Table V. Leaving Group Series for Reaction 1[a]

trans group	leaving group (L)				
Im	py	> Im	> $P(OBu)_3$		
	80	(1)	0.11		
	750	9	(1)		
$P(OBu)_3$	py	≥ $P(OBu)_3$	> pip	>	Im ≈ MeIm
	14	11	7		(1)
	1.2	(1)	0.6		0.08

[a] The solvent was acetone at 21 °C; the numbers are relative reactivities.

Table VI. Trans-Effect Series for Reaction 1[a]

leaving group	trans group (T)				
Im	$P(OBu)_3$	> Im			
	2400	1			
$P(OBu)_3$	$P(OBu)_3$	≥ PBu_3	> Im		
	250 000	210 000	1		
MeIm	$P(OBu)_3$	> RNC[b]	> MeIm		
	3500	16	1		
RNC[b]	RNC	> pip	> py	>	MeIm
	5000	4	2		1
py	$P(OBu)_3$	> pip	≥ py	>	Im
	400	6	5		1

[a] The solvent was acetone at 21 °C except as noted; numbers are relative reactivities. [b] The solvent was toluene at 23 °C; data from: Stynes, D. V., *Inorg. Chem.* 1977, *16*, 1170.

to $P(OBu)_3$, the lability of $P(OBu)_3$ relative to Im increases by a factor of 100. Imidazole is primarily a σ donor with some π-donor properties, whereas $P(OBu)_3$ is both a good σ donor and π acceptor. This means that synergic π bonding occurs in the mixed complex, with the result that $P(OBu)_3$ is extremely inert trans to Im. Trans to $P(OBu)_3$, both Im and $P(OBu)_3$ are labilized (trans effect), but $P(OBu)_3$ becomes more labile because of the loss of the synergic π bonding and the necessity for the $P(OBu)_3$ ligand to compete for π-electron density with the trans $P(OBu)_3$ group.

The trans-effect series is summarized in Table VI. The π-acceptor ligands $P(OBu)_3$ and RNC are high in the series, in agreement with the well-known trans effect found in Pt(II) complexes. $P(OBu)_3$ is the best trans activator yet reported. Both $P(OBu)_3$ and RNC are much less effective, relative to imidazole, when trans to the π-donor Im ligand. As described above, the reason for this is the synergic π bonding present in, e.g., $[P(OBu)_3]FePc(Im)$ that is lost upon dissociation of the Im group. Unfortunately, very little is known about the trans effect in iron porphyrins. Basolo et al.[9] found the order py ≥ pip ≥ MeIm for reaction 7. This agrees with the

$$Fe(TPP)(L)(O_2) + L \rightarrow Fe(TPP)L_2 + O_2 \qquad (7)$$

phthalocyanine series in that MeIm is the poorest trans activator. However, the position of a good π acceptor in this series is unknown. As shown above, the synthesis of mixed-ligand complexes, $[P(OBu)_3]FePc(L)$, was possible because $P(OBu)_3$ is high in the trans-effect series, and this in turn allowed the necessary reactions to be studied to establish the fairly extensive trans-effect series given in Table VI. Similar experiments are in progress with iron porphyrins.

What is known at this time suggests that metalloporphyrins and metallophthalocyanines may have similar trans-effect series, but ones that differ drastically from those of other macrocycles. Although imidazole is trans deactivating in FePc and Fe(Por) complexes, it is apparently trans activating in Fe(TIM), $Fe(DMG)_2$, and Fe(TAAB) complexes.[10] These differences must be related to the ability of the metal and the macrocycle to transmit π-electron density. Since the imidazole ligand trans to dioxygen in HbO_2 and MbO_2 must influence the dynamics and thermodynamics of oxygenation, it is important that an extended trans-effect series for metalloporphyrins be determined and that the position of imidazole in this series be understood.

Acknowledgment. Part of this work was supported by a Dreyfus Teacher-Scholar Grant to D.A.S.

Registry No. $(P(OBu)_3)FePc(P(OBu)_3)$, 61005-31-0; $(P(OBu)_3)FePc(Im)$, 73612-14-3; $(P(OBu)_3)FePc(MeIm)$, 73612-15-4; $(P(OBu)_3)FePc(pip)$, 73612-16-5; $(P(OBu)_3)FePc(py)$, 73612-17-6; $(PBu_3)FePc(P(OBu)_3)$, 73612-18-7; (pip)FePc(pip), 21194-13-8; (pip)FePc(py), 73612-19-8; (py)FePc(py), 20219-84-5; (Im)FePc(py), 73612-20-1; (Im)FePc(Im), 20219-85-6; (MeIm)FePc(MeIm), 55925-76-3; Im, 288-32-4; MeIm, 616-47-7; PBu_3, 102-85-2; pip, 110-89-4.

(9) Weschler, C. J.; Anderson, D. L.; Basolo, F. *J. Am. Chem. Soc.* **1975**, *97*, 6707.
(10) Pang, I. W.; Stynes, D. V. *Inorg. Chem.* **1977**, *16*, 2192. Baldwin, D. A.; Pfeiffer, R. M.; Reichgott, D. W.; Rose, N. J. *J. Am. Chem. Soc.* **1973**, *95*, 5152. Pang, I. W.; Singh, K.; Stynes, D. V. *J. Chem. Soc., Chem. Commun.* **1976**, 132. Pang, I. W.; Stynes, D. V. *Inorg. Chem.* **1977**, *16*, 590.

