0.050 g (2.2 mmol) of sodium metal was stirred for 10 min at ambient temperature before 0.78 g (2.0 mmol) of Mo(CO)$_5$(2-Cl-4-mp) (2) was added. Then the reaction mixture was stirred for 20 h before being evaporated to dryness. The residue was taken up in 25 ml of hexanes and filtered through a 1 cm layer of silica gel in a 30 cm^3 medium sintered glass funnel. The filtrate was rotary evaporated to dryness, giving 0.51 g (62%) of 3 as a pale brown oil.

(2-n-Propylthio-4-methyl-1,3,2-dioxaphosphorinane)pentacarbonylmolybdenum(0), Mo(CO)$_5$(2-n-PrS-4-mp) (4)

A solution of 0.26 ml (2.9 mmol) of 1-propanethiol in 25 ml of THF was stirred at ambient temperature and 1.82 ml of 1.5 M n-butyllithium in hexanes was added from a syringe. This solution was stirred for 10 min before 1.00 g (2.56 mmol) of Mo(CO)$_5$-(P(OCH$_2$CH$_2$CHMeO)Cl) was added. The reaction mixture was stirred at ambient temperature for 19 h

and then rotary evaporated to dryness. The residue was taken up in 10 ml of a 1:1 hexanes–methylene chloride mixture, and this solution was washed with three 50 ml portions of water. The organic layer was dried over magnesium sulfate and then filtered through a 1 cm layer of chromatography grade silica gel in a 30 cm^3 medium sintered glass funnel. After the filtration, the silica gel was washed with 5 ml of the 1:1 hexanes–methylene chloride mixture. The filtrate was rotary evaporated to dryness, yielding 0.80 g (73%) of 4 which crystallized as a white solid on standing in the freezer.

(2-n-Propylamino-4-methyl-1,3,2-dioxaphosphorinane)pentacarbonylmolybdenum(0), Mo(CO)$_5$(2-n-Pr-NH-4-mp) (5)

A solution of 1.03 g (2.64 mmol) of Mo(CO)$_5$-(2-Cl-4-mp) (2), 5.0 ml (61 mmol) of 1-propylamine and 5 ml of THF was stirred for 12 h at ambient temperature. The mixture was then rotary evaporated to dryness, and the residue was taken up in 20 ml of a 1:1 hexane–methylene chloride mixture. The solution was filtered through a 1 cm layer of silica gel in a 30 cm^3 medium sintered glass funnel. The filtrate was rotary evaporated to dryness to yield 0.63 g (58%) of 5 as a pale pink oil.

(2-p-Tolyloxy-4-methyl-1,3,2-dioxaphosphorinane)pentacarbonylmolybdenum(0), Mo(CO)$_5$(2-p-tolyl-O-4-mp), (6)

A solution of 0.28 g (2.6 mmol) of p-cresol in 20 ml of THF was stirred at ambient temperature as 0.27 ml of 9.5 M n-butyllithium in hexanes was added from a syringe. This mixture was stirred for about 5 min and then 1.12 g (2.88 mmol) of Mo(CO)$_5$(2-Cl-4-mp) (2) was added. The mixture was stirred for 15 h and then rotary evaporated to dryness. The residue was taken up in 16 ml of 1:1 hexanes–ether and washed with four 50 ml portions of 5% aqueous sodium carbonate solution and two 25 ml portions of sodium bicarbonate. The organic phase was dried over magnesium sulfate and then filtered. The filtrate was rotary evaporated to dryness to yield 0.96 g (71%) of 6 as a white solid.

(2-p-Tolylthio-4-methyl-1,3,2-dioxaphosphorinane)pentacarbonylmolybdenum(0), Mo(CO)$_5$(2-p-tolyl-thio-4-mp) (7)

A solution of 0.35 g (2.8 mmol) p-thiocresol in 25 ml of THF was stirred at ambient temperature as 1.82 ml of 1.55 M n-butyllithium was added. After about 20 min, 1.00 g (2.56 mmol) of Mo(CO)$_5$(2-Cl-4-mp) was added and the mixture was then stirred for 18 h. Then, the reaction mixture was rotary evaporated to dryness, and the residue was taken up in 5 ml of hexanes and 3 ml of methylene chloride. This mixture was washed twice with 50 ml portions of 5% sodium bicarbonate, and then twice with 50

ml portions of water. The organic layer was dried over magnesium sulfate, filtered through a 1 cm layer of chromatography grade silica gel in a 60 cm³ medium sintered glass funnel and then rotary evaporated to dryness. The oily residue crystallized upon standing in the freezer to yield 0.88 g (72%) of 7 as a white solid.

