duality. A more extensive series should provide an incisive picture of how to sterically and perhaps electronically promote fragmentation in this prototype cluster class.

For all monomers to be 17-electron[9] complexes, an η^1-allyliron interaction should be present only in $C_3H_5Fe(CO)_3$(hexene) and probably the butyne analog[6] although there is a possible continuum of idealized forms that range from symmetrical η^3-allyl to η^1-allyl. ESR spectra for most complexes (solution state) exhibited the same triplet hyperfine structure, arising from two magnetically equivalent hydrogen atoms, presumably the anti[10] set in η^3-allyl and the aliphatic set in η^1-allyl forms,[11] in addition to a phosphorus doublet in phosphine and phosphite derivatives. The spin-orbit contribution to the isotropic g values (Table I), which to a first approximation reflects the ligand field strength around iron, varies only slightly (~10% maximum) with ligand variation which invariance mirrors the *relative* constancy of the iron–iron bond energies.

Relatively large variations in g_0 with temperature were observed, e.g., g_0 for B varied from 2.0459 to 2.0423 in the +25 to −94° range. This effect could be due to an equilibrium between isomers (vide infra) or specific outer sphere solvation[12] but the crucial point here is that the effects have no significant influence on the monomer-dimer equilibrium since there were no deviations from linearity in the ln K vs. $1/T$ plot over 90–130° ranges.

Definitive evidence for the presence of isomers in mononuclear complexes in frozen solutions (glasses) was obtained. In many cases, the ESR spectra of glasses comprised the superposition of signals from two different species with different sets of $g_{\parallel}$ and $g_{\perp}$ (see Table I). Whenever an accurate interpretation of these spectra was possible,[13] the more intense signal had $g_{\parallel} < g_{\perp}$. For complexes with the hexenes, the less intense signal was also characterized by $g_{\parallel} < g_{\perp}$, but for the remaining compounds the order was $g_{\parallel} > g_{\perp}$. In frozen solutions of A in 2-butyne, the two species interconverted rapidly on the ESR time scale at −90° *in the solid state* as seen from the collapse of the overlapping anisotropic spectra to a single isotropic line which was the same as in liquid solutions. A similar phenomenon was observed for B at defects in the crystals of A, where the collapse of the anistropic spectrum to the isotropic line occurred above −30°. Such interconversion processes in the solid state show that the two species observed at low temperature are two isomers of the same composition. For $C_3H_5Fe(CO)_2P(C_6H_5)_3$ in toluene glass, both isomers exhibited triplet hyperfine structure from two equivalent protons but with different values of A_H.

We defer discussion of the nature of the isomers and their unusual fluxional characteristics until X-ray crystal structure determinations for dimeric and monomeric forms and theoretical calculations[14] have been completed. Substituted allyl analogs are being synthesized so that ESR characterization of η^3- and η^1-allyl interactions may be definitive and the catalytic chemistry of the monomeric paramagnetic species is under investigation with respect to scope and mechanism.

Acknowledgment. We gratefully acknowledge support of this research by the National Science Foundation (E.L.M.) and also by the Foundation and the Academy of Sciences of the U.S.S.R. in the Joint U.S.-U.S.S.R. Program in Chemical Catalysis (K.I.Z.).

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(3) (a) H. D. Murdock and E. A. C. Lucken, *Helv. Chim. Acta*, **47**, 1517 (1964). (b) $[C_3H_5Fe(CO)_3]_2$ appears quite stable in crystalline form at 25° but it does slowly decompose at 25° in pentane solvent.

(4) Concentration range was from 0.0003 to 0.1 *M* for total iron; concentration of monomer varied with temperature about three orders of magnitude for a specific total iron concentration.

(5) ESR spectra recorded during this reaction at −10° exhibited an isosbestic point. Accurate kinetic parameters for a variety of olefins are now being determined.

(6) 2-Butyne interaction is very fast compared to hexene adduct formation.

