might be 5-coordinate Si, but more probably there is 6-coordinate Si with Si–F–Si bridging, as has been suggested for $(CH_3)_3N\cdot SiF_4$.[3]

Mutual Displacements and Exchange Reactions. The action of SiF_4 on $SiCl_4\cdot 4TMAO$ was complicated by halogen exchanges, but the resulting mixture of volatiles included $SiCl_4$, which must have been displaced by SiF_4. Similarly, $SiCl_4$ displaced some SiF_4 from its TMAO adducts, leading to empirical formulas such as $SiCl_{1.61}F_{2.40}(TMAO)_{2.14}$ and $SiCl_{1.99}F_{2.01}(TMAO)_{2.59}$. The correlation of higher chloride content with larger TMAO:SiX_4 ratios may not be accidental. More directly, TMAO with $SiCl_2F_2$ in slight excess gave a precipitate (from $HCCl_3$) formulated as $SiCl_{1.9}F_{2.1}(TMAO)_{3.4}$; here the high ratio of TMAO to Si implies a course of reaction influenced more by Cl than by F, but again with much halogen scrambling in the remaining volatile material.

Also, HCl penetrated solid $SiCl_4\cdot 4TMAO$, liberating 80% of the $SiCl_4$ and removing some TMAO from the rest. Action by HCl on $SiF_4\cdot TMAO$ led to halogen scrambling, with volatile products including Cl_3SiF, Cl_2SiF_2, and probably $ClSiF_3$ (not easily separable from the excess HCl). Such scrambling reactions were not unexpected in view of similar effects when H_nSiCl_{4-n} combined with $(CH_3)_3N$.[4,5]

Theory of Bond Energetics. The displacement reactions indicate that TMAO bonds with about equal strength to $SiCl_4$, SiF_4, and their scramble products. Such a similarity was not expected in view of the wide differences between $SiCl_4$ and SiF_4 bonded to other bases, as judged by the following examples: $SiF_4\cdot N(CH_3)_3$, 6 mm decomposition pressure at 0 °C;[6] $SiCl_4\cdot N(CH_3)_3$, liquid $SiCl_4$ appears at −55 °C;[5] $SiF_4\cdot 2P(CH_3)_3$, liquid $P(CH_3)_3$ appears at −50 °C;[7] $SiCl_4\cdot 2P(CH_3)_3$, <2 mm observed pressure at 25 °C.[7]

The energetics of formation of all such acid–base (a·b) adducts are best discussed in terms of the cycle

$$\Delta H_f = V_a + V_b + A_a + A_b - B - C$$

For the present comparison, we may neglect the enthalpies of vaporization V_a and V_b and the small bond-angle adjustment energy A_b for each base. The energy cost A_a of Lewis-acid bond adjustments may be less for SiF_4 than for $SiCl_4$, for which Cl–Cl steric compression is serious, and the solid-state (vapor condensation) energy C also may favor $SiF_4\cdot$base adducts because the dative-bond dipoles will be closer together for stronger attraction between adjacent molecules. Then the wild variable here must be B, which is the b→a dative-bond energy.

Most important for B is the quality of the bond-orbital overlap, for which the hard–soft acid–base concept may be too simple. Good overlap can occur between deep, narrow orbitals or between wide, shallow orbitals, but not between these different shapes. In $(CH_3)_3N$ the lone-pair $2sp^3$ electrons can bond fairly well to SiF_4, wherein strong electron withdrawal by F makes the acceptor orbital deeper and narrower than in $SiCl_4$. The $(CH_3)_3P$ lone-pair electrons have more s character on a larger atom, for poor overlap with SiF_4 but far better with $SiCl_4$.

What is unusual in TMAO is the single-bonded oxygen atom, with any of its three lone electron pairs able to employ almost any combination of s and p orbitals, which may be ideal for a wide variety of Lewis acids, including the very different $SiCl_4$ and SiF_4. With strong donor-bonding action due to the negative charge on oxygen, and with V_b not too high, the overlap versatility of TMAO should lead to many stable Lewis-acid adducts not yet reported in the literature.

Experimental Procedures and Details

General Methods. All volatiles were managed by modified Stock-type high-vacuum methods, with U-tubes and mercury float valves in series for separation of Cl–Si–F compounds by fractional condensation at pressures near 1 mm. At such low pressures, $ClSiF_3$ and SiF_4 were not separable, but the amount of each in a binary mixture could be calculated from the molecular weight. When HCl was a third component, a chloride analysis gave enough further information. The method was gravimetric, with HF added to prevent silicic acid from interfering with true weighing of AgCl. The same method was used for determining excess $SiCl_4$ after the reaction with TMAO in $HCCl_3$.

