Journal of Organometallic Chemistry, 372 (1989) 207–216
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 09988

Synthesis and characterization of transition metal complexes of (2-(2-methoxyethoxy)ethyl)diphenylphosphine and (2-(2-methoxyethoxy)ethyl)dimethylarsine

V. Vijay Sen Reddy, J.E. Whitten, K.A. Redmill, A. Varshney and G.M. Gray *

Department of Chemistry, The University of Alabama at Birmingham, 219-2 UAB Station, Birmingham, AL 35294 (U.S.A.)

(Received January 30th, 1989)

Abstract

Two new, potentially tridentate ligands, $Ph_2P(CH_2CH_2O)_2Me$ (POO) and $Me_2As(CH_2CH_2O)_2Me$ (AsOO), have been synthesized and characterized by multinuclear NMR spectroscopy. Mononuclear complexes of these ligands, *cis*-$(CO)_4Mo(EOO)_2$ (E = P, As), *cis,cis,trans*- and *cis,trans,cis*-$(CO)_2Cl_2Ru(POO)_2$, $[(1,5\text{-cod})Rh(POO)_2][ClO_4]$ and $Cl_2M(POO)_2$, (M = Pd and Pt), have also been prepared and characterized by multinuclear NMR and IR spectroscopy. In all cases, these ligands are coordinated only through the group 15 donor atom. Different procedures have been developed to give either the *cis,cis,trans* or *cis,trans,cis* isomers of $Cl_2(CO)_2Ru(POO)_2$ complex in high yields. The latter isomer is unusual and has not previously been reported with ligands of this type.

The reactions of the *cis*-$(CO)_4Mo(EOO)_2$ complexes with methyllithium have been examined. The carbonyl ligands in these complexes do not react with methyllithium at room temperature. These results are in direct contrast to those of Powell and coworkers who reported facile reactions between methyllithium and the carbonyl ligands in similar *cis*-$(CO)_4Mo(Ph_2PO(CH_2CH_2O)_3PPh_2)$ complexes. These results confirm Powell's conclusions that the number and type of the hard donor atoms in these complexes greatly affect the reactivity of methyllithium towards the carbonyl ligands.

Introduction

A number of studies of the coordination chemistry of ligands containing both ether-O- and P-donor sites have appeared in the recent literature. Ligands that have been studied include those with one P- and one O-donor site [1–10], those with one P- and one or more linear polyether O-donor sites [11,12], those with α,ω-bis(phosphine), -bis(phosphinite) or -bis(phosphite) substituents on a polyether chain [13–20],

0022-328X/89/$03.50

those with one or more phosphine substituents on a crown ether [21–26] and those with phosphorus atoms in the crown ether ring [27–31].

These ligands are of interest for two reasons. One is that the ether group in these ligands can easily be displaced from soft, platinum group metals during catalytic processes. This provides a coordination site for the substrate and often results in significantly higher catalytic activities for complexes of these ligands than for complexes with monodentate phosphine ligands [1,4,8].

A second reason for the interest in complexes of these ligands is that these ligands can be used to prepare binuclear complexes containing both soft and hard metal centers [13,15–17,22]. The ability of these ligands to coordinate to hard metal ions has been used to activate carbonyl ligands in *cis*-$(CO)_4MoL_2$ (L_2 = bis(phosphinite)-polyether or -aminoether) complexes to attack by methyllithium. This ability has also been used to prepare metal complexes that will function as phase transfer, reduction catalysts [11,12].

In this paper, we report the syntheses and characterizations of a variety of transition metal complexes with two new polydentate ligands of the type $R_2E(CH_2CH_2O)_2Me$ ($R_2E = Ph_2P$ (POO) or Me_2As (AsOO)). The coordination behavior of these ligands, as determined by multinuclear NMR and IR spectroscopy will be discussed. The results of a study of the reactions of complexes of the type *cis*-$(CO)_4Mo(EOO)_2$ with methyllithium will also be presented.

Experimental

All of the starting materials, free ligands and solvents were handled under an atmosphere of dry, high-purity nitrogen. The solid products were generally air stable and no special handling precautions were taken. Solutions of these materials were handled under an atmosphere of dry high-purity nitrogen when in solution.

All solvents were of reagent grade and were used as received except for diethyl ether and tetrahydrofuran (THF). These were distilled from sodium-benzophenone prior to use. All starting materials were reagent grade and were used as received except for diphenylphosphine and methanesulfonyl chloride, which were distilled prior to use, and triethylamine, which was distilled from CaH_2. The starting materials Me_2AsCl [32], $(CO)_4Mo(nbd)$ [33], $[(cod)RhCl]_2$ [34] and $Cl_2M(cod)$ [35,36] (nbd = [2.2.1]-bicyclohepta-2,5-diene; cod = 1,5-cyclooctadiene; M = Pd, Pt) were prepared using standard procedures.

