

## TERTIARY PHOSPHINE COMPLEXES OF CYCLOPENTADIENYLMOLYBDENUM CARBONYL HALIDES. STEREOSELECTIVE SYNTHESSES AND ISOMER SEPARATIONS

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### Summary

Pure *cis* and *trans* isomers of  $\text{CpMo}(\text{CO})_2(\text{L})\text{X}$  ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ,  $\text{L} = \text{PPh}_3$  or  $\text{PBu}_3$ ,  $\text{X} = \text{Br}$ , or  $\text{I}$ ) have been separated by chromatography and characterized by infrared and proton NMR spectroscopy. The reactions of *trans*- $\text{CpMo}(\text{CO})_2(\text{L})\text{CH}_3$  with  $\text{HgX}_2$  ( $\text{X} = \text{Cl}$ ,  $\text{Br}$ ,  $\text{I}$ ,  $\text{SCN}$ ) afford *cis*- $\text{CpMo}(\text{CO})_2(\text{L})\text{X}$  in high yield. Both linkage isomers are obtained in the reaction with  $\text{Hg}(\text{SCN})_2$ ,  $\text{L} = \text{PPh}_3$ . The mercuric halides react with  $\text{CpMo}(\text{CO})_2(\text{L})\text{COCH}_3$  to form the metal-metal bonded derivatives *trans*- $\text{CpMo}(\text{CO})_2(\text{L})\text{HgX}$ . Reactions of  $\text{CpMo}(\text{CO})_2(\text{L})\text{CH}_3$  or  $\text{CpMo}(\text{CO})_2(\text{L})\text{COCH}_3$  with bromine or iodine yield the halide complexes  $\text{CpMo}(\text{CO})_2(\text{L})\text{X}$  ( $\text{X} = \text{Br}$  and  $\text{I}$ , respectively), the product mixtures containing high proportions of the *trans* isomers.

### Introduction

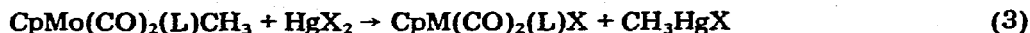
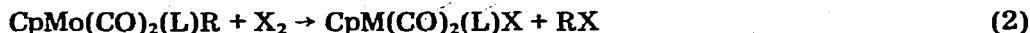
Since the initial report by King in 1963 [1] that  $\text{CpMo}(\text{CO})_2[\text{P}(\text{NMe}_2)_3]\text{I}$  exists in two isomeric forms, a considerable volume of data has been accumulated on complexes of this type containing a variety of Group V donors and one-electron ligands [2]. The basic geometries of these isomers (generally denoted *cis* and *trans*)\* in the solid state have been confirmed by X-ray diffraction studies of *trans*- $\text{CpMo}(\text{CO})_2(\text{PPh}_3)\text{COCH}_3$  [5] and *cis*- $\text{CpMo}(\text{CO})_2[\text{P}(\text{n-butyl})_3]\text{I}$  [6]. The comprehensive proton NMR study by Faller and Anderson [7] demonstrated that the *cis/trans* isomer ratio in solution is a complex function of ligand electronic and steric effects and that *cis*  $\rightleftharpoons$  *trans* interconversions are accomplished by an intramolecular process or processes. The latter conclusion has been supported by related studies conducted in other laboratories [8,9].

\* King [3,4] prefers the terms "lateral" and "diagonal" instead of "cis" and "trans", respectively.

While neither seems entirely satisfactory, the *cis*, *trans* nomenclature has been used almost exclusively in the literature to date and will be employed here.



In the course of our studies of the carbon-13 NMR spectra of a series of these complexes [10] we discovered that pure *cis* and *trans* isomers of  $\text{CpM}(\text{CO})_2(\text{PPh}_3)\text{X}$  ( $\text{M} = \text{Mo}$ ,  $\text{X} = \text{Br}$ ,  $\text{I}$ ;  $\text{M} = \text{W}$ ,  $\text{X} = \text{I}$ ) are separable by careful column chromatography [11]. Further, we noted that *cis* isomers predominated when the complexes were prepared by thermal substitution (eq. 1) while *trans* isomers were formed preferentially in the electrophilic cleavage of alkyls or acyls by halogens (eq. 2). We have extended these studies to include cleavage with



mercury(II) halides and pseudohalides (eq. 3 and 4). The present paper reports details of the isomer separations and the utility of the electrophilic cleavage routes for preparing mixtures heavily enriched in a specific isomer.

