but we are not able to determine if it proceeds via a three-center transition state such as B or an intermediate with a M–SnX_2 bond such as C. The halogen interchange with the migration of the least electronegative halogen from Sn to the transition metal M takes place by a similar series of reactions, which are not illustrated in detail, in D → E. The extrusion of SnY_2 from E, the reverse of A → D, which results only in halogen exchange at M, is E → F although again the individual steps are not illustrated. The reaction D → G which takes place for M = $Fe(CO)_3(PPh_3)$ in the presence of excess L = PPh_3 is the reverse of Kummer and Graham's oxidative addition of tin(IV) halides to $[Fe(CO)_3(PPh_3)_2]$. It provides a rare example of the reductive elimination of tin(IV) halides from a transition-metal complex (we have not been able to trace another), whereas the reverse is well-known.

All of the various steps in Scheme I are probably reversible (cf. ref 15). Together they constitute a series of equilibria, the positions of which vary with metal, halogen, other ligands, and reaction conditions. It is possible that the halogen interchange (D → E) may take place by complete dissociation of SnXY from D followed by its attack on the M–Y bond of the residual M(X)Y moiety. Our inability to detect $M(SnX_3)Y$ species tends to weigh against such a suggestion but does not rule it out.

The absence of $M(SnX_2Y)_2$ derivatives from our reaction mixtures when equimolar amounts of the reactants are used is a clear indication that the SnX_2Y ligand deactivates the second M–Y bond toward SnX_2 insertion. This may be for steric reasons, but it may also be a consequence of the Lewis acid nature of the SnX_2Y ligand[16] and the presence of a Lewis acid–Lewis base interaction between it and Y ligand which is always cis to it in our complexes. Such an interaction would account also for the facile loss of $SnCl_2Br_2$ from $[Fe(CO)_3(PPh_3)(Br)(SnCl_2Br)]$ in the presence of excess PPh_3.

Registry No. $Co(\eta\text{-}C_5H_5)(CO)Br(SnCl_2Br)$, 74007-65-1; $Co(\eta\text{-}C_5H_5)(CO)Br(SnBr_3)$, 12305-13-4; $Co(\eta\text{-}C_5H_5)(CO)I(SnBr_2I)$, 74007-66-2; $Co(\eta\text{-}C_5H_5)(CO)I(SnCl_2I)$, 74007-67-3; $Co(\eta\text{-}C_5H_5)(CO)I(SnI_3)$, 12305-20-3; $Co(\eta\text{-}MeC_5H_4)(CO)Br(SnCl_2Br)$, 74019-24-2; $Co(\eta\text{-}MeC_5H_4)(CO)Br(SnBr_3)$, 74019-25-3; $Co(\eta\text{-}MeC_5H_4)(CO)I(SnBr_2I)$, 74019-26-4; $Co(\eta\text{-}MeC_5H_4)(CO)I(SnCl_2I)$, 74019-27-5; $Co(\eta\text{-}MeC_5H_4)(CO)I(SnI_3)$, 74019-28-6; $Co(\eta\text{-}MeC_5H_4)(PPh_3)I(SnCl_2I)$, 74019-29-7; $Co(\eta\text{-}MeC_5H_4)(PPh_3)I(SnBr_2I)$, 74019-30-0; $Co(\eta\text{-}MeC_5H_4)(PPh_3)I(SnI_3)$, 74019-31-1; $Co(\eta\text{-}C_5H_5)(CO)(C_3F_7)(SnCl_2I)$, 74007-68-4; $Co(\eta\text{-}C_5H_5)(CO)(C_3F_7)(SnBr_2I)$, 74007-69-5; $Co(\eta\text{-}C_5H_5)(CO)(C_3F_7)(SnI_3)$, 74007-70-8; $Fe(CO)_3(PPh_3)Br(SnCl_2Br)$, 74007-71-9; $Fe(CO)_3(PPh_3)Br(SnBr_3)$, 41333-06-6; $Fe(CO)_3(PPh_3)I(SnCl_2I)$, 74007-72-0; $Fe(CO)_3(PPh_3)I(SnBr_2I)$, 74007-73-1; $Fe(CO)_3(PPh_3)I(SnI_3)$, 19601-48-0; $Co(\eta\text{-}C_5H_5)(CO)Br_2$, 12144-83-1; $Co(\eta\text{-}C_5H_5)(CO)I_2$, 12012-77-0; $Co(\eta\text{-}MeC_5H_4)(CO)Br_2$, 74007-74-2; $Co(\eta\text{-}MeC_5H_4)(CO)I_2$, 74007-75-3; $Co(\eta\text{-}MeC_5H_4)(PPh_3)I_2$, 74007-76-4; $Co(\eta\text{-}C_5H_5)(CO)(C_3F_7)I$, 12128-52-8; $Fe(CO)_3(PPh_3)Br_2$, 15388-83-7; $Fe(CO)_3(PPh_3)I_2$, 51744-71-9; $SnBr_2$, 10031-24-0; SnI_2, 10294-70-9; $SnCl_2$, 7772-99-8.