(7) (a) In the formation of this species in our catalytic system, a critical feature is presumed to be the $\eta^3 \rightleftharpoons \eta^1$ allyl interconversion. (b) Conversion to 2-hexene was about 60% after 1 hr. After 48 hr no 1-hexene could be detected by NMR techniques. No solvent was used in these reactions. (c) 1-Hexene isomerization also occurs in the H_2–A system where $C_3H_5FeH(CO)_3$ is probably present but the rate is lower than in the absence of hydrogen. (d) A possible mode of isomerization is η^1-$C_3H_5Fe(CO)_3$(1-hexene) $\rightleftharpoons$ η^1-$C_3H_5FeH'(\eta^1$-$CH_2CH{=}CHCH_2CH_2CH_3)(CO)_3$ $\rightleftharpoons$ η^1-$C_3H_5Fe(CH_2H'CH{=}CHCH_2CH_2CH_3)(CO)_3$ $\rightleftharpoons$ η^3-$C_3H_5Fe(CO)_3$ + 2-hexene. Labeled experiments are in progress to test such hypotheses. (e) With *trans*-3-hexene and A, no isomerization was detected after 2 days.

(8) Monomer–dimer interconversion is fast relative to adduct formation.

(9) In a formal accounting.

(10) Most structure determinations show these protons to be much closer to the metal than the others.

(11) (a) Rotation about the M–C bond is presumed to be fast in η^1-allyl iron. (b) The isotropic hyperfine coupling constants (Table I) are similar for both structures. The variation in a_H of ~30% as ligands were varied corresponds to an electron spin density change from 1.1 to 1.6%.

(12) A. N. Shupick, V. M. Novikov, and K. I. Zamaraev, *Dokl. Acad. Nauk, SSSR*, **214**, 629 (1974).

(13) Agreement between $\frac{1}{3}(g_{\parallel} + 2g_{\perp})$ and g_0 affords additional support for the correctness of the interpretation.

(14) R. Hoffmann. We acknowledge helpful discussions with R. H.

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Species with Strong Heteronuclear Metal–Metal Bonds. Dimers with Tungsten–Molybdenum Bonds of Order 3.5 and 4.0

Sir:

Heteronuclear metal-metal bonded species containing only two metal atoms are of great importance since they constitute the simplest systems in which the effects of substituting one metal atom for another can be studied in detail. Heteronuclear species with metal-metal bond order greater than unity should be especially interesting, but seldom have they been realized. A few years ago in this laboratory the heteronuclear carboxylate dimers $MoW(O_2CR)_4$ were prepared as constituents of mixtures containing the homonuclear molybdenum dimers $Mo_2(O_2CR)_4$.[1] Until recently the separation of such mixtures was unsuccessful.

In more recent work[2] it has been shown that selective iodination of a benzene solution of $Mo_2(O_2CC(CH_3)_3)_4$–$MoW(O_2CC(CH_3)_3)_4$ mixtures effected the desired separation by precipitation of $[MoW(O_2CC(CH_3)_3)_4]I$, essentially free of any corresponding dimolybdenum product. Infrared spectra and magnetic susceptibility data led to the conclusion that the precipitated iodide contained the one-electron oxidized cation $[MoW(O_2CC(CH_3)_3)_4]^+$. It was presumed that the structure and metal-metal bonding in this cation were entirely analogous with that in the compounds $[Mo_2(O_2CC(CH_3)_3)_4]^+I_3^-$[2] and $K_3Mo_2(SO_4)_4 \cdot 3.5H_2O$.[3] We now report the preparation[4] and molecular structure of $[MoW(O_2CC(CH_3)_3)_4]I \cdot CH_3CN$, and its reduction to $MoW(O_2CC(CH_3)_3)_4$, the first pure heteronuclear species containing a quadruple metal-metal bond.[5]