Formation of TMAO Adducts. TMAO in a weighed reaction bulb (with attached stopcock and ground joint leading to the vacuum line) was dehydrated first by evacuation at 40 °C and then by repeated high-vacuum sublimation until no more water came off. Now a measured gas volume of the silicon halide could be brought in, either for contact with the fine crystals or for absorption by a solution. The volatiles were assayed for proof of the formula of the precipitate. For experiments with SiX_4 always in excess, the TMAO solution was slowly dropped into the SiX_4 solution, from a side arm with a stopcock and swivel joint, all under vacuum conditions. After removal of all volatiles, the gain in weight of the reaction tube served as a recheck of the stoichiometry.

Displacement Processes. After 1.316 mmol of $SiCl_4$ had acted on a precipitate composed of 1.451 mmol of TMAO and 1.274 mmol of SiF_4 (4 h at 85 °C), the remaining volatiles (in millimoles) were as follows: SiF_4, 0.359; $ClSiF_3$, 0.236; Cl_2SiF_2, 0.402; Cl_3SiF, 0.527; $SiCl_4$, 0.389. The solid formula was $SiCl_{1.61}F_{2.40}(TMAO)_{2.14}$. With milder heating, another experiment employed $SiF_4\cdot 1.54TMAO$ with equimolar $SiCl_4$ in four nearly equal portions, each time with removal of the volatiles and return of the Cl-rich fractions. This was the experiment that gave the empirical formula of the solid as $SiCl_{1.99}F_{2.01}(TMAO)_{2.59}$. For the experiment leading to the formula $SiCl_{1.9}F_{2.1}(TMAO)_{3.4}$, pure $SiCl_2F_2$ (having the right molecular weight and volatility) was available from earlier experiments. Again there was halogen scrambling; the remaining volatiles (in millimoles) were as follows: SiF_4, 0.015; $ClSiF_3$, 0.136; Cl_2SiF_2, 0.083; Cl_3SiF, 0.158; $SiCl_4$, 0.046.

The displacement of $SiCl_4$ from $SiCl_4\cdot 4TMAO$ by SiF_4 was observed only qualitatively, with the usual halogen scrambling.

These displacement experiments indicate that all five $SiCl_nF_{4-n}$ compounds bond about equally well to TMAO.

Molecular Weights in Solution. Vapor pressure lowering by TMAO in the solvents $HCCl_3$, HCF_2Cl, and H_2CCl_2 gave the average molecular weights in those solvents. The procedure was much like that employed earlier for $(CH_3)_3NSO_2$ in liquid SO_2,[8] but with uncertainties on the order of 10%. In $HCCl_3$ at 19 °C, the mole fraction x was 0.038 (calculated for monomer, 0.075). In HCF_2Cl at −62 °C, $x = 0.014$ (calculated for monomer, 0.032). In H_2CCl_2 at 0 °C, $x = 0.032$ (calculated for monomer, 0.028). Equilibria of the monomer with some dimer, or vice versa, cannot be excluded.

Retention of TMAO Identity. The present results have validity only if TMAO retains its molecular identity when it reacts with the SiX_4 compounds—as it does not when its C–H and N–O bonds are broken in its reaction with SO_2.[9] Also, recent work in this laboratory has shown that it oxidizes PF_3 or $(CF_3)_3P$. The adduct $TMAO\cdot(CF_3)_3PO$ promptly decomposes to give some HCF_3.

When some of the $TMAO\cdot SiX_4$ adducts were treated under vacuum conditions with aqueous KOH (slightly beyond the neutral point), it was possible to pump off the water and sublime off as much as 79% of the original TMAO. Also, granular aluminum acting on one of the basic solutions gave a 68% yield of pure $(CH_3)_3N$ (proved by quantitative conversion to the pure BH_3 complex)—a result that would not have been possible for any $(CH_3)_2NCH_2X$ compound.