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(16) F. Bonati and G. Minghetti, *J. Organomet. Chem.*, **16**, 332 (1969).

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Alkylation and Ligand Substitution Reactions of Binuclear Organosulfur Molybdenum Complexes with Phosphites and Phosphines

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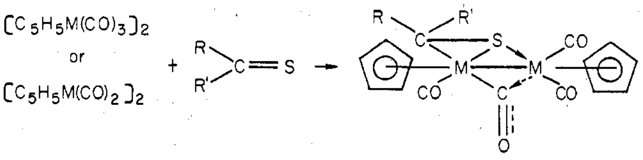
Binuclear organosulfur molybdenum complexes, of formula $(C_5H_5)_2Mo_2(CO)_4(R_2CS)$, which contain a metallathiacyclopropane unit and a semibridging carbonyl group, react with phosphites and alkoxyphosphines to give alkyl migration and ligand substitution products. The alkylated products are of lateral stereochemistry. Mechanisms are proposed for these reactions.

The reaction of thioketones with dicyclopentadienylhexacarbonyl- or dicyclopentadienyltetracarbonyldimolybdenum or -ditungsten results in the formation of complexes of structural type **1** (see Scheme I). These complexes contain a metallathiacyclopropane unit as well as a semibridging carbonyl group.[2] We anticipated that these novel organosulfur complexes would exhibit interesting chemical behavior. For example, would reactions occur which would result in retention or cleavage of the semibridging carbonyl group, metal–metal bond, or the metallathiacyclopropane unit? We now report the results of an investigation of the reactions of organomolybdenum complexes with phosphites and phosphines.

Results and Discussion

Treatment of the binuclear complex **2**, R = OCH_3, with triethyl phosphite in benzene at 60 °C for 15 h affords the mononuclear complex **3**, R = OCH_3, R′ = C_2H_5, in 92% yield (see Scheme II). The yields, melting points, and analytical data for **3** and for the other products of the phosphite and phosphine reactions are given in Table I. Pertinent infrared, magnetic resonance (^1H, ^{13}C, ^{31}P), and mass spectral data are listed in Table II.

Scheme I



1

M = Mo, W

Complex **3**, R = OCH_3, R′ = C_2H_5, has several very interesting structural features. One can consider **3** to be square pyramidal in geometry, if it is assumed that the thiocarbonyl group occupies one coordination site. In that event, two stereoisomers are possible, a lateral (also denoted as cis) and a diagonal (trans).[3-5] The spectral data indicate that the

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(1) E. W. R. Steacie Fellow.

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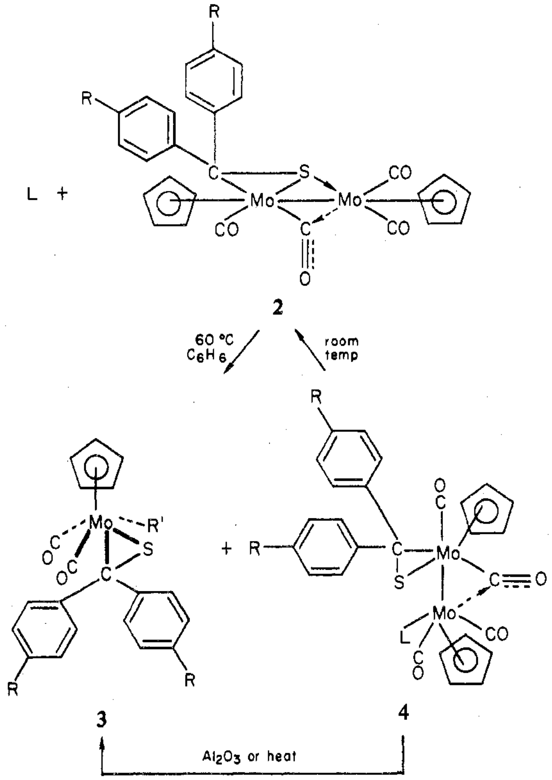
Table I. Products Obtained from Reaction of **2** and **5** with Phosphites and Phosphines

