5:**6**, was dependent on the reaction period of X(N_3^-) treatment (Table I). Another symmetric product, CD(N_3)$_2$ (**4**),[7] was also detected by HPLC analysis at prolonged treatment (12 h) of **2** with N_3^-. Since unreacted **2** reacts with Y to give **6**, the two consecutive first-order reactions **2** → **3** and **3** → **4**, whose rate constants are k_1 and k_2, respectively (Scheme I), were analyzed[8] based on the "time-dependent" product ratio, **4**:**5**:**6** (Scheme I). The rate ratio k_1/k_2 thus evaluated was ca. 13. It was concluded, therefore, that X(N_3^-) attacked the carbon of the sulfonate para to *N*-oxide more rapidly (13 times) than X attacked the sulfonate carbon para to the methylene group. Thus, **3** was accumulated and finally collapsed with the subsequent rapid reaction with Y to afford CDXY (**5**) (Scheme I). Since the technique of regioselective capping has been reported,[3d,e] a variety of excellent enzyme models will be made through this flamingo-type capping when combined with the regioselective capping.[3d,e]

Registry No. 1, 80781-19-7; **2**, 80781-20-0; **3**, 80781-21-1; **4**, 80781-22-2; **5**, 80789-31-7; **6**, 80781-23-3; *N*-benzyl-*N*-methylaniline-*p,p'*-disulfonyl chloride, 80781-24-4; *β*-cyclodextrin, 7585-39-9; *p*-*tert*-butylthiophenolate, 2396-68-1.

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(7) **4**: ν_{N_3} 2080 cm^{-1}. Anal. Calcd for $C_{42}H_{68}O_{34}N_6{\cdot}2H_2O$: C, 41.31; H, 5.94; N, 6.98. Found C, 41.04; H, 5.96; N, 6.78.

(8) Frost, A. A.; Pearson, R. G. "Kinetics and Mechanism"; Wiley: New York, 1953.

Metal–Formaldehyde Chemistry: Coordination, Disproportionation, and Lewis Acid Promoted Transformation to Oxymethylene Derivatives

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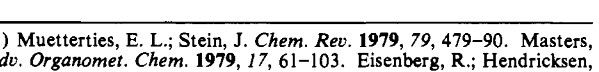
Received August 10, 1981

Notwithstanding that the metal–formaldehyde group, M–CH$_2$O, could play a significant and unexpected role in carbon monoxide reduction,[1] its chemistry is limited to the only formaldehyde complex identified so far, Os(CO)$_2$(PPh$_3$)$_2$(η^2-CH$_2$O).[2] The very close relationship between formyl, formaldehyde, oxymethylene, and hydroxycarbene derivatives makes the genesis and the chemistry of the M–CH$_2$O moiety highly significant in CO metal-promoted chemistry.[1] In this context, it must be noticed that such a unit was invoked as a key species occurring in the homogeneous reduction of CO by zirconium hydrides.[3,4]

The coordination and some elementary transformations of formaldehyde promoted by an early transition metal, namely vanadium(II), are the subject of the present report.

Paraformaldehyde suspended in toluene reacted with vanadocene, cp$_2$V (cp = η^5-C$_5$H$_5$), giving a deep green solution from which crystals of I (eq 1) were isolated.[5] The solution from which complex I crystallizes contains a significant amount of HCOOMe.[6] Before discussing such a vanadocene-promoted transformation of formaldehyde, the nature of complex I must be considered. The structure of I was clarified by analytical, spectroscopic (ν_{C-O} = 1160 cm^{-1}, vs[5]), and X-ray data.[7] Figure 1 shows a simplified drawing of the structure with the most relevant bond distances, the C–O bond length [1.353 (10) Å] being surprisingly shorter than the corresponding one found in Os(CO)$_2$(PPh$_3$)$_2$(η^2-CH$_2$O)[2] [C–O = 1.59 (1) Å; ν_{C-O} = 1017 cm^{-1}], while the C–O bond distance in free formaldehyde is 1.225 Å.[8] The vanadium–carbon bond distance [2.092 (8) Å] has some double-bond character.[9]



$$cp_2V + H{-}[OCH_2]_n{-}OH \longrightarrow cp_2V(\eta^2\text{-}CH_2O) + HCOOMe \quad (1)$$