Surprisingly, solutions of $[MoW(O_2CC(CH_3)_3)_4]I$ in ac-

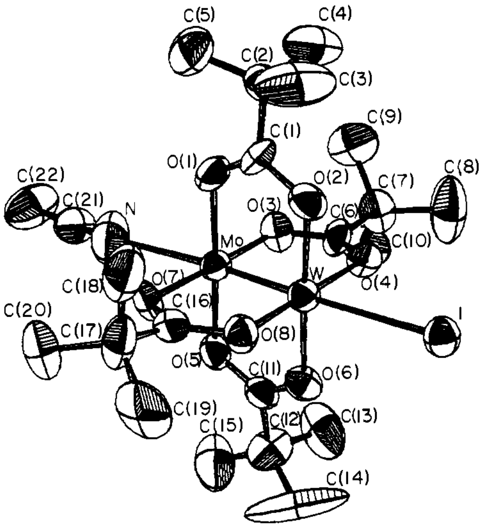

Figure 1. Structure and labeling scheme for the molecular unit [Mo-W($O_2CC(CH_3)_3$)$_4$]I·CH_3CN. Thermal ellipsoids enclose 50% of the electron density.

etonitrile appear to be stable indefinitely[6] in the absence of oxygen and water. On slow evaporation of such solutions red-brown crystals of the acetonitrile adduct are easily obtained. The crystals are orthorhombic with cell dimensions a = 35.59 (3), b = 36.22 (3), and c = 10.01 (1) Å, space group $Fdd2$, and $\rho_{\text{calcd}} = 1.76$ g cm^{-3} for 16 formula units per unit cell. Data were collected using an automated four-circle diffractometer with graphite monochromatized Mo Kα radiation within a 2θ sphere of 45°. Of the 3103 independent reflections checked, 2707 were used in the subsequent structure solution and refinement ($I > 3\sigma_I$). The positions of the three heaviest atoms in the molecular unit were located from analysis of a sharpened three-dimensional Patterson function. The remaining nonhydrogen atoms were located by successive structure factor and electron density map calculations. After refining all nonhydrogen atoms with anisotropic thermal parameters by full-matrix least-squares methods, H atoms were included as fixed atom contributions at 1.0 Å from the bound C atom, and isotropic thermal parameters of 10.0 Å^2 in the final refinement cycles. Refinement converged to final agreement indices of 0.051 and 0.071 for R and R_w, respectively.[7]

The remarkable structure of the molecular unit is depicted in Figure 1. Indeed, the most interesting and fortunate feature of the structure is the discrete molecular character with the I atom uniquely bonded to the W atom, d(W-I) = 3.054 (2) Å, and the N of acetonitrile very weakly bonded to the Mo atom, d(Mo-N) = 2.71 (2) Å, such that disordering of the metal atoms is prevented. The very short Mo-W bond distance, 2.194 (2) Å, is in full accord with the presumed bond order of 3.5 and compares quite favorably with d(Mo-Mo) = 2.164 (2) Å (average) previously reported for the Mo-Mo bond of order 3.5 in $K_3Mo_2(SO_4)_4$·$3.5H_2O$.[3] Other pertinent features of the molecular structure include the average bond distances Mo-O, 2.081 (13), and W-O, 2.064 (13) Å; the bond angles are Mo-W-I, 176.8 (1)°, W-Mo-N, 176.0 (6)°, W-Mo-O (average), 90.7 (3)°, and Mo-W-O (average), 90.7 (4)°. A calculation of deviations from the least-squares planes defined by W, Mo, O(3), O(4), O(7), O(8), C(6), C(16) and by W, Mo, O(1), O(2), O(5), O(6), C(1), C(11) shows that the O atoms bonded to W are in the eclipsed conformation with respect to those bonded to Mo; in particular none of the metal or oxygen atoms deviate from the respective planes by more than 0.02 Å. Thus all features of the structure substantiate the assessment of Mo-W bonding as involving seven electrons in the configuration $\sigma^2\pi^4\delta^1$. However, since iodine is uniquely bonded to tungsten and the W-O distances are at least as short as the Mo-O distances the structure suggests that the Mo-W bonding is polarized such that tungsten bears a higher formal charge or the Mo atom enjoys a greater portion of the bonding electron density. The unusually long Mo-N distance is further evidence of the latter assessment. Apparently the notable stability of [Mo-W($O_2CC(CH_3)_3$)$_4$]I and its CH_3CN adduct as compared to the dimolybdenum derivative, where only [$Mo_2(O_2CC(CH_3)_3)_4$]$^+I_3^-$ has been prepared,[2] can be attributed to this polar character, which should be expected to stabilize a discrete bond to halogen from the metal of higher formal charge. The acetonitrile adduct crystals are paramagnetic as expected, and provide a strong, virtually isotropic ESR spectrum with $\langle g \rangle$ = 1.873 (26 G peak to peak). In contrast to most strongly metal-metal bonded species the electronic spectrum in acetonitrile is relatively featureless with a strong band at 240 nm ($\epsilon \sim 15{,}000$) and a pronounced shoulder at 850 nm ($\epsilon \sim 100$).