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Preparation and Structure of the Dimolybdenum(III) Compound $Mo_2Cl_6(PEt_3)_4$. An Anomaly in Metal–Metal-Bonded Edge-Sharing Bioctahedral Compounds

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The synthetic and structural chemistry of dinuclear transition-metal compounds containing direct metal–metal bonds has been actively investigated for over thirty years.[1] Of interest here

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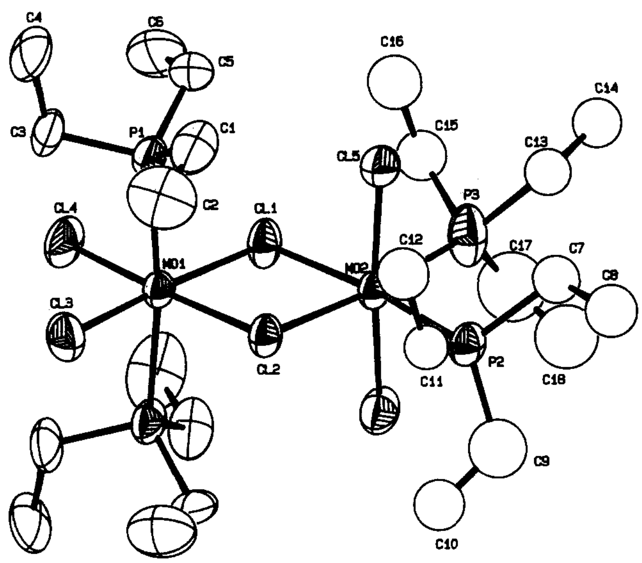
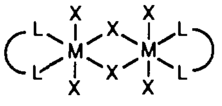


Figure 1. ORTEP view of the $Mo_2Cl_6(PEt_3)_4$ molecule with the atomic numbering scheme employed. Only one orientation of the disordered phosphine ligands bonding through P(2) and P(3) is shown for clarity.

are the edge-sharing bioctahedral complexes with M_2^{6+} cores, representative structures of which are illustrated in I–III (X = anionic ligand; L = neutral monodentate ligand; L-L = neutral bidentate ligand).[2] Note that, in compounds of formula $M_2X_6L_4$, the neutral donors normally occupy axial sites on one metal center and equatorial sites on the second (type II).[3] Examples of the latter include $Ta_2Cl_6(PMe_3)_4$ (d^2–d^2),[4] $Cr_2Cl_6(PEt_3)_4$,[5] $W_2Cl_6(PEt_3)_4$,[6] and $W_2Cl_6py_4$[7] (d^3–d^3), and $Ru_2Cl_6(PBu_3)_4$ (d^5–d^5).[8]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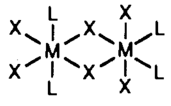
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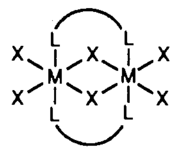
III

For the group 6 derivatives the six available metal electrons can be involved in a direct metal–metal bonding of type $\sigma^2\pi^2\delta^2$ or $\sigma^2\pi^2\delta^{*2}$, depending on the nature of the bridging ligands.[9] $W_2Cl_6(PEt_3)_4$ is diamagnetic and exhibits a strong metal–metal interaction (W–W = 2.7397 (7) Å).[6] However, the corresponding chromium compound is paramagnetic with a nonbonding Cr–Cr separation of 3.637 (2) Å.[5] The question of whether the corresponding molybdenum(III) complex would or would not have a metal–metal bond stimulated the present investigation.[10] Although derivatives of formula $[MoCl_3(PR_3)_2]_n$ (R = Me, Et) have been mentioned briefly by Carmona et al.,[11] no compound with a $Mo_2Cl_6(PR_3)_4$ stoichiometry has been structurally characterized. Molybdenum(III) dimers of type I and III, however, are well-known, and these show Mo–Mo distances in the range 2.5–2.8 Å.[2]