Multinuclear NMR spectra of the ligands and complexes were taken of chloroform-d_1 solutions (ca. 0.1 *M*). The ^1H NMR spectra were taken on a Varian EM 360 L NMR spectrometer, and the ^{31}P and ^{13}C NMR spectra were taken on a Nicolet 300 MHz, wide-bore, FT NMR spectrometer. The ^{13}C and ^1H NMR spectra were referenced to internal tetramethylsilane, and the ^{31}P NMR spectra were referenced to external 85% phosphoric acid. In all cases, downfield was treated as positive. The NMR spectral data of the complexes are summarized in Tables 1 and 2. Infrared spectra in the 2200 to 1800 cm^{-1} region were taken of dilute solutions of the complexes in matched 0.2 mm KBr solution cells on a Perkin–Elmer 283B IR spectrometer. IR spectra of insoluble samples were taken of KBr disks of the complexes on the same instrument. Elemental analyses (C & H) were carried out by Atlantic Microlabs, Atlanta, GA. Solvents of crystallization are included in the

Table 1

^{31}P and phenyl ^{13}C NMR data

Compound	δ (^{31}P) [a] (ppm)	*ipso*		*ortho*		*meta*		*para*
		δ (^{13}C) (ppm)	$\lvert J(PC)\rvert$ (Hz)	δ (^{13}C) (ppm)	$\lvert J(PC)\rvert$ (Hz)	δ (^{13}C) (ppm)	$\lvert J(PC)\rvert$ (Hz)	δ (^{13}C) (ppm)
II	−21.77	138.20 [b]	13 [c]	132.67 [b]	19 [d]	128.55 [b]	11 [e]	128.39 [a]
IV	20.42	136.30 [f]	31 [g]	132.17 [f]	10 [h]	128.34 [f]	7 [i]	129.47 [e]
VIII	14.23	130.78 [f]	46 [g]	132.88 [f]	10 [h]	128.44 [f]	8 [i]	130.69 [a]
IX	18.94	132.12 [f]	42 [g]	134.46 [f]	10 [h]	128.15 [f]	10 [i]	130.32 [a]
		130.90 [f]	42 [g]	132.55 [f]	8 [h]	127.86 [f]	6 [i]	129.03 [a]
X	16.09 [j]	[k]		133.44 [l]		128.89 [l]		131.15 [a]
XI	12.44	129.88 [f]	48 [g]	133.70 [f]	12 [h]	129.29 [f]	10 [i]	130.56 [a]
XII	4.48 [m]	129.33 [f]	63 [g]	133.43 [f]	10 [h]	128.27 [f]	11 [i]	131.01 [a]

[a] Singlet. [b] Doublet. [c] $\lvert {}^1J(PC)\rvert$. [d] $\lvert {}^2J(PC)\rvert$. [e] $\lvert {}^3J(PC)\rvert$. [f] Apparent quintet. [g] $\lvert {}^1J(PC)+{}^3J(PC)\rvert$. [h] $\lvert {}^2J(PC)+{}^4J(PC)\rvert$. [i] $\lvert {}^3J(PC)+{}^5J(PC)\rvert$. [j] Doublet, $\lvert {}^1J(RhP)\rvert = 143$ Hz. [k] Not observed. [l] Broad singlet. [m] Superimposed singlet and doublet, $\lvert {}^1J(PtP)\rvert$ (for doublet) = 3630 Hz.

Table 2

Aliphatic ^{13}C NMR data

R_2E–CH_2–CH_2–O–CH_2–CH_2–O–CH_3

1 2 3 4 5

Compound	C(1)		C(2)		C(3) and C(4) [a]		C(5) [a]	R(Me) [a]
	δ (^{13}C) (ppm)	$\lvert J(PC)\rvert$ (Hz)	δ (^{13}C) (ppm)	$\lvert J(PC)\rvert$ (Hz)	δ (^{13}C) (ppm)	δ (^{13}C) (ppm)	δ (^{13}C) (ppm)	δ (^{13}C) (ppm)
II	28.69 [b]	13 [c]	68.58 [b]	26 [d]	71.86	69.98	59.06	
III	28.52 [a]		69.74 [a]		71.98	69.74	59.08	9.29
IV	32.80 [e]	20 [f]	66.99 [g]		71.70	69.87	58.97	
V	31.18 [a]		67.90 [a]		71.91	70.02	59.01	14.51
VIII	24.25 [e]	28 [f]	66.06 [g]		71.73	69.68	58.95	
IX	24.72 [e]	26 [f]	66.47 [g]		71.81	69.52	58.95	
X	27.28 [e]	30 [f]	67.05 [g]		71.76	70.02	58.95	
XI	25.97 [e]	29 [f]	66.68 [e]	6 [h]	71.79	69.87	59.03	
XII	30.35 [e]	42 [f]	66.98 [g]		71.70	69.78	58.99	