Having established that the pure one-electron oxidized derivatives could be used as a vehicle to separate the heteronuclear species from the dimolybdenum coproducts, it was important to ascertain if the pure MoW(O_2CR)$_4$ could be obtained by reduction of the iodide derivative. The reaction was performed by stirring a solution of [MoW($O_2CC(CH_3)_3$)$_4$]I in acetonitrile with zinc powder at 25° for 12-24 hr. After removing acetonitrile by vacuum distillation the product mixture was separated by extraction of the desired compound into benzene. Pure MoW($O_2CC(CH_3)_3$)$_4$ was obtained as a yellow sublimate (140°, in vacuo) after removal of solvent from the benzene extract. Anal. Calcd for MoW($O_2CC(CH_3)_3$)$_4$: Mo, 14.02; W, 26.87. Found: Mo, 14.01; W, 26.56. In the mass spectrum a set of 15 lines centered at mass number 683 is characteristic of the molecular ion; in this spectrum the parent ion set arising from $Mo_2(O_2CC(CH_3)_3)_4$ is barely detectable (<1% relative intensity). As expected, the pure compound is diamagnetic, and exhibits a ^{1}H NMR spectrum indistinguishable from that of $Mo_2(O_2CC(CH_3)_3)_4$ with a sharp singlet at τ 8.48 in benzene. A more extensive development of the chemistry of MoW(O_2CR)$_4$ and derivatives obtained from it will be the subject of subsequent publications.

Acknowledgments. We express our appreciation to Professor R. A. Jacobson for his valuable advice and assistance during the X-ray structure solution and refinement, and to Mr. James Benson for his aid during the X-ray data collection.

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(3) F. A. Cotton, B. A. Frenz, E. Pedersen, and T. R. Webb, *Inorg. Chem.*, 14, 391 (1975).

(4) In a typical sequence of reactions a 3:1 mixture of W(CO)$_6$:Mo(CO)$_6$ is refluxed in *o*-dichlorobenzene with the calculated quantity of pivalic acid for conversion of all of the metal carbonyls to $M_2(O_2CC(CH_3)_3)_4$. When CO evolution ceases the solution is cooled and allowed to stand until crystallization is complete. Yellow crystals containing ca. 70 mol % Mo-W($O_2CC(CH_3)_3$)$_4$ and 30 mol % $Mo_2(O_2CC(CH_3)_3)_4$ are thus obtained. This mixture then is dissolved in benzene (carefully purified by vacuum distillation) and sufficient iodine added to react only with the mixed metal species. The gray crystalline [MoW($O_2CC(CH_3)_3$)$_4$]I precipitates within a few minutes and is filtered and washed with benzene. Subsequently the iodide product is dissolved in acetonitrile, filtered, and crystallized as the adduct [MoW($O_2CC(CH_3)_3$)$_4$]I·CH_3CN upon slow removal of solvent. Because all of the indicated compounds are extremely sensitive to oxygen and moisture the solvents must be carefully purified and all manipulations performed with scrupulous exclusion of oxygen or water.

