Figure 1. Plot of log K vs. $1/N$ for the adsorption of 139 organic compounds from aqueous solution onto CAL activated carbon at 25 °C.

for glycine, L-serine, and L-threonine. The equation of the line is

$$1/N = (-0.186 \pm 0.008) \log K + (0.572 \pm 0.011) \quad (11)$$

$$r = 0.973 \qquad s = 0.0477$$

In this equation, the errors are in the 95% confidence intervals, r is the correlation coefficient, and s is the standard deviation. Figure 1 indicates that eq 10 is also valid for compounds other than hydrocarbons. This result can be explained by considering that the adsorption of solute takes place by precipitation of the hydrocarbon portion of the solute.

Next we have checked the propriety of the numerical values in eq 11. McAuliffe[5] measured the solubilities in water at room temperature of paraffin, cycloparaffin, olefin, acetylene, cyclo-olefin, and aromatic hydrocarbons. The solubility data for 60 hydrocarbons excluding methane, ethane, and ethene have been given to a NEC PC-8001 computer to determine the constants a and b in eq 7. The data could be expressed by the following equation:

$$\log C_s = (-0.0300 \pm 0.0049)V_s + (5.43 \pm 0.60) \quad (12)$$

$$r = 0.847 \qquad s = 0.450$$

where C_s is the solubility expressed in mg/1000 g of water and V_s is the molar volume expressed in mL/mol. Since the solubility of hydrocarbon is usually low, the solubility in mg/1000 g of water is nearly equal to the solubility in mg/1000 mL of solution. The coefficient of log K in eq 10 was calculated from eq 12 ($-1/b = -1/5.43 = -0.184$). This excellent agreement with the experimental value (-0.186) indicates that the assumption that the hydrophobic adsorption takes place by precipitation of the hydrocarbon portion of the solute is valid. The value of m in eq 2 was calculated from the adsorption data of anisole ($m = 0.0488$).[14] The value of W_0 was determined as the micropore volume of the adsorbent ($W_0 = 0.317$ mL/g).[14] The ρ value was calculated as the average of the densities of the 60 hydrocarbons ($\rho = 0.717$ g/mL). The value of second term of eq 10 calculated from these values (W_0, ρ, m, $a = -0.0300$, $b = 5.43$, $R = 1.99$, and $T = 298$) was 0.594 and was in agreement with the experimental value (0.572).

It can be seen from Figure 1 that the plots of glycine, serine, etc., deviate downward from the line because of the very small

contribution of hydrophobic hydration to the adsorption.

These results indicate that the hydrophobic adsorption isotherm can be expressed by the following equation with only one parameter:

$$\log X = \log K + (0.572 - 0.186 \log K) \log C \quad (13)$$

These relationships were applicable to many other adsorbent-adsorbate systems. Equation 10 is an important equation characterizing hydrophobic adsorption isotherm and becomes a very powerful tool in the investigation of hydrophobic adsorption.

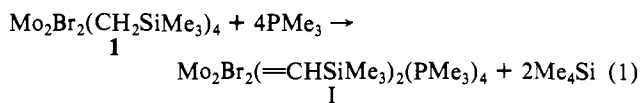## Bis[(trimethylsilyl)methylidene]tetrakis(trimethylphosphine)dibromodimolybdenum (M≡M)

K. J. Ahmed, M. H. Chisholm,* I. P. Rothwell, and J. C. Huffman

*Department of Chemistry and Molecular Structure Center
Indiana University, Bloomington, Indiana 47405*

Received June 18, 1982

We have proposed[1] that reactivity patterns presently well documented in mononuclear transition-metal chemistry will also be found for dinuclear compounds containing M-M multiple bonds. We wish here, in further support of this hypothesis, to report a phosphine-promoted α-hydrogen elimination reaction in the formation of a dinuclear bis-carbene compound. Interesting analogies with Schrock's[2] findings for related mononuclear early transition-metal chemistry are apparent.