reactant complex	phosphite or phosphine	product	yield,[a] %	mp, °C	anal. [calcd (found)] %C	%H	%S	%P
2, R = OCH_3	$P(OC_2H_5)_3$	**3**, R = OCH_3, R′ = C_2H_5	92	81–83	57.14 (57.51)	4.80 (4.78)	6.36 (6.31)	
	$P(OC_4H_9)_3$	**3**, R = OCH_3, R′ = C_4H_9	57	144–146	58.46 (58.49)	5.30 (5.67)	6.02 (6.39)	
	$PhP(OC_2H_5)_2$	**3**, R = OCH_3, R′ = C_2H_5	44	81–83				
		4, R = OCH_3, L = $PhP(OC_2H_5)_2$	35					
	$Ph_2POC_2H_5$	**4**, R = OCH_3, L = $Ph_2POC_2H_5$	72	105–107	55.97 (55.54)	4.26 (4.60)	3.47 (3.67)	3.35 (3.25)
	$P(OPh)_3$	**4**, R = OCH_3, L = $P(OPh)_3$	15[b]	130 dec	56.30 (57.08)	3.92 (4.08)	3.26 (3.44)	
2, R = H	$P(OC_2H_5)_3$	**3**, R = H, R′ = C_2H_5	82	114–116	59.46 (59.68)	4.54 (4.68)	7.20 (6.93)	
2, R = CH_3	$P(OC_2H_5)_3$	**3**, R = CH_3, R′ = C_2H_5	55	127–128	61.01 (61.05)	5.12 (5.06)	6.79 (7.28)	
		4, R = CH_3, L = $P(OC_2H_5)_3$	29	160 dec	50.86 (51.15)	4.76 (4.95)	3.88 (3.47)	
5	$P(OC_2H_5)_3$	**6**	46	67–69	55.07 (55.23)	6.32 (6.04)	7.73 (7.52)	
		7	10	108–109	46.88 (47.23)	5.38 (5.27)	4.17 (3.82)	

[a] Yields are of analytically pure materials. Satisfactory analytical data could not be obtained for **4**, R = OCH_3, L = $PhP(OC_2H_5)_2$, due to reverse reaction. [b] Unreacted starting material was recovered.

Scheme II



L = $P(OC_2H_5)_3$, $PhP(OC_2H_5)_2$, $Ph_2POC_2H_5$, $P(O\text{-}n\text{-}C_4H_9)_3$
R = H, CH_3, OCH_3
R′ = C_2H_5, C_4H_9

phosphite reaction product, **3**, R = OCH_3, R′ = C_2H_5, is lateral. The infrared spectrum displays two terminal metal–carbonyl stretching absorption bands ($I_a/I_s = 0.9$).[3] What is particularly fascinating are the nuclear magnetic resonance spectra (^1H, ^{13}C), which clearly reveal the nonequivalence of the aryl groups and the nonequivalence of the methylene protons of the ethyl group. The ethyl group gives an ABX_3 pattern in the proton magnetic resonance spectrum, and there are two singlets for the methoxy groups as well as two AB quartets for the protons of the two substituted benzene rings (Figure 1). The carbon magnetic resonance spectrum shows eight aromatic carbon signals, two methoxy carbon and two carbonyl carbon resonances. The resonance signal for the metallathiacyclopropane carbon (δ 65.11) occurs at significantly higher field than the signal for the corresponding carbon of **2**, R = OCH_3 (δ 106.93). While there may be some π character in the carbon–sulfur bond of **2**, R = OCH_3, the chemical shift for the metallathiacyclopropane carbon of **3**, R = OCH_3, R′ = C_2H_5, is indicative of an essentially pure σ-bonding situation in the mononuclear complex.

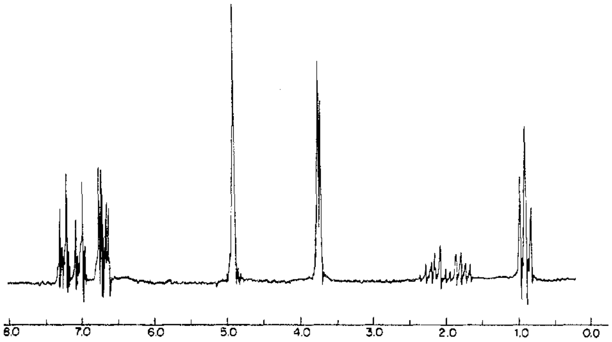


Figure 1. Proton magnetic resonance spectrum (Varian HA-100) of **3**, R = OCH_3, R′ = C_2H_5.

The *n*-butyl analogue, **3**, R = OCH_3, R′ = *n*-C_4H_9, was formed in good yield from the reaction of **2**, R = OCH_3, with tri-*n*-butyl phosphite. The spectral properties for the *n*-butyl complex are similar to those for **3**, R = OCH_3, R′ = C_2H_5. The triethyl and tri-*n*-butyl phosphite reactions did not yield any other stable, isolable complexes (discussed below).

These phosphite reaction products arise from migration of the alkyl group of the phosphite from oxygen to the metal (with metal–metal bond cleavage). It was of interest to determine the effect of successive substitution, of phenyl for ethoxy groups of triethyl phosphite, on the facility of the alkyl migration process.

Use of diethoxyphenylphosphine as the reactant with **2**, R = OCH_3, gave **3**, R = OCH_3, R′ = C_2H_5, but in substantially lower yield (44%) than in the case of triethyl phosphite. Also formed was the ligand substitution product **4**, R = OCH_3, L = $PhP(OC_2H_5)_2$, in which the phosphorus–molybdenum donor bond has replaced the sulfur–metal donor bond of **2**, R = OCH_3. Complex **4**, R = OCH_3, L = $PhP(OC_2H_5)_2$, proved to be relatively unstable and reverted back to **2**, R = OCH_3, on standing at room temperature (nitrogen atmosphere). Interestingly, the brownish green complex **4**, R = OCH_3, L = $PhP(OC_2H_5)_2$, decomposed in part during column chromatography on alumina to give the mononuclear complex **3**, R = OCH_3, R′ = C_2H_5.