[a] Singlet. [b] Doublet. [c] $\lvert {}^1J(PC)\rvert$. [d] $\lvert {}^2J(PC)\rvert$. [e] Apparent quintet. [f] $\lvert {}^1J(PC)+{}^3J(PC)\rvert$. [g] Broad singlet. [h] $\lvert {}^2J(PC)+{}^4J(PC)\rvert$.

calculated analyses only if the solvent was observed in the NMR or IR spectra of the analytical sample.

$MeS(O)_2O(CH_2CH_2O)_2Me$ (I)

A solution of 19.1 g (167 mmol) of CH_3SO_2Cl in 100 ml of dry Et_2O was added dropwise to a solution of 20.0 g (167 mmol) of $HO(CH_2CH_2O)_2Me$ and 16.9 g (167 mmol) of Et_3N in 75 ml of Et_2O over a 60 min period. This mixture was stirred for 30 min and then filtered. The filtrate was evaporated to dryness to yield 37.8 g (100%) of pure I. ^1H NMR: δ 4.33 (2H, m), 3.65 (6H, m), 3.34 (3H, s), 3.03 (3H, s).

$Ph_2P(CH_2CH_2O)_2Me$ (POO) (II)

A solution of 18.8 g (101 mmol) of Ph_2PH in 100 ml of Et_2O was stirred at −78°C as 80.0 ml (128 mmol) of a 1.6 *M* solution of n-BuLi in hexanes was added

dropwise over a 30 min period. This bright yellow mixture was stirred for 30 min at −78 °C, and then a solution of 20.0 g (101 mmol) of I in 100 ml of Et_2O was added dropwise over a 1 h period. The reaction mixture was stirred for 1 h at ambient temperature and then poured into 200 ml of deionized water. The organic layer separated, dried with anhydrous $MgSO_4$ and filtered. The filtrate was evaporated to dryness, and the residue was distilled at 120 °C at 0.01 mm of Hg to yield 24.0 g (83.2%) of pure II. ^{1}H NMR: δ 7.30 (10H, m), 3.51 (6H, m), 3.34 (3H, s), 2.40 (2H, t, $|^3J(HH)| = 8$ Hz).

$Me_2As(CH_2CH_2O)_2Me$ (AsOO) (III)

A mixture 2.92 g (74.8 mmol) of K in 50 ml of 1,2-dimethoxyethane was stirred as a solution of 5.00 g (35.6 mmol) of Me_2AsCl in 50 ml of 1,2-dimethoxyethane was added dropwise over a 1 h period. This mixture was stirred overnight, and then a solution of 7.05 g (35.6 mmol) of I in 50 ml of Et_2O was added dropwise over a 1 h period. This mixture was stirred for 45 min and then evaporated to dryness. The residue was treated with 50 ml of a 1/1 dichloromethane/hexanes mixture and 150 ml of water. The organic layer was washed with three, 150 ml portions of water, dried with anhydrous $MgSO_4$ and then filtered. The filtrate was evaporated to dryness to yield 3.04 g of crude III. This material was distilled at 106–108 °C at 25 mm of Hg to yield 2.05 g (25.7%) of pure III. ^{1}H NMR: δ 3.60 (2H, t, $|^3J(HH)| = 7$ Hz), 3.52 (4H, s), 3.33 (3H, s), 1.72 (2H, t, $|^3J(HH)| = 7$ Hz), 0.98 (6H, s).

cis-$(CO)_4Mo(Ph_2P(CH_2CH_2O)_2Me)_2$ (IV)

A mixture of 1.47 g (4.88 mmol) of $(CO)_4$Mo(nbd) and 2.18 g (9.77 mmol) of II in 50 ml of hexanes was stirred at ambient temperature for 12 h and then evaporated to dryness. A solution of the residue in 50 ml of a 1/1 CH_2Cl_2 · hexanes mixture was filtered through a 1 cm column of silica gel in a 30 cc medium fritted glass funnel to yield 1.93 g (50.4%) of IV as a yellow oil. ^{1}H NMR: δ 7.20 (20H, m), 3.31 (12H, m), 3.25 (6H, s), 2.40 (4H, m). ^{13}C NMR(CO): δ 215.01 (apparent quintet, $|^2J(PC) + {}^2J(P'C)| = 29$ Hz), 209.61 (t, $|^2J(PC)| = 10$ Hz). ν(CO) (CH_2Cl_2): 2022m, 1945sh, 1912vs, 1870sh cm^{-1}.