Triethylammonium (2-Oxy-4-methyl-1,3,2-dioxaphosphorinane)pentacarbonylmolybdenum(0), [Et₃-NH]⁺[Mo(CO)₅(2-O⁻-4-mp)] (8)

A mixture of 1.00 g (2.56 mmol) of Mo(CO)₅-(2-Cl-4-mp) (2), 10 ml of acetone, 10 ml of triethylamine and 5 ml of deionized water was stirred at ambient temperature for 18 h. The volume of the reaction mixture was then reduced to 10 ml under vacuum, and this mixture was treated with 15 ml of methanol and filtered to remove 0.38 g of insoluble solid. The filtrate was evaporated to dryness under high vacuum at ambient temperature to yield 0.20 g (16%) of 8 as a white solid.

(2-Chloro-4-methyl-1,3,2-dioxaphosphorinane)pentacarbonylchromium(0), Cr(CO)₅(2-Cl-4-mp) (9)

Method A

A mixture of 4.10 g (17.6 mmol) of Cr(CO)₅-(CH₃CN) and 2.72 g (17.6 mmol) of 2-Cl-4-mp (1) in 35 ml of degassed methylene chloride was stirred for 15 h. After rotary evaporation, the residue was distilled at 98 °C (0.1 mm of Hg) to yield 4.91 g (80.5%) of 9.

Method B

A solution of 5.00 g (22.7 mmol) of chromium hexacarbonyl in 300 ml of THF was irradiated with a medium-pressure 450 watt mercury-vapor quartz lamp, and the gas evolution was monitored. When the evolution ceased, 3.51 g (22.73 mmol) of 2-Cl-4-mp (1) was added, and the photolysis was continued until all gas evolution ceased. Then the mixture was rotary evaporated to dryness. The residue was dissolved in hexanes and filtered through a 1 cm layer of silica gel in a 30 cm³ medium sintered glass funnel. The filtrate was rotary evaporated and distilled at 93–95 °C (0.05 mm of Hg). The distillate crystallized on standing in the freezer, giving 3.18 g (40.4%) of 9.

Attempted Method C

An attempt was made to synthesize the complex in the same manner as the molybdenum compound. Infrared spectra, however, revealed that no CO substitution had occured after a 24 h reflux.

(2-n-Propyloxy-4-methyl-1,3,2-dioxaphosphorinane)-pentacarbonylchromium(0), Cr(CO)₅(2-n-PrO-4-mp) (10)

The synthesis was similar to that of the Mo analogue 4 with 1.00 g (2.88 mmol) of Cr(CO)₅-

(2-Cl-4-mp) (9) and 0.073 g (3.2 mmol) of sodium in 10 ml of 1-propanol yielding 0.72 g (67%) of 10 as a pale green oil.

(2-n-Propylthio-4-methyl-1,3,2-dioxaphosphorinane)-pentacarbonylchromium(0), Cr(CO)₅(2-n-PrS-4-mp) (11)

The synthesis was similar to that of the Mo analogue 5 with 0.33 ml of 9.5 M n-butyllithium and 0.29 ml (3.20 mmol) of 1-propanethiol and 1.00 g (2.88 mmol) of Cr(CO)₅(2-Cl-4-mp) (9) yielding 0.52 g (47%) of 11 as a pale yellow oil.

(2-n-Propylamino-4-methyl-1,3,2-dioxaphosphorinane)pentacarbonylchromium(0), Cr(CO)₅(2-n-PrNH-4-mp) (12)

A solution of 0.51 g (1.5 mmol) of Cr(CO)₅(2-Cl-4-mp) and 5.0 ml of 1-propylamine (61 mmol) in 5 ml of acetonitrile was stirred at ambient temperature for 12 h before being rotary evaporated to dryness. The residue was taken up in 12 ml of a 1:1 methylene chloride–hexanes mixture, and the mixture was filtered through a 1 cm layer of chromatography grade alumina in a 15 cm³ medium sintered glass funnel. The filtrate was rotary evaporated to dryness to yield 0.48 g (87%) of 12 as a pale yellow oil.

(2-p-Tolyloxy-4-methyl-1,3,2-dioxaphosphorinane)-pentacarbonylchromium(0), Cr(CO)₅(2-p-tolyl-O-4-mp) (13)

The synthesis was similar to that of the Mo analogue 6 with 0.31 g (2.9 mmol) of p-cresol, 0.33 ml of 9.5 M n-butyllithium and 1.00 g (2.88 mmol) of Cr(CO)₅(2-Cl-4-mp) (9) yielding 0.40 g (33%) of 13 as a white solid.

(2-p-Tolylthio-4-methyl-1,3,2-dioxaphosphorinane)-pentacarbonylchromium(0), Cr(CO)₅(2-p-tolyl-S-4-dmp) (14)

The synthesis was similar to that of the Mo analogue 7 with 1.00 g (2.88 mmol) of Cr(CO)₅(2-Cl-4-mp) (9), 0.36 g (2.9 mmol of p-thiocresol and 1.86 ml of 1.55 M n-butyllithium yielding 0.98 g (78%) of 14 as a pale green solid.