## Experimental

All operations were conducted under nitrogen or argon atmospheres, including admission of argon to evacuated flasks. Solvents were dried by standard methods and argon purged before use.  $\text{Mo}(\text{CO})_6$  was a generous gift of Climax Molybdenum Company. Phosphorus ligands were purchased from Stem Chemical Company and used as received. The complexes  $\text{CpMo}(\text{CO})_3\text{CH}_3$  [12],  $\text{CpMo}(\text{CO})_2(\text{L})\text{COCH}_3$  [13,14] and  $\text{CpMo}(\text{CO})_2(\text{L})\text{CH}_3$  [13] were prepared by the literature methods cited. The products  $\text{CpMo}(\text{CO})_2(\text{L})\text{X}$  and  $\text{CpMo}(\text{CO})_2(\text{PPh}_3)\text{HgX}$  were identified by comparison of infrared and NMR spectra with authentic samples prepared by literature methods [7,15,16]. Elemental analyses for the new complexes  $\text{CpMo}(\text{CO})_2(\text{PPh}_3)\text{—SCN}$ ,  $\text{—NCS}$  and  $\text{CpMo}(\text{CO})_2(\text{PBU}_3)\text{HgX}$  were conducted by Galbraith Microanalytical Laboratories, Knoxville, Tennessee.

Infrared spectra were recorded on Perkin—Elmer 337 or 521 spectrometers using matched 0.1 mm KBr solution cells. Spectra were calibrated vs. the 1944.0 and 1601.4  $\text{cm}^{-1}$  bands of polystyrene film. NMR spectra were recorded on a Varian Associates T-60 instrument, using deuteriochloroform solvent with TMS as the internal standard. Infrared and NMR data are collected in Table 1. Examples of typical synthetic and isomer separation procedures are given below. Yields and isomer ratios for all the reported reactions are given in Table 2.

TABLE 1  
PROTON NMR <sup>a</sup> AND INFRARED SPECTRA <sup>b</sup> FOR CpMo(CO)<sub>2</sub>(L)X COMPLEXES

Geometry	L	X	δ(Cp) <sup>c</sup>	ν(CO)
<i>cis</i>	PPh <sub>3</sub>	Cl	5.35	1980vs, 1895s
<i>cis</i>	PPh <sub>3</sub>	Br	5.37	1980 vs, 1890 s
<i>trans</i>	PPh <sub>3</sub>	Br	5.08(1.5)	1980 s, 1890 vs
<i>cis</i>	PPh <sub>3</sub>	I	5.35	1975 vs, 1890 s
<i>trans</i>	PPh <sub>3</sub>	I	5.07(1.5)	1975 s, 1890 vs
<i>cis</i>	PPh <sub>3</sub>	NCS	5.51	1981 vs, 1896 s <sup>d</sup>
<i>cis</i>	PPh <sub>3</sub>	SCN	5.54	1975 vs, 1891 s <sup>e</sup>
<i>cis</i>	PPh <sub>3</sub>	CN	5.42	1985 vs, 1905 s <sup>f</sup>
<i>trans</i>	PPh <sub>3</sub>	CN	5.20(2.0)	1985 s, 1905 vs <sup>f</sup>
<i>trans</i>	PPh <sub>3</sub>	HgCl	5.12(1.5)	1935 s, 1865 vs
<i>trans</i>	PPh <sub>3</sub>	HgBr	5.12(1.5)	1940 s, 1860 vs
<i>trans</i>	PPh <sub>3</sub>	HgI	5.12(1.5)	1930 s, 1860 vs
<i>cis</i>	PBu <sub>3</sub>	Br	5.46	1960 vs, 1870 s
<i>trans</i>	PBu <sub>3</sub>	Br	5.30(2.0)	1960(s), 1870 vs
<i>cis</i>	PBu <sub>3</sub>	I	5.46	1970 vs, 1880 s
<i>trans</i>	PBu <sub>3</sub>	I	5.28(1.5)	1970 s, 1880 vs
<i>trans</i>	PBu <sub>3</sub>	HgCl	5.23(1.5)	1930 s, 1850 vs
<i>trans</i>	PBu <sub>3</sub>	HgBr	5.25(2.0)	1932 s, 1851 vs
<i>trans</i>	PBu <sub>3</sub>	HgI	5.20(1.5)	1930s, 1854 vs

<sup>a</sup> Varian Associates T-60 spectrometer. CDCl<sub>3</sub> solvent, TMS internal standard. <sup>b</sup> Chloroform solution.