I

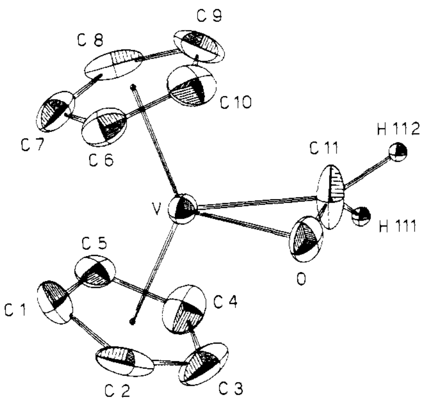
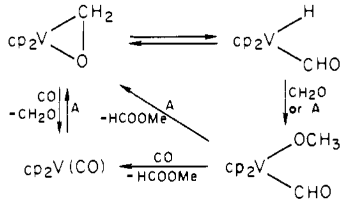


Figure 1. ORTEP drawing of Cp$_2$V(CH$_2$O).[8] Selected bond lengths (Å): C11–O = 1.353 (10), V–C11 = 2.092 (8), V–O = 1.955 (5), V–cp$_1$(⊥) = 1.964 (9), V–cp$_2$(⊥) = 1.945 (9) Å.

Scheme I



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(1) Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479–90. Masters, C. *Adv. Organomet. Chem.* **1979**, *17*, 61–103. Eisenberg, R.; Hendricksen, D. E. *Adv. Catal.* **1979**, *28*, 79–172. Henrici-Olivé, G.; Olivé, S. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 136–41.

(2) Brown, K. L.; Clark, G. R.; Headford, C. E. L.; Marsden, K.; Roper, W. R. *J. Am. Chem. Soc.* **1979**, *101*, 503–5.

(3) Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 2716–24. Walczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121–7 and references cited therein.

(4) Fachinetti, G.; Floriani, C.; Roselli, A.; Pucci, S. *J. Chem. Soc., Chem. Commun.* **1978**, 269–70.

(5) A toluene solution (150 mL) of vanadocene (7.32 g) was stirred for 2 days with paraformaldehyde (1.50 g). The color of the solution changed from violet to deep green. The filtered solution was concentrated in vacuo at room temperature until a crystalline solid started to separate. Then the solution was kept on standing for 4 h at room temperature, for 2 days at −30 °C, and for 8 h at −80 °C. The deep green crystals obtained (4.55 g) are highly sensitive to air. Anal. Calcd for cp$_2$V(CH$_2$O), C$_{11}$H$_{12}$OV: C, 62.55; H, 5.69. Found: C, 62.75; H, 5.78. Molecular weight 211 (mass spectrometry); the IR spectrum (Nujol) shows a strong band for the C–O vibration at 1160 cm^{-1}. Complex I is thermally labile. A THF solution (30 mL) of complex I (0.21 g, 0.99 mmol) reacted with iodine (0.30 g, 1.18 mmol) to give cp$_2$VI$_2$ and paraformaldehyde.

(6) The solution from which complex I was isolated contains, as shown by GLC, mass, and IR spectra, HCOOMe, whose maximum amount was reached when the yield in complex I was very low. It must be noticed that a toluene solution of I does not form HCOOMe on standing, except when paraformaldehyde is added. A 0.60-g sample (2.80 mmol) of complex I dissolved in toluene (60 mL) was stirred with paraformaldehyde (5 g) for 3 days. The solution became violet, and the toluene was found to contain ca 2.0 mmol of HCOOMe. Vanadocene complexes I and II promote the disproportionation of paraformaldehyde to HCOOMe in very high yield; this cannot substantiate, however, the existence of catalytic processes.