Triethylammonium (2-Oxy-4-methyl-1,3,2-dioxaphosphorinane)pentacarbonylchromium(0), [Et₃-NH]⁺[Cr(CO)₅(2-O⁻-4-mp) (15)

A mixture of 1.00 g (2.88 mmol) of Cr(CO)₅-(2-Cl-4-mp) (9), 10 ml of acetone, 10 ml of triethylamine and 5 ml of deionized water was stirred for 65 h at ambient temperature. The reaction mixture was then evaporated to dryness, and the residue was taken up in 25 ml of a 1:1 hexanes–methylene chloride mixture. This mixture was washed with three 50 ml portions of water. The organic layer was dried over magnesium sulfate, filtered and the filtrate

TABLE I. Carbonyl ^{13}C, ^{31}P and ^{95}Mo NMR Data for the $M(CO)_5(2\text{-RE-4-mp})$ Complexes

M	ER	trans CO		cis CO		P	Mo	
		$\delta(^{13}C)^b$ (ppm)	$\lvert^2J_{PC}\rvert$ (Hz)	$\delta(^{13}C)^b$ (ppm)	$\lvert^2J_{PC}\rvert$ (Hz)	$\delta(^{31}P)^c$ (ppm)	$\delta(^{95}Mo)^b$ (ppm)	$\lvert^1J_{MoP}\rvert$ (Hz)
Mo	Cl (2)	208.40	52.6	203.14	14.0	163.90	−1749.5	243.6
Mo	O-n-Pr (3)	208.90	40.2	204.71	13.9	156.26	−1844.6	197.8
Mo	S-n-Pr (4)	209.39	41.1	204.44	12.4	194.86	−1766.6	204.4
Mo	NH-n-Pr (5)	208.84	33.5	205.27	12.8	152.61	−1844.5	194.1
Mo	O-p-tolyl (6)	208.60	44.2	204.03	13.8	153.86	−1828.5	227.5
Mo	S-p-tolyl (7)	209.45	45.4	203.96	12.6	188.91	−1754.2	212.7
Mo	O⁻Et₃NH⁺ (8)	212.10	29.2	207.51	14.4	133.73	−1848.9	195.1
Cr	Cl (9)	218.69	<1	213.58	21.0	189.60		
Cr	O-n-Pr (10)	219.82	<1	215.54	21.1	172.28		
Cr	S-n-Pr (11)	220.14	<1	215.14	18.5	215.04		
Cr	NH-n-Pr (12)	219.85	6.9	216.28	19.8	171.89		
Cr	O-p-tolyl (13)	219.52	<1	214.82	21.5	174.11		
Cr	S-p-tolyl (14)	220.80	1.4	214.63	18.9	209.46		
Cr	O⁻Et₃NH⁺ (15)	223.13	<1	218.79	22.3	147.35		

^{a}Spectra run on 0.20 M d_1-chloroform solutions. ^{b}Doublet. ^{c}Singlet.

TABLE II. Infrared Stretching Frequencies and Cotton–Kraihanzel Stretching Force Constants for the $M(CO)_5(2\text{-RE-4-mp})$ Complexes

RE	$A_1^{1\ a}$ (cm^{-1})	B_1^b (cm^{-1})	$A_1^{2\ c}$ (cm^{-1})	E^c (cm^{-1})	k_1 (mdyne/A)	k_2 (mdyne/A)	k_i (mdyne/A)	B_1 (calc.) (cm^{-1})
M = Mo								
Cl (2)	2089	^{d}	1980	1972	16.04	16.28	0.29	2008
O-n-Pr (3)	2081	1996	1967	1957	15.85	16.07	0.30	1995
S-n-Pr (4)	2081	1997	1967	1959	15.84	16.10	0.30	1996
NH-n-Pr (5)	2076	1985	1959	1945	15.74	15.91	0.31	1985
O-p-tolyl (6)	2083	1999	1966	1961	15.82	16.13	0.30	1998
S-p-tolyl (7)	2081	1997	1966	1960	15.82	16.11	0.29	1997
M = Cr								
Cl (9)	2083	^{d}	1978	1968	16.01	16.21	0.28	2003
O-n-Pr (10)	2076	1993	1962	1952	15.77	15.99	0.30	1990
S-n-Pr (11)	2071	1991	1963	1954	15.77	16.99	0.28	1990
NH-n-Pr (12)	2067	1975	1955	1943	15.69	15.76	0.31	1975
O-p-tolyl (13)	2076	1992	1964	1953	15.80	16.00	0.30	1990
S-p-tolyl (14)	2073	1992	1962	1954	15.76	16.00	0.29	1990

^{a}Medium. ^{b}Very weak. ^{c}Strong. ^{d}Not observed.

evaporated to dryness to yield 0.71 g (57%) of **15** as a pale yellow solid.