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Preparation and Stereochemistry of Bis(carboxylato)bis(tertiary phosphine)bis(disilylamido)dimolybdenum(II) Complexes

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Received December 7, 1979

Tetrakis(acetato)dimolybdenum, $Mo_2(O_2CMe)_4$, reacts with the lithium silylamides $LiN(SiMe_3)_2$, $LiN(SiMe_2H)_2$, or $LiN(SiMe_3)(Me)$ in the presence of tertiary phosphines (PMe_3, PMe_2Ph, or PEt_3) to give complexes of the type $Mo_2(O_2CMe)_2(NR_2)_2(PR_3)_2$. The stereochemistry of the red, pentane-soluble complexes has been determined by ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ nuclear magnetic resonance and infrared spectroscopy. When the silylamide is $N(SiMe_2H)_2$, the phosphines and silylamide groups are oriented trans relative to the metal–metal bond. In contrast, when the silylamide is $N(SiMe_3)_2$ or $N(SiMe_3)(Me)$, the phosphine and silylamide groups are trans to each other on the same molybdenum atom. Tetrakis(pivalato)dimolybdenum, $Mo_2(O_2CCMe_3)_4$, behaves similarly with one exception; i.e., the $N(SiMe_3)_2$ complexes are of the type $Mo_2(O_2CCMe_3)_3[N(SiMe_3)_2](PR_3)$. The stereochemistry of these complexes is independent of the carboxylate or phosphine group but dependent upon the nature of the silylamide. This effect is ascribed to a trans influence.

Compounds of the general type $Mo_2(O_2CR)_2(R')_2(PR''_3)_2$, where R, R′, and R″ are uninegative groups, are of some interest since a number of geometrical isomers are possible. Only a few complexes of this general type have been de-

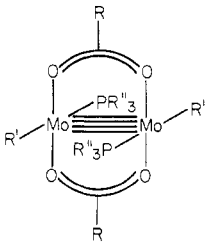
0020-1669/80/1319-2165$01.00/0

Table I. Analytical and Some Physical Properties of $Mo_2(O_2CR)_{2,3}(NR_2)_{2,1}(PR_3)_{2,1}$

compd	mp, °C	analysis[a] required C	H	N	found C	H	N	IR[b] ($\nu_{as}(CO_2)$)
$Mo_2(O_2CMe)_2[N(SiMe_3)_2]_2(PMe_3)_2$ (A)	105 dec	33.7	7.72	3.58	33.6	7.50	3.62	1520
$Mo_2(O_2CCF_3)_2[N(SiMe_3)_2]_2(PMe_3)_2$ (B)	110 dec	29.7	6.11	3.14[c]	29.4	5.97	3.03	1600
$Mo_2(O_2CMe)_2[N(SiMe_3)_2]_2(PMe_2Ph)_2$ (C)	148 dec	42.4	7.11	3.09	41.9	6.76	2.93	1510
$Mo_2(O_2CMe)_2[N(SiMe_3)_2]_2(PEt_3)_2$ (D)	156 dec	38.8	8.37	3.23	38.9	8.14	3.23	1520
$Mo_2(O_2CMe)_2[N(SiMe_3)(Me)]_2(PMe_3)_2$ (E)	150 dec	32.4	7.26	4.20[d]	31.9	7.14	3.89	1520
$Mo_2(O_2CCMe_3)_2[N(SiMe_3)(Me)]_2(PMe_3)_2$ (F)	162–165	38.4	8.06	3.73	38.5	7.72	3.11	1480
$Mo_2(O_2CCMe_3)_2[N(SiMe_3)(Me)]_2(PEt_3)_2$ (G)	170–172 dec	43.2	8.63	3.36	43.0	8.39	3.47	1480
$Mo_2(O_2CMe)_2[N(SiMe_2H)_2]_2(PMe_3)_2$ (H)	110 dec	29.7	7.21	3.85[e]	29.4	6.89	3.67	1520
$Mo_2(O_2CMe)_2[N(SiMe_2H)_2]_2(PMe_2Ph)_2$ (I)	125 dec	39.5	6.59	3.29	39.9	6.86	3.23	1520
$Mo_2(O_2CCMe_3)_2[N(SiMe_2H)_2]_2(PMe_3)_2$ (J)		35.6	7.96	3.45	34.9	7.67	3.04	1475
$Mo_2(O_2CCMe_3)_2[N(SiMe_2H)_2]_2(PMe_2Ph)_2$ (K)		43.7	7.28	3.00	42.8	6.75	2.26	1475
$Mo_2(O_2CCMe_3)_2[N(SiMe_2H)_2]_2(PEt_3)_2$ (L)	142 dec	40.3	8.50	3.13	40.3	8.36	3.16	1475
$Mo_2(O_2CCMe_3)_3[N(SiMe_3)_2](PMe_3)$ (M)	178–180	38.9	8.70	1.89	39.7	7.19	1.88	1475
$Mo_2(O_2CCMe_3)_3[N(SiMe_3)_2](PEt_3)$ (N)	148–151	41.4	7.76	1.81	42.1	7.61	1.91	1475
$Mo_2(O_2CCMe_3)_3[N(SiMe_3)_2](PMe_2Ph)(PhMe)$[f] (O)	130–134	48.8	7.23	1.58	48.2	7.00	1.54	1475

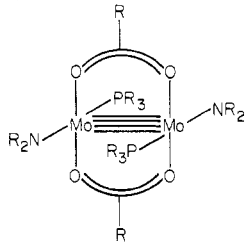
[a] Percent. [b] Recorded as Nujol mulls, cm^{-1}. [c] P: required, 6.95; found, 6.82. [d] P: required, 9.29; found, 8.92. [e] P: required, 8.52; found, 8.52. [f] Toluene of crystallization found in the ^1H NMR spectrum in PhH-d_6.