(5) Reports of the preparation of $MoCr(O_2CR)_4$ derivatives have been made, but none has been substantiated as pure compounds, free of $Mo_2(O_2CR)_4$ which always appears to accompany formation of the heteronuclear species; cf. ref 1 and C. D. Garner and R. G. Senior, *J. Chem. Soc., Chem. Commun.*, 580 (1974).

(6) This stability is in contrast to that observed for the species $[Mo_2(O_2CR)_4]^+$ obtained by electrochemical oxidation of $Mo_2(O_2CR)_4$ in acetonitrile; cf. F. A. Cotton and E. Pedersen, *Inorg. Chem.*, **14**, 399 (1975).

(7) Details of the X-ray structure elucidation, including tables of final atomic and thermal parameters and structure factors will be provided in a full publication.

(8) On leave from the University of Zagreb, Zagreb, Croatia, Yugoslavia.

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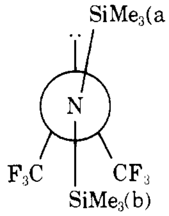
Stereochemistry of *N*,*N*-Bis(trimethylsilyl)amino- and *N*-*tert*-Butyl-*N*-(trimethylsilyl)aminobis(trifluoromethyl)phosphine

Sir:

The structures[1] and stereochemistry[2] of aminophosphines have received considerable attention in recent years. Our interest in this area is being extended to include compounds containing the silicon-nitrogen-phophorus linkage.[3] The new silylaminophosphines, $(Me_3Si)_2NP(CF_3)_2$ (**1**) and $(Me_3Si)(t\text{-}Bu)NP(CF_3)_2$ (**2**), were prepared by the reaction of $(CF_3)_2PCl$ with the *N*-lithium derivative of the appropriate silylamine.[4]

At ambient temperature the ^1H NMR spectrum of **1** consists of a single broad resonance which on cooling broadens further before splitting into two sharp lines and a multiplet (Figure 1a). By recording the ^1H spectra at both 60 and 100 MHz it was determined that: (i) the 2.8 Hz spacing between the two sharp lines is a coupling constant, as is the 0.7 Hz splitting within the multiplet, and (ii) the separation (6.3 Hz at 100 MHz, 3.7 Hz at 60 MHz) between the doublet and the multiplet results from a chemical shift difference. The ^{19}F NMR spectrum of **1** is a doublet (+59.2 ppm from $CFCl_3$, J_{PCF} = 93.1 Hz) which remains unchanged down to −130°.

These observations are consistent with hindered rotation about the N-P bond and the characteristic[1,2] ground state structure, in which the CF_3 groups are isochronous and the Me_3Si groups are anisochronous. The doublet Me_3Si resonance in the ^1H NMR spectrum of **1** can be assigned to the Me_3Si(a) group with J_{PNSiCH} = 2.8 Hz. Such an assignment is based on the observations[5,6] that the analogous *P*-N-C-*H* and *P*-N-^{13}C coupling constants in dimethylaminophosphines are larger when the methyl resides cis to the phosphorus lone pair than for the trans conformation. For the Me_3Si(b) group J_{PNSiCH} ~0 and $J_{FCPNSiCH}$ = 0.7 Hz. Possibly the proximity of the Me_3Si(b) and CF_3 groups promotes a through space interaction. A similar preferential phosphorus coupling has been found to exist in the low temperature ^1H NMR spectra of $(Me_3Si)_2NPCl_2$ and a long range proton-fluorine coupling has been observed in the aminoarsine $(Me_3Si)_2NAs(CF_3)_2$.[3]