The 2-chloro-4-methyl-1,3,2-dioxaphosphorinane ligand was characterized by comparison of its ^1H NMR spectra with literature spectra [13].

All of the complexes were characterized by ^{13}C, ^{17}O, ^{31}P and ^{95}Mo NMR spectroscopy, and the NMR spectral data for the complexes are summarized in Table I. The multinuclear NMR spectra of 0.50 M d_1-chloroform solutions of the complexes in nitrogen-

filled 10 mm NMR tubes were run on a Nicolet, 300 MHz, wide-bore, multinuclear NMR spectrometer. The instrumental parameters for data acquisition and work up and the standards used have been previously reported [24].

Infrared spectra of dilute 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 cm^{-1} using a Perkin-Elmer 283B infrared spectrometer. The method used to assign the

TABLE III. Rate Data for the Reactions of the $M(CO)_5$(2-Cl-4-mp) Complexes with 1-Propylamine in d_1-Chloroform

M	[complex] (mol l^{-1})	[1-propylamine] (mol l^{-1})	Initial rate (mol l^{-1} s^{-1})	k (l mol^{-1} s^{-1})
Mo (2)	0.20	0.40	4.2×10^{-5}	5.2×10^{-4}
	0.20	0.40	3.8×10^{-5}	4.7×10^{-4}
	0.20	0.80	1.1×10^{-4}	7.1×10^{-4}
	0.20	0.80	1.1×10^{-4}	7.0×10^{-4}
	0.40	0.80	2.6×10^{-4}	8.0×10^{-4}
	0.40	0.80	2.4×10^{-4}	7.6×10^{-4}
Cr (9)	0.10	0.20	7.3×10^{-7}	3.6×10^{-5}
	0.20	0.40	2.5×10^{-6}	3.1×10^{-5}
	0.20	0.56	4.2×10^{-6}	3.8×10^{-5}
	0.40	0.80	6.7×10^{-6}	4.1×10^{-5}

observed absorptions to the symmetry modes has been previously described [12]. Infrared stretching force constants were calculated from the A_1^1, A_1^2 and E absorption frequencies using the Cotton—Kraihanzel approximation [25]. The IR absorptions and approximate stretching force constants are summarized in Table II.

Mass spectra of all of the complexes, except for 8 and 15 which are 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 given in the Supplementary Material.

The initial rates and rate constants for the reactions of the 2-Cl-4-mp complexes with 1-propylamine were measured using ^{31}P NMR spectroscopy as has previously been described [12]. Each reaction was studied using at least three different sets of amine/complex concentrations. Both initial reaction rates and rate constants were calculated and are summarized in Table III.

The correlations between the various NMR chemical shifts and coupling constants and the IR CO stretching force constants were run using the ABSTAT^{TM} release 4 program of Anderson—Bell. Linear regression analyses were run for all of the correlations and the levels of confidence determined by an analysis of variance of the regression using the F test. All levels of confidence are measures of the likelyhood that the correlation in question is valid.
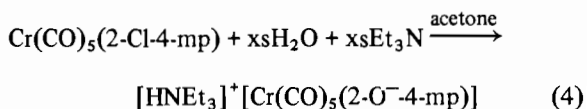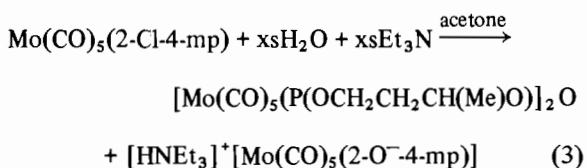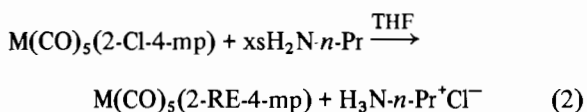
Results

Syntheses

The thermal reaction of $Mo(CO)_6$ and 2-Cl-4-mp forms $Mo(CO)_5$(2-Cl-4-mp) (2) in moderate yield. The thermal reaction of $Cr(CO)_6$ with 2-Cl-4-mp does not produce any $Cr(CO)_5$(2-Cl-4-mp) (9) even after a 24 h reflux. Instead, 9 can be synthesized by the reaction of 2-Cl-4-mp with $Cr(CO)_5$(MeCN).

The Cr complex may also be synthesized by the photochemical reaction of the hexacarbonyl with 2-Cl-4-mp, however the yield of 9 is poor.