scribed,[1,2] and the crystal structures of two of them, $Mo_2(O_2CMe)_2(CH_2SiMe_3)_2(PMe_3)_2$[3] (Ia) and $Mo_2(O_2CPh)_2(Br)_2(P(n\text{-}Bu)_3)_2$[4] (Ib), have been determined. A related azaindolyl derivative (Ic) has also been crystallographically determined.[5] In the solid state the complexes have a conformation in which the bridging ligands are trans to each other bridging the molybdenum–molybdenum quadruple bond. The other four groups are also trans to each other across the metal–metal bond as shown above. In this paper we describe the synthesis of a series of silylamide derivatives of the type $Mo_2(O_2CR)_2(NR'_2)_2(PR''_3)_2$ and show that in solution two geometrical isomers can be isolated depending upon the substituents on the amide nitrogen atom.

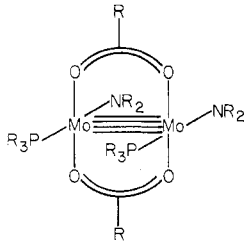


Ia, R = Me, R′ = CH_2SiMe_3, R″ = Me
b, R = Ph, R′ = Br, R″ = *n*-Bu
c, O_2CR = azaindolyl, R′ = Cl, R″ = Et

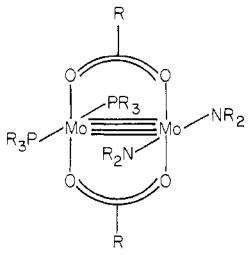
Addition of lithium bis(trimethylsilyl)amide to tetrakis(acetato)dimolybdenum in the presence of trimethylphosphine and diethyl ether gives red $Mo_2(O_2CMe)_2[N(SiMe_3)_2]_2(PMe_3)_2$. The trifluoroacetate, $Mo_2(O_2CCF_3)_2[N(SiMe_3)_2]_2(PMe_3)_2$, was prepared similarly from $Mo_2(O_2CCF_3)_4$. Analytical and spectroscopic data for all new compounds are collected in Tables I and II. The stereochemistry of these complexes is suggested by the spectroscopy. The acetate ($\nu_{as}(CO_2)$ = 1520 cm^{-1}) and trifluoroacetate ($\nu_{as}(CO_2)$ = 1600 cm^{-1}; ^{19}F NMR δ −70.3) ligands are bidentate[6,7] and presumably bridging the binuclear unit as is found in the related Me_3SiCH_2 (Ia) and Br derivatives (Ib). The arrangement of the other pairs of ligands about the five-coordinate molybdenum atoms can be of three types, i.e., trans (II) or cis (III)



II



III



IV

with respect to the metal–metal bond or trans with respect to each other on the same molybdenum atom (IV). The proton and carbon nuclear magnetic resonance spectra will yield a clear-cut distinction between stereochemistry II or IV and III or IV but not between II or III. However, isomer III is rather unlikely since the steric hindrance between the voluminous $(Me_3Si)_2N$ groups on adjacent molybdenum atoms will be far too great. Consequently we will consider only isomers II and IV. In the trimethylphosphine complex of isomer II, the ^1H and $^{13}C\{^1H\}$ spectra in the PMe_3 region will both yield doublets, the spin systems being AX_9 and AX, respectively. In contrast, isomer IV will yield a "virtually coupled" triplet in the ^1H and a triplet in the $^{13}C\{^1H\}$ NMR spectra in the PMe_3 region since the spin systems will now be $X_9AA'X'_9$ and XAA′, respectively.[8-10]

The observation of a "virtually coupled" triplet in the ^1H and a triplet in the $^{13}C\{^1H\}$ NMR spectra of $Mo_2(O_2CMe)_2[N(SiMe_3)_2]_2(PMe_3)_2$ strongly suggests that isomer IV is the only species present in solution. The triplet pattern

(1) Andersen, R. A.; Jones, R. A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1978**, 446.
(2) San Filippo, J.; Sniadoch, H. J. *Inorg. Chem.* **1976**, *15*, 2209.
(3) Hursthouse, M. B.; Malik, K. M. A. *Acta Crystallogr., Sect. B* **1979**, *B35*, 2709.
(4) Potenza, J. A.; Johnson, R. J.; San Filippo, J. *Inorg. Chem.* **1976**, *15*, 2215.
(5) Cotton, F. A.; Lay, D. G.; Millar, M. *Inorg. Chem.* **1978**, *17*, 186.
(6) Girolami, G. S.; Mainz, V. V.; Andersen, R. A. *Inorg. Chem.* **1980**, *19*, 805.
(7) Robinson, S. D.; Uttley, M. F. *J. Chem. Soc., Dalton Trans.* **1973**, 1912.
(8) Harris, R. K. *Can. J. Chem.* **1964**, *42*, 2275.
(9) Axelson, D. E.; Holloway, C. E. *J. Chem. Soc., Chem. Commun.* **1973**, 455.
(10) Redfield, D. A.; Nelson, J. H.; Cary, L. W. *Inorg. Nucl. Chem. Lett.* **1974**, 727.