<sup>c</sup> Singlet unless *J*(PH) given in parentheses to indicate doublet. <sup>d</sup> ν(CN) 2085 vs. <sup>e</sup> ν(CN) 2108 m. <sup>f</sup> ν(CN) 2105 mw.

### Reaction of CpMo(CO)<sub>2</sub>(PPh<sub>3</sub>)CH<sub>3</sub> with iodine

The molybdenum complex (0.50 g, 1.01 mmol) was dissolved in 25 ml chloroform under argon and the solution cooled to 0°C. Iodine (0.25 g, 0.98 mmol) was dissolved in 40 ml of chloroform and added dropwise to the vigorously

TABLE 2  
ISOMER RATIOS OF CpMo(CO)<sub>2</sub>(L)X AS A FUNCTION OF PREPARATIVE METHOD <sup>a,b</sup>

L	X	Thermal substitution <sup>b</sup>		X <sub>2</sub> cleavage		HgX <sub>2</sub> cleavage	
		<i>cis/trans</i>	Yield(%)	<i>cis/trans</i>	Yield( <i>f</i> ) <sup>c</sup>	<i>cis/trans</i>	Yield(%) <sup>c,d</sup>
PPh <sub>3</sub>	Cl	100 : 0	81	100 : 0	12	100 : 0	83
PPh <sub>3</sub>	Br	95 : 5	77	25 : 75	70	100 : 0	53
PPh <sub>3</sub>	I	60 : 40	74	25 : 75	67	100 : 0	48
PPh <sub>3</sub>	NCS					100 : 0	34
PPh <sub>3</sub>	SCN					100 : 0	15
PPh <sub>3</sub>	CN					80 : 20	trace
PBu <sub>3</sub>	Cl					100 : 0	72
PBu <sub>3</sub>	Br	95 : 5	80	35 : 65	44	100 : 0	90
PBu <sub>3</sub>	I	95 : 5	74	60 : 40	53	100 : 0	35
PPh <sub>3</sub>	HgCl <sup>e</sup>					0 : 100	93
PPh <sub>3</sub>	HgBr <sup>e</sup>					0 : 100	62
PPh <sub>3</sub>	HgI <sup>e</sup>					0 : 100	36
PBu <sub>3</sub>	HgCl <sup>e</sup>					0 : 100	48
PBu <sub>3</sub>	HgBr <sup>e</sup>					0 : 100	45
PBu <sub>3</sub>	HgI <sup>e</sup>					0 : 100	19

<sup>a</sup> Ratios determined by integration of proton NMR spectra in the C<sub>5</sub>H<sub>5</sub> region. <sup>b</sup> Refluxing benzene.

<sup>c</sup> Isolated yield, not optimized. <sup>d</sup> 2–3% of the "absent" isomer would not be detectable by NMR.

<sup>e</sup> From CpMo(CO)<sub>2</sub>(L)COCH<sub>3</sub> and HgX<sub>2</sub>.

stirred  $\text{CpMo}(\text{CO})_2(\text{PPh}_3)\text{CH}_3$  solution over a 30 min period. After 2 h the solvent was removed by rotary evaporation (room temperature). The resulting red-orange solid was dissolved in the minimum amount of chloroform and chromatographed on Brockman Activity Grade 1 alumina. A single red-orange band was eluted with 1 : 1 chloroform/hexane. Removal and solvent and crystallization from chloroform/hexane afforded 0.41 g of a 25 : 75 *cis/trans* mixture of  $\text{CpMo}(\text{CO})_2(\text{PPh}_3)\text{I}$  (67% yield).