The displacement of the Cl groups from the $M(CO)_5$(2-Cl-4-mp) (M = Mo (2) and Cr (9)) complexes by alcohols, thiols, amines and water are summarized in eqns. 1—4. These reactions are similar to those previously reported for the Mo(CO)$_5$(2-Cl-

$$M(CO)_5\text{(2-Cl-4-mp)} + M'ER \xrightarrow{\text{THF}}$$

$$M(CO)_5\text{(2-RE-4-mp)} + M'Cl \qquad (1)$$
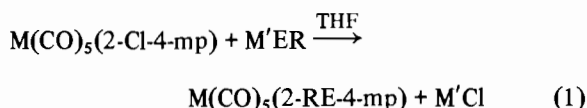
M = Cr, Mo; M'ER = NaO-*n*-Pr, LiS-*n*-Pr, LiO-*p*-tolyl, LiS-*p*-tolyl

$$M(CO)_5\text{(2-Cl-4-mp)} + xsH_2N\text{-}n\text{-Pr} \xrightarrow{\text{THF}}$$

$$M(CO)_5\text{(2-RE-4-mp)} + H_3N\text{-}n\text{-Pr}^+Cl^- \qquad (2)$$

$$Mo(CO)_5\text{(2-Cl-4-mp)} + xsH_2O + xsEt_3N \xrightarrow{\text{acetone}}$$

$$[Mo(CO)_5(P(OCH_2CH_2CH(Me)O)]_2O$$

$$+ [HNEt_3]^+[Mo(CO)_5\text{(2-O}^-\text{-4-mp)}] \qquad (3)$$

$$Cr(CO)_5\text{(2-Cl-4-mp)} + xsH_2O + xsEt_3N \xrightarrow{\text{acetone}}$$

$$[HNEt_3]^+[Cr(CO)_5\text{(2-O}^-\text{-4-mp)}] \qquad (4)$$

5,5-dmp) complexes with similar ligands [11, 12] with the exception of the hydrolysis of $Mo(CO)_5$-(2-Cl-4-mp) shown in eqn. 3. This reaction gave only a 16% yield of the expected salt and produced a significant amount of a second material. Multinuclear NMR and IR spectroscopic studies suggest that this material is the dinuclear diphosphoxane complex, $[Mo(CO)_5(P(OCH_2CH_2CH(Me)O)]_2O$. The hydrolysis of $Cr(CO)_5$(2-Cl-4-mp) under similar reaction conditions did not produce the Cr analog of this material and gave a good yield of the expected salt 15.

Quantative studies of the rates of the nucleophilic displacements of Cl from the $M(CO)_5(2-Cl-4-mp)$ complexes with 1-propylamine have been carried out with ^{31}P NMR spectroscopy, using a previously described method [12], and the results are summarized in Table III. Although the initial rates show some dependance upon the polarity of the reaction medium, both reactions appear to be first order in both complex and amine and thus to proceed by S_N2 mechanisms. The rate constants show that Cl displacement from the Mo complex (2) is significantly more rapid than from the Cr complex (9).

Carbonyl ^{13}C NMR Spectra

The ^{13}C NMR data for the *cis* and *trans* COs of the $M(CO)_5(2-RE-4-mp)$ complexes are reported in Table I. Both the *cis* and *trans* CO resonances of the Mo complexes are found approximately 10 ppm upfield of the corresponding resonances of the Cr complexes. According to the Bodner–Todd theory of CO chemical shifts [26, 27], this suggests that the Cr donates more electron density from its d orbitals into the CO π^*-antibonding orbitals than does the Mo. These results are consistent with those from other ^{13}C NMR studies of Cr and Mo carbonyl complexes of other P-donor ligands [13, 14].

The magnitudes of the $^2J_{PC}$ coupling constants of the *trans* COs of the $Cr(CO)_5(2-RE-4-mp)$ complexes are much smaller than those of the *trans* CO ligands of the $Mo(CO)_5(2-RE-4-mp)$ complexes. In contrast, the magnitudes of the $^2J_{PC}$ coupling constants of the *cis* COs of the $Cr(CO)_5(2-RE-4-mp)$ complexes are significantly larger than those of the *cis* CO ligands of the $Mo(CO)_5(2-RE-4-mp)$ complexes. These results are similar to those which have been obtained from ^{13}C NMR studies of Cr and Mo carbonyl complexes of other P-donor ligands [13, 14].

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

The $^{31}P\{^1H\}$ NMR data for the $M(CO)_5(2-RE-4-mp)$ complexes are summarized in Table I. The ^{31}P NMR spectrum of each complex contains a singlet resonance, and this was used as a check on the purity of the complex. The ^{31}P resonances of the $Cr(CO)_5(2-RE-4-mp)$ complexes are found 13.6 to 25.7 ppm downfield of the ^{31}P resonances of the $Mo(CO)_5(2-RE-4-mp)$ complexes. The chemical shifts of the ^{31}P resonances of the $M(CO)_5(2-RE-4-mp)$ complexes are extremely sensitive to the nature of the E group with the ^{31}P resonances of the E = S complexes found farthest downfield and those of the E = O and NH complexes found farthest upfield. This behavior indicates that the electronegativity of the E group is not the predominate factor which affects the chemical shifts of the ^{31}P resonance in these complexes. The chemical shifts of the ^{31}P resonances of the $Mo(CO)_5(2-RE-5,5-dmp)$ complexes also exhibit this unusual behavior [12].