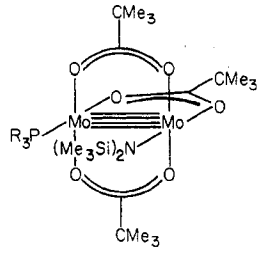
Table II. Proton and Carbon NMR Spectra of $Mo_2(O_2CR)_{2,3}(NR_2)_{2,1}(PR_3)_{2,1}$

compd	^1H[a-c]	assignt	$^{13}C\{^1H\}$[b,d]
A	2.75 s (3)	O_2CMe	24.1 s[e]
	1.27 t (9), J_{PH} = 8	PMe_3	15.2 t, J_{PC} = 23
	0.31 s (18)	$N(SiMe_3)_2$	7.40 s
B	1.24 t (9), J_{PH} = 9	PMe_3	15.7 t, J_{PC} = 24
	0.33 s (18)	$N(SiMe_3)_2$	6.96 s
C	2.72 s (3)	O_2CMe	24.5 s[e]
	1.69 t (6), J_{PH} = 8	PMe_2Ph	15.3 t,[f] J_{PC} = 25
	0.42 s (18)	$N(SiMe_3)_2$	7.88 s
D	2.89 s (3)	O_2CMe	25.7 s[e]
	1.99 m (6)	$P(CH_2Me)_3$	17.8 t, J_{PC} = 19
	1.52 m (9)	$P(CH_2Me)_3$	9.50 s
	0.52 s (18)	$N(SiMe_3)_2$	9.00 s
E	2.79 s (3)	O_2CMe	23.8 s[e]
	1.25 br, d (9), J_{PH} = 12	PMe_3	11.9 t, J_{PC} = 24
	3.47 s (3)	$N(SiMe_3)(Me)$	42.8 s
	0.37 s (9)	$N(SiMe_3)(Me)$	4.10 s
F	1.71 s (9)	O_2CCMe_3	28.8 s[e]
		O_2CCMe_3	40.8 s
	1.29 t (9), J_{PH} = 8	PMe_3	14.4 t, J_{PC} = 21
	0.27 s (9)	$N(SiMe_3)(Me)$	2.10 s
	3.45 s (3)	$N(SiMe_3)(Me)$	42.8 s
H	2.77 s (3)	O_2CMe	24.1 s[e]
	1.17 d (9), J_{PH} = 12	PMe_3	14.6 d, J_{PC} = 29
	4.77 h (2), J_{HH} = 2	$N(SiMe_2H)_2$	
	0.43 d (12), J_{HH} = 2	$N(SiMe_2H)_2$	3.39 s
J	1.77 s (9)	O_2CCMe_3	29.0 s[e]
		O_2CCMe_3	40.8 s
	1.23 d (9), J_{PH} = 8	PMe_3	14.6 d, J_{PC} = 13
	4.97 h (2), J_{HH} = 2	$N(SiMe_2H)_2$	
	0.59 d (12), J_{HH} = 2	$N(SiMe_2H)_2$	3.94 s
K	1.67 s (9)	O_2CCMe_3	28.9 s[e]
		O_2CCMe_3	40.8 s
	1.49 d (6), J_{PH} = 5	PMe_2Ph	13.9 br, d[f]
		$N(SiMe_2H)_2$	
	0.42 d (12), J_{HH} = 2	$N(SiMe_2H)_2$	3.52 s
M	1.71 s (18), 1.56 s (9)	O_2CCMe_3	28.7 s, 28.5 s[e]
		O_2CCMe_3	40.6 s, 40.3 s
	1.04 d (9), J_{PH} = 7	PMe_3	12.5 d, J_{PC} = 24
	0.47 s (18)	$N(SiMe_3)_2$	6.46 s
N	1.81 s (18), 1.42 s (9)	O_2CCMe_3	28.9 s, 28.6 s[e]
		O_2CCMe_3	40.9 s, 40.5 s
	1.27 m (6)	$P(CH_2Me)_3$	16.6 d, J_{PC} = 21
	1.00 m (9)	$P(CH_2Me)_3$	8.08 s
	0.41 s (18)	$N(SiMe_3)_2$	6.37 s
O	1.77 s (18), 1.56 s (9)	O_2CCMe_3	28.9 s, 28.6 s[e]
		O_2CCMe_3	40.98 s, 40.65 s
	1.17 d (6), J_{PH} = 5	PMe_2Ph	14.2 d,[f] J_{PC} = 10
	0.37 s (18)	$N(SiMe_3)_2$	6.20 s

[a] In benzene at 60 or 180 MHz, expressed in δ values (positive numbers are to high frequency) relative to Me_4Si, δ 0. [b] Multiplicity: s = singlet, d = doublet, t = triplet, h = heptet, m = multiplet, br = broad (*J* in Hz). [c] Value in parentheses is the area ratio. [d] In benzene-d_6 at 25.1 MHz, expressed in δ values (positive numbers are to high frequency) relative to Me_4Si, δ 0. [e] Quaternary (carboxylate) carbon atom resonance was not observed. [f] Phenyl ring proton and carbon atom resonances were not observed.

in the ^1H NMR spectrum is not due to accidental overlap of a pair of doublets as the $^1H\{^{31}P\}$ NMR spectrum consists of a single resonance. Further, the $^{31}P\{^1H\}$ NMR spectrum yields a single resonance as do all of the derivatives examined in this study (see Experimental Section for chemical shifts). The other $(Me_3Si)_2N$ derivatives, $Mo_2(O_2CR)_2(N(SiMe_3)_2)_2(L)_2$, where R = CF_3 and L = PMe_3, R = Me and L = PMe_2Ph, and R = Me and L = PEt_3, yield similar spectroscopic parameters (Table II), and these complexes are assigned a similar structure, viz., IV. The stereochemistry of the triethylphosphine complex is obtained only from the $^{13}C\{^1H\}$ NMR spectrum (a triplet centered at δ 17.8 due to the α-carbon atom and a singlet due to the β-carbon atom at δ 9.50) as the proton spectrum is too complex to be useful as a stereochemical probe.[11]

In contrast to the disubstituted products obtained from tetrakis(acetato)dimolybdenum and lithium bis(trimethylsilyl)amide, reaction of the lithium reagent with tetrakis(pivalato)dimolybdenum takes a different course. The monosubstituted derivative (V) is obtained with PMe_3, PMe_2Ph,



V

or PEt_3. The pivalate groups are bidentate ($\nu_{as}(CO_2)$ = 1475–1480 cm^{-1}). Further, the *tert*-butyl protons of the pivalate ligands which are trans to each other are deshielded (δ 1.7–1.8) relative to those that are trans to the amide and phosphine ligands (δ 1.4–1.5).