cis-$(CO)_4Mo(Me_2As(CH_2CH_2O)_2Me)_2$ (V)

Following the procedure for IV, 1.25 g (4.17 mmol) of $(CO)_4$Mo(nbd) and 1.73 g (8.34 mmol) of III yielded 2.10 g (80.7%) of V as a green oil. ^{1}H NMR: δ 3.75 (2H, t, $|^3J(HH)| = 7$ Hz), 3.53 (4H, s), 3.35 (3H, s), 2.00 (2H, t, $|^3J(HH)| = 7$ Hz), 1.40 (6H, s). ^{13}C NMR(CO): δ 215.92 (s), 209.82 (s). ν(CO) (THF): 2012m, 1905sh, 1896s, 1873s cm^{-1}.

$[Cl_2(CO)_2Ru]_n$ (VI)

A solution of 10.0 g (41.0 mmol) of $RuCl_3 \cdot nH_2O$ in 50 ml of 90% HCO_2H and 50 ml of conc. hydrochloric acid was refluxed for 18 h. Then, 25 ml of HCO_2H and 25 ml of hydrochloric acid was added, and the reflux was continued for 4 h until the color of the solution changed to yellow. The solution was evaporated to dryness, and the yellow solid residue was extracted with methanol in a Soxhlet extractor for 24 h. Evaporation of the methanol solution to dryness yielded 9.34 g (100%) of yellow-orange VI. IR (KBr disk): ν(CO) 2082, 2023 cm^{-1}.

$[Cl_2(CO)_3Ru] \cdot 0.75THF$ (VII)

The yellow solid from the reaction of $RuCl_3 \cdot nH_2O$, HCO_2H and conc. hydrochloric acid was prepared as described for VI. This material (1.90 g) was washed with 50 ml of acetone and filtered to remove VI (0.30 g). The colorless filtrate was evaporated to dryness, and the residue was recrystallized from a THF/hexanes mixture to yield 1.68 g (68.7%) of pure, white VII. Anal. Found: C, 23.21; H 1.96. $C_6H_6Cl_2O_{3.75}Ru$ calc. C, 23.23; H, 1.94%. IR ($CHCl_3$): ν(CO) 2138, 2069 cm^{-1}.

cis,cis,trans-$Cl_2(CO)_2Ru(Ph_2P(CH_2CH_2O)_2Me)_2$ (VIII)

A solution of 0.25 g (0.44 mmol) of VII and 0.25 g (0.88 mmol) of II in 25 ml of THF was stirred at room temperature for 16 h and then evaporated to dryness. Recrystallization of the residue from a THF/hexanes mixture yielded 0.34 g (96%) or pure VIII (m.p. 180 °C). Anal. Found: C, 53.40; H, 5.59. $C_{36}H_{42}Cl_2O_6P_2Ru$ calc: C, 53.74; H, 5.26%. ^1H NMR: δ 7.65 (20H, m), 3.40 (16H, m), 3.25 (6H, s). ^{13}C NMR (CO): 192.20 (t, $|^2J(PC| = 11$ Hz). ν(CO) (CH_2Cl_2): 2059s, 1997s cm^{-1}.

cis,trans,cis-$Cl_2(CO)_2Ru(Ph_2P(CH_2CH_2O)_2Me)_2$ (IX)

A mixture of 0.25 g (1.1 mmol) of VI in 20 ml of CH_3CN was refluxed for 15 h. Then 0.85 g (2.9 mmol) of II was added and the reflux was continued for 15 h. The reaction mixture was then evaporated to dryness, and the residue was washed with diethyl ether. The pale yellow residue was recrystallized from a $CHCl_3$/hexanes mixture to yield 0.71 g (81%) of pure IX (m.p. 140–142 °C). Anal. Found: C, 53.76; H, 5.51. $C_{36}H_{42}Cl_2O_6P_2Ru$ calc: C, 53.73; H, 5.26%. ^1H NMR: 7.40 (20H, m), 3.33 (16H, m), 3.25 (6H, s). ^{13}C NMR (CO): δ 198.75 (t, $|^2J(PC)| = 13$ Hz). ν(CO) (CH_2Cl_2): 1959 cm^{-1}.

