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Preparation and Multinuclear NMR and IR Spectroscopic Characterization of some Complexes of Acetyldiphenylphosphine, Diphenyl(2-thienyl)phosphine, Bis(2-thienyl)phenylphosphine and Cyanodiphenylphosphine

ASHIMA VARSHNEY and GARY M. GRAY*

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

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Abstract

The syntheses and multinuclear NMR and IR spectroscopic characterizations of some mononuclear Mo, Pd and Pt complexes of acetyldiphenylphosphine, diphenyl(2-thienyl)phosphine, bis(2-thienyl)phenylphosphine and cyanodiphenylphosphine are presented. The NMR and IR spectra of the Mo carbonyl complexes indicate that the electron-donor ability of the P substituents increases in the order CN < C(O)Me < 2-thienyl < Ph. The reactions of free and coordinated acetyldiphenylphosphine with amines and borohydrides are reported. These reactions do not lead to the desired imino and hydroxymethyl complexes but rather result in P–C bond cleavage. Attempts to form dinuclear complexes with bridging 2-thienylphosphine ligands from mononuclear complexes with P-coordinated ligands have not been successful. The products of the reactions result from ligand exchange between the mononuclear precursors and contain only P-coordinated ligands. The structure suggested for a previously reported homodinuclear complex containing a bridging cyanodiphenylphosphine ligand, $[(CO)_5Mo(Ph_2PCN)]_2$, has been confirmed by multinuclear NMR and IR spectroscopic studies. An attempt to form a heterodinuclear MoPt complex with bridging cyanophosphine ligands has not been successful. The products of this reaction result from ligand exchange between the mononuclear precursors.

Introduction

There has been considerable interest in recent years in dinuclear transition metal complexes in which the two metals are coordinated to a bidentate ligand that has a single atom bridge between the two donor sites. The metal centers in these complexes are close to one another and can form metal–metal bonds. The reactions of small molecules, such as H_2, CO, CO_2 and SO_2, with the dinuclear complexes are often quite different from those with similar mononuclear complexes because of these metal–metal interactions. Thus, these complexes may serve as catalysts for reactions that require the activation of small molecules and that are not efficiently catalyzed by mononuclear complexes.

Many of the complexes that have been studied contain bridging ligands with equivalent P-donor sites such as $Ph_2PCH_2PPh_2$ [1], Ph_2POPPh_2 [2], $(RO)_2POP(OR)_2$ (R = H, alkyl) [3] and $Ph_2PNHPPh_2$ [4]. Because the ligands contain two soft P-donor sites, the binuclear complexes which are formed generally contain two similar, soft metal centers. Recently, dinuclear complexes with the bridging ligands 2-(Ph_2P)pyridine [5], 2,6-$(Ph_2P)_2$pyridine [6], and $Ph_2PCH_2NEt_2$ [7], which have two different donor sites separated by a single atom bridge, have been reported. These ligands have the potential to form heteronuclear complexes containing both a hard and a soft metal center due to the differing coordinating abilities of the donor sites.

A number of other ligands containing both a P-donor site and either an N-, O- or S-donor site have been reported in the literature. We have attempted to form bimetallic complexes with four of these ligands: $Ph_2PC(O)Me$ (1), Ph_2P(2-thienyl) (2), PhP(2-thienyl)$_2$ (3) and Ph_2PCN (4). These ligands were chosen for study because they contain different coordination sites and can potentially form both A-frame and non-A-frame complexes. In this paper, we report the results of our study of the coordination chemistry of these ligands. The syntheses and multinuclear NMR and IR spectroscopic data for mononuclear Mo, Pd and Pt complexes of the ligands are presented. Also discussed are the abilities of the ligands to serve as bidentate, bridging ligands in dinuclear transition metal complexes.

Experimental

All reactions and purifications were run under an inert atmosphere (N_2 or Ar). Tetrahydrofuran (THF)

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*Author to whom correspondence should be addressed.

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and diethyl ether were distilled from sodium-benzophenone under N_2. Benzene, hexanes and dichloromethane were distilled from calcium hydride under N_2. Literature methods were used to prepare ([2.2.1]-bicyclohepta-2,5-diene)tetracarbonylmolybdenum(O) (Mo(CO)$_4$(nbd)) [8], *cis*-bis(piperidine)-tetracarbonylmolybdenum(O) (*cis*-Mo(CO)$_4$(pip)$_2$) [9], dichloro-bis(benzonitrile)palladium(II) (PdCl$_2$-(PhCN)$_2$) [10], dichloro(1,5-cyclooctadiene)platinum(II) (PtCl$_2$(cod)) [11], acetyldiphenylphosphine (**1**) [12], diphenyl(2-thienyl)phosphine (**2**) and bis(2-thienyl)phenylphosphine (**3**) [13] and cyanodiphenylphosphine (**4**) [14].