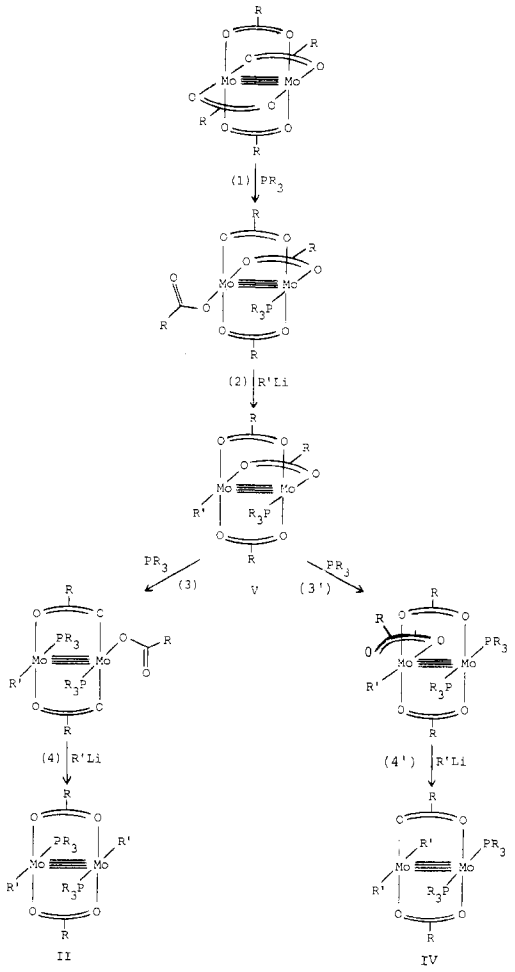
The sterically smaller amide $LiN(SiMe_3)(Me)$ gives a series of trimethylphosphine complexes with tetrakis(acetato)- or tetrakis(pivalato)dimolybdenum, $Mo_2(O_2CMe)_2[N(SiMe_3)(Me)]_2(PMe_3)_2$ and $Mo_2(O_2CCMe_3)_2[N(SiMe_3)(Me)]_2(PMe_3)_2$. The stereochemistry of these two complexes is similar to the bis(trimethylsilyl)amide analogues, viz., isomer IV (Table II). The chemical shift of the pivalate protons is δ 1.71. This observation strengthens our contention that the disubstituted complexes do indeed have trans bidentate pivalate and, by implication, acetate and trifluoroacetate groups (II–IV) rather than cis ones.

The amide $LiN(SiMe_2H)_2$ gives complexes of the same stoichiometry, $Mo_2(O_2CR)_2[N(SiMe_2H)_2]_2(PR_3)_2$, but of a different stereochemistry, viz., II. The complex $Mo_2(O_2CMe)_2[N(SiMe_2H)_2]_2(PMe_3)_2$ contains bidentate acetate groups ($\nu_{as}(CO_2)$ = 1520 cm^{-1}). The ^1H and $^{13}C\{^1H\}$ NMR spectra each show a simple doublet in the trimethylphosphine region (Table II) as expected for stereochemistry II with phosphines and amides trans relative to the metal–metal bond. The pivalate derivatives with trimethylphosphine or dimethylphenylphosphine, $Mo_2(O_2CCMe_3)_2[N(SiMe_2H)_2]_2(PR_3)_2$, have a similar stereochemistry (the chemical shifts of the *tert*-butyl protons are δ 1.77 and 1.67, respectively).

The observation of two geometrical isomers (II or IV) which is dependent upon the substituents on the amide nitrogen atom, though independent of the type of phosphine or carboxylate ligand, requires some comment. A reasonable pathway, on the assumption of a stepwise displacement of two carboxylate groups, is shown in Scheme I. In the first step (1), the phosphine displaces one arm of a bidentate acetate. We have recently shown that some phosphines (PMe_3, PMe_2Ph, or PEt_3) are capable of causing this rearrangement when the carboxylate group is trifluoroacetate.[6] The monodentate carboxylate undergoes nucleophilic substitution (step 2) with an alkyl[1] (Me_3SiCH_2 or Me_3CCH_2) or amide, giving the monosubstituted species. This species can be isolated with the pivalate and bis(trimethylsilyl)amide (V). At this point the tris(carboxylate) has a choice between two pathways (3 or 3′) followed by pathway 4 or 4′, giving a final product in which the two phosphines and two anionic ligands are related as in II or IV. Pathways 3 and 4 give the species where the phosphine are trans with respect to the metal–metal bond. This is the isomer found when R is Me_3SiCH_2, Me_3CCH_2, or $(Me_2SiH)_2N$. If, however, pathways 3′ and 4′ are followed, the isomer which

(11) Balimann, G.; Motschi, H.; Pregosin, P. S. *Inorg. Chim. Acta* **1977**, *23*, 191.