$[(cod)Rh(Ph_2P(CH_2CH_2O)_2Me)_2 \cdot H_2O$ ($X \cdot H_2O$)

A solution of 1.41 g (4.49 mmol) of (cod)Rh(acac) in 20 ml of THF was stirred at room temperature as a solution of 0.65 g (4.6 mmol) of 70% perchloric acid in 11 ml of THF was added dropwise over a 30 s period. Then, a solution of 2.60 g (9.03 mmol) of II in 10 ml of THF was added dropwise over a 30 s period. This solution was stirred for 30 min and then reduced in volume to 20 ml. Et_2O was slowly added until a precipitate began to form and then the mixture was cooled to −10 °C. Filtration yielded 2.64 g (65.0%) of $X \cdot H_2O$ as a orange solid (m.p. 97 °C with decomp.). Anal. Found: C, 55.71; H, 6.10. $C_{42}H_{56}ClO_9P_2Rh$ calc: C, 55.68; H, 6.18%. ^1H NMR: δ 7.30 (20H, bs), 4.74 (4H, bs), 3.60 (12H, m), 3.29 (6H, s), 2.20 (8H, bs), 1.95 (4H, m).

$Cl_2Pd(Ph_2P(CH_2CH_2O)_2Me)_2$ (XI)

A mixture of 0.250 g (0.876 mmol) of $Cl_2Pd(cod)$ and 0.504 g (1.75 mmol) of II in CH_2Cl_2 was stirred at room temperature for 24 h and then evaporated to dryness. The residue was washed with methanol, and the pale yellow solid residue was recrystallized from a CH_2Cl_2/methanol mixture to yield 0.350 g (53.0%) of pure XI (m.p. 95–100 °C). Anal. Found: C, 54.10; H, 5.59. $C_{34}H_{42}Cl_2O_4P_2Pd$ calc: C, 54.15; H, 5.58%. ^1H NMR: δ 7.45 (20H, m), 3.50 (12H, m), 3.26 (6H, s), 2.78 (4H, m).

cis-$Cl_2Pt(Ph_2P(CH_2CH_2O)_2Me)_2$ (XII)

Following the procedure for XI, 1.00 g (2.67 mmol) of $Cl_2Pt(cod)$ and 1.54 g (5.40 mmol) of II in THF yielded 1.56 g (68.6%) of pure XII (m.p. 128–130 °C)

after recrystallization from a CH_2Cl_2/hexanes mixture. Anal. Found: C, 48.31; H, 5.10. $C_{34}H_{42}Cl_2O_4P_2Pt$ calc: C, 48.46; H, 5.02%. ^1H NMR: δ 7.21 (20H, m), 3.81 (4H, m), 3.42 (8H, bs), 3.32 (6H, s), 2.63 (4H, m).

Results and discussion

Ligands

The POO and AsOO ligands were synthesized as shown in eq. 1.

$$MsO(CH_2CH_2O)_2Me + MER_2 \rightarrow R_2E(CH_2CH_2O)_2Me \quad (1)$$

POO, II (M = Li, E = P, R = Ph); AsOO, III (M = K, E = As, R = Me)

The POO ligand is obtained in excellent yield and high purity using this method. The AsOO ligand is obtained in much lower yield, perhaps because the reaction of chlorodimethylarsine with potassium is not a good method to form dimethylarsenide. It may be possible to improve the yield of AsOO by using excess chlorodimethylarsine and potassium.

The ligands were characterized by multinuclear NMR spectroscopy, and the results are given in Tables 1 and 2. The purities of the ligands were determined from their ^1H NMR and ^{13}C NMR spectra. The ^{13}C NMR resonances of the ligands have been assigned by comparison with related systems and on the basis of their chemical shifts and P–C coupling constants. These assignments are straightforward for all of the resonances except for those of the C(3) and C(4) methylene carbons. The C(3) resonance has arbitrarily been assigned as the downfield resonance.

Complexes

A number of different, mononuclear transition metal complexes containing two POO ligands or two AsOO ligands have been prepared and are discussed below. In all of the complexes, the ligands are monodentate and coordinated through the group 15 donor atom (P or As). This is seen in the coordination chemical shifts of ^{31}P NMR resonance, the ^{13}C NMR resonances of the C(1) and C(2) methylene, the *ipso* phenyl and the As methyl groups, and the ^1H NMR resonance of the C(1) methylene group. The absence of coordination of the ether oxygens to the metal is indicated by the similar chemical shifts of both the ^1H and ^{13}C NMR resonances of the C(2), C(3) and C(4) methylenes and the methyl of the free and complexed ligands. The P nuclei in the complexes with two POO ligands are chemically equivalent but magnetically inequivalent and the ^{13}C NMR resonances of the C(1) methylene and *ipso, ortho* and *meta* phenyl Cs are apparent quintets (the A portion of an AXX' spin system) [37].