*Reaction of  $\text{CpMo}(\text{CO})_2(\text{PBu}_3)\text{CH}_3$  with  $\text{HgBr}_2$*

The molybdenum complex (0.38 g, 0.87 mmol) and  $\text{HgBr}_2$  (0.43 g, 1.2 mmol) were dissolved in 50 ml  $\text{CHCl}_3$  and stirred under argon for 1 h at room temperature. The NMR spectrum of an aliquot of the reaction mixture indicated the presence of *cis*- $\text{CpMo}(\text{CO})_2(\text{PBu}_3)\text{Br}$  and  $\text{CH}_3\text{HgBr}$  [17]. Solvent was removed at reduced pressure ( $T$  15–20°C). The resultant solid was extracted with 3 five ml portions of  $\text{CHCl}_3$  and chromatographed on alumina (1 : 1 chloroform/hexane). A single red-orange band was collected. Removal of solvent at reduced pressure followed by crystallization from hexane/diethyl ether afforded 0.39 g of *cis*- $\text{CpMo}(\text{CO})_2(\text{PBu}_3)\text{Br}$  (90% yield). No attempt was made to isolate  $\text{CH}_3\text{HgBr}$ .

*Reaction of  $\text{CpMo}(\text{CO})_2(\text{PPh}_3)\text{CH}_3$  with  $\text{Hg}(\text{SCN})_2$*

The molybdenum complex (1.5 g, 3.0 mmol) and  $\text{Hg}(\text{SCN})_2$  (1.1 g, 3.5 mmol) were dissolved in 100 ml  $\text{CHCl}_3$  and stirred under argon for 2 h, during which time the color of the solution changed from yellow to orange. An NMR spectrum of the crude reaction mixture (after solvent removal) showed the expected phenyl resonances, two singlets in the  $\text{C}_5\text{H}_5$  region (vide infra) and a sharp singlet at  $\delta$  1.22 ppm attributable to  $\text{CH}_3\text{HgSCN}$ . The reaction mixture was dissolved in 15 ml chloroform and gravity filtered to remove approximately 0.5 g of grey-green material which was also insoluble in acetone and water. The chloroform solubles were chromatographed (3 × 20 cm column, Brockman Activity Grade 1 Alumina) using 1 : 3 chloroform/hexane as eluant. The first, yellow-orange, band afforded 0.54 g of *cis*- $\text{CpMo}(\text{CO})_2(\text{PPh}_3)\text{NCS}$  as bright orange plates upon crystallization from chloroform/hexane (34% yield), m.p. 166–168°C (dec.). Found: C, 57.48; H, 3.52; P, 6.0; S, 6.18.  $\text{C}_{26}\text{H}_{20}\text{MoNO}_2\text{PS}$  calcd.: C, 58.10; H, 3.72; P, 5.77; S, 5.96%. The second band (red-orange) similarly gave 0.25 g (15% yield) of *cis*- $\text{CpMo}(\text{CO})_2(\text{PPh}_3)\text{SCN}$  as rust red microcrystals, m.p. 138–139°C (dec.). Found: C, 56.95; H, 3.88; P, 5.46; S, 5.65.  $\text{C}_{26}\text{H}_{20}\text{MoNO}_2\text{PS}$ , calcd.: C, 58.10; H, 3.72; P, 5.77; S, 5.96%. Infrared and NMR data are given in Table 1. Integrated absorption intensities of the CN stretching bands were found to be  $14.8 \times 10^4 \text{ M}^{-1} \text{ cm}^{-2}$  and  $3.4 \times 10^4 \text{ M}^{-1} \text{ cm}^{-2}$  for the N- and S-bonded isomers, respectively.

