is observed for all investigated complexes (Figure 5b). Analogous regularity with carboxylato carbon chemical shifts has been also established (Figure 6). However, in the latter case the d-electron magnetic anisotropy has a stronger influence.

^{13}C chemical shifts of the glycinato ligand, so obtained, systematized according to trans ligators, are presented in Figure 7. It is interesting to note that trans influence on chemical shifts is more pronounced when different ligators are facing the glycinato ligand. This fact signifies that apart from the influence exerted on the closer carbon, there is a smaller opposite influence upon carbon which is further away.

The corrected ^{13}C chemical shifts most probably are determined by the value of paramagnetic shielding term on carbon nuclei, since this term has the greatest bearing on the ^{13}C chemical shift.[27] In this way, trans-ligator influence should change the paramagnetic shielding term. This term depends upon electron density on carbon nuclei, electron excitation energy, and bond order,[27] and it is questionable which of these properties is the most affected by trans ligator. This problem may be approached by considering the changes in ^{1}H and ^{13}C chemical shifts of the glycinato ligand when bonding with cobalt. Namely, one should expect cobalt to transmit part of its positive electric charge onto the ligands,[28] thus decreasing ligand electron density. Consequently a smaller proton shielding due to the lowering of the diamagnetic shielding term, as well as a lesser shielding of carbon nucleus because of a paramagnetic shielding term increase might be expected. For the glycinato anion both the ^{13}C chemical shifts[28] [$\delta(^{13}C_\alpha) = 45.4$ and $\delta(^{13}C_{oo}) = 183.5$] and the proton chemical shifts[29] [$\delta(^{1}H_\alpha) = 3.1$] have been reported. These values should be compared with the shifts in the *fac*-[Co(gly)$_3$] complex in which there is no contribution of magnetic anisotropy to the glycinato nuclei chemical shielding (Table I). As it may be seen, proton and ^{13}C chemical shifts move to lower field after complex formation. This fact signifies that changes in electron density may be used to determine chemical shifts of the nuclei under consideration. (On the basis of ^{14}N chemical shifts it was shown[5] that the glycine nitrogen shielding is determined by changes in the excitation energy and that after bonding to cobalt(III) a shift toward a higher field is observed. Such a difference is not surprising, since the nitrogen σ orbital directly participates in the metal–ligand bond, whereas carbon orbitals probably do not partake significantly in these molecular orbitals.) Consequently, trans-ligand influence on ^{13}C chemical shifts of the glycinato ligand probably operates through an inductive change of carbon electron density. In line with this, Figure 7 shows the relative change of charge densities on glycinato carbons when δ represents a charge which corresponds to a ~0.3 ppm shift change. From the scheme on Figure 7, it may be concluded that nitrogen in the trans position increases the relative density on the closest carbon, while oxygen performs an opposite influence. Such a finding is consistent with the perceived trans-ligand influence on the rate of the amine proton isotope exchange.[30] Research carried out by other authors[14,15] regarding the influence of trans ligands on the chemical shift of various nuclei speaks in favor of the proposed explanation.

Finally, we have studied the possible influence of the complex ion electric field on ^{1}H and ^{13}C chemical shifts, the reason being that this effect had been used in explaining the corresponding amino acid chemical shifts.[29] One of the basic phenomena caused by the electric field is the polarization of C–H bonds, which causes ^{1}H and ^{13}C chemical shifts to move in opposite directions.[11,29] However, the latter phenomenon has not been observed in complexes examined, neither before nor after making corrections of chemical shifts for the influence of magnetic anisotropy. No shift dependence on complex ion charge had been found, as well. Hence, the electric field influence is relatively weak in the investigated complexes.

A general conclusion which presents itself on the basis of the results obtained in this study is the necessity of performing a correction of chemical shifts of the nuclei of the ligands for the contribution from the magnetic anisotropy of the central ion in the complex. This task should be carried out before approaching the study of other influences.

Registry No. [Co(en)$_3$]Cl$_3$, 13408-73-6; [Co(gly)(en)$_2$]Cl$_2$, 14408-57-2; *trans*(*O*)-[Co(gly)$_2$(en)]Cl, 57298-57-4; *cis*(*O*)-*C*$_2$-[Co(gly)$_2$(en)]Cl, 57298-58-5; *cis*(*O*)-*C*$_1$-[Co(gly)$_2$(en)]Cl, 57335-06-5; *mer*-[Co(gly)$_3$], 30364-77-3; *fac*-[Co(gly)$_3$], 21520-57-0; *cis*(*N*)-*C*$_1$-K[Co(ox)(gly)$_2$], 65816-56-0; *cis*(*N*)-*C*$_2$-K[Co(ox)(gly)$_2$], 65816-57-1; *trans*(*N*)-K[Co(ox)(gly)$_2$], 16986-03-1; K$_2$[Co(ox)$_2$(gly)], 46846-80-4; K$_3$[Co(ox)$_3$], 14239-07-7.