cis-Bis(acetyldiphenylphosphine)tetracarbonylmolybdenum(O), cis-Mo(CO)$_4$(Ph$_2$PC(O)Me)$_2$ (5)

A solution of 5.00 g (21.9 mmol) of **1** in 25 ml of hexanes was stirred at ambient temperature as 3.29 g (11.0 mmol) of Mo(CO)$_4$(nbd) were added. The yellow precipitate that formed was collected by filtration. Recrystallization from a dichloromethane–hexanes mixture gave 5.16 g (71.0%) of analytically pure **5** as a yellow microcrystalline solid. *Anal.* Calc. for $C_{32}H_{26}MoO_6P_2$: C, 57.00; H, 3.90. Found: C, 57.20; H, 4.05%.

cis-Bis(diphenyl(2-thienyl)phosphine)tetracarbonylmolybdenum(O), cis-Mo(CO)$_4$(Ph$_2$P(2-C$_4$H$_3$S))$_2$ (6)

A solution of 0.84 g (2.8 mmol) of Mo(CO)$_4$(nbd) in 20 ml of THF was added dropwise to 1.50 g (5.59 mmol) of **2** in 20 ml of THF over a 15 min period at ambient temperature. The reaction mixture was stirred overnight and then evaporated to dryness. A solution of the residue in 30 ml of a THF–hexanes mixture was filtered through a short silica gel column and then evaporated to dryness to yield crude **6** (2.0 g, 95%). Recrystallization of **6** from a dichloromethane–hexanes mixture yielded analytically pure **6**. *Anal.* Calc. for $C_{36}H_{28}MoO_4P_2S_2$: C, 58.00; H, 3.50. Found: C, 57.74; H, 3.86%.

cis-Bis(bis(2-thienyl)phenylphosphine)tetracarbonylmolybdenum(O), cis-Mo(CO)$_4$(PhP(2-C$_4$H$_3$S)$_2$)$_2$ (7)

A suspension of 0.69 g (1.9 mmol) of *cis*-Mo(CO)$_4$-(pip)$_2$ in 10 ml of dichloromethane was slowly added to a solution of 1.00 g (3.65 mmol) of **3** in 5 ml of dichloromethane at room temperature. The clear red solution was saturated with hexanes and then cooled at −20 °C. Analytically pure **7** (0.94 g, 82%) was obtained as pale yellow crystals. *Anal.* Calc. for $C_{32}H_{22}MoO_4P_2S_2$: C, 50.79; H, 2.91. Found: C, 50.53; H. 3.12%.

Dichloro-bis(diphenyl(2-thienyl)phosphine)-palladium(II), Pd(Ph$_2$P(2-C$_4$H$_3$S))$_2$Cl$_2$ (8)

A solution of 0.36 g (0.93 mmol) of Pd(PhCN)$_2$-Cl$_2$ in 5 ml of dichloromethane was added dropwise to a solution of 0.50 g (1.9 mmol) of **2** in 5 ml of dichloromethane over a 10 min period at room temperature. During the addition, the color of the solution changed from red to yellow and a yellow precipitate formed. This solid was collected by N_2-pressure filtration. The filtrate was reduced in volume and cooled to −20 °C to yield a second crop of analytically pure **8**·0.5CH$_2$Cl$_2$. The total yield of the reaction was 0.55 g (78%). *Anal.* Calc. for $C_{32.5}H_{29}Cl_3PdP_2S_2$: C, 50.81; H, 3.57. Found: C, 50.96; H, 3.75%.

Dichloro-bis(bis(2-thienyl)phenylphosphine)-palladium(II), Pd(PhP(2-C$_4$H$_3$S)$_2$)$_2$Cl$_2$ (9)

A solution of 0.70 g (1.8 mmol) of Pd(PhCN)$_2$Cl$_2$ in 3 ml of dichloromethane was added dropwise to a solution of 1.0 g (3.6 mmol) of **3** in 5 ml of dichloromethane over a 10 min period at room temperature. At the completion of the addition, a yellow precipitate of the product had formed and was collected. The filtrate was treated with hexanes and cooled to −10 °C to yield a second crop of analytically pure **9**. The total yield of the reaction was 0.84 g (64%). *Anal.* Calc. for $C_{28}H_{22}Cl_2PdP_2S_4$: C, 46.33; H, 3.03. Found: C, 46.35; H, 3.39%.