(7) Crystal Structure Information: monoclinic, space group *C*2/*c*; a = 13.634 (3) Å, b = 6.812 (1) Å, c = 20.528 (4) Å, β = 103.24 (2)°, V = 1855.9 (6) Å^3, Z = 8; Siemens AED diffractometer, niobium-filtered Mo Kα radiation, λ = 0.71069 Å, θ–2θ scan type, $6 < 2\theta < 50°$, 1626 unique reflections. No absorption correction was applied. The structure was refined by full-matrix least-squares techniques: 820 reflections with $I > 2\sigma(I)$; 118 variables (anisotropic thermal parameters for all nonhydrogen atoms, hydrogen atoms included with U fixed at 0.09 Å^2 and not refined); R = 0.048; R_w = 0.049. No peak above the general background was found in the final difference synthesis. The mathematical and computational details may be found in ref 9.

(8) Wells, A. F. "Structural Inorganic Chemistry", 3rd ed.; Oxford Press: Oxford, England, 1962; p 717.

(9) The structural features of the V(CH$_2$O) moiety are highly reminiscent of a η^2-C,O bonded formyl group: Gambarotta, S.; Pasquali, M.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1981**, *20*, 165–71 and 1173–8. Fachinetti, G.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Ibid.* **1979**, *18*, 2282–7.

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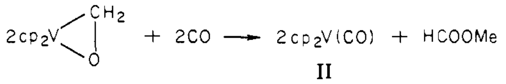
Formaldehyde in complex I is displaced by carbon monoxide in the form of methyl formate[10] (eq 2). In reaction 2, which is

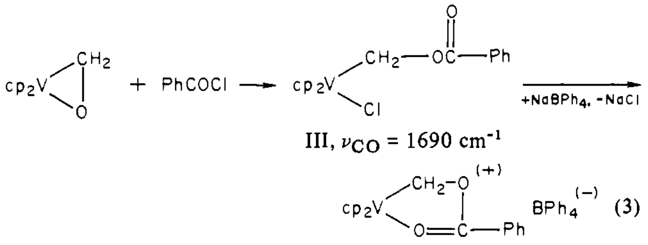

(2)

I

II

rather slow, the vanadocene moiety is transformed into the corresponding monocarbonyl, II.[11] Complex II itself is active in promoting the slow transformation of paraformaldehyde into HCOOMe.[12] Disproportionation of formaldehyde to HCOOMe can be viewed as the classic Cannizzaro reaction in the version call "the Tishchenko reaction".[13] The occurrence of such a transformation would suggest that the formation of HCOOMe from H_2/CO catalyzed by transition-metal complexes could be the consequence of a preliminary metal-promoted formation of formaldehyde.[14] In case of an early transition metal,[3] the data cited above can be easily explained by Scheme I[15] (A ≡ paraformaldehyde). The scheme requires, mostly, the conversion of a formaldehydo into a hydrido–formyl complex. Such a transformation was observed both for the osmium complex $Os(CO)_2(PPh_3)_2(\eta^2\text{-}CH_2O)$[2] and in the oxidative addition of CH_2O to an iridium complex to form $(PMe_3)_4Ir(H)(CHO)^+$.[16]

The interaction of a Lewis acid on the metal-bonded CH_2O may represent a useful modeling reaction as concerns its possible activation by a bifunctional acid–base system.[1] This reaction would simulate the change from η^2-C,O to a bridging bonding mode of formaldehyde[4] and other possible pathways that formaldehyde, eventually formed from CO and H_2 on a metal center, could evolve through by a subsequent action of Lewis acids. Electrophiles attack the oxygen in complex I by a rather unexpected reaction because of the high oxophilicity of vanadium. Reaction 3 describes the transformation of η^2-C,O-bonded formaldehyde into an acyloxymethylene complex.[17] Complexes III and IV are unexpectedly stable being vanadium(IV) derivatives containing metal–carbon σ bonds.[17] The transformation of formaldehyde into an acyloxymethylene group was recently proposed as the intermediate step in the ruthenium-catalyzed reduction of CO to ethylene glycol esters.[18] Conversion of the formaldehydo group into oxymethylene derivatives, $cp_2V\text{–}CH_2OX$, exemplified in reaction 3, can be achieved by different Lewis acids [$X = BF_3$, $^1/_2TiCl_4$]. Detailed investigations both on the action of different acids on complex I and on the reaction of carbon monoxide with the resulting oxymethylene complexes are in progress.