^{95}Mo NMR Spectra

The ^{95}Mo NMR data for the $Mo(CO)_5(2-RE-4-mp)$ complexes are summarized in Table I. The ^{95}Mo NMR spectrum of each of the complexes consists of a doublet with a $|^1J_{MoP}|$ of 195 to 243 Hz. The line widths of the ^{95}Mo resonances (5–21 Hz) are among the narrowest reported for Mo complexes in which the Mo is not in a spherically symmetric environment. The chemical shifts of the Mo resonances are sensitive to the nature of the E group with the resonance moving downfield in the order $O > N \gg S > Cl$. This behavior is similar to that reported for the ^{95}Mo resonances of other $Mo(CO)_5$-(R_2PER') complexes [10, 12].

Carbonyl IR Spectra

The infrared spectra of the CO region (2100–1900 cm^{-1}) of the $M(CO)_5(2-RE-4-mp)$ complexes contain four absorptions which are assigned to the two A_1, the B_1 and the E symmetry modes as has been previously described. The Cotton–Kraihanzel force constants [25] for these absorptions have been calculated using the data for the A_1^1, A_1^2 and E absorptions. In order to ensure that the correct assignments for the stretching modes have been made, the force constants have been used to calculate the position of the B_1 absorption. The observed stretching frequencies, the stretching force constants and the calculated position for the B_1 absorption are summarized in Table II. The lower force constants of the Cr complexes relative to those of the Mo complexes are in agreement with the ^{13}C NMR results which suggest that Cr donates more electron density from its d orbitals to the CO π^*-antibonding orbitals than does Mo.

Discussion

Multinuclear NMR and IR Spectroscopic Studies

Previous studies of complexes of the type $Mo(CO)_5(R_2PER')$ have demonstrated that fair to good linear correlations exist between the IR stretching force constants and the NMR chemical shifts of the ^{13}C resonances of the *cis* and *trans* CO ligands [10, 12]. The correlation coefficients and levels of confidence of these correlations for the $M(CO)_5(2-RE-4-mp)$ (M = Cr, Mo) complexes are summarized in Table IV. The correlation coefficients are similar to those previously reported for the $Mo(CO)_5(2-RE-5,5-dmp)$ complexes, however the levels of confidence are lower as fewer data points are used in the calculations. As was reported for the 2-RE-5,5-dmp complexes, the correlations involving the ^{13}C NMR chemical shifts or the IR stretching force constants of the *trans* CO ligands improve greatly when the data for the E = S complexes are dropped from the correlations. According to the

TABLE IV. Correlations between the ^{13}C NMR Chemical Shifts and IR Stretching Force Constants of the *cis* and *trans* COs of the $M(CO)_5$ (2-RE-4-mp) Complexes

M	Parameter 1	Parameter 2	Linear correlation coefficient[a,b]	Level of confidence (%)
Cr	$\delta\,^{13}C$ *trans* CO	^{13}C *cis* CO	0.9291 (0.9596)	99.75
	$\delta\,^{13}C$ *trans* CO	k_1	−0.8938 (−0.9775)	98.37
	$\delta\,^{13}C$ *cis* CO	k_2	−0.9451	99.56
	k_1	k_2	0.9142 (0.9499)	98.93
Mo	$\delta\,^{13}C$ *trans* CO	^{13}C *cis* CO	0.9002 (0.9495)	99.43
	$\delta\,^{13}C$ *trans* CO	k_1	−0.6447 (−0.8866)	83.31
	$\delta\,^{13}C$ *cis* CO	k_2	−0.9651	99.82
	k_1	k_2	0.9077 (0.9308)	98.76

[a]Correlations involving only chemical shift data use data for 7 compounds while those involving k_1 or k_2 use data for 6 compounds. [b]Coefficients in parentheses are those calculated using all data except that for the E = S complexes.