Dichloro-bis(diphenyl(2-thienyl)phosphine)-platinum(II), Pt(Ph$_2$P(2-C$_4$H$_3$S))$_2$Cl$_2$ (10)

A suspension of 0.50 g (1.3 mmol) of Pt(cod)Cl$_2$ in 10 ml of dichloromethane was added dropwise to a solution of 0.72 g (2.6 mmol) of **2** in 15 ml of dichloromethane over a 10 min period at room temperature. The analytically pure, white product, **10**·0.25CH$_2$Cl$_2$, was collected by vacuum filtration on completion of the reaction. The reaction yield was 0.68 g (64%). *Anal.* Calc. for $C_{32.25}H_{28.5}Cl_{2.5}P_2PtS_2$: C, 47.01; H, 3.22. Found: C, 47.19; H, 3.12%.

cis-Bis[μ-(cyanodiphenylphosphine)-P,N]octacarbonyldimolybdenum(O), cis-[Mo(CO)$_4$(μ-(Ph$_2$PCN)-P,N)]$_2$ (11)

A solution of 1.13 g (3.76 mmol) of Mo(CO)$_4$-(nbd) in 10 ml of benzene was added dropwise to a solution of 0.80 g (3.8 mmol) of **4** in 10 ml of benzene over a 30 min period at room temperature. Filtration of the reaction mixture then yielded 1.41 g (89%) of analytically pure **11**. *Anal.* Calc. for $C_{34}H_{20}$-$Mo_2N_2O_8P_2$: C, 48.69; H, 2.39; N, 3.34. Found: C, 48.61; H, 2.53; N, 3.42%.

cis-Bis(cyanodiphenylphosphine)tetracarbonylmolybdenum(O), cis-Mo(CO)$_4$(Ph$_2$PCN)$_2$ (12)

A solution of 3.55 g (11.8 mmol) of Mo(CO)$_4$-(nbd) in 10 ml of THF was added dropwise to a solution of 5.00 g (23.6 mmol) of **4** in 15 ml of THF over a 30 min period at room temperature. The reaction mixture was then evaporated to dryness. The residue was recrystallized from a dichloromethane–hexanes mixture to yield 4.94 g (66.2%) of analytically pure **12**. *Anal.* Calc. for $C_{30}H_{20}MoN_2P_2$: C, 57.16; H, 3.20. Found: C, 56.69; H, 3.31%.

Reaction of $Ph_2PC(O)Me$ (1) with n-PrNH$_2$

A solution of 0.50 g (2.2 mmol) of **1** and 0.13 g (2.2 mmol) of n-propylamine in 25 ml of benzene was stirred at ambient temperature overnight before being evaporated to dryness. The residue was analyzed by ^1H NMR and IR spectroscopy.

Reduction of $Ph_2PC(O)Me$ (1) with $NaBH_4$

To a stirred solution of 0.50 g (2.2 mmol) of **1** in 20 ml of ethanol was added 0.08 g of sodium borohydride. This mixture was stirred for 2 days and then evaporated to dryness. The residue was taken up in 50 ml of dichloromethane and washed with two 100 ml portions of water. The solution was then dried over anhydrous magnesium sulfate, filtered and evaporated to dryness. The residue was characterized by ^1H NMR and IR spectroscopy.

Reaction of cis-$Mo(CO)_4(Ph_2PC(O)Me)_2$ (5) with n-PrNH$_2$

A solution of 2.80 g (4.35 mmol) of **5** and 0.51 g (8.70 mmol) of n-propylamine in 25 ml of benzene was stirred at ambient temperature for two days. The yellow reaction mixture was then evaporated to dryness, and the residue was characterized by ^1H NMR and IR spectroscopy. Recrystallization of the residue from a dichloromethane–hexanes mixture yielded 0.50 g (20%) of *cis*-$Mo(CO)_4(Ph_2PH)_2$ as identified by its ^1H NMR and IR spectra.

Reduction of cis-$Mo(CO)_4(Ph_2PC(O)Me)_2$ (5) with $(n\text{-}Bu)_4NBH_4$

A solution of 0.78 g (6.18 mmol) of tetra-n-butylammonium borohydride in 20 ml of dichloromethane was added dropwise to a stirred solution of 2.00 g (3.09 mmol) of **5** in 20 ml of dichloromethane over a 30 min period at ambient temperature. The solution was stirred at ambient temperature for 24 h and then refluxed for 2 h. Next the reaction mixture was washed with 100 ml portions of 0.10 M hydrochloric acid, 5% aqueous potassium carbonate and 5% aqueous sodium bicarbonate in that order. The solution was then dried over anhydrous magnesium sulfate, filtered and evaporated to dryness. The oily residue was characterized by ^1H NMR and IR spectroscopy.

Reaction of cis-$Mo(CO)_4(Ph_2P(2\text{-}C_4H_3S))_2$ (6) and $Pd(PhCN)_2Cl_2$

A mixture of 0.50 g (0.67 mmol) of **6** and 0.26 g (0.67 mmol) of $Pd(PhCN)_2Cl_2$ was dissolved in 25 ml of THF at room temperature to yield a brown–black solution. This solution was refluxed for 50 min and then was filtered to remove the small amount (<0.1 g) of green precipitate that had formed. The filtrate was evaporated to dryness under high vacuum to yield a green–black residue. The residue was analyzed by ^{31}P NMR and IR spectroscopy.