*Reactions of  $\text{CpMo}(\text{CO})_2(\text{PBu}_3)\text{COCH}_3$  with  $\text{HgCl}_2$ ,  $\text{HgBr}_2$  and  $\text{HgI}_2$*

The molybdenum compound (0.57 g, 1.24 mmol) and  $\text{HgCl}_2$  (0.060 g, 2.2 mmol) were dissolved in 30 ml of  $\text{CHCl}_3$  and stirred under argon at room temperature for 1 h. Solvent was removed at aspirator vacuum (room temperature and below) and the solid extracted with three 5 ml portions of chloroform. The solution was placed on an alumina column and the chromatogram developed with 1 : 1 chloroform/hexane. A single yellow band was collected. Solvent re-

moval followed by crystallization from chloroform/hexane gave *trans*-CpMo(CO)<sub>2</sub>-(PBu<sub>3</sub>)HgCl as bright yellow needles, m.p. 139–140°C, 0.39 g, 48% yield. Found: C, 34.95; H, 5.03; P, 4.76. C<sub>19</sub>H<sub>32</sub>ClHgMoP calcd.: C, 34.82; H, 4.92; P, 4.73%. Use of HgBr<sub>2</sub> under otherwise identical conditions afforded *trans*-CpMo(CO)<sub>2</sub>-(PBu<sub>3</sub>)HgBr as bright yellow microcrystals, m.p. 125–126°C. Found: C, 32.38; H, 4.70; P, 3.96%. C<sub>19</sub>H<sub>32</sub>BrHgMoP calcd.: C, 32.61; H, 4.61; P, 4.42%. *trans*-CpMo(CO)<sub>2</sub>(PPh<sub>3</sub>)HgI (yellow needles) melted 115–117°C with decomposition. Found: C, 30.77, H, 4.48, P, 3.96. C<sub>19</sub>H<sub>32</sub>HgIMoP calcd.: C, 30.55; H, 4.32; P, 4.15%.

#### Chromatographic separation of CpMo(CO)<sub>2</sub>(PBu<sub>3</sub>)I isomers

200 mg of a 3 : 2 *cis/trans* mixture of the subject compound was dissolved in 1 : 1 benzene/hexane and chromatographed on Brockman Activity Grade 1 neutral alumina (1 × 20 cm column). Two bands developed, the first red-purple, the second orange. These were collected, solvent removed and the products crystallized from ether/hexane to afford 85 mg of *cis*-CpMo(CO)<sub>2</sub>(PBu<sub>3</sub>)I and 60 mg of *trans*-CpMo(CO)<sub>2</sub>(PBu<sub>3</sub>)I, respectively. Pure *cis* and *trans* isomers of CpMo(CO)<sub>2</sub>(PPh<sub>3</sub>)X (X = Br, I) and CpW(CO)<sub>2</sub>(PPh<sub>3</sub>)I were separated under identical conditions [11]. The latter complexes do not isomerize in the solid state for periods of at least 2 years. Both *cis*- and *trans*-CpMo(CO)<sub>2</sub>(PBu<sub>3</sub>)I isomerize to the thermodynamic 90 : 10 *cis/trans* mixture in the solid state at 25°C within 4 weeks. At 0°C they are stable towards isomerization for several months.

#### Reaction of CpMo(CO)<sub>2</sub>(PPh<sub>3</sub>)CH<sub>3</sub> with Hg(CN)<sub>2</sub>

No reaction was observed in chloroform (25–60°C), THF (25°C), or acetone (25°C). The molybdenum methyl complex (1.0 g, 2 mmol) and Hg(CN)<sub>2</sub> (1.6 g, 6.4 mmol) were dissolved in 50 ml acetone and the solution refluxed for 3 h. Solvent was removed by rotary evaporation. The resulting solid was extracted with five 25 ml portions of chloroform leaving behind a considerable quantity of grey-green non-carbonyl containing residue. The extracts were combined and solvent removed to afford a yellow oil which could not be recrystallized from a variety of solvents. Infrared and proton NMR spectra (Table 1) indicated the presence of a 4 : 1 mixture of *cis* and *trans*-CpMo(CO)<sub>2</sub>(PPh<sub>3</sub>)CN. A singlet in the NMR spectrum at 1.07 ppm was attributed to CH<sub>3</sub>HgCN [17]. Chromatography on neutral alumina with a variety of solvent combinations failed to free the molybdenum containing product from the mercury byproduct.

