due to the more effective trapping of $H_2C^+OO^-$ by the increased amount of ester (reactions 2a and 2c). However, the dioxolane product is still predominant which is indicative that the relative dipolarophilicities toward $H_2C^+OO^-$ are $CH_2=CHOCH_3$ > $HCOOCH_3$ > $CH_3COOCH_2CH_3$. Such an order is not unreasonable since esters are generally very poor dipolarophiles toward carbonyl oxides,[4] while electron-rich enol ethers have an extensive 1,3-dipolar cycloaddition chemistry.[12]

In order to explore whether the dioxolane might be formed by a reaction between starting alkene and ozonide (perhaps assisted by adventitious catalyst), 60 mmol of methyl vinyl ether in 50 mL of methyl formate was ozonized with 20 mmol of ozone. A workup of 25 mL of this reaction mixture showed no difference in the product composition (Table I, run 3) compared to the second half of the solution, which was analyzed 20 h later. The increased dioxolane yield compared to run 2 is consistent with the higher effective concentration of the starting alkene. The mutual stability of the dioxolane and ozonide observed under these conditions makes it unlikely that a catalyzed reaction between them leads to the dioxolane. Moreover, the high yields of dioxolanes and the change in product yields with solvent (Table I) are plausible for a kinetic scheme which derives these products from the cleavage fragments of the primary ozonide recombining with themselves, the solvent, or the initial alkene in a competitive manner. Experiments with labeled vinyl ethers are in progress to explore this reaction scheme further.

(12) Huisgen, R. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 565, 633; *Angew. Chem.* **1963**, *75*, 604, 741.

Figure 1. ORTEP plot of **3** (Scheme I). The phenyl groups of which C301 and C401 are the ipso carbon atoms are not shown. Selected bond lengths in angstroms: Mo1–Mo2, 3.282; P1–Mo1, 2.398; P1–Mo2,, 2.417; Mo1–H1, 1.96; Mo2–H1, 1.78; P2–Mo1, 2.382. Angle Mo1–P1–Mo2, 86.0°.

Figure 2. ORTEP plot of **4** (Scheme I). The phenyl groups of which C301 and C401 are the ipso carbon atoms are not shown. Selected bond lengths in angstroms: Mo1–Mo2, 2.532; P1–Mo1, 2.376; P2–Mo1, 2.385; P1–Mo2, 2.363; P2–Mo2, 2.368; C7–Mo1, 2.082; C7–Mo2, 2.099. Selected bond angles: Mo1–C7–Mo2, 74.5°; Mo1–P1–Mo2, 64.6°; Mo1–P2–Mo2, 64.4°.

Scheme I

Linked Bis(μ-phosphido) and Related Ligands for Metallic Clusters. 3. Synthesis and Chemistry of a Bis(μ-phosphido)(μ-carbonyl)dimolybdenum(Mo≡Mo) System[1]

Evan P. Kyba,* J. Douglas Mather, Karen L. Hassett, Jeffrey S. McKennis, and Raymond E. Davis*

*Department of Chemistry
The University of Texas at Austin
Austin, Texas 78712*

Received April 13, 1984

The chemistry of the $[CpMo(CO)_mX_n]_2$ system has generated considerable attention lately, due to the multifaceted bonding arrangements engendered by such molecules.[2] As part of our recent development of the chemistry of linked bis(bridging) di- and polymetal systems,[1,3a] we investigated the thermal reaction of the bis(secondary phosphine) 1^{3b-d} and $[CpMo(CO)_3]_2$ (**2**), which led to the isolation of two novel Mo_2 complexes. We describe these herein, along with some of the chemistry exhibited by these species (Scheme I).

(1) For the preceding paper in this series, see: Kyba, E. P.; Davis, R. E.; Hassett, K. L.; McKennis, J. S.; Sheikh, B. *Phosphorus Sulfur* **1983**, *18*, 275.