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Coordination Complexes of Tetrakis(trifluoroacetato)dimolybdenum. A Solution ^{1}H, ^{19}F, and ^{31}P Nuclear Magnetic Resonance and Infrared Spectroscopic Study

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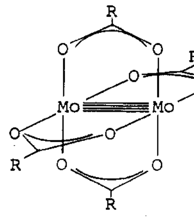
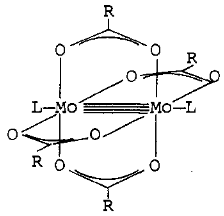
New coordination complexes of the type Mo$_2$(O$_2$CCF$_3$)$_4$(L)$_2$ where L is Me$_3$P, Me$_2$PhP, MePh$_2$P, Ph$_3$P, Et$_3$P, (c-Hx)$_3$P (c-Hx = cyclohexyl), (*t*-Bu)$_3$P, (Me$_3$Si)$_3$P, Me$_3$PO, and quinuclidine have been prepared. These complexes fall into two classes, viz., class I or class II. Class I complexes are formed with MePh$_2$P, Ph$_3$P, (c-Hx)$_3$P, (*t*-Bu)$_3$P, (Me$_3$Si)$_3$P, Me$_3$PO, and quinuclidine. Solution infrared and ^{19}F NMR studies show that these complexes are of the classical type (axial coordination) as shown by X-ray crystallography for L = pyridine, some years ago. Solution ^{31}P{^{1}H} NMR spectroscopy of these phosphine adducts indicates that they are extensively dissociated in CDCl$_3$. Class II complexes (L = Me$_3$P, Me$_2$PhP, or Et$_3$P) exist in solution (CDCl$_3$) with bidentate and monodentate trifluoroacetate groups as determined by infrared and ^{19}F NMR spectroscopy. At least two isomers are present as shown by ^{31}P{^{1}H} and ^{1}H{^{31}P} NMR spectroscopy. Some bidentate phosphine complexes are also described.

Base-free molybdenum(II) carboxylates, Mo$_2$(O$_2$CR)$_4$, where R = H,[1] Me,[2,3] CF$_3$,[4] Ph,[5] *t*-Bu,[5] or CH$_2$NH$_3$$^+$,[6] have been shown to be of structure A by X-ray crystallography. A number of other carboxylates have been prepared, and these



A



B

are thought to have the same structure, viz., A.[7,8] Some Lewis-base coordination complexes, $Mo_2(O_2CR)_4(L)_2$, where R is Ph and L is diethylene glycol dimethyl ether[9] or R is CF_3 and L is pyridine[10] have been shown to possess structure B by X-ray crystallography. Other diadducts of the carboxylates have been prepared, and they are thought to have structure B; viz., the Lewis bases coordinate to the vacant axial sites in the base-free compound.[7,8,11-13] A characteristic feature of the diadducts which have been crystallographically examined is that the molybdenum–donor atom bond length is rather long, implying a weak interaction. The only detailed solution spectroscopic study of Lewis-base complexes of molybdenum carboxylates is that of 2,2′-bipyridine and $Mo_2(O_2CCF_3)_4$.[14] That study is complicated by the presence of a number of species in solution which depends upon reaction time, solvent, etc.

Solution spectroscopic studies of acetates or benzoates have been limited by their insolubility in common aromatic or chlorinated hydrocarbon solvents. The trifluoroacetates and their complexes are quite soluble in these solvents so that infrared and nuclear magnetic resonance spectroscopy can be used to investigate their solution behavior. The trifluoroacetates are convenient spectroscopic labels since a bidentate CF_3CO_2 group absorbs at ca. 1600 cm^{-1} whereas a monodentate CF_3CO_2 group absorbs at ca. 1680 cm^{-1} in the infrared.[15] The ^{19}F nuclear magnetic resonance spectra are also useful since bidentate CF_3CO_2 groups resonate at ca. δ −70[16] and monodentate CF_3CO_2 groups resonate at ca. δ −74.[17-19] In this paper we describe the application of these and other [$^{31}P\{^1H\}$ and $^1H\{^{31}P\}$] spectroscopic techniques to a study of the solution behavior of $Mo_2(O_2CCF_3)_4(L)_2$ complexes where L is a monodentate phosphine, amine, or phosphine oxide. Some bidentate phosphine complexes are also described.

Monodentate Lewis Bases. General Data. All of the monodentate, Lewis-base complexes of $Mo_2(O_2CCF_3)_4$ prepared in this study yield 1:2 coordination complexes. Physical properties are shown in Tables I–III. The complexes have conductivities in the range 0.1–2.6 Ω^{-1} mol^{-1} cm^2 in chloroform at 20 °C on solutions of ca. 10^{-4} M (reckoned as dimer). As reference points, n-Bu_4NI and base-free $Mo_2(O_2CCF_3)_4$ have conductivities of 20 and 0.4 Ω^{-1} mol^{-1} cm^2 (ca. 10^{-4} M) in chloroform, respectively. Thus, the complexes are essentially nonconducting at these low concentrations. The infrared spectra in the solid state (Nujol mull) and in solution ($CHCl_3$) are nearly or completely superimposable in each case, implying that the structure of each complex is the same in both phases.