Addition of PMe$_3$ ($\geq$4 equiv) to a hexane or toluene solution of 1,2-Mo$_2$Br$_2$(CH$_2$SiMe$_3$)$_4$[3] causes an immediate reaction, even at -78 °C, and the solution turns from orange-red to dark green. When the reaction was carried out in a sealed NMR tube in benzene-d_6, Me$_4$Si (2 equiv) was detected by ^{1}H NMR spectroscopy. Analysis of the volatiles in this reaction by GC-MS revealed only benzene-d_6, PMe$_3$, and Me$_4$Si. Significantly, the latter was not enriched in Me$_4$Si-d_1, suggesting that the hydrogen atom required to form Me$_4$Si was originating from a Me$_3$SiCH$_2$ ligand. The ^{31}P NMR spectrum obtained on the NMR tube reaction described above showed the formation of a major product, ca. 85% based on ^{31}P signal intensities, having an AA'BB' spectrum and two minor products showing ^{31}P singlets. (One of the minor products has been shown to be Mo$_2$Br$_4$(PMe$_3$)$_4$ (M-M quadruple bond).) On a preparative scale, crystallization of the crude reaction product from hexane gave the (trimethylsilyl)methylidene complex, I, as amber crystals in 60% yield based on eq 1.[4]

$$\text{Mo}_2\text{Br}_2(\text{CH}_2\text{SiMe}_3)_4 + 4\text{PMe}_3 \rightarrow$$
$$\mathbf{1}$$
$$\text{Mo}_2\text{Br}_2(\!=\!\text{CHSiMe}_3)_2(\text{PMe}_3)_4 + 2\text{Me}_4\text{Si} \quad (1)$$
$$\text{I}$$

(1) Chisholm, M. H. *ACS Symp. Ser.* **1981**, *No. 155*, 17.
(2) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98.
(3) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Rothwell, I. P. *Organometallics* **1982**, *1*, 251.
(4) All operations were carried out by using dried and deoxygenated atmospheres and solvents. Mo$_2$Br$_2$(CH$_2$SiMe$_3$)$_4$ (0.94 g, 1.34 mmol) was dissolved in toluene (40 mL). With the use of a calibrated vacuum manifold, PMe$_3$ (5.36 mmol) was condensed onto this solution frozen at -178 °C. The mixture was allowed to warm to room temperature slowly, and the resultant green solution was stirred for 1.5 h. The solvent was stripped and the residue extracted with hexane (100 mL). A small quantity of insoluble material was removed by filtration, the filtrate was reduced in volume to ca. 20 mL, and the solution was cooled to ca. -15 °C. The green-yellow microcrystalline precipitate so formed was collected and recrystallized from hexane slowly (cooling from 50 to 18 °C), yielding amber crystals, Mo$_2$Br$_2$(CHSiMe$_3$)$_2$-(PMe$_3$)$_4$.

(14) Abe, I.; Hayashi, K.; Kitagawa, M.; Urahata, T. *Nippon Kagaku Kaishi* **1979**, 830–835.

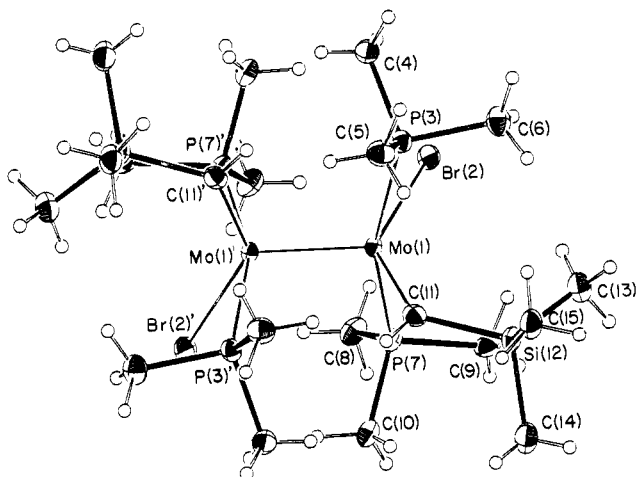**Figure 1.** ORTEP view of the $Mo_2Br_2(=CHSiMe_3)_2(PMe_3)_4$ molecule viewed down the C_2 axis of symmetry. Some pertinent bond distances (Å) and angles (deg) are as follows: Mo–Mo = 2.276 (1), Mo–Br = 2.636 (1), Mo(1)–P(3) = 2.535 (2), Mo(1)–P(7) = 2.534 (2), Mo(1)–C(11) = 1.949 (5), Mo–Mo–Br = 116.54 (3), Mo(1)′–Mo(1)–P(3) = 101.54 (4), Mo(1)′–Mo(1)–P(7) = 97.98 (4), Mo(1)′–Mo(1)–C(11) = 109.0 (2), Mo(1)–C(11)–Si(12) = 129.8 (3), Mo(1)–C(11)–H(19) = 120 (3).