Reaction of **2**, R = OCH_3, with ethoxydiphenylphosphine afforded **4**, R = OCH_3, L = $Ph_2POC_2H_5$, but none of the mononuclear complex **3**, R = OCH_3, R′ = C_2H_5. The ligand substitution product, **4**, R = OCH_3, L = $Ph_2POC_2H_5$, was more stable than the diethoxyphenylphosphine analogue. The infrared spectrum of **4**, R = OCH_3, L = $Ph_2POC_2H_5$, showed a weak absorption at 1804 cm^{-1}, suggesting that the semibridging carbonyl group was retained in the conversion of **2**,

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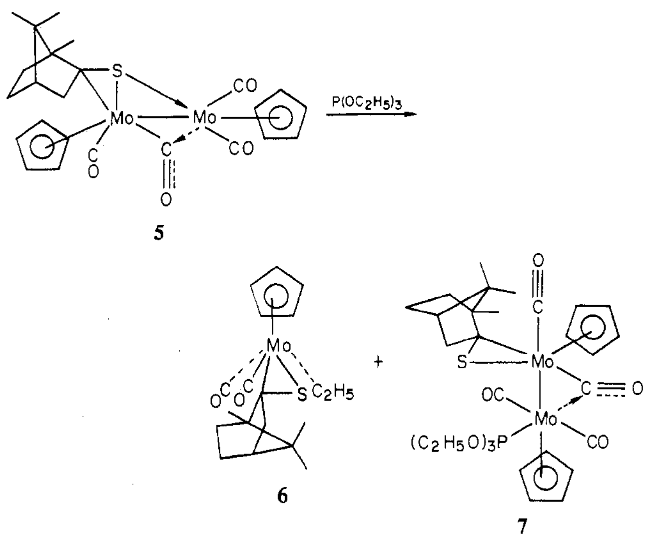
(5) A. Pfister, H. Behrens, and M. Moll, *Z. Anorg. Allg. Chem.*, **428**, 53 (1977).