Reaction of cis-$Mo(CO)_4(Ph_2P(2\text{-}C_4H_3S))_2$ (6) and $Pt(cod)Cl_2$

A mixture of 0.50 g (0.67 mmol) of **6** and 0.25 g (0.67 mmol) of $Pt(cod)Cl_2$ in 25 ml of THF was refluxed for 2 h to yield a brownish red solution. The solution was evaporated to dryness under high vacuum. The residue was analyzed by ^{31}P NMR and IR spectroscopy.

Reaction of cis-$Mo(CO)_4(Ph_2PCN)_2$ (11) and $Pt(cod)Cl_2$

A mixture of 0.50 g (0.79 mmol) of **11** and 0.30 g (0.79 mmol) of $Pt(cod)Cl_2$ in 50 ml of benzene and 10 ml of THF was stirred overnight after which it was refluxed for 75 min. The mixture was then evaporated to dryness. The residue was washed with THF and filtered to yield 0.17 g of insoluble material. The filtrate was evaporated to dryness to yield 0.57 g of material. The insoluble material was analyzed by IR while the soluble material was analyzed by ^{31}P NMR and IR spectroscopy.

Spectroscopic Characterization of the Complexes

The complexes in this study were characterized by multinuclear NMR spectroscopy and IR spectroscopy. The NMR spectra were taken of approximately 0.1 M solutions of the complexes in d_1-chloroform solutions on a wide-bore, Nicolet 300 MHz Fourier Transform NMR spectrometer. The ^{31}P NMR data for the complexes are reported in Table I and are referenced to external 85% phosphoric acid (downfield being positive). The ^{13}C NMR data for the carbonyl ligands and the C(1) atom of the Ph groups in the Mo carbonyl complexes are reported in Table II. IR spectra of dilute dichloromethane solutions of the Mo carbonyl complexes in a 0.2 mm KBr solution cell *versus* pure dichloromethane in a matched cell were run from 2100 to 1800 cm^{-1} on a Perkin-Elmer 283B IR spectrometer.

TABLE I. ^{31}P NMR Chemical Shifts for **1–4** and their Mo, Pd and Pt Complexes[a]

Ligand	L	$Mo(CO)_4L_2$	PdL_2Cl_2	PtL_2Cl_2
$Ph_2PC(O)Me$ (**1**)	19.15	49.01		
$Ph_2P(2\text{-}C_4H_3S)$ (**2**)	−19.41	26.85	12.98	4.98
$PhP(2\text{-}C_4H_3S)_2$ (**3**)	−33.59	15.59	2.26	
Ph_2PCN (**4**)	−33.80	30.43		
Ph_3P		38.66		

[a] All chemical shifts given in ppm relative to an external 80% H_3PO_4 reference. Downfield shifts from the standard are positive and upfield shifts are negative.

TABLE II. ^{13}C NMR Data for the *cis*-$Mo(CO)_4L_2$ Complexes

L	*trans* CO		*cis* CO		phenyl C(1)	
	$\delta^{13}C$ (ppm)	$\lvert J(PC)\rvert^a$ (Hz)	$\delta^{13}C$ (ppm)	$\lvert ^2J(PC)\rvert$ (Hz)	$\delta^{13}C$ (ppm)	$\lvert J(PC)\rvert^b$ (Hz)
$Ph_2PC(O)Me$ (1)	213.42	17	208.22	9	131.51	33
$Ph_2P(2\text{-}C_4H_3S)$ (2)	214.57	17	209.63	9	136.82	35
$PhP(2\text{-}C_4H_3S)_2$ (3)	214.15	17	209.20	9	138.04	38
Ph_2PCN (4)	210.80	20	206.77	9	130.59	43
Ph_3P	215.06	17	210.23	9	136.23	32

$^a\lvert J(PC)\rvert = \lvert ^2J(PC) + {}^2J(P'C)\rvert$. $^b\lvert J(PC)\rvert = \lvert ^1J(PC) + {}^3J(P'C)\rvert$.