Class I Complexes. The coordination complexes in this class are of the type $Mo_2(O_2CCF_3)_4(L)_2$ where L is $MePh_2P$, Ph_3P, $(t\text{-}Bu)_3P$, $(SiMe_3)_3P$, quinuclidine (1-azabicyclo[2.2.2]octane), $(c\text{-}Hx)_3P$, or Me_3PO. Solution infrared spectra contain a single $\nu_{asy}(CO_2)$ stretching frequency at ca. 1600 cm^{-1} (Table II). This frequency is essentially identical with that found for base-free $Mo_2(O_2CCF_3)_4$ and is indicative of bidentate coordination. No absorptions are found in the region where monodentate CF_3CO_2 groups absorb. This conclusion is supported by the ^{19}F NMR spectra (Table II) since only single resonances at ca. δ −70 are observed. The data suggest that the CF_3CO_2 groups are equivalent and bidentate and that these complexes are doubtless of structure B. This conclusion is supported by $^{31}P\{^1H\}$ NMR spectra of the phosphine complexes, as a single resonance is observed for each complex (Table III). The coordination chemical shifts, defined as the ^{31}P chemical shift of the complex less that of free ligand, are approximately zero. This low value implies that the phosphine ligands are only weakly coordinated at the axial positions of the binuclear unit. The inherently small ^1H NMR chemical shifts of coordinated pyridine (δ 8.04, 7.19, and 7.66 for the α, β, and γ protons, respectively) or quinuclidine (δ 2.39, 1.43, and 1.67 for the α, β, and γ protons, respectively) protons relative to free pyridine (δ 8.50, 7.06, and 7.46) or quinuclidine (δ 2.83, 1.49, and 1.71) do not allow us to say whether these ligands are bonded weakly or strongly to the molybdenum atom in solution. A crystal structure analysis of $Mo_2(O_2CCF_3)_4(py)_2$ indicates that the Mo–N bond length is rather long.[10] Dissociation in solution is probable for both of these diadducts though we cannot be certain.

The spectroscopic data, taken in their entirety, show that all Class I complexes have structure B and the Lewis bases are appreciably dissociated in solution. The phosphine oxide complex $Mo_2(O_2CCF_3)_4(OPMe_3)_2$ appears to contradict this generalization since the ^{31}P coordination chemical shift is rather large (ca. 12), indicating that this complex is not dissociated in solution. The ^{31}P coordination chemical shift of a number of monodentate, tertiary phosphine oxide complexes ranges from 5.8 to 25.7.[20,21]

Trimethylphosphine oxide is a weaker base in aqueous solution ($pK_a = 0$)[22] than pyridine ($pK_a = 5.2$),[23] quinuclidine ($pK_a = 10.6$),[24] or tertiary phosphines (Ph_3P, $pK_a = 2.7$; Me_3P, $pK_a = 8.7$).[25] If ligand basicity is the only factor which affects the extent of dissociation, then the Me_3PO complex should be more rather than less dissociated in solution. Trimethylphosphine oxide is the smallest ligand in the series, and this could be the reason for its apparent stronger coordination in solution.

Class II Complexes. The 1:2 complexes, $Mo_2(O_2CCF_3)_4(L)_2$, where L is Me_3P, Me_2PhP, or Et_3P, are of a new type since nonaxial phosphine coordination is observed. Solution infrared spectra of the three phosphine complexes are similar, showing absorptions due to mono- and bidentate CF_3CO_2 groups at ca. 1670 and 1600 cm^{-1}, respectively (Table II). The

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Table I. Some Physical Properties of $Mo_2(O_2CCF_3)_4(L)_x$

$(L)_x$	color	mp, °C	anal.			
			calcd		found	
			% C	% H	% C	% H
$(PMe_3)_2$	orange	198–201	21.1	2.28	21.5	2.52
$(PMe_3)_3$	purple	120 dec	23.4	3.12	23.8	3.42
$(PMe_2Ph)_2$	orange	180 dec	31.3	2.41	30.4	2.40
$(PEt_3)_2$	orange	154–159	27.3	3.44	28.5	3.86
$(PMePh_2)_2$	orange-yellow	93–95	39.1	2.51	40.1	2.90
$(PPh_3)_2$	yellow	183–184	45.2	2.59	45.5	3.03
$[P(c\text{-}Hx)_3]_2$	yellow	179–181	43.9	5.52	45.1	5.76
$[P(t\text{-}Bu)_3]_2$	orange-yellow	200–205	36.7	5.19	37.4	5.31
$[P(SiMe_3)_3]_2$	orange-yellow	160 dec	27.3	4.75	27.3	4.63
$(OPMe_3)_2$	orange-yellow	208–209	20.3	2.19	20.7	2.34
$(quin)_2$	orange-yellow	195–200	30.5	3.03[a]	31.7	3.30[b]
$(Me_2PCH_2PMe_2)_2$	pink-red	240 dec	23.6	3.08	22.9	2.96
$Ph_2PCH_2PPh_2$	yellow	230–235	38.5	2.16	38.6	2.47
$Me_2PCH_2CH_2PMe_2$	orange	242–243	21.2	2.03	21.4	2.24
$(Me_2PCH_2CH_2PMe_2)_2$	blue		25.4	3.42	25.2	3.29
$(Me_2PCH_2CH_2PMe_2)_3$	pink-purple		28.5	4.42	27.5	4.19

[a] N, 3.16%. [b] N, 3.23%.