## Results and discussion

Separation of the *cis* and *trans* isomers of CpMo(CO)<sub>2</sub>(L)X complexes is described in the Experimental. The identity of the isomers was proven according to well-established infrared and proton NMR criteria [2,7–9,11]. The data are given in Table 1. The higher frequency (symmetric) CO stretching vibration is more intense than the lower frequency (antisymmetric) stretch for the *cis* isomers, while the opposite is true for the *trans* isomers (3,4,18). The *cis* and *trans* isomers afford well-separated singlet and doublet [*J*(PH) 1.5–2.0 Hz] C<sub>5</sub>H<sub>5</sub> resonances respectively in their proton NMR spectra. Carbon-13 NMR data of re-

presentative complexes are in complete accord with these assignments, as described elsewhere [10,11]. The triphenylphosphine complexes are stable with respect to thermal isomerization in the solid state and in solution at or near room temperature. Both *cis*- and *trans*-CpMo(CO)<sub>2</sub>(PBU<sub>3</sub>)I isomerize in the solid state at room temperature, necessitating their storage at 0°C or below. At elevated temperatures *cis* ⇌ *trans* isomerization is rapid, the thermodynamic equilibrium ratios being achieved within 2–4 h in refluxing acetone or benzene in all cases. The equilibrium isomer ratios were equal within experimental error to those given in Table 2 for thermal substitution.

Preparation of the subject complexes by thermal substitution (eq. 1) leads to product mixtures in which the *cis* isomer predominates. Since the *cis* isomer is thermodynamically favored at high temperatures and isomerization is rapid relative to substitution, the product ratios in these cases reflect thermodynamic control. In view of the kinetic stability of both isomers at lower temperatures (*vide supra*), synthetic routes employing milder conditions offered the possibility of selective formation of product mixtures rich in either geometric isomer. Electrophilic cleavage of metal–carbon σ bonds by halogens or mercury(II) salts is known for a variety of systems [19–22] and proved to be applicable to these goals.

Cleavage of methyl or acetyl complexes with bromine or iodine at 0°C in chloroform solution (eq. 2) leads to product mixtures rich in the *trans* isomers (Table 2), providing a valuable route to these complexes. Combined with the separation techniques described in the experimental section, this process provides for the first time a route to the pure *trans* isomers of many of the subject complexes, notably the bromide and tri(*n*-butyl)phosphine derivatives. In sharp contrast to the halogen cleavage reactions, treatment of the methyl complexes CpMo(CO)<sub>2</sub>(L)CH<sub>3</sub> with mercuric bromide or iodide in chloroform at room temperature (eq. 3) \* leads to the exclusive formation of *cis*-CpMo(CO)<sub>2</sub>(L)X in good to excellent yield. It is thus possible to prepare the bromide and iodide complexes in high isomeric purity by judicious choice of the cleaving agent.

Based on the above observations, we hoped to be able to prepare the *trans* chloride CpMo(CO)<sub>2</sub>(PPh<sub>3</sub>)Cl, but chlorine cleavage of CpMo(CO)<sub>2</sub>(PPh<sub>3</sub>)CH<sub>3</sub> (even at –40°C) leads to the *cis* isomer only, in addition to considerable decomposition. The reaction of CpMo(CO)<sub>2</sub>(PPh<sub>3</sub>)CH<sub>3</sub> with mercuric chloride affords *cis*-CpMo(CO)<sub>2</sub>(PPh<sub>3</sub>)Cl and a small amount of *trans*-CpMo(CO)<sub>2</sub>(PPh<sub>3</sub>)HgCl, the latter being the only example of a mercury bonded derivative encountered in the cleavages of the methyl complexes.

The acetyl complexes CpMo(CO)<sub>2</sub>(L)COCH<sub>3</sub> are cleaved by Br<sub>2</sub> or I<sub>2</sub> to afford heavily *trans* halide complex mixtures [11], but yield cleanly the metal–metal bonded *trans*-CpMo(CO)<sub>2</sub>(L)HgX compounds when treated with HgX<sub>2</sub>. This result is in obvious contrast to the behavior of the methyl complexes. King and Bisnette have reported a similar anomaly in the reaction of CpMo(CO)<sub>3</sub>CH<sub>2</sub>SCH<sub>3</sub> with HgCl<sub>2</sub>, the product [23] being the metal–metal bonded derivative CpMo(CO)<sub>3</sub>HgCl. These authors were unable to obtain identifiable products from the reactions of tricarbonylalkyl derivatives CpMo(CO)<sub>3</sub>R (R = C<sub>2</sub>H<sub>5</sub> or CF<sub>3</sub>) with HgCl<sub>2</sub>. We find CpMo(CO)<sub>3</sub>CH<sub>3</sub> and CpW(CO)<sub>3</sub>CH<sub>3</sub> to be unreactive toward any