TABLE III. Infrared Data for the *cis*-$Mo(CO)_4L_2$ Complexes

L	CO Stretching frequencies (cm^{-1})				Force constants (mdyne/Å)			Calculated
	A_1^1	A_1^2	B_1	B_2	k_1	k_2	k_i	A_1^2 (cm^{-1})
$Ph_2PC(O)Me$ (1)	2031	1925	1932	1899	14.89	15.73	0.32	1922
$Ph_2P(2\text{-}C_4H_3S)$ (2)	2026	1911	1926	1888	14.73	15.64	0.33	1912
$PhP(2\text{-}C_4H_3S)_2$ (3)	2028	1915	1929	1895	14.83	15.68	0.32	1918
Ph_2PCN (4)	2044	1936	1955	1913	15.08	16.03	0.30	1936
Ph_3P	2023	1911	1922	1885	14.69	15.59	0.33	1909

Approximate stretching force constants for these absorptions were calculated using the Cotton–Kraihanzel approximation [15] using the frequencies of the A_1^1, B_1 and B_2 absorptions for the various possible assignments of the symmetry modes. The force constants were then used to calculate the frequency of the A_1^2 absorption, which was not used in the force constant calculations. The assignments of symmetry modes that gave reasonable values for the force constants and good agreement (±3 cm^{-1}) between the observed and calculated frequencies for the A_1^2 band are reported in Table III. The Table also contains the calculated force constants and positions of the A_1^2 absorption.

Results and Discussion

Complexes of Acetyldiphenylphosphine, $Ph_2PC(O)Me$ (1)

Acetyldiphenylphosphine (1) was chosen for this study with a view to functionalize the carbonyl group, either via reduction or Schiff base formation, and to create a second coordination site one atom removed from the P. The reaction of 1 with $n\text{-}PrNH_2$ in benzene at room temperature failed to yield the desired Schiff base, but instead yielded diphenylphosphine and *N*-propyl acetamide (as identified by characteristic ^1H NMR resonances and IR absorptions in the spectra of the reaction mixture). This reaction is summarized in eqn. (1). The reduction of 1 with sodium borohydride in ethanol also failed to yield

$$Ph_2PC(Me){=}N\text{–n-Pr} \not\leftarrow Ph_2PC(O)Me + n\text{-}PrNH_2 \longrightarrow Ph_2PH + MeC(O)NH\text{–n-Pr} \quad (1)$$

the desired product and instead resulted in cleavage of the P–C bond to form diphenylphosphine (as identified by characteristic ^1H NMR resonances and IR absorptions in the spectra of the reaction mixture). This reaction is summarized in eqn. (2).

$$Ph_2PC(Me)OH \not\leftarrow Ph_2PC(O)Me + n\text{-}Bu_4NBH_4 \longrightarrow Ph_2PH + ? \quad (2)$$

Because the P–acetyl bond of the free ligand appeared to be unstable, we attempted to stabilize the ligand through coordination to a molybdenum carbonyl group. The synthesis of *cis*-$Mo(CO)_4(Ph_2PC(O)Me)_2$ (5) is shown in eqn. (3).

$$Mo(O)_4(nbd) + 2Ph_2PC(O)Me \xrightarrow{\text{hexanes}} cis\text{-}Mo(CO)_4(Ph_2PC(O)Me)_2 \quad (3)$$

The reactions of 2 with n-propylamine and tetra-n-butylammonium borohydride are shown in eqns. (4) and (5), respectively. The products of both reactions were analogous to those observed with 1. These compounds were either isolated or were identified by their characteristic ^1H NMR and IR resonances in the spectra of the reaction mixtures.

$$cis\text{-Mo(CO)}_4\text{(Ph}_2\text{PC(O)Me)}_2 + 2\text{n-PrNH}_2 \longrightarrow cis\text{-Mo(CO)}_4\text{(Ph}_2\text{PH)}_2 + \text{MeC(O)NH-n-Pr} \quad (4)$$

$$cis\text{-Mo(CO)}_4\text{(Ph}_2\text{PC(O)Me)}_2 + \text{n-Bu}_4\text{NBH}_4 \longrightarrow cis\text{-Mo(CO)}_4\text{(Ph}_2\text{PH)}_2 + ? \quad (5)$$

Apparently, the coordination of **1** to the molybdenum carbonyl group does not result in stabilization of the P–acetyl bond in **1**.

Complexes of Diphenyl(2-thienyl)phosphine, $Ph_2P(2\text{-}C_4H_3S)$ (3) and Bis(2-thienyl)phenylphosphine, $PhP(2\text{-}C_4H_3S)_2$ (4)

The diphenyl(2-thienyl)phosphine (3) and bis(2-thienyl)phenylphosphine (4) ligands contain a P-donor site and an S-donor site separated by a single C. Studies of the coordination of these ligands to transition metals should allow a comparison of the relative coordinating abilities of the P- and S-donor sites in these complexes and may allow the synthesis of A-frame complexes with bridging thienylphosphine ligands. Nickel(II) and cobalt(II) complexes of the types (ML_2X_2) and rhodium complexes of the types $RhCl(CO)(L)_2$ (L = 2, 3) in which these ligands are P-coordinated, have previously been reported [16]. The syntheses of Mo, Pd and Pt complexes of the thienylphosphines are shown in eqns. (6)–(9).