Table II. Infrared and ^{19}F NMR Spectra of $Mo_2(O_2CCF_3)_4(L)_x$

$(L)_x$	infrared[a]		^{19}F NMR[d]
	$\nu_{asy}(O_2CCF_3)$[b]	$\nu_{asy}(O_2CCF_3)$[c]	
$(PMe_3)_2$	1663 s, 1570 s	1672 s br, 1599 s, 1580 m	−69.9, −73.1, −73.8
$(PMe_3)_3$	1705 s, 1670 s, 1610 w, 1575 m	1675 s br, 1600 m, 1582 m	see text
$(PMe_2Ph)_2$	1645 s, 1596 s, 1574 s	1670 s br, 1595 s, 1580 m	−69.7, −72.7, −73.2
$(PEt_3)_2$	1660 s, 1607 m, 1575 s	1662 s br, 1600 m, 1580 s	−69.8, −73.7
$(PMePh_2)_2$	1596	1600	−70.5
$(PPh_3)_2$	1600	1600	−70.1
$[P(c\text{-}Hx)_3]_2$	1600	1598	−70.7
$[P(t\text{-}Bu)_3]_2$	1600	1600	−70.6
$[P(SiMe_3)_3]_2$	1600	1598	−70.1
$(OPMe_3)_2$	1600	1600	−70.6
$(quin)_2$	1600	1600	−70.3
$(py)_2$	1595	1600	−69.8
$(Me_2PCH_2PMe_2)_2$	1670 s, 1650 s, 1634 m, 1605 m, 1585 m	1652 s, 1605 m, 1588 m	−69.5, −69.9, −73.6 (1:2:10)
$Ph_2PCH_2PPh_2$	1650 s, 1600 s	1662 w, 1600 s	−70.6, −72.8 (10:1)
$Me_2PCH_2CH_2PMe_2$	1636 s, 1598 s, 1578 s	1665 s br, 1605 s	
$(Me_2PCH_2CH_2PMe_2)_2$	1700 s, 1680 s 1600 w, 1582 w		−74.1, −75.8
$(Me_2PCH_2CH_2PMe_2)_3$	1682 s, 1587 w		−75.1

[a] s = strong, m = medium, w = weak, br = broad. [b] Nujol mull, cm^{-1}. [c] Chloroform solution, cm^{-1}. [d] Chloroform-d_1 solution at −55 °C; expressed in δ units relative to $CFCl_3$ (δ 0), negative values being to low frequency.

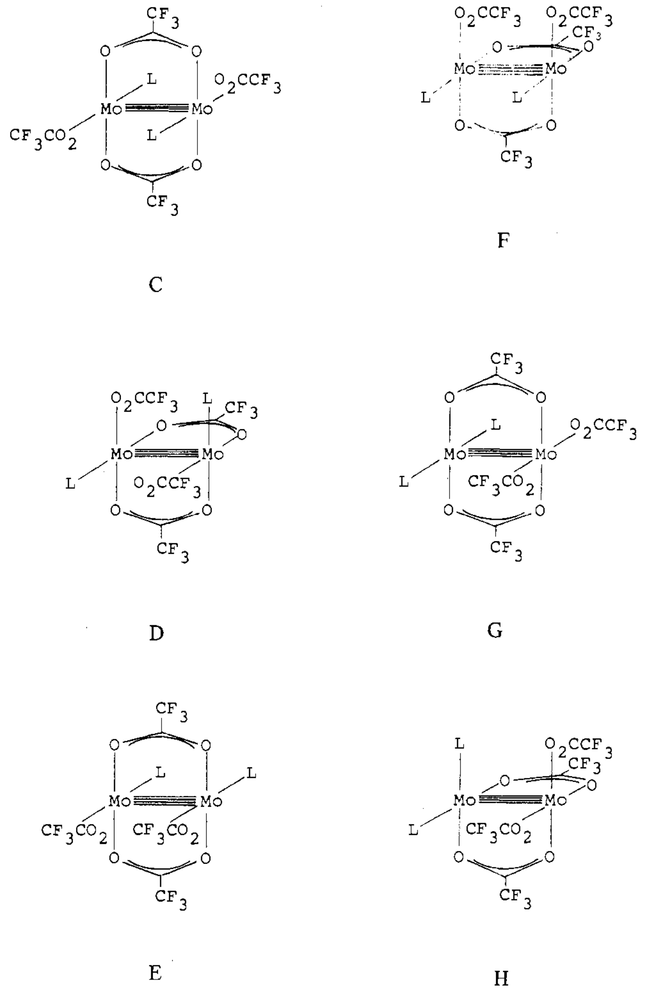
Table III. $^{31}P\{^1H\}$ and $^1H\{^{31}P\}$ NMR Spectra of $Mo_2(O_2CCF_3)_4(L)_x$

$(L)_x$	$^{31}P\{^1H\}$ NMR[a]		Δ[b]	$^1H\{^{31}P\}$ NMR[c]
	complex	free ligand		
$(PMe_3)_2$ (−11 °C)	−4.40, −5.90	−63.0	58.6, 57.1	1.52, 1.48 (Me)
$(PMe_2Ph)_2$	4.30, 2.20	−46.9	51.2, 49.1	7.43 br (Ph), 1.80 br (Me)
$(PEt_3)_2$	18.1, 17.2	−20.4	38.5, 37.6	1.92 q, J_{HH} = 7.4 Hz 1.89 q, J_{HH} = 7.2 Hz 1.03 t, J_{HH} = 7.4 Hz 1.02 t, J_{HH} = 7.2 Hz
$(PMePh_2)_2$	−29.6	−28.1	−1.5	7.39 (Ph), 1.61 (Me)
$(PPh_3)_2$	−1.00	−5.90	4.9	7.30
$[P(c\text{-}Hx)_3]_2$	12.8	10.0	2.8	complex
$[P(t\text{-}Bu)_3]_2$	59.3	61.9	−2.6	1.17
$[P(SiMe_3)_3]_2$	−250	−251	1.0	0.18
$(OPMe_3)_2$	48.6	36.4	12.2	1.28
$(Me_2PCH_2PMe_2)_2$	10.9, 8.76, 4.85 (1:5:10)	−41.6	52.5, 50.4, 46.5	
$Ph_2PCH_2PPh_2$	23.3, 21.2, −26.1 (5:1:5)	−23.6	46.9, 44.8, −2.5	
$Me_2PCH_2CH_2PMe_2$	4.29, 3.68, 1.88 (3:5:1)	−42.4	46.7, 46.1, 44.3	
$(Me_2PCH_2CH_2PMe_2)_2$	3.64	−42.4	46.0	
$(Me_2PCH_2CH_2PMe_2)_3$	5.43, 3.47, 3.16, (1:2:2)	−42.4	47.8, 45.9, 45.6	