Table II. Pertinent Spectral Data for the Reaction Products

product	IR, ν_{CO}, cm^{-1} (solvent)	NMR,[a] δ			MS (*m/e*)
		^1H	^{13}C	^{31}P	
3, $R = OCH_3$, $R' = C_2H_5$	1946 s, 1844 s (CCl_4)	0.91 (t, 3 H, CH_3), 1.78, 2.18 (m, 2 H, CH_2, AB of ABX_3), 3.74 (s, 3 H, OCH_3), 3.77 (s, 3 H, OCH_3), 4.94 (s, 5 H, C_5H_5), 6.71, 6.74, 7.05, 7.27 (all doublets, 8 H, aromatic protons, J = 8 Hz)	13.26 (CH_3), 34.07 (CH_2), 55.16 (OCH_3), 55.25 (OCH_3), 65.11 (c-CMoS), 94.17 (C_5H_5), 112.72, 113.41, 128.08, 133.56, 135.12, 145.87, 156.81, 158.07 (aromatic carbons), 245.10, 246.35 (carbonyl carbons)		504 $[M]^+$, 476 $[M - CO]^+$, 448 $[M - 2CO]^+$
3, $R = OCH_3$, $R' = C_4H_9$	1940 s, 1835 s ($CHCl_3$)	0.9–2.4 (m, 9 H, C_4H_9), 3.78 (s, 3 H, OCH_3), 3.81 (s, 3 H, OCH_3), 4.96 (s, 5 H, C_5H_5), 6.71, 6.74, 7.05, 7.29 (all doublets, 8 H, aromatic protons, $J = 8$ Hz)	13.49 (CH_3), 21.72, 30.82, 39.24 (methylene carbons), 55.11 (OCH_3), 55.23 (OCH_3), 66.32 (c-CMoS), 94.21 (C_5H_5), 112.73, 113.41, 128.15, 133.62, 135.24, 146.01, 156.85, 158.12 (aromatic carbons), 245.28, 246.43 (carbonyl carbons)		532 $[M]^+$, 504 $[M - CO]^+$, 476 $[M - CO]^+$, 476 $[M - 2CO]^+$, 420 $[M - 2CO - C_4H_8]^+$
3, $R = H$, $R' = C_2H_5$	1942 s, 1840 s (CH_2Cl_2)	0.87 (t, 3 H, CH_3), 1.79, 2.19 (m, 2 H, CH_2, AB of ABX_3), 4.89 (s, 5 H, C_5H_5), 7.10–7.30 (m, 10 H, aromatic protons)	13.07 (CH_3), 34.09 (CH_2), 64.97 (c-CMoS), 94.24 (C_5H_5), 124.64, 126.37, 127.03, 127.40, 128.06, 128.28, 142.56, 153.05 (aromatic carbons), 244.92, 246.02 (carbonyl carbons)		444 $[M]^+$, 416 $[M - CO]^+$, 388 $[M - 2CO]^+$
3, $R = CH_3$, $R' = C_2H_5$	1938 s, 1833 s ($CHCl_3$)	0.92 (t, 3 H, CH_3), 1.86, 2.26 (m, 2 H, CH_2, AB of ABX_3), 2.67 (s, 3 H, $C\mathit{H}_3C_6H_4$), 2.69 (s, 3 H, $C\mathit{H}_3C_6H_4$), 4.93 (s, 5 H, C_5H_5), 6.89–7.33 (m, 8 H, aromatic protons)	13.19 ($\mathit{C}H_3CH_2$), 20.90 ($\mathit{C}H_3C_6H_4$), 34.04 (CH_2), 65.07 (c-CMoS), 94.28 (C_5H_5), 127.00, 128.15, 128.67, 132.45, 135.98, 136.47 (aromatic carbons), 245.00, 246.25 (carbonyl carbons)		472 $[M]^+$, 444 $[M - CO]^+$, 416 $[M - 2CO]^+$
4, $R = OCH_3$, $L = PhP(OC_2H_5)_2$	1935 s, 1830 s, 1805 w ($CHCl_3$)	1.35 (t, 6 H, CH_3), 3.76 (s, br, 6 H, OCH_3), 3.95 (m, 4 H, CH_2O), 4.37 (d, 5 H, C_5H_5, $J_{P-H} = 1.5$ Hz), 4.90 (s, 5 H, C_5H_5), 6.60–7.25 (m, 13 H, aromatic protons)			
4, $R = OCH_3$, $L = Ph_2POC_2H_5$	1933 s, 1826 s, 1804 w (CH_2Cl_2)	1.45 (t, 3 H, CH_3), 3.75 (s, 3 H, OCH_3), 3.79 (s, 3 H, OCH_3), 3.90 (m, 2 H, CH_2O), 4.33 (d, 5 H, C_5H_5, $J_{P-H} = 2.0$ Hz), 5.05 (s, 5 H, C_5H_5), 6.67–7.60 (m, 18 H, aromatic protons)	55.09 (OCH_3), 55.25 (OCH_3), 94.04 (C_5H_5), 95.44 (C_5H_5), 102.40 (c-CMoS), 238.02, 238.39, 244.50, 245.75 (carbonyl carbons)	−52.80	
4, $R = OCH_3$, $L = P(OPh)_3$	1941 s, 1857 s, 1817 w (CCl_4)	3.75 (s, 3 H, OCH_3), 3.78 (s, 3 H, OCH_3), 4.21 (d, 5 H, C_5H_5, $J_{P-H} = 1.0$ Hz), 5.09 (s, 5 H, C_5H_5), 6.62–7.48 (m, 23 H, aromatic carbons)		−40.19	
4, $R = CH_3$, $L = P(OC_2H_5)_3$	1945 s, 1850 s, 1806 m (C_6H_{14})	1.37 (t, 9 H, $CH_2C\mathit{H}_3$), 2.26 (s, 6 H, $C\mathit{H}_3C_6H_4$), 4.02 (m, 6 H, OCH_2), 4.39 (d, 5 H, C_5H_5, $J_{P-H} = 1.5$ Hz), 5.22 (s, 5 H, C_5H_5), 6.88–7.20 (m, 8 H, aromatic protons)			600 $[M - (CH_3C_6H_4)_2CS]^+$
6	1928 s, 1828 s ($CHCl_3$)	0.8–2.6 (m, 21 H, C_2H_5 and thiocamphor protons), 5.32 (s, 5 H, C_5H_5)			414 $[M]^+$, 386 $[M - CO]^+$, 358 $[M - 2CO]^+$
7	1918 s, 1849 s, 1837 ms, 1804 w (C_6H_{14})	0.75–2.40 (m, 16 H, thiocamphor protons), 1.30 (t, 9 H, $C\mathit{H}_3CH_2$), 4.98 (d, 5 H, C_5H_5, $J_{P-H} = 1.5$ Hz), 5.40 (s, 5 H, C_2H_5)	92.50 (C_5H_5), 93.47 (C_5H_5), 105.42 (c-CMoS), 234.40, 237.66, 242.24, 246.30 (carbonyl carbons)		

[a] $CDCl_3$ solution with $(CH_3)_4Si$ as internal standard for the ^1H and ^{13}C spectra. ^{31}P reference is 85% H_3PO_4.