I has been characterized by elemental analyses, NMR spectroscopy (^{1}H, ^{13}C, ^{31}P), and a single-crystal X-ray study.[5] An ORTEP view of the molecule found in the crystal is shown in Figure 1. The molecule has rigorous C_2 symmetry, and the two ends of the molecule are virtually eclipsed, presumably because this minimizes PMe_3–PMe_3 steric repulsions.[6] The solid-state structure is readily reconciled with the observed NMR data and the latter indicate that there is restricted rotation about the Mo–Mo bond.

The Mo–Mo distance of 2.276 (1) Å is indicative of a Mo≡Mo bond,[7] which rather interestingly can be viewed as arising in one of two ways: (i) If the Me_3SiCH ligand is counted as a dianion, then the formal oxidation state for Mo is 3+, giving rise to a d^3–d^3 triple bond of configuration $\sigma^2\pi^4$. (ii) If the Me_3SiCH ligand is viewed as a neutral two-electron donor, the oxidation state of Mo is 1+, giving rise to a d^5–d^5 dimer and a Mo≡Mo bond of configuration $\sigma^2\pi^4\delta^2\delta^{*2}$. However, the two electrons on each molybdenum that might be used to form δ and δ^* Mo–Mo bonds occupy molybdenum d_{xy} orbitals, which have the appropriate symmetry to backbond to the vacant carbon p_z atomic orbitals. The short Mo–C distance, 1.949 (5) Å, and the alignment of the planar Mo–C(H)Si groups provide good evidence for Mo-to-C double bonds.

A number of interesting points emerge: (1) The close relationship between mononuclear and dinuclear chemistry is seen in a comparison of I and II and their respective formation in reactions 1 and 2,[8] respectively. In both I and II, the metal atoms form triple, double, and single bonds and two dative bonds with PMe_3 ligands. The structural analogy between I and W(≡CCMe$_3$)(=CHCMe$_3$)(CH$_2$CMe$_3$)(Me$_2$PCH$_2$CH$_2$PMe$_2$)[9] is most

$$W(\equiv CCMe_3)(CH_2CMe_3)_3 + 2PMe_3 \rightarrow$$
$$\underset{\textbf{2}}{W(\equiv CCMe_3)(=CHCMe_3)(CH_2CMe_3)(PMe_3)_2 + CMe_4}$$
$$\underset{II}{}$$

$$(2)$$

striking: in both molecules, each metal atom is in a distorted square-based pyramidal geometry with the M≡X function occupying the axial position. (2) In I, each molybdenum attains a share of 16 valence electrons, and the Me_3SiCH ligand is not of the "grossly distorted" type of alkylidene ligand commonly observed when an electron-deficient early transition metal shows incipient M–H and M≡CR bond formation.[10] This is quite evident from the relatively small Mo–C–Si angle of 129° and the relatively long Mo–C bond distance 1.949 (5) Å when compared to "distorted" alkylidene ligands bound to tungsten. (3) The remarkably low chemical shift value, δ 14 downfield from Me_4Si, of the Me_3SiCH ligand is reconcilable with its position directly over the Mo≡Mo bond.[11]
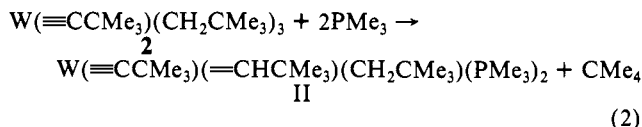
Further studies are in progress.[12]