[a] Chloroform-d_1 solution at −55 °C; expressed in δ units relative to 85% H_3PO_4 (δ 0), negative values being to low frequency. [b] Coordination chemical shift (ppm). [c] Chloroform-d_1 solution at −55 °C; expressed in δ units relative to Me_4Si (δ 0), negative values being to high field.

^{19}F NMR spectra also show that mono- and bidentate CF_3CO_2 groups are present in equal amounts (Table II). The triethylphosphine complex, $Mo_2(O_2CCF_3)_4(PEt_3)_2$, gives two equal area resonances at δ −69.8 and −73.7, the former due to bidentate and the latter due to monodentate CF_3CO_2 coordination. The ^{19}F NMR spectra of the Me_3P and Me_2PhP

Chart I. Possible Isomers of $Mo_2(O_2CCF_3)_4(L)_2$



complexes are slightly more complex as a single resonance is observed in the bidentate CF_3CO_2 region and a pair of resonances is observed in the monodentate region from +25 to −55 °C. In the Me_3P complex, the area ratio of the δ −69.7:−73.1:−73.8 resonances is ca. 1:0.3:0.7, and in the Me_2PhP complex, the area ratio of the δ −69.7:−72.7:−73.2 resonances is ca. 1:0.4:0.6. Clearly at least two isomers exist in solution with bi- and monodentate trifluoroacetate groups for the latter two complexes.

If we allow a pair of CF_3CO_2 groups to be bidentate while filling the remaining equatorial sites with two monodentate CF_3CO_2 groups and two tertiary phosphine ligands, we can generate six possible isomers C–H in Chart I (D has an enantiomer). The monodentate CF_3CO_2 groups are shown as not being bonded to the axial sites about molybdenum though this need not be the case. The $^{31}P\{^1H\}$ and ^1H NMR spectra should allow us to distinguish among the various possibilities. The $^{31}P\{^1H\}$ NMR spectrum of the Et_3P complex shows two resonances at δ 18.1 and 17.2 in an area ratio of 1:1.5 at −55 °C. The large coordination chemical shifts and absence of a resonance due to free phosphine are indicative of strongly bound phosphine. The $^{31}P\{^1H\}$ NMR spectra of the Me_2PhP (−55 °C) and Me_3P (−11 °C) are similar; viz., two types of phosphine environments are observed. Matters, however, are not so simple since cooling the Me_3P complex to −55 °C yields a ^{31}P NMR spectrum which contains five resonances at δ −4.59, −6.03, −7.03, −8.16, and −10.0 in approximate area ratio 5:3:1:4:1. At least in the Me_3P complex all of the isomers could be present in appreciable concentration at −55 °C whereas in the Me_2PhP or Et_3P complexes, at this temperature, only two isomers are required to satisfy the observations.

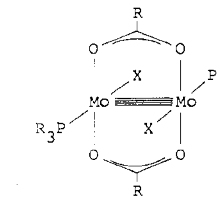
The ^1H NMR spectra of the methyl–phosphine complexes should in principle be informative since isomers C–F should yield simple doublets whereas G or H are examples of $X_9AA'X'_9$ spin systems.[26] In practice, the spectra are uninformative since broadened, featureless spectra are observed. Decoupling the ^{31}P nuclei yields sharp signals which mirror the $^{31}P\{^1H\}$ NMR spectra, a pair of resonances being observed for the methyl protons in the Me_3P and Me_2PhP complexes and a pair of overlapping A_2B_3 multiplets for the Et_3P complex (Table III). Unfortunately, decoupling the ^{31}P nuclei results in loss of all stereochemical information.

The $^{13}C\{^1H\}$ nuclear magnetic resonance experiment is also potentially applicable for stereochemical studies. The carbon atoms of the phosphine ligands in isomers C–F should give rise to AX spectra and those in isomers G or H should give rise to AXX′ spectra[27] (A is ^{13}C and X and X′ are ^{31}P nuclei). The $^{13}C\{^1H\}$ at −10 °C of the trimethylphosphine complex shows an apparent 1:2:1 triplet centered at δ 10.8, the separation between each resonance being 14.6 Hz. This apparent AXX′ spectrum, however, could be due to at least a pair of overlapping AX spectra. The $^{13}C\{^1H\}$ at −50 °C of the Me_2PhP complex shows a seven-line pattern, the chemical shifts being δ 9.48, 9.17, 9.04, 8.86, 8.71, 8.58, and 8.39. The spectrum is clearly not susceptible to a straightforward analysis.