Scheme III



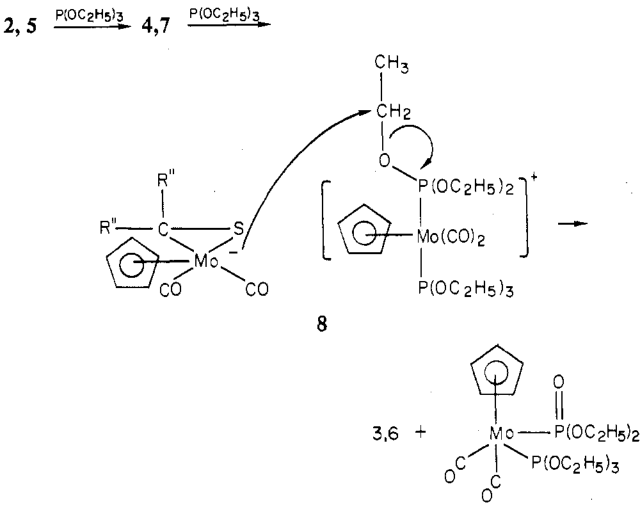
R = OCH_3, to **4**, R = OCH_3, L = $Ph_2POC_2H_5$. In the proton NMR spectrum of the latter, there are two signals (δ 4.33, 5.05) for the cyclopentadienyl protons, with the higher field one being that of the ring bound to the molybdenum bearing the $Ph_2POC_2H_5$ ligand. It is noteworthy that the carbon resonance for the metallathiacyclopropane carbon of **4**, R = OCH_3, L = $Ph_2POC_2H_5$, is at a similar chemical shift to that of **2**, R = OCH_3. The phosphorus-31 magnetic resonance spectrum of **4**, R = OCH_3, L = $Ph_2POC_2H_5$, displayed a singlet at δ -52.80.

Triphenyl phosphite reacted with **2**, R = OCH_3, to give **4**, R = OCH_3, L = $P(OPh)_3$, but not the σ-phenyl compound, **3**, R = OCH_3, R′ = Ph. Exposure of **2**, R = H, to triethyl phosphite resulted in the formation of **3**, R = H, R′ = C_2H_5, while the 4,4′-dimethyl-substituted complex **2**, R = CH_3, gave **3**, R = CH_3, R′ = C_2H_5, and the ligand substitution product, **4**, R = CH_3, L = $P(OC_2H_5)_3$. The latter, over a period of weeks, lost triethyl phosphite, giving back starting material (i.e., **2**, R = OCH_3), while thermolysis afforded **3**, R = CH_3, R′ = C_2H_5, and other unidentified byproducts. The thiocamphor complex, **5**, reacted with triethyl phosphite in an analogous manner to that of **2**, producing complexes **6** and **7**. (See Scheme III.)

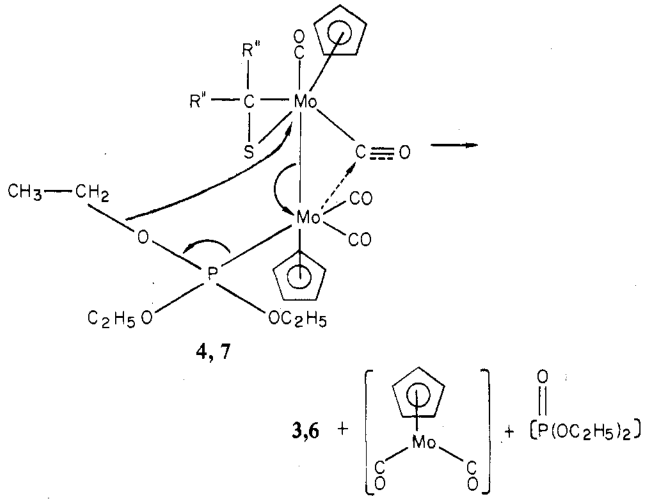
Surprisingly, no reaction—not even ligand substitution—occurred on thermal reaction (refluxing benzene) of **2**, R = OCH_3, or **5** with tri-*p*-tolylphosphine (16-h reaction time) or tris(*p*-fluorophenyl)phosphine (36 h).

A possible mechanism for the formation of the mononuclear complexes (**3**, **6**) is outlined in Scheme IV (illustrated for L = $P(OC_2H_5)_3$). The initial step probably involves generation of the ligand substitution product (**4**, **7**). Reaction of the latter with additional phosphite would afford the ionic intermediate, **8**. Carbon–oxygen bond cleavage of **8** would result in the formation of the mononuclear sulfur complex (**3**, **6**) and the phosphonate **9**. While the Michaelis–Arbusov process[6,7] is an attractive one for accounting for the formation of **3** and **6**, the failure to detect **9** (a known compound[7]) in any of these reactions and the stereospecificity of the process (i.e., only one isomer of **3** or **6** is formed) renders this pathway as a less likely one. Furthermore, it should be noted that in several cases (e.g., reaction of **2**, R = OCH_3, with $P(OC_2H_5)_3$), an *organic* compound containing a P═O bond (IR: ν_{PO} 1165–1166 cm^{-1})[4] was eluted off the chromatographic column but could not be successfully characterized.

Scheme IV



Scheme V



An alternative intramolecular pathway for the formation of **3** or **6** should also be considered (Scheme V). The ligand substitution complexes (**4**, **7**) could undergo stereospecific alkyl transfer from oxygen to molybdenum.