(2) For recent work, see inter alia: (a) D'Errico, J. J.; Messerle, L.; Curtis, M. D. *Inorg. Chem.* **1983**, *22*, 851–852. (b) Messerle, L.; Curtis, M. D. *J. Am. Chem. Soc.* **1982**, *104*, 889–891. (c) Green, M.; Orpen, A. G.; Schaverien, C. J.; Williams, I. D. *J. Chem. Soc., Chem. Commun.* **1983**, 181–183. (d) Alper, H.; Einstein, F. W. B.; Petrignani, J.-F.; Willis, A. C. *Organometallics* **1983**, *2*, 1422–1426. (e) Curtis, M. D.; Messerle, L.; Fotinos, N. A.; Gerlach, R. F. In "Reactivity of Metal–Metal Bonds"; Chisholm, M. H., Ed.; American Chemical Society: Washington, DC, 1981; ACS Symp. Ser. No. 155, Chapter 12.

(3) (a) McKennis, J. S.; Kyba, E. P. *Organometallic* **1983**, *2*, 1249–1251. (b) Kyba, E. P.; John, A. M.; Brown, S. B.; Hudson, C. W.; McPhaul, M. J.; Harding, A.; Larsen, K.; Niedzwiecki, S.; Davis, R. E. *J. Am. Chem. Soc.* **1980**, *102*, 139–147. (c) Mann, F. G.; Mercer, A. J. H. *J. Chem. Soc., Perkin Trans. 1* **1972**, 2548–2555. (d) A much superior method for the synthesis of **1** has been developed: Kyba, E. P.; Rines, S. P., submitted for publication.
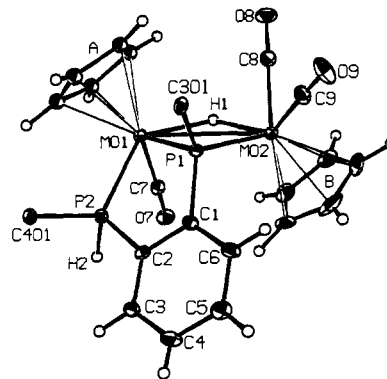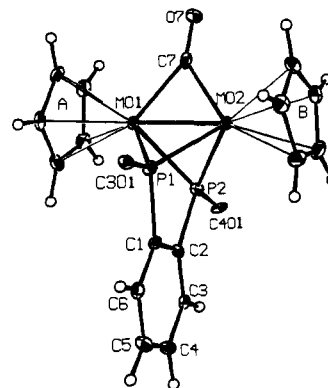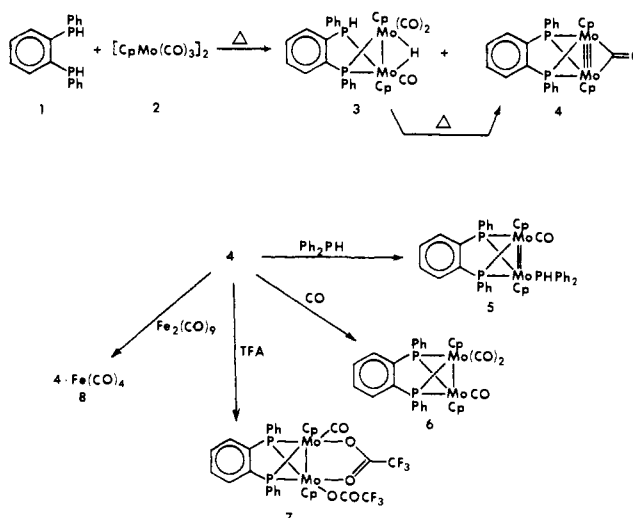
The reaction of equimolar quantities of **1** and **2** in degassed boiling mesitylene for 4 h gave **3** (56%), following workup and alumina chromatography (benzene eluent).[4] When the reaction was carried out for 12 h, **4** was isolated in 47% yield, following chromatography on alumina (CH_2Cl_2 eluent).[4] We also estab-

lished that pure **3** is transformed into **4** under these reaction conditions.[4]