The situation for the Me_3P complex is further complicated by the observation that a 1:3 complex, $Mo_2(O_2CCF_3)_4(PMe_3)_3$, can be isolated. The ^{19}F NMR spectrum (−55 °C) consists of resonances at δ −69.8, −72.5, −73.3, and −73.8 in approximate area ratio 2:3:5:10. The first resonance can be reasonably ascribed to a bidentate and the latter three resonances to monodentate trifluoroacetate groups. The $^{31}P\{^1H\}$ NMR spectrum at −55 °C is exceedingly complex as it appears to consist of an A component, a pair of AB components, and an AB_2 component. We have not attempted a detailed analysis of the spectrum.

The thermal instability (the solutions discolor when heated to >40 °C) precludes a high-temperature study. The complexes are rather insoluble in solvents of low dielectric constant (such as aliphatic or aromatic hydrocarbons). Further, the complexes show extremely complex behavior in solvents of high dielectric constants such as acetone or acetonitrile probably due to competition of the solvent for coordination sites about the binuclear unit.

The complex behavior dooms to failure any attempt to decide the number and stereochemistry of the isomers present in solution. Some molybdenum phosphine complexes with two bidentate carboxylate groups have been crystallographically characterized, I[28] and J.[29] These are similar to isomer C in



I, R = Me, X = CH_2SiMe_3, R_3P = Me_3P

J, R = Ph, X = Br, R_3P = $(n\text{-}Bu)_3P$

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Chart II. Graph of Ligand Size vs. Basicity

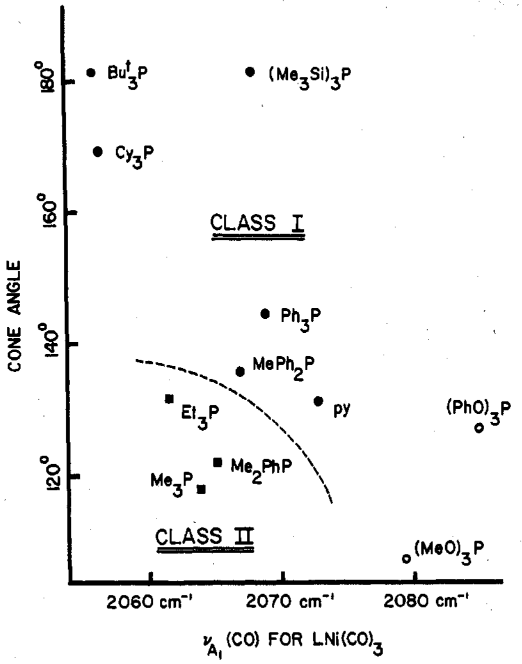

Chart I, the most symmetrical isomer. This isomer is doubtless present in solution. The detailed solution stereochemistry unfortunately remains unknown, and we know of no way to answer this question.

The essential point, however, remains: viz., monodentate phosphine complexes of $Mo_2(O_2CCF_3)_4$ can be segregated into two distinct types. Class I complexes possess axial coordination whereas those of Class II prefer equatorial coordination. A combination of ligand size and basicity is required to account for this behavior. This can be readily seen from Chart II. The cone angles and ν(CO) values (smaller values indicating greater σ-donor and poorer π-acceptor properties) are taken from Tolman.[37] Only those phosphines which are good Lewis bases and are sterically small give complexes of Class II. This duality is nicely illustrated by our inability to isolate a 1:2 complex with the small but poor Lewis bases, $P(OMe)_3$ or $P(OPh)_3$. The observation that quinuclidine gives a Class I complex does not appear to fit the above generalization. The nickel-tricarbonyl(quinuclidine) complex does not appear to have been described, so we cannot fit it into Chart II. It is the best base in aqueous solution of all the ligands used in this study ($pK_a = 10.6$),[24] and its size is similar to that of pyridine or triethylphosphine.[30] Hence we would expect that $Mo_2(O_2CCF_3)_4(quin)_2$ (quin = quinuclidine) would be a Class II complex which it is not. Quinuclidine is a poor π-acceptor ligand, and the ligands that yield Class II complexes have π-accepting capabilities. The importance of π-accepting abilities of Lewis bases has been used to explain the variations in bond length and acidity in complexes of $Rh_2(O_2CR)_4$.[31,32] Thus, it appears that Class II complexes are formed with ligands that have just the right combination of σ-base, π-acid, and steric requirements. These observations are of considerable practical importance since synthesis of binuclear molybdenum(II) alkyl or aryl derivatives is only successful with those phosphines that afford Class II complexes.[33,34]

Bidentate Phosphine Complexes. Coordination complexes of $Mo_2(O_2CCF_3)_4$ with some bidentate phosphines have also been prepared (Table I). Infrared and ^{19}F and $^{31}P\{^1H\}$ NMR spectra (Tables II and III) of two of these, $Mo_2(O_2CCF_3)_4(Me_2PCH_2PMe_2)_2$ and $Mo_2(O_2CCF_3)_4(Me_2PCH_2CH_2PMe_2)_2$, indicate that the predominant species in solution contain monodentate trifluoroacetate groups and chelating phosphine ligands. They are probably similar to those previously described, viz., $Mo_2Cl_4(Ph_2PCH_2PPh_2)_2$[35] and $Mo_2Br_4(Ph_2PCH_2CH_2AsPh_2)_2$,[36] acetate replacing halide. The NMR spectra of the other complexes listed in Table I are exceedingly complex, and we have not examined these in detail.

Experimental Section

All 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, and at 72.9 MHz for phosphorus. All operations were performed under argon.