TABLE V. Correlations between Similar NMR Chemical Shifts and IR Force Constants of the $M(CO)_5$(2-RE-4-mp) and the $Mo(CO)_5$(2-RE-5,5-dmp) Complexes

Parameter	Linear regression coefficient[a]	Level of confidence (%)
$Cr(CO)_5$(2-RE-4-mp) *vs.* $Mo(CO)_5$(2-RE-4-mp)		
$\delta\,^{13}C$ *trans* CO	0.9943	>99.99
$\delta\,^{13}C$ *cis* CO	0.9992	>99.99
$\delta\,^{31}P$	0.9902	>99.99
k_1 (*trans* CO)	0.9792	99.94
k_2 (*cis* CO)	0.9902	99.99
$Cr(CO)_5$(2-RE-4-mp) *vs.* $Mo(CO)_5$(2-RE-5,5-dmp)		
$\delta\,^{13}C$ *trans* CO	0.9847	>99.99
$\delta\,^{13}C$ *cis* CO	0.9966	>99.99
$\delta\,^{31}P$	0.9861	>99.99
k_1 (*trans* CO)	0.9657	99.83
k_2 (*cis* CO)	0.9641	99.81
$Mo(CO)_5$(2-RE-4-mp) *vs.* $Mo(CO)_5$(2-RE-5,5-dmp)		
$\delta\,^{13}C$ *trans* CO	0.9842	>99.99
$\delta\,^{13}C$ *cis* CO	0.9977	>99.99
$\delta\,^{31}P$	0.9826	>99.99
$\delta\,^{95}Mo$	0.9717	99.97
k_1 (trans CO)	0.9869	99.97
k_2 (*cis* CO)	0.9963	99.98

[a]Correlations with chemical shifts used data for 7 compounds while those with k_1 and k_2 use data for six compounds.

Bodner–Todd theory of CO NMR chemical shifts [26, 27], these correlations indicate that the amount of electron density donated into the CO π^*-antibonding orbitals increases as the E atom varies, with $Cl < S < O < NH$.

Linear correlations between the NMR chemical shifts of analogous resonances in the $M(CO)_5$(2-RE-4-mp) (M = Cr, Mo) and $Mo(CO)_5$(2-RE-5,5-dmp) complexes have been studied and the linear correlation coefficients and levels of confidence are given in Table V. The linear correlations between the two sets of CO stretching force constants for the three complexes are also reported. These correlations are all excellent with levels of confidence $\geqslant 99.8\%$, and this indicates that similar electronic and steric factors are affecting the NMR chemical shifts and IR stretching force constants in these complexes. This is not surprising since the only differences in the sets of complexes are in the central metal atoms and in the number and position of the Me groups on the phosphorinane ring.

Nucleophilic Displacement of Chlorides from P-Donor Ligands

We have previously reported that the rate of chloride displacement from $Mo(CO)_5(R_2PCl)$ complexes by 1-propylamine is four orders of magnitude greater for the Ph_2PCl complexes than for the 2-Cl-5,5-dmp complexes [12]. These relative rates are surprising since both the higher electronegativity and the smaller size of the phosphorinane group relative to the two phenyl groups might be expected to favor a more rapid displacement of the chloride from the 2-Cl-5,5-dmp complex. Similar rates of chloride displacement from $R_2P(O)Cl$ (R = alkyl, alkoxy) compounds had been rationalized by assuming significant π-donation of electron density from the filled p-orbitals on O to the empty d-orbitals on P [28]. However, the IR and NMR data for the $Mo(CO)_5(R_2PCl)$ complexes indicate that there is less electron density on the P in the 2-RE-5,5-dmp complexes than in the Ph_2PER complexes. Thus, an alternate explanation is necessary for the relative rates of chloride displacement which are observed in these complexes.

One possibility is that the rate determining step in the S_N2 displacement of chloride from the $Mo(CO)_5(Ph_2PCl)$ and $Mo(CO)_5(2-Cl-4-mp)$ complexes is not the attack of the entering group on the complexes to form a five coordinate transition state

but rather is the loss of chloride from this transition state. If this is the case, a decrease in the electron density at the P will cause a decrease in the rate of chloride displacement. This hypothesis is supported by the relative rates of chloride displacement observed for the two $M(CO)_5(2\text{-Cl-4-mp})$ complexes and the NMR and IR spectra of the complexes. The rate of chloride displacement by 1-propylamine from the $Mo(CO)_5(2\text{-Cl-4-mp})$ complex is an order of magnitude larger than that from the $Cr(CO)_5(2\text{-Cl-mp})$ complex. The downfield shifts of the *cis* and *trans* CO ^{13}C and ^{31}P NMR resonances and the lower IR CO stretching force constants of the Cr complexes relative to the Mo complexes indicate that the Cr is donating more electron density into the CO π^*-antibonding orbitals and less into the P d-orbitals. Thus, the decrease in rate which occurs as Mo is replaced by Cr is paralleled by a decrease in the electron density at P.

Steric factors also have a significant affect upon the rates of chloride displacement in these complexes. The rate of chloride displacement from the $Mo(CO)_5(2\text{-Cl-4-mp})$ complex is two orders of magnitude greater than the rate of chloride displacement from the 2-Cl-5,5-dmp complex. The chemical shifts of the *cis* and *trans* CO ^{13}C, ^{31}P and ^{95}Mo NMR resonances and the IR CO stretching force constants of the 2-Cl-4-mp and 2-Cl-5,5-mp complexes are nearly identical and correlate well which suggests that the effect is not electronic in nature. The large difference in rates of chloride displacement from complexes which only differ by the number and position of the Me substituents on the phosphorinane ring suggests that steric interaction is occurring with the Me substituents, and that this interaction is significantly stronger when two Me groups are present at the 5 position than when one Me is present at the 4 position.