Experimental Section

General Data. A Fisher-Johns apparatus was used for melting point determinations. Elemental analyses were carried out by M-H-W Laboratories, Phoenix, Ariz., Canadian Microanalytical Service, Vancouver, Canada, and Butterworth Microanalytical Consultancy, Teddington, Great Britian. Infrared spectra were obtained by using a Unicam SP 1100 spectrometer, equipped with a calibration standard. Proton magnetic resonance spectral determinations were made with a Varian T60 or HA 100 spectrometer, while carbon magnetic resonance spectra were recorded in the fully and partially decoupled modes with a Varian FT-80 spectrometer. The latter was also employed for phosphorus magnetic resonance determinations. Mass spectra were determined on an AEI MS902 spectrometer.

The reactant complexes (**2**, **5**) were synthesized as described previously.[2] All of the phosphites and phosphines were commercial materials and were used as received. Solvents were purified and dried by standard methods. All reactions were effected under an atmosphere of dry nitrogen.

Reaction of 2, R = OCH_3, with Triethyl Phosphite. A mixture of 2.38 g (3.44 mmol) of **2**, R = OCH_3, and 2.36 g (14.2 mmol) of triethyl phosphite in benzene (50 mL) was heated at 60 °C for 15 h. The reaction mixture was cooled and filtered, and the filtrate was concentrated to ca. 5 mL and then chromatographed on alumina (EM reagents, activity grade 1, 70–230 mesh) with hexane. Elution with hexane–benzene (3:1) gave the product as a fluffy orange solid. A

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(7) R. J. Haines and C. R. Nolte, *J. Organomet. Chem.*, **24**, 725 (1970).

narrow green band, which was moving down the column at a much slower rate than **3**, R = OCH_3, R′ = C_2H_5, was then eluted with benzene. However, as the chromatography continued, the green band disappeared and only additional **3**, R = OCH_3, R′ = C_2H_5, was isolated. The total yield of the mononuclear complex **3**, R = OCH_3, R′ = C_2H_5, was 1.60 g (92%). Elution with benzene–methylene complex chloride (1:1), or pure methylene chloride, gave an unidentified organic compound (IR: $\nu_{P=O}$ 1166 cm^{-1}).

Reaction of 2, R = OCH_3, with Tri-*n*-butyl Phosphite. A mixture of 2.82 g (4.07 mmol) of **2**, R = OCH_3, and tri-*n*-butyl phosphite (4.54 g, 18.0 mmol) in benzene was reacted and worked up as described for triethyl phosphite, except that silica gel was used as the chromatographic absorbent. Pure **3**, R = OCH_3, R′ = C_4H_9, was obtained as a crystalline orange solid, yield 1.23 g (57%).

Reaction of 2, R = OCH_3, with Diethoxyphenylphosphine. Diethoxyphenylphosphine (1.50 g, 7.58 mmol) and **2**, R = OCH_3 (1.303 g, 1.88 mmol), in benzene (50 mL) were heated for 15 h at 60 °C. After cooling, filtration, and filtrate concentration, the crude mixture was chromatographed on alumina (Fisher activity grade I, 80–200 mesh) with 2:1 hexane–benzene. Elution with 2:1 hexane–benzene gave 0.54 g of impure **3**, R = OCH_3, R′ = C_2H_5 (contaminated with a small quantity of an organic material). The green-brown ligand substitution product **4**, R = OCH_3, L = $PhP(OC_2H_5)_2$, was eluted with benzene. Thin-layer chromatography of the latter indicated that it was impure and rechromatography using 1:1 hexane–benzene resulted in the isolation of **3**, R = OCH_3, R′ = C_2H_5, and 0.57 g (35%) of quite pure **4**, R = OCH_3, L = $PhP(OC_2H_5)_2$. However, the latter was gradually converted back to **2**, R = OCH_3, on standing. Consequently, attempts to obtain satisfactory analyses for **4**, R = OCH_3, L = $PhP(OC_2H_5)_2$, were futile.

Pure **3**, R = OCH_3, R′ = C_2H_5 (0.414 g, 44%), was obtained by rechromatography of the crude complex using 3:1 hexane–*commercial* (not rigorously purified) benzene.

Reaction of 2, R = OCH_3, with Ethoxydiphenylphosphine. Complex **2**, R = OCH_3 (0.774 g, 1.12 mmol), and ethoxydiphenylphosphine (1.06 g, 4.60 mmol) were reacted and worked up as described for the reaction of the complex with triethyl phosphite. Elution with 1:1 hexane–benzene gave 0.74 g (72%) of **4**, R = OCH_3, L = $Ph_2POC_2H_5$. Slow coversion of the latter to **2**, R = OCH_3, occurred over a period of weeks.