Scheme I



has a phosphine trans to another phosphine on the same metal atom is obtained. This is the isolated isomer when R is $(Me_3Si)_2N$ or $(Me_3Si)(Me)N$.

The third step is the key to understanding the substitution behavior in these binuclear carboxylate species. The crucial question is why one arm of the carboxylate group trans to an anionic ligand is displaced in one case (step 3) whereas in the other case (step 3′) the carboxylate arm trans to a phosphine is displaced. The substitution behavior is reminiscent of the substitution chemistry at square-planar Pt(II) which is dominated by a trans influence[12a] or effect.[12b] The geometry about the molybdenum atoms in Ib is not exactly square planar (ignoring the metal–metal bond) since the Br–Mo–P angle is 142°. However, the Br–Mo–O and P–Mo–O bond angles are essentially 90°, and the corresponding angles in the amide derivatives are most likely similar. Thus these molecules can be viewed as consisting of two distorted square-planar MoO_2PN units joined by a metal–metal bond. If this is accepted, then the type of isomer can be rationalized on the basis of a trans influence operating in Mo(II), d^4 chemistry. Accordingly, if the anionic ligand, R′ in the scheme, is a good trans-influence group (relative to PR_3) the molybdenum–oxygen bond trans to it is weakened and pathway 3 is followed. If, on the other hand, the anionic ligand R′ is a poor trans-influence group (relative to PR_3), pathway 3′ is followed. The suggested trans influence also rationalizes the formation of trans-carboxylate groups rather than cis ones. Some crystallographic data is available that lends support to the trans-influence suggestion. The Mo–Cl bond length in Ic (chloride trans to a phosphine) is 2.436 (2) Å whereas the Mo–Cl bond length in *trans*-$Mo_2Cl_4(Ph_2PCH_2PPh_2)_2$ (chloride trans to chloride) is 2.39 (1) Å.[13] The bond length data show that a molybdenum–chloride bond trans to a phosphine is lengthened by ca. 0.04 Å relative to one trans to a chloride ligand.

On the basis of the experiments described here and elsewhere,[1] the trans-influence series may be written $Me_3SiCH_2 \approx Me_3CCH_2 \approx (Me_2SiH)_2N > PR_3 > (Me_3Si)(Me)N \approx (Me_3Si)_2N > O_2CR$. It is well-known in Pt(II) that the trans-influence order is $RCH_2 > PR_3 > O_2CR$.[14] This general order is also observed here.[15] The placement of the silylamide ligands on either side of a tertiary phosphine in the series has no precedent since no silylamide derivatives of platinum have been described. However, this prediction is subject to experimental test. Until such time we offer the postulate of a trans influence as a reasonable way to account for the stereochemical results disclosed in this paper.

Experimental Section

Analyses were by the microanalytical laboratory of this department. The infrared spectra were recorded on a Perkin-Elmer 257 instrument. The nuclear magnetic resonance spectra were recorded on a modified Bruker 1180 machine operating at 180 MHz for proton, 169.4 MHz for fluorine, 72.9 MHz for phosphorus, and 45.29 MHz for carbon spectra. Some of the proton or carbon spectra were recorded at 60 (Varian T-60) or 25.1 MHz (Nicolet TT-23), respectively. The ^{19}F and $^{31}P\{^1H\}$ NMR spectra were recorded in benzene solution, and the chemical shifts are expressed in δ values relative to $CFCl_3$ and 85% H_3PO_4, respectively. All operations were performed under argon.

Bis(acetato)bis[bis(trimethylsilyl)amido]bis(trimethylphosphine)-dimolybdenum(II) (A). Trimethylphosphine (0.22 mL, 0.0022 mol) was added to a suspension of tetrakis(acetato)dimolybdenum (0.47 g, 0.0011 mol) in diethyl ether (25 mL) at 0 °C. Lithium bis(trimethylsilyl)amide–1.0-diethyl ether complex (0.52 g, 0.0022 mol) in diethyl ether (25 mL) was added to the above suspension. The solution turned red, and the suspension was stirred at 0 °C for 4 h. The diethyl ether was removed under vacuum, the residue was extracted with pentane (50 mL) and filtered, and the filtrate was concentrated to ca. 45 mL and cooled to −10 °C. The red *prisms* were collected and dried under vacuum. The yield was 0.50 g (58%). The $^{31}P\{^1H\}$ NMR spectrum gave a singlet at δ −6.27.

Bis(trifluoroacetato)bis[bis(trimethylsilyl)amido]bis(trimethylphosphine)dimolybdenum(II) (B). Trimethylphosphine (0.29 mL, 0.0022 mol) was added to tetrakis(trifluoroacetato)dimolybdenum (0.73 g, 0.0011 mol) in diethyl ether (25 mL). To the orange suspension was added lithium bis(trimethylsilyl)amide–0.32-diethyl ether complex (0.42 g, 0.0022 mol) in diethyl ether (25 mL) at 0 °C. The red solution was stirred for 4 h at 0 °C. The diethyl ether was removed under vacuum, the solid was extracted with pentane (50 mL) and filtered, and the filtrate was concentrated to ca. 35 mL and cooled to −10 °C. The red *prisms* (0.59 g, 60%) were collected and dried under vacuum. The $^{31}P\{^1H\}$ NMR spectrum gave a singlet at δ −7.30.