Table I. Positional Parameters and *B*(eq) for $Mo_2Cl_6(PEt_3)_4$

atom	*x*	*y*	*z*	*B*(eq),[a] Å²
Mo(1)	0.09056 (6)	$^1/_4$	0.0928 (1)	4.09 (7)
Mo(2)	−0.06141 (6)	$^1/_4$	−0.1029 (1)	4.03 (7)
Cl(1)	0.0615 (2)	$^1/_4$	−0.1334 (4)	5.4 (2)
Cl(2)	−0.0300 (2)	$^1/_4$	0.1261 (4)	4.6 (2)
Cl(3)	0.1090 (2)	$^1/_4$	0.3135 (4)	6.4 (3)
Cl(4)	0.2045 (2)	$^1/_4$	0.0447 (5)	7.0 (3)
Cl(5)	−0.0643 (2)	0.1267 (2)	−0.1123 (3)	6.4 (2)
P(1)	0.0979 (2)	0.1158 (2)	0.0999 (4)	6.0 (2)
P(2)	−0.1811 (2)	$^1/_4$	−0.0339 (4)	5.0 (2)
P(3)	−0.0740 (3)	$^1/_4$	−0.3409 (5)	7.9 (4)
C(1)	0.0278 (7)	0.0679 (7)	0.168 (2)	8 (1)
C(2)	0.014 (1)	0.081 (1)	0.303 (2)	12 (1)
C(3)	0.1698 (7)	0.0918 (7)	0.194 (2)	8 (1)
C(4)	0.183 (1)	0.0126 (8)	0.206 (2)	13 (2)
C(5)	0.1068 (8)	0.0690 (8)	−0.049 (1)	8 (1)
C(6)	0.168 (1)	0.089 (1)	−0.122 (2)	13 (1)
C(7)	−0.234 (1)	0.195 (1)	−0.144 (2)	6.9 (7)*
C(8)	−0.306 (2)	0.191 (2)	−0.096 (3)	8.5 (8)*
C(9)	−0.222 (2)	0.336 (2)	−0.007 (4)	11 (1)*
C(10)	−0.197 (2)	0.376 (2)	0.092 (3)	8 (1)*
C(11)	−0.195 (1)	0.208 (1)	0.128 (2)	6.0 (6)*
C(12)	−0.177 (2)	0.136 (2)	0.142 (3)	8 (1)*
C(13)	−0.137 (2)	0.179 (2)	−0.393 (3)	6.7 (8)*
C(14)	−0.136 (1)	0.165 (2)	−0.540 (3)	7.5 (7)*
C(15)	0.001 (2)	0.212 (1)	−0.418 (3)	7.8 (7)*
C(16)	0.019 (2)	0.137 (2)	−0.391 (3)	9.1 (9)*
C(17)	−0.086 (3)	0.322 (3)	−0.437 (5)	15 (2)*
C(18)	−0.146 (3)	0.350 (3)	−0.424 (5)	12 (2)*

[a] Starred values belong to atoms whose positions were refined isotropically with a site occupancy of 0.5.

Table II. Intramolecular Distances (Å) and Angles (deg) for $Mo_2Cl_6(PEt_3)_4$

	Distances		
Mo(1)–Cl(1)	2.479 (4)	Mo(2)–Cl(1)	2.524 (4)
Mo(1)–Cl(2)	2.481 (4)	Mo(2)–Cl(2)	2.518 (4)
Mo(1)–Cl(3)	2.378 (5)	Mo(2)–Cl(5)	2.384 (3)
Mo(1)–Cl(4)	2.375 (5)	Mo(2)–P(2)	2.546 (4)
Mo(1)–P(1)	2.596 (3)	Mo(2)–P(3)	2.545 (6)
	Angles		
Cl(1)–Mo(1)–Cl(2)	84.4 (1)	Cl(1)–Mo(2)–Cl(5)	91.07 (9)
Cl(1)–Mo(1)–Cl(3)	175.2 (2)	Cl(1)–Mo(2)–P(2)	170.6 (2)
Cl(1)–Mo(1)–Cl(4)	91.4 (2)	Cl(1)–Mo(2)–P(3)	88.4 (2)
Cl(1)–Mo(1)–P(1)	92.4 (1)	Cl(2)–Mo(2)–Cl(5)	92.7 (1)
Cl(2)–Mo(1)–Cl(3)	90.9 (2)	Cl(2)–Mo(2)–P(2)	88.0 (1)
Cl(2)–Mo(1)–Cl(4)	175.8 (2)	Cl(2)–Mo(2)–P(3)	171.1 (2)
Cl(2)–Mo(1)–P(1)	93.02 (8)	Cl(5)–Mo(2)–Cl(5)′	174.4 (2)
Cl(3)–Mo(1)–Cl(4)	93.4 (2)	Cl(5)–Mo(2)–P(2)	89.36 (9)
Cl(3)–Mo(1)–P(1)	87.8 (1)	Cl(5)–Mo(2)–P(3)	87.5 (1)
Cl(4)–Mo(1)–P(1)	87.14 (8)	P(2)–Mo(2)–P(3)	101.0 (2)
P(1)–Mo(1)–P(1)′	172.6 (2)	Mo(1)–Cl(1)–Mo(2)	96.4 (1)
Cl(1)–Mo(2)–Cl(2)	82.7 (1)	Mo(1)–Cl(2)–Mo(2)	96.5 (1)