Bis(trimethylphosphine)tetrakis(trifluoroacetato)dimolybdenum(II). Trimethylphosphine (0.40 mL, 0.0038 mol) was added to tetrakis(trifluoroacetato)dimolybdenum (0.40 g, 0.000 62 mol) dissolved in diethyl ether (20 mL). The purple solution was stirred for 15 min, and the volatile material was removed under vacuum. The orange-purple solid was dissolved in diethyl ether (20 mL) and the solution was taken to dryness. The orange residue was dissolved in diethyl ether, and the solution was filtered and cooled to −10 °C. The orange needles were collected and dried under vacuum, yield 0.44 g (89%). Bis(dimethylphenylphosphine)tetrakis(trifluoroacetato)dimolybdenum was prepared similarly, yield 83%.

Bis(methyldiphenylphosphine)tetrakis(trifluoroacetato)dimolybdenum(II). Methyldiphenylphosphine (0.30 mL, 0.0016 mol) was added to tetrakis(trifluoroacetato)dimolybdenum (0.55 g, 0.000 85 mol) in diethyl ether (30 mL). The solution was stirred for 30 min and filtered, and the filtrate was evaporated to ca. 10 mL. Cooling (−10 °C) gave orange-yellow prisms in 86% (0.76 g) yield. The $(t\text{-}Bu)_3P$ and $(Me_3Si)_3P$ complexes were prepared similarly.

Bis(triethylphosphine)tetrakis(trifluoroacetato)dimolybdenum(II). Neat triethylphosphine (2.0 mL, 0.0017 mol) was added to tetrakis(trifluoroacetato)dimolybdenum (0.43 g, 0.000 67 mol), and the suspension was heated to ca. 100 °C. The solution was cooled slowly to room temperature and the orange prisms were collected and dried under vacuum. The yield was 0.56 g (95%).

Bis(triphenylphosphine)tetrakis(trifluoroacetato)dimolybdenum(II). Tetrakis(trifluoroacetato)dimolybdenum (0.57 g, 0.000 88 mol) and triphenylphosphine (0.46 g, 0.0018 mol) were intimately mixed and heated to form a homogeneous solid. After the solution was cooled, to room temperature, the solid was pulverized, dissolved in toluene (30 mL), and cooled (−10 °C). The yellow prisms were collected and dried under vacuum. The yield was 87% (0.90 g). Bis(tricyclohexylphosphine)tetrakis(trifluoroacetato)dimolybdenum was prepared similarly.

Bis(trimethylphosphine oxide)tetrakis(trifluoroacetato)dimolybdenum(II). Trimethylphosphine oxide (0.22 g, 0.0024 mol) and tetrakis(trifluoroacetato)dimolybdenum (0.40 g, 0.000 62 mol) were intimately mixed, and dichloromethane (30 mL) was added. The solution was gently refluxed for 30 min. Cooling to −70 °C yielded orange-yellow prisms in 73% (0.38 g) yield. Bis(quinuclidine)tetrakis(trifluoroacetato)dimolybdenum was prepared similarly.

Tris(trimethylphosphine)tetrakis(trifluoroacetato)dimolybdenum(II). Trimethylphosphine (0.40 mL, 0.0039 mol) was added to tetrakis-

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(trifluoroacetato)dimolybdenum (0.27 g, 0.000 34 mol) in diethyl ether (30 mL). The solution was stirred for 30 min and cooled to −70 °C. The purple solid was collected and dried under vacuum. The yield was 0.17 g (58%).

Bis[bis(dimethylphosphino)methane]tetrakis(trifluoroacetato)dimolybdenum(II). Addition of bis(dimethylphosphino)methane (1.0 mL, 0.0074 mol) to tetrakis(trifluoroacetato)dimolybdenum (0.92 g, 0.0014 mol) in diethyl ether (30 mL) resulted in formation of a pink precipitate. The solid was collected, dissolved in chloroform (50 mL), and filtered. The filtrate was concentrated to ca. 30 mL and cooled (−10 °C). The pink-red prisms were collected and dried under vacuum. The yield was 87% (1.1 g).

[Bis(diphenylphosphino)methane]tetrakis(trifluoroacetato)dimolybdenum(II). Tetrakis(trifluoroacetato)dimolybdenum (0.50 g, 0.00078 mol) and bis(diphenylphosphino)methane (0.60 g, 0.0015 mol) were intimately mixed, and the mixture was heated until a homogeneous solution formed. After the solution was cooled to room temperature, the solid was pulverized and washed with cold benzene (40 mL). The residue was dissolved in hot benzene, and the solution was filtered and slowly cooled to room temperature. The microcrystalline solid was collected and dried under vacuum. The yield was 0.42 g (52%).