Red, crystalline **3** exhibited two doublets in the $^{31}P\{H\}$ NMR spectrum (CDCl$_3$) at δ 212 and 79 (J = 43 Hz) and a metal hydride absorption in the ^{1}H NMR spectrum (CDCl$_3$) at δ -12.45 (dd, J = 45.0, 12.8 Hz). Its structure was established by X-ray crystallography and is shown as an ORTEP plot in Figure 1.[4] The Mo—Mo distance of 3.282 (1) Å is in the range expected for a single bond[5] and corresponds closely to that in (μ-PMe$_2$)(μ-H)(η^5-Cp)$_2$(CO)$_4$Mo$_2$, 3.26 Å.[6] The data were of sufficient quality[7] that the bridging hydrogen atom position was located and refined, but its unsymmetrical binding must be viewed with caution.[8]

Deep-green **4** featured a single absorption in the carbonyl stretching region (1710 cm^{-1}, CH$_2$Cl$_2$ solution) and a sharp singlet at δ 185 in the $^{31}P\{H\}$ NMR spectrum. The results of an X-ray structure determination on **4** are shown in an ORTEP plot (Figure 2).[4] The Mo—Mo bond length of 2.532 (1) Å may be somewhat longer than expected for a $\sigma^2\pi^4$ triple bond formulation,[9] but since this is the first example of such a bond which contains μ-phosphido groups, there are no good models with which to compare this complex. A recently described phosphido-bridged Mo$_2$ quadruple bond was also found to be longer than usually observed.[10] An alternative Mo(II)—Mo(II) single bond formulation would be expected to have a bond length in excess of 3.0 Å.[2]

Consonant with the metal—metal unsaturation, we find that **4** is reactive toward both nucleophiles and electrophiles. Reaction of **4** with 1 equiv of diphenylphosphine gave an air-sensitive complex formulated as **5** based on its spectroscopic data: $^{31}P\{H\}$ NMR (CDCl$_3$) δ 134 (t, J = 6 Hz), 117 (dd, J = 12, 6 Hz), and 57 (dd, J = 12, 5 Hz, ^{1}H-coupled, $^1J_{PH}$ = 358 Hz).[4] Reaction with carbon monoxide (1 atm, C$_6$H$_6$ solution, 16 h) produced a new species formulated as **6**. The spectroscopic data indicated identical environments for the phosphorus atoms but different ones for the Cp protons as shown in **6**: $^{31}P\{H\}$ NMR (CH$_2$Cl$_2$) δ 102 (s); ^{1}H NMR (C$_6$D$_6$) δ 5.40 (s, Cp), 4.50 (s, Cp).[4] Reaction of **4** with excess trifluoroacetic acid gave quantitatively a complex that we formulate as **7**, which featured $^{31}P\{H\}$ NMR (CDCl$_3$) absorptions at δ 155 (d) and 134 (d, J = 43 Hz).[4] We are in the process of confirming this structure by X-ray crystallography.[11] Finally, reaction of **4** with Fe$_2$(CO)$_9$ in THF at 25 °C for 2 h followed by heating at reflux for 2 h gave a high yield of a green crystalline material **8**, which analyzed for [4 + Fe(CO)$_4$]: $^{31}P\{H\}$ NMR (CH$_2$Cl$_2$, 35 °C) δ 138 (br s); (CH$_2$Cl$_2$, -80 °C) δ 194 (br s), 85 (br s).[4] We are currently investigating the structure of this fluxional complex, as well as other aspects of the chemistry of **4** and its congeners.

(5) See ref 2, 13–18 in Alper et al.[2d]

(6) Doedens, R. J.; Dahl, L. F. *J. Am. Chem. Soc.* **1965**, *87*, 2576–2581.

(7) Frenz, B. A.; Ibers, J. A. In "Transition Metal Hydrides"; Muetterties, E. L., Ed.; Marcel Dekker: New York, 1971.