Bis(acetato)bis[bis(trimethylsilyl)amido]bis(dimethylphenylphosphine)dimolybdenum(II) (C). To tetrakis(acetato)dimolybdenum (0.35 g, 0.00082 mol) in diethyl ether (25 mL) were added dimethylphosphine (0.23 mL, 0.0016 mol) and lithium bis(trimethylsilyl)amide–1.5-diethyl ether complex (0.97 g, 0.0033 mol) in diethyl ether (25 mL) at 0 °C. The suspension was stirred for 12 h at 0 °C. The diethyl ether was evaporated and the residue was extracted with pentane (40 mL) and filtered. The filtrate was concentrated to ca.

(12) (a) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335. (b) Basolo, F.; Pearson, R. G. "Mechanisms of Inorganic Reactions"; Wiley: New York, 1967.

(13) Abbott, E. H.; Bose, K. S.; Cotton, F. A.; Hall, W. T.; Sekutowski, J. C. *Inorg. Chem.* **1978**, *17*, 3240.

(14) Cardin, C. J.; Cardin, D. J.; Lappert, M. F.; Muir, K. W. *J. Chem. Soc., Dalton Trans.* **1978**, 46. Wozniak, B.; Ruddick, J. D.; Wilkinson, G. *J. Chem. Soc. A* **1971**, 3116. Adkins, P. W.; Green, J. C.; Green, M. L. H. *Ibid.* **1968**, 2275. Eaborn, C.; Odell, K. J.; Pidcock, A. *J. Chem. Soc., Dalton Trans.* **1979**, 758. Church, M. J.; Mays, M. J. *J. Chem. Soc. A* **1968**, 3074.

(15) We use the term trans influence in a general sense since we cannot make a clear distinction between its thermodynamic (influence) or kinetic (effect) origin. However, Scheme I suggests that the isomer distribution is due to relative rates. Therefore trans effect might be most appropriate.

20 mL, and cooling (−10 °C) gave red *prisms* in 45% (0.33 g) yield. Bis(acetato)bis[bis(trimethylsilyl)amido]bis(triethylphosphine)dimolybdenum (D) was prepared similarly. The $^{31}P\{^1H\}$ NMR spectrum of D consists of a singlet at δ 18.5.

Bis(acetato)bis[(trimethylsilyl)methylamido]bis(trimethylphosphine)dimolybdenum(II) (E). Lithium (trimethylsilyl)methylamide (0.29 g, 0.0027 mol) in diethyl ether (25 mL) was added to a suspension of tetrakis(acetato)dimolybdenum (0.38 g, 0.000 90 mol) and trimethylphosphine (0.18 mL, 0.0018 mol) in diethyl ether (25 mL) at 0 °C. After the solution was stirred for 5 h (0 °C), the diethyl ether was removed under vacuum from the purple suspension. Pentane (50 mL) was added to the residue which was filtered, and the filtrate was evaporated to ca. 10 mL and cooled (−10 °C). The red *prisms* (0.24 g, 40%) were collected and dried under vacuum.

Bis(pivalato)bis[(trimethylsilyl)methylamido]bis(trimethylphosphine)dimolybdenum(II) (F). To tetrakis(pivalato)dimolybdenum (0.29 g, 0.000 49 mol) dissolved in diethyl ether (25 mL) was added trimethylphosphine (0.10 mL, 0.0015 mol) at 0 °C. Lithium (trimethylsilyl)methylamide (0.16 g, 0.0015 mol) in diethyl ether (25 mL) was added and stirred at 0 °C for 8 h. The diethyl ether was removed from the blue-red suspension under vacuum. The residue was extracted with pentane (50 mL) and filtered, and the filtrate was concentrated to ca. 5 mL and cooled to −10 °C. The red *prisms* were collected and dried under vacuum. The yield was 0.29 g (80%). Bis(pivalato)bis[(trimethylsilyl)methylamido]bis(triethylphosphine)dimolybdenum(II) (G) was prepared similarly. The $^{31}P\{^1H\}$ NMR spectrum of G yielded a singlet at δ 20.2.

Bis(acetato)bis[bis(dimethylsilyl)amido]bis(dimethylphenylphosphine)dimolybdenum(II) (I). Lithium bis(dimethylsilyl)amide (0.26 g, 0.0019 mol) in diethyl ether (25 mL) was added to a suspension of tetrakis(acetato)dimolybdenum (0.40 g, 0.000 93 mol) and dimethylphenylphosphine (0.27 mL, 0.0019 mol) in diethyl ether (25 mL) at 0 °C. After the solution was stirred at 0 °C for 12 h, the diethyl ether was removed under vacuum. The residue was extracted with pentane (100 mL) and filtered. The filtrate was concentrated to ca. 90 mL and cooled (−10 °C). The red *prisms* were collected and dried under vacuum. The yield was 0.16 g (20%). Bis(acetato)bis[bis(dimethylsilyl)amido]bis(trimethylphosphine)dimolybdenum(II) (H) was prepared similarly.

Bis(pivalato)bis[bis(dimethylsilyl)amido]bis(trimethylphosphine)dimolybdenum(II) (J). To tetrakis(pivalato)dimolybdenum (0.26 g, 0.000 44 mol) in diethyl ether (25 mL) at 0 °C were added trimethylphosphine (0.09 mL, 0.000 87 mol) and lithium bis(dimethylsilyl)amide–0.58-diethyl ether complex (0.16 g, 0.000 87 mol) in diethyl ether (25 mL). After the solution was stirred for 4 h (0 °C), the diethyl ether was removed under vacuum. The residue was extracted with pentane (100 mL) and filtered, and the filtrate was concentrated to ca. 70 mL and cooled (−10 °C). The red *prisms* were collected and dried under vacuum. The yield was 0.28 g (80%). Bis(pivalato)bis[bis(dimethylsilyl)amido]bis(triethylphosphine)dimolybdenum(II) (L) was prepared similarly. The latter complex yielded a singlet in the $^{31}P\{^1H\}$ NMR spectrum at δ 23.4.