Reaction of 1,2-Bis(dimethylphosphino)ethane with Tetrakis(trifluoroacetato)dimolybdenum(II). Addition of 1,2-bis(dimethylphosphino)ethane (1.0 mL, 0.0067 mol) to tetrakis(trifluoroacetato)dimolybdenum (0.76 g, 0.0012 mol) in diethyl ether (50 mL) resulted in a blue-purple solid and a pink solution. The volatile material was removed under vacuum. Chloroform (40 mL) was added to the residue, and the pink solution was separated from the blue residue by filtration. The blue residue was washed with chloroform (40 mL), and the extracts were combined, concentrated to ca. 20 mL, and cooled (−10 °C). The 1:3 complex tris[1,2-bis(dimethylphosphino)ethane]tetrakis(trifluoroacetato)dimolybdenum was isolated as pink-purple needles in 20% (0.26 g) yield. Dichloromethane (40 mL) was added to the blue residue, resulting in a blue solution and an orange solid which were separated by filtration. The orange residue was washed with dichloromethane (10 mL), and the blue filtrate and washings were combined, concentrated to ca. 10 mL, and cooled (−10 °C). The 1:2 complex bis[1,2-bis(dimethylphosphino)ethane]tetrakis(trifluoroacetato)dimolybdenum was isolated as blue prisms. The yield was 45% (0.50 g). The orange residue was dissolved in absolute ethanol (15 mL), filtered, concentrated to ca. 5 mL, and cooled (−10 °C), yielding the 1:1 complex [1,2-bis(dimethylphosphino)ethane]tetrakis(trifluoroacetato)dimolybdenum(II) as orange crystals. The yield was 20% (0.19 g).

Acknowledgment. We thank the Regents of the University of California for a fellowship (G.S.G. and V.V.M.) and the National Science Foundation for a departmental grant for purchase of the nuclear magnetic resonance spectrometer used in this work.

Note Added in Proof. We have been informed that a crystal structure analysis of $(CF_3CO_2)_4Mo_2(PEt_2Ph)_2$ shows that this diadduct has structure C (L = PEt_2Ph, Chart I) in the solid state: Lay, D. G.; Cotton, F. A., personal communication, Nov 26, 1979. The cone angle (136°)[37] and ν(CO) of $Ni(CO)_3PEt_2Ph$, 2064 cm^{-1}, clearly show that PEt_2Ph is a Class II phosphine in agreement with the X-ray analysis.

Registry No. $Mo_2(O_2CCF_3)_4(PMe_3)_2$, 72509-74-1; $Mo_2(O_2CCF_3)_4(PMe_2Ph)_2$, 72509-70-7; $Mo_2(O_2CCF_3)_4(PMePh_2)_2$, 72453-45-3; $Mo_2(O_2CCF_3)_4[P(t\text{-}Bu)_3]_2$, 72453-46-4; $Mo_2(O_2CCF_3)_4[P(SiMe_3)_3]_2$, 72453-47-5; $Mo_2(O_2CCF_3)_4(PEt_3)_2$, 72509-73-0; $Mo_2(O_2CCF_3)_4(PPh_3)_2$, 41772-59-2; $Mo_2(O_2CCF_3)_4[P(c\text{-}Hx)_3]_2$, 72453-48-6; $Mo_2(O_2CCF_3)_4(OPMe_3)_2$, 72453-49-7; $Mo_2(O_2CCF_3)_4(quin)_2$, 72453-50-0; $Mo_2(O_2CCF_3)_4(PMe_3)_3$, 72509-72-9; $Mo_2(O_2CCF_3)_4(Me_2PCH_2PMe_2)_2$, 72467-43-7; $Mo_2(O_2CCF_3)_4(Ph_2PCH_2PPh_2)$, 72509-69-4; $Mo_2(O_2CCF_3)_4(Me_2PCH_2CH_2PMe_2)_3$, 72509-68-3; $Mo_2(O_2CCF_3)_4(Me_2PCH_2CH_2PMe_2)_2$, 72453-51-1; $Mo_2(O_2CCF_3)_4(Me_2PCH_2CH_2PMe_2)$, 72509-71-8; $Mo_2(O_2CCF_3)_4(py)_2$, 39176-71-1; $Mo_2(O_2CCF_3)_4$, 35489-62-4.

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Photoelectron and Electronic Spectra of $Rh_2Cl_2(CO)_4$ and $Rh_2Cl_2(PF_3)_4$. Assignments from SCF–Xα–SW Calculations

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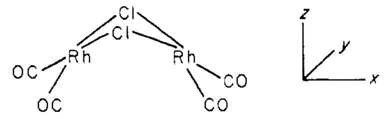
Transition-state SCF–Xα–SW calculations of ionization energies for $Rh_2Cl_2(CO)_4$ are found to be in good agreement with the UV photoelectron spectrum. A detailed assignment of the spectrum and that of $Rh_2Cl_2(PF_3)_4$ is given, based on the calculations and He I/He II intensity variations. The Xα–SW results also appear to agree closely with the recently reported electronic spectrum of $Rh_2Cl_2(CO)_4$. This consistency with experiment lends credence to the simple orbital explanation, based on the calculations, which was previously given for the folded structure of $Rh_2Cl_2(CO)_4$. Comparison of the Xα–SW electronic structure with that since obtained for $Rh_2Cl_2(CO)_4$ by an HF LCAO method reveals a number of similarities.

Introduction

J.G.N. and D.J.G. have previously[2] reported calculations of $Rh_2Cl_2(CO)_4$ (I). Our chief goal at that time was to present the simple orbital explanation revealed by the calculations for the observed folding of this type of molecule along the bridging ligand axis. No spectroscopic data were then available with which to compare the calculations. J.F.N., R.J.S., and M.J.T. have now obtained the UV photoelectron spectra of $Rh_2Cl_2(CO)_4$ and $Rh_2Cl_2(PF_3)_4$, as part of a systematic comparison of such spectra for analogous CO and PF_3 complexes.[3-5] In this paper we report these spectra and use the Xα–SW predictions of ionization energies to assign them. We also comment on two recent papers which deal with the electronic structure of $Rh_2Cl_2(CO)_4$, the first reporting the



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