(8) Peterson, J. L.; Williams, J. M. *Inorg. Chem.* **1978**, *17*, 1308–1312.

(9) (a) Cotton, F. A. *J. Chem. Educ.* **1983**, *60*, 713–720. (b) Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982. (b) Cotton, F. A. *Acc. Chem. Res.* **1978**, *11*, 225–232.

(10) Jones, R. A.; Lasch, J. G.; Norman, N. C.; Whittlesey, B. R.; Wright, T. C. *J. Am. Chem. Soc.* **1983**, *103*, 6184–6185.

(11) Since submission of this work for publication, we have indeed confirmed the structure of **7** by X-ray crystallography.

Use of Deuterium Labeling To Assess the Roles of Tetramethylammonium Cation, Dimethylformamide, and Water as Proton Donors for Electrogenerated *tert*-Butyl Carbanions. Evidence for the Formation of an Ylide (Trimethylammonium Methylide)

Kenneth L. Vieira, Mohammad S. Mubarak, and Dennis G. Peters*

Department of Chemistry, Indiana University Bloomington, Indiana 47405

Received March 2, 1984

Recently, in studying[1] the reduction of *tert*-butyl bromide at mercury in dimethylformamide containing tetramethylammonium perchlorate, we became interested in assessing the roles of the solvent, the supporting-electrolyte cation, and water (typically present as an impurity at concentrations ranging from approximately 10 to 50 mM, depending on the procedures used to dry and handle the solvent) as proton donors for the electrolytically generated *tert*-butyl carbanion. From electrolyses involving deuterated reagents, we conclude that the solvent (dimethylformamide) is a poor source of protons for *tert*-butyl carbanions, that water is the dominant proton donor, that the tetramethylammonium cation is the second most important source, and that only a small percentage of the carbanions is protonated by the starting material under the conditions of our experiments.

In a paper by de la Torre and Sease,[2] who summarize earlier work dealing with the elucidation of the roles of proton donors in organic electrochemistry, the reduction of iodobenzene at a mercury cathode in dimethylformamide containing tetraethylammonium bromide and various concentrations of H$_2$O and D$_2$O was scrutinized to ascertain the source of protons for electrogenerated phenyl carbanions; these authors found that water is the best proton donor, that the tetraethylammonium cation is a significant source of protons, and that dimethylformamide can serve as a proton donor only if both water and the tetraethylammonium ion are either absent or present at low concentrations. To the best of our knowledge, there have been no previous electrochemical investigations of the role as a proton donor of the tetramethylammonium cation—which, instead of undergoing a Hofmann elimination after deprotonation, would be converted to a nitrogen ylide (trimethylammonium methylide)—nor have there been any reported efforts with deuterated solvent to determine whether dimethylformamide functions as a source of protons for electrogenerated alkyl carbanions.

A normal dc polarogram for *tert*-butyl bromide in dimethylformamide containing 0.1 M tetramethylammonium perchlorate exhibits two waves of nearly identical height with half-wave potentials of -1.23 and -1.46 V;[3] the first wave signals the formation of the *tert*-butyl radical and the second wave is attributable to production of the *tert*-butyl carbanion. Earlier polarographic studies by Fry and Krieger[4] have indicated that *tert*-butyl bromide can undergo stepwise reduction in dimethyl sulfoxide containing various tetraalkylammonium salts. Our electrolysis of *tert*-butyl

(1) Vieira, K. L. Ph.D. Thesis, Indiana University, Bloomington, 1984.

(2) de la Torre, R. A.; Sease, J. W. *J. Am. Chem. Soc.* **1979**, *101*, 1687–1690.

(3) All potentials are quoted with respect to a reference electrode consisting of a saturated cadmium amalgam in contact with dimethylformamide saturated with both cadmium chloride and sodium chloride; this electrode has a potential of -0.75 V vs. the aqueous saturated calomel electrode.

(4) Fry, A. J.; Krieger, R. L. *J. Org. Chem.* **1976**, *41*, 54–57.