(5) Anal. Calcd (found): C, 29.00 (29.09); H, 6.81 (6.83); Br, 19.29 (19.30). ^{1}H NMR (toluene-d_8 solvent, 16 °C) δ 0.80 (s, SiMe$_3$), 1.45 (d, J = 7Hz), 1.55 (d, J = 7Hz, PMe$_3$), 14.1 (m, =CHSi); ^{13}C{^{1}H} NMR δ 283 (m, =CHSi), 17.5 (d, J_{P-C} = 23 Hz, PMe$_3$), 19.5 (d, J_{P-C} = 24 Hz); (iii) ^{31}P{^{1}H} NMR δ –17 and –28 (J = 140 Hz (δ relative to H$_3$PO$_4$ external reference)). Crystal data at –165 °C: a = 20.461 (11) Å, b = 9.918 (4) Å, c = 20.468 (11) Å, α = 120.67 (2)°, Z = 4, d_{calcd} = 1.540 g cm^{-3}, and space group $A2/a$. Of the 2802 reflections collected, the 1629 having $F > 2.33\sigma(F)$ were used in the full-matrix refinement. Final residuals are R_F = 0.023 and R_{wF} = 0.027.

(6) The eclipsed conformation is also seen in Re$_2$Cl$_4$(PR$_3$)$_4$ compounds, which have Re≡Re bonds of configuration $\sigma^2\pi^4\delta^2\delta^{*2}$ and has been rationalized in terms of minimizing PR$_3$–PR$_3$ steric repulsions (R = Me or Et). See: Cotton, F. A.; Walton, R. A. In "Multiple Bonds between Metal Atoms"; Wiley: New York, **1982**.

(7) For a listing of Mo–Mo distances in compounds containing a central (Mo≡Mo)$^{6+}$ unit, see Cotton and Walton in ref 6.

(8) Clark, D. N.; Schrock, R. R. *J. Am. Chem. Soc.* **1978**, *100*, 6774.

(9) Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1979**, 2454.

(10) Wengrovins, J. H.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* **1982**, *104*, 1739 and references therein.

(11) McGlinchey, M. J. *Inorg. Chem.* **1980**, *19*, 1392.

(12) We thank the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

O-Methylation and O-Protonation of Coordinated Nitric Oxide. Observation of an Anion-Assisted O–H to M–H Tautomerization

Robert E. Stevens and Wayne L. Gladfelter*

Department of Chemistry, University of Minnesota
Minneapolis, Minnesota 55455
Received August 16, 1982

The reactivity of the nitric oxide ligand coordinated to transition metals is varied.[1] Not only is it susceptible to nucleophilic attack in some complexes, but it also reacts with electrophiles in others. Several studies of the reaction of protons with various M–NO groups have resulted in products containing a new N–H bond.[2-4] For instance, treatment of OsCl(CO)(PPh$_3$)$_2$(NO) with HCl yields OsCl$_2$(CO)(PPh$_3$)$_2$(HNO),[2] which has been structurally characterized[4] and found to contain an HNO ligand coordinated to the Os via the nitrogen. Until recently studies of the reactions of coordinated NO have been limited to mononuclear complexes. We have undertaken studies of the reactivity of cluster-bound nitrosyl ligands and report here the reactions of [Ru$_3$(CO)$_{10}$(NO)]$^-$, 1 (Scheme I), with electrophiles that lead to the first well-defined compounds resulting from O-methylation or O-protonation of coordinated NO.

A 20-mL methylene chloride solution of PPN[Ru$_3$(CO)$_{10}$(NO)] (182 mg, 0.158 mmol), prepared by the reaction of PPNNO$_2$ with Ru$_3$(CO)$_{12}$,[5] was reacted with a stoichiometric amount of CF$_3$-SO$_3$CH$_3$ at room temperature. The initially deep yellow-green solution became bright lemon yellow upon addition of the CF$_3$-

(1) McCleverty, J. A. *Chem. Rev.* **1979**, *79*, 53.

(2) Grundy, K. R.; Reed, C. A.; Roper, W. R. *J. Chem. Soc., Chem. Commun.* **1970**, 1501.

(3) Enemark, J. H.; Feltham, R. D.; Riker-Nappier, J.; Bizot, K. F. *Inorg. Chem.* **1975**, *14*, 624.

(4) Wilson, R. D.; Ibers, J. A. *Inorg. Chem.* **1979**, *18*, 336.

(5) Stevens, R. E.; Yanta, T. J.; Gladfelter, W. L. *J. Am. Chem. Soc.* **1981**, *103*, 4981.