Tris(pivalato)[bis(trimethylsilyl)amido](trimethylphosphine)dimolybdenum(II) (M). Lithium bis(trimethylsilyl)amide (0.20 g, 0.0012 mol) in toluene (25 mL) was added to a solution of tetrakis(pivalato)dimolybdenum (0.36 g, 0.000 60 mol) and trimethylphosphine (0.12 mL, 0.0012 mol) in toluene (25 mL) at room temperature. After the solution was stirred for 8 h, the toluene was removed under vacuum, and the residue was extracted with pentane (50 mL). After filtration, the filtrate was concentrated to ca. 20 mL and cooled (−10 °C). The orange *prisms* were collected and dried under vacuum. The yield was 0.24 g (55%). Tris(pivalato)[bis(trimethylsilyl)amido](triethylphosphine)dimolybdenum(II) (N) was prepared similarly. The $^{31}P\{^1H\}$ NMR spectrum of N consisted of a singlet at δ 18.2.

Tris(pivalato)[bis(trimethylsilyl)amido](dimethylphenylphosphine)dimolybdenum(II) (O). Lithium bis(trimethylsilyl)amide–1.46-diethyl ether complex (0.41 g, 0.0014 mol) in toluene (25 mL) was added to a solution of tetrakis(pivalato)dimolybenum (0.42 g, 0.000 70 mol) and dimethylphenylphosphine (0.20 mL, 0.0014 mol) in toluene (25 mL). The red suspension was stirred for 7 h. The toluene was removed under vacuum, and the residue was exposed to vacuum for 8 h. The residue was extracted with pentane (35 mL) and filtered, and the filtrate was concentrated to ca. 20 mL and cooled (−10 °C). The red crystals were collected and were dissolved with pentane (50 mL) and filtered, the filtrate was concentrated to ca. 15 mL, and cooling (−10 °C) yielded red *prisms* (0.28 g, 54%).

Acknowledgment. We thank the Regents of the University of California for a fellowship (V.V.M.) and the National Science Foundation for a departmental grant which was used to purchase the nuclear magnetic resonance spectrometers used in this study.

Registry No. A, 73622-29-4; B, 73622-30-7; C, 73622-31-8; D, 73622-32-9; E, 73651-42-0; F, 73622-33-0; G, 73622-34-1; H, 73622-35-2; I, 73622-36-3; J, 73622-37-4; K, 73622-38-5; L, 73622-39-6; M, 73728-24-2; N, 73728-23-1; O, 73728-25-3; tetrakis(acetato)dimolybdenum, 14221-06-8; tetrakis(trifluoroacetato)-dimolybdenum, 36608-07-8; tetrakis(pivalato)dimolybdenum, 55946-68-4; lithium bis(trimethylsilyl)amide, 4039-32-1; lithium (trimethylsilyl)methylamide, 10568-44-2; lithium bis(dimethylsilyl)amide, 73612-22-3.

Notes

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Derivatives of (η^5-Cyclopentadienyl)molybdenum Tricarbonyl Hydride and Chloride, η^5-$C_5H_5Mo(CO)_3X$ (X = H, Cl), Containing a Bicyclic Phosphorus–Nitrogen Ligand

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Received July 13, 1979

Substitution reactions of η^5-$C_5H_5Mo(CO)_3X$ (X = H, Cl) with bidentate group 5a ligands in 1:1 molar ratio have been well investigated only for X = Cl. In this case, derivatives of two types have been obtained, depending on whether only carbon monoxide is displaced or the chloride ion as well; ionic products are formed in the latter case. Bis(phosphine) ligands have been found to give both neutral and ionic compounds,[2] with the most π-accepting ones, such as $(F_2P)_2NCH_3$, leading to the substitution of CO only.[2c] In contrast, the bidentate ligands which have little or no back-bonding capacity such as bipyridines and pyridine Schiff bases have resulted only in cationic products.[2a,3]

The combination of a π-accepting center with a σ-donating site is now realized in the tautomeric open form B of the bicyclophosphorane $(C_6H_5)HP(OCH_2CH_2)_2N$, **1**.[4] We wish to report that in its reaction with $C_5H_5Mo(CO)_3Cl$, **1** exhibits

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(2) (a) P. M. Treichel, K. W. Barnett, and R. L. Shubkin, *J. Organomet. Chem.*, **7**, 449 (1967); (b) R. J. Haines, R. S. Nyholm, and M. H. B. Stiddard, *J. Chem. Soc. A*, 94 (1967); (c) R. B. King and J. Gimeno, *Inorg. Chem.*, **17**, 2396 (1978); (d) P. W. Lednor, W. Beck, H. G. Fick, and H. Zippel, *Chem. Ber.*, **111**, 615 (1978).

(3) H. Brunner and W. A. Herrmann, *Chem. Ber.*, **105**, 3600 (1972).

(4) (a) D. Bondoux, I. Tkatchenko, D. Houalla, R. Wolf, C. Pradat, J. G. Riess, and B. F. Mentzen, *J. Chem. Soc., Chem. Commun.*, 1023 (1978); (b) C. Pradat, J. G. Riess, D. Bondoux, B. F. Mentzen, I. Tkatchenko, and D. Houalla, *J. Am. Chem. Soc.*, **101**, 2234 (1979).

0020-1669/80/1319-2169$01.00/0