$$\text{Mo(CO)}_4\text{(nbd)} + \underset{\mathbf{2}}{2\text{Ph}_2\text{P(2-C}_4\text{H}_3\text{S)}} \longrightarrow \underset{\mathbf{6}}{cis\text{-Mo(CO)}_4\text{(Ph}_2\text{P(2-C}_4\text{H}_3\text{S))}_2} \quad (6)$$

$$cis\text{-Mo(CO)}_4\text{(pip)}_2 + \underset{\mathbf{3}}{2\text{PhP(2-C}_4\text{H}_3\text{S)}_2} \longrightarrow \underset{\mathbf{7}}{cis\text{-Mo(CO)}_4\text{(PhP(2-C}_4\text{H}_3\text{S)}_2\text{)}_2} \quad (7)$$

$$\text{Pd(PhCN)}_2\text{Cl}_2 + \underset{\mathbf{2,3}}{2\text{Ph}_{2-n}\text{P(2-C}_4\text{H}_3\text{S)}_n} \longrightarrow \underset{\mathbf{8,9}}{\text{Pd(Ph}_{2-n}\text{P(2-C}_4\text{H}_3\text{S)}_n\text{)}_2\text{Cl}_2} \quad (8)$$

$n = 1, 2$

$$\text{Pt(cod)Cl}_2 + \underset{\mathbf{2}}{2\text{Ph}_2\text{P(2-C}_4\text{H}_3\text{S)}} \longrightarrow \underset{\mathbf{10}}{cis\text{-Pt(Ph}_2\text{P(2-C}_4\text{H}_3\text{S))}_2\text{Cl}_2} \quad (9)$$

The ^{31}P NMR spectra of the complexes indicate that the ligands are P-coordinated in all of the complexes. The CO IR stretching frequencies and ^{13}C NMR spectra of the Mo complexes indicate that their geometry is *cis*. The $|^1J(\text{Pt–P})| = 3681$ Hz of the Pt complex also suggests a *cis* configuration. The spectroscopic data of the Pd complexes do not provide any indication as to their geometries.

An attempt was made to form bimetallic Mo–Pd complexes by reacting *cis*-$Mo(CO)_4(Ph_2P(2\text{-}C_4H_3S))_2$ (**6**) with $Pd(PhCN)_2Cl_2$. Mixing the two complexes in either tetrahydrofuran or dichloromethane results in an immediate reaction as evidenced by the color change from yellow to brown–black. Both ^{31}P NMR and IR spectroscopic studies of the reaction mixture indicate that the major products of the reaction are *trans*-$Mo(CO)_4(Ph_2P(2\text{-}C_4H_3S))_2$ ($\delta\,^{31}P = 38.93$ ppm, $\nu(CO) = 1952, 1906$ cm^{-1}), $Mo(CO)_5(Ph_2P(2\text{-}C_4H_3S))$ ($\delta\,^{31}P = 25.43$ ppm, $\nu(CO) = 2076, 1950$ cm^{-1}) and **8** ($\delta\,^{31}P = 13.01$ ppm) as well as the starting material **6** ($\delta\,^{31}P = 26.25$ ppm). The variety of products of this reaction as well as the rate at which the reaction occurs suggests that a bimetallic complex with a P,S-bridging **2** may initially form but is not stable and decomposes to monometallic Mo and Pd complexes.

The reaction of *cis*-$Mo(CO)_4(Ph_2P(2\text{-}C_4H_3S))_2$ (**6**) with $Pt(cod)Cl_2$ in both THF and dichloromethane has also been studied. It was hoped that the absence of the benzonitrile byproduct and the Pt–S bonding, which is expected to be stronger than the Pd–S bonding, would allow a bimetallic Mo–Pt complex to be isolated. However, a ^{31}P NMR study of the reaction mixture indicated that the major products were *trans*-$Mo(CO)_4(Ph_2P(C_4H_3S))_2$, $Mo(CO)_5(Ph_2P(C_4H_3S))$, and **10** ($\delta\,^{31}P = 4.96$ ppm, $|^1J(PC)| = 3645$ Hz). It is likely that the mechanism of this reaction also involves the initial formation of a bimetallic complex with a P,S-bridging **2**.

Complexes of Cyanodiphenylphosphine, Ph_2PCN (4)