\* CH<sub>3</sub>HgX products were observed by NMR monitoring of crude reaction mixtures (Experimental). These were removed by chromatography and crystallization.

of the Hg(II) derivatives studied herein. It thus appears that the presence of the phosphorus donor ligand enhances reactivity toward mercuric salts and the presence of a heteroatom (oxygen or sulfur) in the R group promotes formation of the Mo—Hg bond in these systems.

An obvious question regarding the exclusive formation of the *cis* isomers in the mercuric halide cleavage reactions is whether an isomeric mixture is formed and then rapidly isomerized. As noted above, thermal isomerization does not occur at 25°C nor is the isomerization process brought about by normal laboratory light. Control experiments showed that, in addition, neither  $\text{HgX}_2$  nor  $\text{CH}_3\text{HgX}$  bring about the *trans*  $\rightleftharpoons$  *cis* isomerization at a detectable rate. Thus there is a unique reaction path from *trans*- $\text{CpMo}(\text{CO})_2(\text{L})\text{CH}_3$  to *cis*- $\text{CpMo}(\text{CO})_2(\text{L})\text{X}$  via the Hg(II) reagents. The mechanisms of these processes are not obvious and must await further study.

We were encouraged by the rapidity and high yields obtained in the mercuric halide reactions to extend this preparative route to complexes containing pseudo-halide ligands. Mercury(II) thiocyanate and  $\text{CpMo}(\text{CO})_2(\text{PPh}_3)\text{CH}_3$  react in chloroform at room temperature to afford the linkage isomers *cis*- $\text{CpMo}(\text{CO})_2(\text{PPh}_3)\text{NCS}$  and *cis*- $\text{CpMo}(\text{CO})_2(\text{PPh}_3)\text{SCN}$ . The *cis* stereochemistries of the products were assigned on the basis of the infrared and NMR criteria discussed above for the halide complexes. The mode of bonding for the SCN group was assigned on the basis of the integrated absorption intensities of the C—N stretching frequencies. The generally observed range of values is 8–12 and  $1\text{--}6 \times 10^4 \text{ M}^{-1} \text{ cm}^{-2}$  for N- and S-bonded isomers respectively, in other complexes [24]. The values obtained for  $\text{CpMo}(\text{CO})_2(\text{PPh}_3)\text{—NCS}$  ( $14.8 \times 10^4$ ) and  $\text{—SCN}$  ( $3.4 \times 10^4$ ) are obviously consistent with this criterion. The geometries of the product complexes are of course consistent with the other  $\text{HgX}_2$  cleavage products. The linkage isomers are not interconverted under the reaction conditions or in benzene or chloroform solution at 50°C, demonstrating that they are both primary products of the initial cleavage process. In refluxing benzene the S-bonded isomer is slowly converted to the N-bonded form, but decomposition at this elevated temperature precluded a quantitative study of the thermal isomerization process. Similar observations have been reported by Sloan and Wojcicki for  $\text{CpMo}(\text{CO})_3\text{—NCS}$  and  $\text{—SCN}$  [25].

Mercury(II) cyanide and  $\text{CpMo}(\text{CO})_2(\text{PPh}_3)\text{CH}_3$  do not react at room temperature in chloroform, THF or acetone solution. In refluxing acetone an 80 : 20 mixture *cis*- and *trans*- $\text{CpMo}(\text{CO})_2(\text{PPh}_3)\text{CN}$  is formed in low yield. The presence of the *trans* isomer as a product of this reaction is surprising in light of the other results obtained. The more forcing conditions required for the cleavage reaction could have resulted in *cis*  $\rightleftharpoons$  *trans* isomerization subsequent to the formation of the initial product. However, the low yields obtained and our inability to isolate these complexes in pure form precluded a detailed study of their interconversions.

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