Reaction of 2, R = OCH_3, with Triphenyl Phosphite. A benzene (60 mL) solution of **2**, R = OCH_3 (3.85 g, 5.56 mmol), and triphenyl phosphite (7.09 g, 22.8 mmol) was refluxed for 3 days. The solution was cooled and filtered, and the concentrated filtrate was chromatographed on alumina (EM reagents 70–230 mesh). Elution with benzene afforded recovered starting material, followed by **4**, R = OCH_3, L = $(PhO)_3P$. The latter was further purified by crystallization from hexane; yield 0.81 g (15%).

Reaction of 2, R = H, with Triethyl Phosphite. Complex **2**, R = H (1.00 g, 1.58 mmol), and triethyl phosphite (1.24 g, 7.46 mmol) were reacted and worked up as described for the reaction of **2**, R = OCH_3, with $(C_2H_5O)_3P$ (except for the substitution of Baker for EM alumina). Elution with 2:1 hexane–benzene afforded 0.53 g (82%) of orange **3**, R = H, R′ = C_2H_5. A narrow green-brown band was eluted off the column with 5:1 benzene–hexane but was too unstable to be isolated in analytically pure form.

Reaction of 2, R = CH_3, with Triethyl Phosphite. A mixture of triethyl phosphite (0.70 g, 4.2 mmol) and **2**, R = CH_3 (1.01 g, 1.53 mmol), in benzene was reacted and worked up as described for the reaction of **2**, R = OCH_3, with tri-*n*-butyl phosphite. Elution with 4:1 hexane–benzene gave 0.394 g (55%) of orange **3**, R = CH_3, R′ = C_2H_5. Elution with benzene afforded **4**, R = CH_3, L = $(C_2H_5O)_3P$, which required further purification by recrystallization from 5:1 hexane–methylene chloride; yield 0.37 g (29%).

Reaction of 5 with Triethyl Phosphite. The thiocamphor complex **5** (1.67 g, 2.70 mmol) and triethyl phosphite (1.92 g, 11.6 mmol) were reacted and worked up as described for the reaction of **2**, R = OCH_3, with triethyl phosphite to give 0.514 g (46%) of **6** and 0.205 g (10%) of **7**.

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Registry No. **2**, R = OCH_3, 72186-35-7; **2**, R = H, 72186-34-6; **2**, R = CH_3, 72186-31-3; **3**, R = OCH_3, R′ = C_2H_5, 73985-98-5; **3**, R = OCH_3, R′ = C_4H_9, 73985-99-6; **3**, R = H, R′ = C_2H_5, 73986-00-2; **3**, R = CH_3, R′ = C_2H_5, 73986-01-3; **4**, R = OCH_3, L = $PhP(OC_2H_5)_2$, 73986-02-4; **4**, R = OCH_3, L = $Ph_2POC_2H_5$, 73986-03-5; **4**, R = OCH_3, L = $(PhO)_3P$, 73986-04-6; **4**, R = CH_3, L = $(C_2H_5O)_3P$, 73986-05-7; **5**, 72186-45-9; **6**, 73986-41-1; **7**, 73986-40-0; $P(OC_2H_5)_3$, 122-52-1; $P(OC_4H_9)_3$, 102-85-2; $PhP(OC_2H_5)_2$, 1638-86-4; $Ph_2P(OC_2H_5)$, 719-80-2.

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Syntheses and Characterization of $Mo(ONPh)(S_2CNEt_2)_2$, a Valence Isomer of $MoO(NPh)(S_2CNEt_2)_2$

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Nitrobenzene reacts rapidly with $Mo(CO)_2(S_2CNEt_2)_2$ in CH_2Cl_2 to yield $MoO(ONC_6H_5)(S_2CNEt_2)_2$. Reduction of this complex with triphenylphosphine affords triphenylphosphine oxide and $Mo(ONC_6H_5)(S_2CNEt_2)_2$, a compound which also results from the reaction of nitrosobenzene and $Mo(CO)_2(S_2CNEt_2)_2$. NMR evidence points to η^2 coordination of the nitrosobenzene in this complex. $Mo(ONPh)(S_2CNEt_2)_2$ and its Mo(VI) relative, $MoO(NPh)(S_2CNEt_2)_2$, comprise a unique pair of isomeric compounds displaying identical ligating atoms at the metal center but differing both in formal oxidation state and in the nature of the bonding within the ligands. However, efforts to bring about isomerization of these compounds by either thermal or photolytic reactions have failed.

Introduction

Recently, we reported the synthesis and X-ray structure of $Mo(NC_6H_5)_2(S_2CNEt_2)_2$.[1] The two Mo–N bond lengths and the Mo–N–C bond angles in that complex are different and the NC_6H_5 ligands are mutually cis. In addition, the two nitrogen atoms were found to be separated by 2.78 Å, indicating the absence of bonding between these atoms. We were intrigued by the thought that $Mo(NPh)_2(S_2CNEt_2)_2$ could be regarded as a valence isomer of the hypothetical azobenzene complex $Mo(PhNNPh)(S_2CNEt_2)_2$. Side-on coordination of *trans*-azobenzene has been found in $Cp_2Mo(PhNNPh)$.[2] A related dithiocarbamate complex, $Mo(EtO_2CN$-

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