Cyanodiphenylphosphine (**4**) was chosen for study because it can coordinate to metals through both the P and N atoms, which are separated by a single C atom, and because it contains both soft (P) and hard (N) donor sites. Jones and Coskran have prepared a number of complexes of the general type $[M(CO)_4(R_2PCN)]_2$ (M = Cr, Mo; R = Ph, Me, Me_2N, EtO) [17]. On the basis of their ^1H NMR spectra and elemental analyses, these complexes are suggested to contain symmetrically bridging cyanophosphine ligands. In order to confirm their suggested structure, the bimetallic complex of **4** has been resynthesized. The complex was initially and unintentionally synthesized by the reaction of $Mo(CO)_4(nbd)$ with two equivalents of **4** in hexanes as shown in eqn. (10). The hexanes-insoluble bimetallic complex was apparently kinetically trapped by the precipitation

$$\begin{tikzcd} \mathrm{Mo(CO)_4(nbd)} + \underset{\mathbf{4}}{\mathrm{Ph_2PCN}} \arrow[d, "\mathrm{PhH}"] \\ \underset{\mathbf{11}}{[\mathrm{Mo(CO)_4(Ph_2PCN)}]_2} \\ \mathrm{Mo(CO)_4(nbd)} + \underset{\mathbf{4}}{2\mathrm{Ph_2PCN}} \arrow[u, "\mathrm{hexanes}"] \end{tikzcd} \qquad (10)$$

reaction even though excess ligand was present. The bimetallic complex was also synthesized by the reaction of Mo(CO)(nbd) with one equivalent of **4** in benzene, a modification of the method of Jones and Coskran [17].

The coordination mode of **4** in the bimetallic complex was determined from the multinuclear NMR and IR spectra of the complex. The ν(CO) stretching frequencies of **11** at 2032, 1943 and 1891 cm^{-1} indicate that the complex has a *cis* arrangement of the CO ligands. The single ^{31}P NMR chemical shift of the complex at 48.11 ppm indicates that a single P environment is present and that the P is coordinated to Mo. The presence of three doublets in a 1:1:2 ratio below 200 ppm in the ^{13}C NMR spectrum of the complex indicates that there are three different CO environments in the complex. The largest ($\delta^{13}\mathrm{C} = 205.20$ ppm, $|^2J(\mathrm{PC})| = 9$ Hz) appears to be due to COs *trans* to CO and *cis* to P. One of the smaller doublets ($\delta^{13}\mathrm{C} = 211.50$ ppm, $|^2J(\mathrm{PC})| = 37$ Hz) appears to be due to a CO *trans* to P while the other ($\delta^{13}\mathrm{C} = 214.31$ ppm, $|^2J(\mathrm{PC})| = 8$ Hz) appears to be due to a CO *trans* to N and *cis* to P. Both the ^{13}C NMR resonance of the CN group ($\delta^{13}\mathrm{C} = 125.97$ ppm, $|^1J(\mathrm{PC})| = 22$ Hz, $|^3J(\mathrm{PC})| = 3$ Hz) and the ^{95}Mo NMR resonance ($\delta^{95}\mathrm{Mo} = -1429.5$ ppm, $|^1J(\mathrm{PMo})| = 109$ Hz, $|^3J(\mathrm{PMo})| = 55$ Hz) indicate that the P atoms are unsymmetrically coordinated with respect to both the Mo and CN groups. This data is consistent with a bimetallic complex containing a head to tail arrangement of the ligands as proposed by Jones and Coskran and shown below [17].

$$\begin{tikzcd} \mathrm{Ph_2P{-}C{\equiv}N} \arrow[r] \arrow[d] & \mathrm{Mo(CO)_4} \\ \mathrm{(CO)_4Mo} & \mathrm{N{\equiv}C{-}PPh_2} \arrow[l] \arrow[u] \end{tikzcd}$$

$$\mathrm{Mo(CO)_4(nbd)} + \underset{\mathbf{4}}{2\mathrm{Ph_2PCN}} \xrightarrow{\mathrm{THF}} \underset{\mathbf{12}}{cis\text{-}\mathrm{Mo(CO)_4(Ph_2PCN)_2}} \qquad (11)$$

The *cis* disubstituted Mo complex of **4** was synthesized in high yield as shown in eqn. (11). Attempts to synthesize disubstituted Pd and Pt complexes of **4** gave products that were either not soluble (Pt) or that appeared to hydrolyze during purification (Pd) and could not be obtained analytically pure.

In order to determine the hydrolytic stability of the P–CN bonds in **12**, the hydrolysis reaction shown in eqn. (12) was carried out. The course of the hydrolysis was followed by TLC, and the reaction appeared to be complete in approximately 24 h. The hydrolysis of **12** is significantly slower than the hydrolysis of *cis*-Mo(CO)$_4$(Ph$_2$PCl)$_2$ to give the same product which is complete in approximately 30 min under the same conditions.

$$\underset{\mathbf{12}}{cis\text{-}\mathrm{Mo(CO)_4(Ph_2PCN)_2}} + xs\mathrm{Et_3N} + xs\mathrm{H_2O} \xrightarrow{\mathrm{THF}} [\mathrm{Et_3NH}][\mathrm{Mo(CO)_4(Ph_2PO)_2H}] \qquad (12)$$