We report here the synthesis and structural characterization of the compound $Mo_2Cl_6(PEt_3)_4$, the first dinuclear compound of molybdenum(III) with structure II. The key result of our structural study is that, in contrast to reported type I and type III dimolybdenum(III) complexes, $Mo_2Cl_6(PEt_3)_4$ *does not exhibit a significant metal–metal interaction.*

Results and Discussion

Compound $Mo_2Cl_6(PEt_3)_4$ has been obtained by reacting $MoCl_3(THF)_3$ with 2 equiv of the phosphine in THF, followed by evaporation to dryness and brief reflux (ca. 10 min) of the residue in toluene. A longer thermal treatment results in partial decomposition. The compound crystallizes from the toluene so-

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(3) However, the (d^1–d^1) zirconium(III) chloro–phosphine complexes $Zr_2Cl_6(PR_3)_4$ (R = *n*-Bu, Et; R_3 = Me_2Ph) adopt eq,eq,eq,eq rather than eq,eq,ax,ax structures. See: (a) Wengrovius, J. H.; Schrock, R. R.; Day, C. S. *Inorg. Chem.* **1981**, *20*, 1844. (b) Cotton, F. A.; Diebold, M. P.; Kibala, P. A. *Inorg. Chem.* **1988**, *27*, 799.

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lution upon cooling to yield well-formed, slightly air-sensitive, golden brown crystals. The molybdenum(III) mononuclear compound $MoCl_3(PEt_3)_2(THF)$ is probably the product of the first step. Similar compounds have been previously described.[12] During the thermal treatment in toluene, a THF molecule is probably lost, resulting in dimer formation (see eq 1). This

$$MoCl_3(THF)_3 + 2PEt_3 \xrightarrow{THF/rt} MoCl_3(PEt_3)_2(THF) \xrightarrow[-THF]{toluene/\Delta} Mo_2Cl_6(PEt_3)_4 \quad (1)$$

reactivity parallels the one recently reported by us for MoX_3(dppe)(THF) [X = Cl, Br; dppe = bis(diphenylphosphino)ethane], where the Mo_2X_6(dppe)$_2$ compounds of structure I are obtained.[13]

The X-ray molecular structure of $Mo_2Cl_6(PEt_3)_4$ is shown in Figure 1. The positional and equivalent isotropic displacement parameters are listed in Table I, and selected bond distances and angles are assembled in Table II. Like the other systems of stoichiometry $M_2X_6L_4$ listed above, this compound adopts the configuration with two axial and two equatorial neutral donors. The metal–metal separation is 3.730 (1) Å, indicative of little or no interaction between the metal centers. The lack of strong interaction is also indicated by the large Mo(1)–Cl–Mo(2) angles [average 96.4 (1)°]. Among the Mo–Cl distances the following, expected trends, which are a combination of terminal vs bridging bond strength and trans influence effects, are observed: terminal [average 2.379 (5) Å] < bridging, trans to Cl [average 2.480 (4) Å] < bridging, trans to P [average 2.521 (4) Å]. For the Mo–P distances, the trans-to-P distance [2.596 (3) Å] is longer, as expected, than the trans-to-Cl distances [average 2.546 (6) Å].

Compound $Mo_2Cl_6(PEt_3)_4$ is paramagnetic. The room-temperature magnetic susceptibility in the solid state corresponds to an effective magnetic moment of 5.05 μ_B/dimer or 3.57 μ_B/Mo atom, which is lower than the expected value for magnetically dilute Mo^{3+} centers. Either a direct metal–metal interaction or a through-the-bridge antiferromagnetic exchange could explain the reduced magnetic moment. On the basis of the long Mo–Mo distance, the latter explanation would seem to be the more logical one. Variable-temperature magnetic studies for $Mo_2Cl_6(PEt_3)_4$ and for $Cr_2Cl_6(PEt_3)_4$ are planned for the near future.[14] It seems safe to conclude, however, that the reason for compound $Mo_2Cl_6(PEt_3)_4$ not having a strong Mo–Mo bond has to do with the stabilization of the $t_{2g}{}^3$ configuration in a pseudooctahedral Mo(III) center vs the stabilization that can be attained by forming the Mo–Mo bond. The same argument can be used to rationalize the lack of bonding in the chromium compound[5] and the strong bonding in the tungsten compound.[6]