The *cis*-$(CO)_4Mo(EOO)_2$ (E = P, IV; E = As, V) complexes were synthesized by the reaction of the ligands with $(CO)_4Mo(nbd)$ as shown in eq. 2. The complexes were initially obtained as oils that slowly solidified upon standing. The complexes

$$(CO)_4Mo(nbd) + 2\ EOO \rightarrow cis\text{-}(CO)_4Mo(EOO)_2 \quad (2)$$

IV (E = P),
V (E = As)

could not be purified by recrystallization and were identified by their multinuclear NMR and IR spectra. The presence of two ^{13}C NMR resonances above 200 ppm

and of four IR absorptions in the 2100–1800 cm^{-1} region demonstrated that these were *cis* complexes [38].

Powell and coworkers have shown that cation binding by the polyether groups of bis(phosphonite)- and bis(phosphite)-polyether ligands in *cis*-$(CO)_4MoL$ complexes activates the CO ligands towards nucleophilic attack by PhLi or MeLi [13,15–17]. Because IV and V contain the same number of O-donor groups as does the most effective ligand reported by Powell, it was hoped that the CO ligands in these complexes would also be activated towards attack by MeLi. However, addition of MeLi to these complexes in dry diethyl ether or toluene caused no change in their IR spectra in the carbonyl region. This lack of reactivity of the CO ligands in IV and V towards MeLi may be due to the lack of a crown ether-type ring or to the separation of the ether oxygens from the P or As by ethylene groups. Either of these differences might reduce the binding constants for the lithium cations sufficiently that activation of the CO ligands does not occur. In order to determine if either of these is responsible, we are studying the reactions of analogous complexes with cyclic bis(phosphine)polyether ligands with MeLi.

Our attempts to prepare $Cl_2(CO)_2Ru(POO)_2$ complexes were hindered by the fact that the preparation reported for $[Cl_2(CO)_2Ru]_n$, VI, by Colton et al. [39] does not give this material in our hands. Instead, this procedure gives a mixture containing mostly $[Cl_2(CO)_3Ru]_2$ with a minor amount of VI. These two materials were separated by extracting the mixture with acetone to remove the soluble $[Cl_2(CO)_3Ru]_2$. Recrystallization of the residue from the acetone wash from a THF/hexanes mixture gives a good yield of $Cl_2(CO)_3Ru \cdot 0.75THF$ (VII). Alternatively, the mixture can be converted to VI via Soxhlet extraction of the mixture with methanol.

These two different Ru precursors were reacted with II as shown in eqs. 3 and 4. The products of these reactions have different

$$\underset{\text{(VII)}}{Cl_2(CO)_3Ru \cdot 0.75THF} + 2\ POO \rightarrow \underset{\text{(VIII)}}{\textit{cis,cis,trans}\text{-}Cl_2(CO)_2Ru(POO)_2} \quad (3)$$

$$\underset{\text{(VI)}}{[Cl_2(CO)_2Ru]_n} \xrightarrow[\text{reflux}]{\text{MeCN}} \xrightarrow{2\ POO} \underset{\text{(IX)}}{\textit{cis,trans,cis}\text{-}Cl_2(CO)_2Ru(POO)_2} \quad (4)$$

geometries. The geometry of VIII was assigned as *cis,cis,trans* by comparison of its ^{31}P NMR and IR spectra to those of *cis,cis,trans*-$Cl_2(CO)_2Ru(Ph_2PCH_2\overline{CHCH_2\text{-}CH_2CH_2O})_2$ (δ (^{31}P) = 13.6 ppm, ν(CO) = 2049, 1979 cm^{-1}) [4]. The ^{13}C NMR resonance of the CO ligands in VIII further confirms this assignment because a single, 1/2/1 triplet resonance is observed for the two CO ligands. This will only occur for *cis* CO ligands (from the IR) if the POO ligands are *trans* to one another and if the chlorides are *trans* to the carbonyls.

The geometry of IX was assigned on the basis of its ^{31}P and ^{13}C NMR and IR spectra. The IR spectrum of IX contains a single absorption at 1959 cm^{-1} that indicates that the two CO ligands are *trans* to each other. The ^{31}P NMR resonance of IX is 4.7 ppm downfield of that of VIII. This suggests that the POO ligands are not *trans* to each other as in VIII, and thus must be *trans* to the chloride ligands. The ^{13}C NMR resonance of the CO ligands in IX further confirms this assignment because a single, 1/2/1 triplet resonance is observed as is expected for CO ligands *trans* to one another and *cis* to two POO ligands. The similarity of $|^2J(PC)|$ of

VIII (11 Hz) to that of IX (13 Hz) suggests that the CO and POO ligands are *cis* in both complexes.