Conclusions

The rates of the S_N2 displacement of chloride from the $M(CO)_5(R_2PCl)$ complexes decrease in the order $R_2PCl = Ph_2PCl > 2\text{-Cl-4-mp} > 2\text{-Cl-5,5-dmp}$ for M = Mo and in the order Mo > Cr for $R_2PCl =$ 4-Cl-4-mp. Both the steric and electronic properties of the R groups have significant effects on the rate of this reaction. The decrease in rate with a decrease in the electron density on the P suggests that the rate determining step in these reactions is not the attack of the nucleophile on the complex to form a five coordinate transition state, but rather the dissociation of chloride from this transition state. The two order of magnitude difference in the rates of chloride displacement from the $Mo(CO)_5(2\text{-Cl-4-mp})$ and $Mo(CO)_5(2\text{-Cl-5,5-dmp})$ complexes suggests that

steric interactions with the Me substituents of the phosphorinane ring also exert a significant affect on the rates of the reactions.

Supplementary Material

Mass spectral data for the complexes **2–7** and **9–14** (1 page).

References

1 C. S. Kraihanzel, *J. Organomet. Chem.*, *73*, 137 (1974) and refs. therein.
2 G. Johanssen, O. Stelzer and E. Unger, *Chem. Ber.*, *108*, 1259 (1975).
3 P. W. Ledner, W. Beck and G. Theil, *Inorg. Chim. Acta*, *20*, L11 (1976).
4 G. M. Gray and C. S. Kraihanzel, *J. Organomet. Chem.*, *146*, 23 (1978).
5 G. M. Gray and C. S. Kraihanzel, *J. Organomet. Chem.*, *187*, 51 (1980).
6 H. Noth, H. Reith and V. Thorn, *J. Organomet. Chem.*, *159*, 165 (1978).
7 E. Lindner and J. C. Wuhrmann, *Chem. Ber.*, *114*, 2272 (1981).
8 E. H. Wong and F. C. Bradley, *Inorg. Chem.*, *20*, 2333 (1981).
9 P. M Treichel and L. D. Rosenheim, *Inorg. Chem.*, *20*, 1539 (1981).
10 G. M. Gray, *Inorg. Chim. Acta*, *81*, 157 (1984).
11 C. M. Bartish and C. S. Kraihanzel, *Inorg. Chem.*, *12*, 391 (1973).
12 G. M. Gray, J. W. Box and J. E. Whitten, *Inorg. Chim. Acta*, *118*, 21 (1986).
13 G. M. Bodner, *Inorg. Chem.*, *14*, 2694 (1975).
14 G. M. Bodner, M. P. May and L. E. McKinney, *Inorg. Chem.*, *19*, 1951 (1980).
15 P. Jaitner and W. Wohlgenannt, *Monat. Chem.*, *113*, 699 (1982).
16 A. M. Bond, S. W. Carr, R. Colton and D. P. Kelley, *Inorg. Chem.*, *22*, 989 (1983).
17 A. F. Masters, G. E. Bossard, T. A. George, R. T. C. Brownlee, M. J. O'Connor and A. G. Wedd, *Inorg. Chem.*, *22*, 908 (1983).
18 G. M. Gray and C. S. Kraihanzel, *J. Organomet. Chem.*, *241*, 201 (1983).
19 G. M. Gray and C. S. Kraihanzel, *Inorg. Chem.*, *22*, 2959 (1983).
20 G. M. Gray and R. J. Gray, *Organometallics*, *2*, 1026 (1983).
21 G. M. Gray, R. J. Gray and D. C. Berndt, *J. Magn. Reson.*, *57*, 347 (1984).
22 U. Koelle, *J. Organomet. Chem.*, *133*, 53 (1977).
23 D. W. White, R. D. Bertrand, G. K. McEwen and J. G. Verkade, *J. Am. Chem. Soc.*, *92*, 7125 (1970).
24 G. M. Gray and K. A. Redmill, *Magn. Reson. Chem.*, *24*, 527 (1986).
25 F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, *84*, 4432 (1962).
26 G. M. Bodner and L. J. Todd, *Inorg. Chem.*, *13*, 1335 (1974).
27 J. P. Hickey, J. R. Wilkinson and L. J. Todd, *J. Organomet. Chem.*, *179*, 159 (1979).
28 R. F. Hudson and L. Keay, *J. Chem. Soc.*, *1960*, 1859.