This situation is reminiscent of the face-sharing bioctahedral group 6 $M_2X_9{}^{3-}$ anions and derivatives,[15] where the magnetic properties range from the magnetically dilute Cr^{3+} in the $Cr_2{}^{6+}$ species to the diamagnetic behavior (only small TIP) of the $W_2{}^{6+}$ species, the corresponding $Mo_2{}^{6+}$ species exhibiting intermediate behavior. Concerning the various Mo(III) dimers, we observe that the face-sharing bioctahedral geometry allows a closer approach of the two metals toward each other with respect to the edge-sharing bioctahedral geometry, favoring a stronger direct interaction and ultimately a further reduction of the magnetic susceptibility. In fact, the room-temperature effective magnetic moment per Mo atom in selected compounds are (Mo–Mo distance in brackets) 0.6 μ_B for $Cs_3[Cl_3Mo(\mu\text{-}Cl)_3MoCl_3]$[16] [2.655 (11) Å],[17] 0.8 μ_B for $Cs_3[Br_3Mo(\mu\text{-}Br)_3MoBr_3]$[16] [2.816 (9) Å],[17] and 1.29 μ_B for $NMe_4[(PMe_3)I_2Mo(\mu\text{-}I)_3MoI_2(PMe_3)]$ [3.021 (4) Å].[18] For the edge-sharing bioctahedral $Mo_2Cl_6(PEt_3)_4$ molecule described here, the Mo–Mo separation is longer [3.730 (1) Å] and the room-temperature magnetic moment higher (3.57 μ_B/Mo atom).

It is interesting to observe that the Mo_2Br_6(dppe)$_2$ derivative of structure I (showing a strong metal–metal interaction) can be reconverted to the mononuclear THF adduct when refluxed in THF.[13a] This effect has been attributed to a slightly longer, and presumably weaker, Mo–Mo bond due to the larger size of the bridging bromo ligands, with respect, for instance, to the corresponding chloro-bridged dimer.[19] In this respect one would predict that $Mo_2Cl_6(PEt_3)_4$ should also easily break down to mononuclear species in a donor solvent. $Mo_2Cl_6(PEt_3)_4$ is stable in THF at room temperature for a short period of time. Brief warming to the reflux temperature or standing at room temperature for a longer period of time causes a reaction to take place, but the product(s) of this reaction is (are) different from the $MoCl_3(PEt_3)_2(THF)$ precursor, as shown by UV/vis spectroscopy. The interaction of $Mo_2Cl_6(PEt_3)_4$ with additional PEt_3 also generates a change in the UV spectrum. However, $Mo_2Cl_6(PEt_3)_4$ has been obtained in moderate yields, according to the procedure outlined in eq 1, by using a $PEt_3/MoCl_3(THF)_3$ ratio of 3:1. In fact, the product, including the crystal for the X-ray study, was obtained for the first time by this procedure.

It is indeed striking that such a slight change in the molecular formula (e.g. 2 mol of a bidentate ligand vs 4 mol of a monodentate one) causes such a dramatic change in the metal–metal interaction. One important difference between the various structures is the relative disposition of the neutral ligands: eq,eq,eq,eq in Mo_2Cl_6(dppe)$_2$ (Mo–Mo = 2.762 (1) Å),[19] ax,ax,eq,eq in $Mo_2Cl_6(PEt_3)_4$ (Mo–Mo = 3.730 (1) Å), and ax,ax,ax,ax in Mo_2Cl_6(dppm)$_2$ [Mo–Mo = 2.789 (1) Å; dppm = bis(diphenylphosphino)methane].[9b] Other differences are the presence of bidentate vs monodentate ligands and aryl vs alkyl groups. A detailed analysis of all the electronic and steric factors requires the structural characterization of a more extensive body of compounds, as well as theoretical calculations, possibly accompanied by detailed magnetic studies. These are ongoing in other laboratories.[14]