In addition to the unusual geometry exhibited by IX, the P-phenyl groups in this complex are chemically inequivalent and exhibit two sets of ^{13}C NMR resonances. The reason for this is not clear as only one set of ^{13}C NMR resonances is observed for the aliphatic carbons of the ligands. It is possible that the two sets of phenyl ^{13}C NMR resonances are inequivalent due to restricted rotation about the Ru–P bond. This would be more likely to occur in IX than in VIII because the bulky POO ligands are *cis* to each other in IX but are *trans* to each other in VIII.

The cationic rhodium complex of the POO ligand, $[(cod)Rh(POO)_2]ClO_4$ was synthesized by the method of Schrock and Osborn [40] as shown in eq. 5. The product precipitates in analytically pure form from the

$$(cod)Rh(acac) + 2\ POO + HClO_4 \rightarrow \underset{(X)}{[(cod)Rh(POO)_2]ClO_4} \quad (5)$$

reaction mixture. Attempts to recrystallize the material to remove the water of crystallization resulted in decomposition of the complex. The chemical shift of the

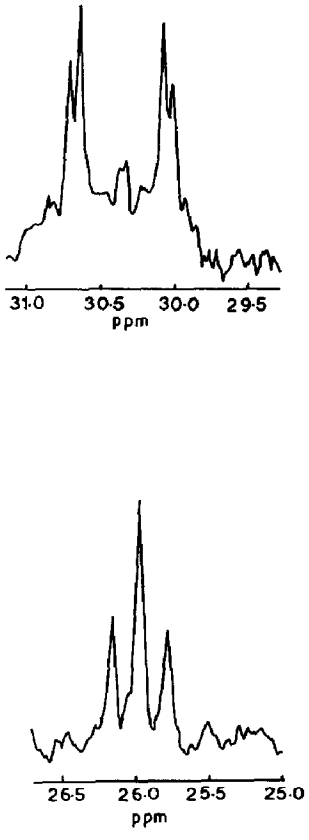

Fig. 1. The C(1) ^{13}C NMR resonances of the *cis*-$Cl_2Pt(POO)_2$ (XII) (top) and *trans*-$Cl_2Pd(POO)_2$ (XI) (bottom) complexes.

^{31}P NMR resonance and $|^1J(RhP)|$ for X are similar to those of the diastereomers of $[(cod)Rh(Ph_2PCH_2\overline{CHCH_2CH_2CH_2O})_2]PF_6$ (δ (^{31}P) = 15.6, 14.5 ppm, $|^1J(RhP)| = 141.9$, 137.7 Hz).

The $Cl_2Pd(POO)_2$ and *cis*-$Cl_2Pt(POO)_2$ complexes were synthesized in good yields as shown in eq. 6. The large $|^1J(PtP)|$ (3630 Hz) of XII indicates that the POO ligands are *cis* in XII.

$$Cl_2M(cod) + 2\ POO \rightarrow Cl_2M(POO)_2 \quad (6)$$

XI (M = Pd),
XII (M = Pt)

The geometry of XI is more difficult to determine than that of XII. The ^{31}P NMR spectrum of pure XI contains two resonances at 24.80 and 12.44 ppm in a 1/7 ratio. The downfield resonance is assigned as due to the *cis* isomer and the upfield resonance as due to the *trans* isomer. This assignment is supported by a comparison of the ^{13}C NMR resonances observed for the *ipso* C(1) groups of XII and the major isomer of XI. Both of these resonances, as shown in Fig. 1, are apparent quintets. However, the diffences in intensities of the lines in these apparent quintets indicate that $|^2J(PP)|$ is very different in these complexes. This is consistent with the major isomer of XI having a *trans* geometry.

Conclusions

The EOO ligands coordinate to group 6 metal carbonyls and Pt-group metals solely through the group 15-donor atom. These ligands do not activate the CO ligands in the *cis*-$(CO)_4Mo(EOO)_2$ complexes towards attack by MeLi.

Acknowledgement

This research was supported by grants from Research Corporation, The Petroleum Research Fund of the American Chemical Society and the Graduate School of UAB. We thank Johnson Matthey for a generous loan of the Pt-group metal salts.