The reaction of **12** with Pt(cod)Cl$_2$ was carried out in an attempt to prepare a dinuclear MoPt complex similar to the binuclear Mo$_2$ complexes reported by Jones and Coskran [17]. The reaction of the two complexes yielded both a THF-soluble and a THF-insoluble material. Both the ^{31}P NMR and IR spectra of the THF-soluble material suggest that it is a mixture of the starting Mo complex, **11**, and Mo(CO)$_5$(PhPCN) ($\delta^{31}\mathrm{P} = 28.83$ ppm, $\nu(\mathrm{CO}) = 2084$, 1964 cm^{-1}). The IR spectra of the THF-insoluble material does not contain any CO absorptions which suggest that this material is a Pt complex of some sort. The total insolubility of this material has precluded further characterization. The above results suggest that, as is the case for the thienylphosphine ligands, the bridged complexes are not stable and decompose into mononuclear complexes with the transfer of the ligands from the Mo complex.

Multinuclear NMR and IR Studies

The ligands used in this study are also of interest because they should exhibit a wide range of electron-donor abilities due to the variations in the electron-donor abilities of the P substituents. The variations in the chemical shifts of the carbonyl ^{13}C resonances and the force constants of the carbonyl IR stretching absorptions of the Mo carbonyl complexes of these ligands can be related to variations in the electron-donor abilities of these ligands [18–20]. As the donor ability of the ligand increases, the carbonyl ^{13}C NMR resonances are deshielded (move downfield) while the carbonyl IR stretching force constants decrease. As can be seen from the data in Table IV,

TABLE IV. Results for the Linear Regression Analyses of the Correlations between the Carbonyl IR Stretching Force Constants and ^{13}C NMR Chemical Shifts for the *cis*-$Mo(CO)_4L_2$ Complexes

Correlation	r	Level of confidence[a]
$\delta^{13}C$ (*trans* CO) *vs.* $\delta^{13}C$ (*cis* CO)	0.979	99.6
$\delta^{13}C$ (*trans* CO) *vs.* k_1 (*trans* CO)	−0.981	99.7
$\delta^{13}C$ (*trans* CO) *vs.* k_2 (*cis* CO)	−0.998	99.9
$\delta^{13}C$ (*cis* CO) *vs.* k_1 (*trans* CO)	−0.990	99.9
$\delta^{13}C$ (*cis* CO) *vs.* k_2 (*cis* CO)	−0.964	99.2
k_1 (*trans* CO) *vs.* k_2 (*cis* CO)	0.969	99.3

[a]% probability that the correlation is real.

excellent correlations are observed between the chemical shift and force constant data as the ligands are varied. The data for *cis*-$Mo(CO)_4(Ph_3P)_2$ is included to improve the statistics and to provide a reference to a known compound. The correlations suggest that the electron donor abilities of the $Ph_{3-n}PR_n$ (R = CN, C(O)Me, 2-thienyl; $n = 0$–2) ligands increase in the order of R = CN ≪ C(O)Me < 2-thienyl < Ph.

The relative electron-donor abilities observed for the 2-thienyl and Ph groups are consistent with those determined from studies of the rates of quaternization of the free ligands [21]. However, studies of electronic spectra of Ni complexes of these ligands have suggested exactly the opposite ordering of electron-donor abilities [16a]. As suggested in the latter study, the relative electron-donor abilities of phenyl and 2-thienyl groups toward P may depend on whether the electron donation is occurring primarily through σ (inductive) or π (resonance) orbitals. If this is the case, the effects of variations in the P-substituents in the Mo complexes in this study would appear to be due to variations in the inductive abilities of the P-substituents.

Conclusions

The abilities of three unusual types of bifunctional P-ligands to form dinuclear transition metal complexes have been evaluated in this research. Attempts to form bifunctional phosphine/imine or hydroxymethylphosphine ligands from $Ph_2C(O)Me$ were unsuccessful due to the lability of the P–acetyl bond. Attempts to form dinuclear complexes from mononuclear complexes containing P-coordinated $Ph_2P(2\text{-}C_4H_3S)$ and mononuclear complexes with easily displaced olefin ligands instead resulted in ligand exchange. This is apparently due to the fact that the thiophene S is a very weak sigma donor. Spectroscopic studies have confirmed that the 1:1 reaction product of Ph_2PCN and $Mo(CO)_4(nbd)$ is $[(CO)_4Mo(Ph_2PCN)]_2$ with head to tail, P,N-bridging Ph_2CN as had been previously suggested. Attempts to form bimetallic MoPt complexes containing this ligand instead result in ligand exchange between the mononuclear precursors.

The NMR and IR spectral data for the Mo carbonyl complexes of the acetyl-, 2-thienyl- and cyano-functionalized phosphine ligands used in this study provided insight into the effect of the functional groups in the electron-donor abilities of the P-ligands. These studies indicated that the order of electron-donor ability of the ligands increased as the substituents were varied in the order CN < C(O)Me < 2-thienyl < Ph.

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