The bonding/nonbonding situation that we have described here for Mo(III) dimers of structures I/II/III is reminiscent of a similar situation encountered for rhenium, where a strong bonding interaction [Re–Re = 2.616 (1) Å] was observed for Re_2Cl_6(dppm)$_2$, of structure III,[20] compared with the weak interaction [Re–Re = 3.809 (1) Å] in Re_2Cl_6(dppe)$_2$, of structure I.[21] Since the usual occurrence in edge-sharing bioctahedral molecules of second- and third-row transition metals is that of strong M–M bonding, the Re_2Cl_6(dppe)$_2$ molecule (the only exception to this rule until the start of the present investigation) had been described as a *puzzling anomaly*.[2] There is no complete agreement yet as to the causes of this "anomaly".[2,22] The two rhenium molecules mentioned above have the important difference that in one, that is the type III molecule, the two metal atoms are buttressed by the two dppm ligands. The comparison between $Mo_2Cl_6(PEt_3)_4$ (type II, long Mo–Mo separation) and Mo_2Cl_6(dppe)$_2$ (type I, short Mo–Mo separation) is even more striking in that both molecules are unbuttressed. Until an explanation for this difference is found, the $Mo_2Cl_6(PEt_3)_4$ molecule can be regarded as a second puzzling anomaly,[2] as far as metal–metal bonding in edge-sharing bioctahedral compounds goes.[23]

Experimental Section

All operations were carried out under an atmosphere of dinitrogen. Solvents were dehydrated by conventional methods and distilled under

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Table III. Crystal Data for $Mo_2Cl_6(PEt_3)_4$

formula	$C_{24}H_{60}Cl_6Mo_2P_4$
fw	877.23
space group	*Pnma*
a, Å	20.368 (2)
b, Å	19.308 (2)
c, Å	10.6404 (7)
V, Å^3	4185 (1)
Z	4
d_{calc}, g/cm^3	1.39
μ(Cu Kα), cm^{-1}	101.83
radiation (monochromated in incident beam)	Cu Kα (λ = 1.541 78 Å)
temp, °C	20
transm factors: max, min	1.000, 0.641
R^a	0.052
R_w^b	0.072

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

dinitrogen prior to use. Instruments used were as follows: FTIR, Nicolet 5DXC; magnetic susceptibility balance, Johnson Matthey; UV/vis, Schimadzu UV-240, X-ray diffractometer, Enraf-Nonius CAD-4. The elemental analysis was by Midwest Microlab, Indianapolis, IN. $MoCl_3(THF)_3$ was prepared according to the literature.[24] PEt_3 was purchased from Strem Chemicals and used as received.

Preparation of $Mo_2Cl_6(PEt_3)_4$. $MoCl_3(THF)_3$ (0.62 g, 1.47 mmol) was reacted with PEt_3 (0.45 mL, 3.05 mmol) in 10 mL of THF. After being stirred for 2 h, the clear yellow solution was evaporated under reduced pressure to a residue. After addition of toluene (10 mL), the resulting yellow-orange solution was refluxed for 10 min. The color of the solution turned dark pine green. Golden brown crystals of the pure product crystallized upon cooling to room temperature. Yield: 0.31 g (48%). An additional crop (0.06 g) was obtained by cooling the mother solution to −20 °C. Anal. Calcd for $C_{24}H_{60}Cl_6Mo_2P_4$: C, 32.9; H, 6.9; Cl, 24.2; P, 14.1. Found: C, 33.2; H, 6.9; Cl, 23.2; P, 13.5. $\chi_g = 11.69 \times 10^{-6}$ cgsu; $\mu_{eff} = 5.05\ \mu_B$ (molar diamagnetic correction -480×10^{-6} cgsu).

IR (Nujol mull; cm^{-1}): 1420 m, 1280 w, 1265 m, 1045 s, 765 s, 750 sh, 735 m, 720 s. UV/vis [toluene; nm (ϵ/cm^{-1} mol^{-1} L)]: 302 (9200), 345 (6000), 370 (5500), 606 (340).

X-ray Crystallography. A single crystal was glued to the inside of a thin-walled glass capillary, which was then sealed under dinitrogen and mounted on the diffractometer. The cell determination, data collection and reduction, and semiempirical absorption correction[25] were routine. Systematic absences from the data indicated the space group as either *Pnma* or *Pn*2$_1$*a* (nonstandard setting of *Pna*2$_1$). The centrosymmetric choice was suggested by intensity statistics and was adopted for the refinement. The successful refinement shows that this was the correct choice. The structure was solved by direct methods and refined by alternate full-matrix least-squares cycles and difference Fourier maps. The two equatorial phosphine ligands [those binding through atoms P(2) and P(3)] had all the ethyl groups disordered among two symmetry-related positions. All the carbon atoms of these groups were refined at half-occupancy and were left isotropic. Hydrogen atoms were not included in the refinement. Selected crystal data are in Table III, positional and equivalent isotropic thermal parameters are listed in Table I, and selected bond distances and angles are assembled in Table II.