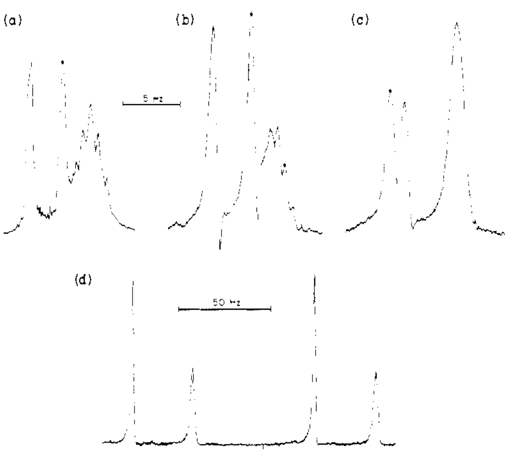
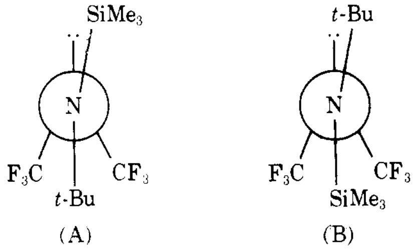


Figure 1. NMR spectra of $(Me_3Si)_2NP(CF_3)_2$ (**1**) and $(Me_3Si)(t\text{-}Bu)NP(CF_3)_2$ (**2**): (a) 60-MHz ^1H spectrum of **1** at −40°; (b) 60-MHz ^1H spectrum of the Me_3Si group of **2** at ambient temperature; (c) 60-MHz ^1H spectrum of the *t*-Bu group of **2** at ambient temperature; (d) 56.45-MHz ^{19}F spectrum of **2** at ambient temperature.

Typically $\Delta G_{NP}^{\ddagger}$ values for other acyclic aminophosphines fall in the range 7-10 kcal/mol.[2] The high $\Delta G_{NP}^{\ddagger}$ value of 15.3 kcal/mol which is calculated[7] for **1** is most reasonably attributed to the steric bulk of the Me_3Si moiety.

Compound **2** is apparently unique among aminophosphines since both the ^1H and ^{19}F NMR spectra (Figure 1) indicate the presence of two rotational isomers at ambient temperature. The Me_3Si region of the ^1H spectrum is strikingly similar to that observed at low temperature for **1** except that the doublet:multiplet ratio is ca. 1.3:1 rather than 1:1. Two *tert*-butyl resonances, a doublet and a broad singlet, of unequal intensities are also observed. The ^{19}F NMR spectrum consists of two doublets (+54.9 ppm, J_{PCF} = 100.0 Hz, and 55.4 ppm, J_{PCF} = 101.0 Hz) in the intensity ratio 1.3:1. These results are consistent with the existence of two rotamers of slightly different energy which undergo slow interconversion on the NMR time scale at ambient temperature.



In view of the earlier discussion of the angular dependence of coupling constants the more intense Me_3Si doublet (J_{PNSiCH} = 3.2 Hz) and the *tert*-butyl singlet are attributed to rotamer A in which the Me_3Si group is cis to the phosphorus lone pair. Similarly the doublet in the *tert*-butyl region (J_{PNCCH} = 1.2 Hz) and the Me_3Si multiplet ($J_{FCPNSiCH}$ = 0.7 Hz) are ascribed to rotamer B. Furthermore, it is noted that the less intense doublet in the ^{19}F spectrum (presumably resulting from rotamer B) has the larger peak width which correlates with the larger H-F coupling observed for the less intense Me_3Si resonance in the ^1H spectrum.

The high temperature ^1H NMR spectrum of **2** revealed a coalescence of the *tert*-butyl signals at +110° from which a value of $\Delta G_{NP}^{\ddagger}$ = 20.8 kcal/mol is calculated.[7] This very high value of $\Delta G_{NP}^{\ddagger}$ is not easily explained. The shorter