References

1 J.C. Jeffrey and T.B. Rauchfuss, Inorg. Chem., 18 (1979) 2658.
2 G.K. Anderson and R. Kumar, Inorg. Chem., 23 (1984) 4064.
3 E. Lindner and B. Andres, Chem. Ber., 120 (1987) 761.
4 E. Lindner, U. Schober, R. Fawzi, W. Hiller, U. Englert and P. Wegner, Chem. Ber., 120 (1987) 1621.
5 E. Lindner, U. Schober and M. Stangle, J. Organomet. Chem., 331 (1987) C13.
6 E. Lindner and S. Meyer, J. Organomet. Chem., 339 (1988) 193.
7 E. Lindner and B. Andres, Chem. Ber., 121 (1988) 829.
8 E. Lindner, A. Sickinger and P. Wegner, J. Organomet. Chem., 349 (1988) 75.
9 E. Lindner and U. Schober, Inorg. Chem., 27 (1988) 212.
10 G.K. Anderson and R. Kumar, Inorg. Chim. Acta, 146 (1988) 89.
11 T. Okana, M. Yamamoto, T. Noguchi, H. Konishi and J. Kiji, Chem. Lett., (1982) 977.
12 T. Okano, Y. Moriyama, H. Konishi and J. Kiji, Chem. Lett., (1986) 1463.
13 J. Powell, A. Kuksis, C.J. May, S.C. Nyburg and S.J. Smith, J. Am. Chem. Soc., 103 (1981) 5941.
14 W.E. Hill, J.G. Taylor, C.A. McAuliffe, K.W. Muir and L. Manojlovic-Muir, J. Chem. Soc., Dalton Trans., (1982) 833.
15 J. Powell, S.C. Nyburg and S.J. Smith, Inorg. Chim. Acta, 76 (1983) L75.
16 J. Powell, K.S. Ng, W.W. Ng and S.C. Nyburg, J. Organomet. Chem., 243 (1983) C4.

17 J. Powell, M. Gregg, A. Kuskis and P. Meindl, J. Am. Chem. Soc., 105 (1983) 1064.
18 D.H.M.W. Thewissen, K. Timmer, J.G. Noltes, J.W. Marsman and R.M. Laine, Inorg. Chim. Acta, 97 (1985) 143.
19 K. Timmer and D.H.W. Thewissen, Inorg. Chim. Acta, 100 (1985) 235.
20 W.E. Hill, J.G. Taylor, C.P. Falshaw, T.J. King, B. Beagley, D.M. Tonge, R.G. Pritchard and C.A. McAuliffe, J. Chem. Soc., Dalton Trans., (1986) 2289.
21 E.M. Hyde, B.L. Shaw and I. Shephard, J. Chem. Soc., Dalton Trans., (1978) 1696.
22 J. Powell and C.J. May, J. Am. Chem. Soc., 104 (1982) 2636.
23 S.J. McLain, J. Am. Chem. Soc., 105 (1983) 6355.
24 B.A. Boyce, A. Carroy, J.-M. Lehn and D. Parker, J. Chem. Soc., Chem. Commun., (1984) 1546.
25 S.J. McLain, Inorg. Chem., 25 (1986) 3124.
26 A. Carroy, C.R. Langick, J.-M. Lehn, K.E. Matthes and D. Parker, Helv. Chim. Acta, 69 (1986) 580.
27 T.A. DelDonno and W. Rosen, Inorg. Chem., 17 (1978) 3714.
28 E.P. Kyba, D.C. Alexander and A. Hohn, Organometallics, 1 (1983) 1619.
29 M. Ciampolini, N. Nardi, P.L. Orioli, S. Mangani and F. Zanobini, J. Chem. Soc., Dalton Trans., (1984) 2265.
30 C. Mealli, M. Sabat, F. Zanobini, M. Ciampolini and N. Nardi, J. Chem. Soc., Dalton Trans., (1985) 479.
31 L. Wei, A. Bell, S. Warner, I.D. Williams and S.J. Lippard, J. Am. Chem. Soc., 108 (1986) 8302.
32 W. Steinkopf and W. Mieg, Chem. Ber., 53 (1920) 1013.
33 W. Erhl, R. Rinck and H. Vahrenkamp, J. Organomet. Chem., 43 (1972) 343.
34 J. Chatt and L.M. Venanzi, J. Chem. Soc., (1957) 4735.
35 H.A. Tayim and J.C. Bailar, Jr., J. Am. Chem. Soc., 60 (1938) 882.
36 J. Chatt, L.M. Vallarino and L.M. Venanzi, J. Chem. Soc., (1957) 3413.
37 D.A. Redfield, J.H. Nelson and L.W. Cary, Inorg. Nucl. Chem. Lett., 10 (1974) 727.
38 F.A. Cotton and C.S. Kraihanzel, J. Am. Chem. Soc., 84 (1962) 4432.
39 R. Colton and R.H. Farthing, Aust. J. Chem., 20 (1967) 1283.
40 R.R. Schrock and J.A. Osborn, J. Am. Chem. Soc., 93 (1971) 2397.