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Supplementary Material Available: For $Mo_2Cl_6(PEt_3)_4$, full tables of crystal data, anisotropic displacement parameters, and bond distances and angles (4 pages); tables of observed and calculated structure factors (19 pages). Ordering information is given on any current masthead page.

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Syntheses of *closo*-1-Methylphosphadodecaborane(12), $B_{11}H_{11}PCH_3$, and *nido*-7-Methylphosphaundecaborane(13), $B_{10}H_{12}PCH_3$, from the $[B_{11}H_{13}]^{2-}$ Anion and Their Molecular Structures

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The anion $[B_{11}H_{14}]^-$ can function as both a Brønsted base and a Brønsted acid. Protonation[1] of $[B_{11}B_{14}]^-$ at low temperature yields *nido*-undecaborane(15), $B_{11}H_{15}$, while deprotonation[2] yields the tridecahydroundecaborate(2−) dianion, $[B_{11}H_{13}]^{2-}$. Recently reported syntheses[3] of alkali-metal salts of $[B_{11}H_{14}]^-$ from the reaction of pentaborane(9), B_5H_9, with MH (M = Na, K) provide a good source for obtaining $[B_{11}H_{13}]^{2-}$ in a relatively simple way and have prompted renewed studies of the chemistry of this dianion. From the reaction of $[B_{11}H_{13}]^{2-}$ with $P(CH_3)Cl_2$ in tetrahydrofuran we have obtained *closo*-1-methyl-phosphadodecaborane(12), $B_{11}H_{11}PCH_3$. However, from the reaction in diethyl ether, *nido*-7-methylphosphaundecaborane(12), $B_{10}H_{12}PCH_3$, was obtained, a phosphaborane prepared previously by a different route.[4] While molecular structures of these types of phosphaboranes have been proposed based upon ^{11}B NMR spectra, no actual structure determinations have been reported. In the present report, syntheses of $B_{11}H_{11}PCH_3$ and $B_{10}H_{12}PCH_3$ and their molecular structures as determined by single-crystal X-ray analyses are described.

Experimental Section

Materials were handled by using standard vacuum-line and inert-atmosphere techniques. B_5H_9 (Callery Chemical Co.) was purified by passing it through a U-trap maintained at −78 °C and collected in a second U-trap cooled to −111 °C. NaH (Aldrich) was obtained as a mineral oil dispersion. The oil was washed away with dry pentane, and the hydride was stored in a controlled-atmosphere glovebox until use. Glyme (1,2-dimethoxyethane), tetrahydrofuran (THF), and toluene were distilled from sodium benzophenone ketyl before use. Hexane was distilled from CaH_2 before use. ^{11}B and 2D ^{11}B–^{11}B NMR (δ($Et_2O{\cdot}BF_3$) = 0.00 ppm), ^{1}H (δ(TMS) = 0.00 ppm), and ^{31}P (δ(H_3PO_4) = 0.00 ppm) NMR spectra were obtained on a Bruker MSL-300 NMR spectrometer. Infrared spectra were obtained on a Mattson Cygnus 25 spectrometer. Mass spectra were obtained on VG 70-250S and Kratos MS-30 mass spectrometers.

X-ray diffraction data were collected with an Enraf-Nonius CAD4 diffractometer. Crystallographic parameters are given in Table I. Computations were carried out on a PDP 11/44 computer using the SDP structure determination package. All data were corrected for Lorentz and polarization effects, and the structures were solved by a combination of the direct-method MULTAN 11/82 and difference Fourier techniques with analytical atomic scattering factors used throughout. Full-matrix least-squares refinements were employed.

$[B_{11}H_{13}]^{2-}$. From the reaction of NaH with B_5H_9 in glyme $Na[B_{11}H_{14}]$ (10.35 mmol) was prepared according to a previously reported procedure.[2] Then, in the glovebox, NaH (282.3 mg, 88% activity, 10.53 mmol of active NaH) was added to a tip tube attached to the reaction vessel containing the $Na[B_{11}H_{14}]$. Glyme (20 mL) was condensed into the flask at −196 °C. The vessel was allowed to warm to room temperature until all the $Na[B_{11}H_{14}]$ had dissolved. Then the tip tube was tilted so as to introduce the NaH into the solution. The resulting slurry was stirred for

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