III, $\nu_{CO} = 1690\ cm^{-1}$

IV, $\nu_{CO} = 1600\ cm^{-1}$

(3)

Studies on metal–formaldehyde species will give interesting information on the products formed from CO and H_2, supposing that such systems produce formaldehyde as a primary intermediate in such a complex reaction.[19] Disproportionation, conversion to oxymethylene derivatives, and reductive coupling of formaldehyde may represent general pathways through which metallic systems are able to operate in synthesis gas conversion.

Acknowledgment. This work was supported by Italian National Research Council (CNR).

Registry No. I, 80737-39-9; II, 53339-41-6; III, 80737-40-2; IV, 80737-42-4; $H\text{-}[OCH_2]_n\text{-}OH$, 30525-89-4; Cp_2V, 1277-47-0; PhCOCl, 98-88-4.

Supplementary Material Available: Tables of positional (SI) and thermal (SII) parameters for $Cp_2V(CH_2O)$ and a listing of structure factor amplitudes (9 pages). Ordering information is given on any current masthead page.

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[10] Reaction 2 can be followed by the IR spectrum of a toluene solution (30 mL) of complex I (0.60 g) treated with carbon monoxide. The appearance of two bands, at 1880 and at 1730 cm^{-1}, in a few hours are diagnostic for the presence of $cp_2V(CO)$ and HCOOMe, respectively. The absorption of CO was found to be 0.85 mol per mol of vanadium in 24 hours. After 2 days HCOOMe can be distilled from the solution and determined by a standard procedure.

[11] Fachinetti, G.; Del Nero, S.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1976**, 1046–9.

[12] Paraformaldehyde added to a toluene solution of $cp_2V(CO)$ causes a partial but significant displacement of CO from the complex, which promotes its disproportionation to HCOOMe.

[13] March, J. "Advanced Organic Chemistry: Reaction, Mechanisms and Structure"; McGraw-hill: New York, 1968; p 910.

[14] Disproportionation of metal-bonded CH_2O can occur by a mechanism like that recently proposed for the disproportionation of metal–formyl groups: Casey, C. P.; Andrews, M. A.; McAlister, D. R. *J. Am. Chem. Soc.* **1979**, *101*, 3371–3. Casey, C. P.; Neumann, S. M.; Andrews, M. A.; McAlister, D. R. *Pure Appl. Chem.* **1980**, *52*, 625–33.

[15] The steps depicted in the scheme are supported by the results given in ref 6, 9, 10, and 12 and by the observation that vanadocene is unreactive with HCOOMe.

[16] Thorn, D. L. *J. Am. Chem. Soc.* **1980**, *102*, 7109–10 and references cited therein.

[17] A toluene solution (50 mL) of I (0.91 g, 4.31 mmol) was reacted with distilled PhCOCl (0.50 mL, 4.31 mmol). The resulting green-yellow solution gave in a few seconds light green needles of $cp_2V(Cl)(CH_2O_2CPh)$ (0.85 g). Anal. Calcd for $C_{18}H_{17}O_2VCl$: C, 61.45; H, 4.83; Cl, 10.10. Found: C, 60.47; H, 5.17; Cl, 11.16. $\nu_{C\text{–}O}$ (Nujol) = 1690 cm^{-1} (vs). Complex III (0.52 g, 1.48 mmol) dissolved in THF (50 mL) was reacted with $NaBPh_4$ (0.60 g, 1.75 mmol). The resulting solution was kept standing overnight. A crystalline deep blue solid formed (0.35 g). Anal. Calcd for $[Cp_2\underbrace{V\text{–}CH_2OC(O)}\text{-}Ph](BPh_4)$, $C_{42}H_{37}O_2VB$: C, 79.37; H, 5.83. Found: C, 78.97; H, 5.89. $\nu_{C\text{–}O}$ (Nujol) = 1600 cm^{-1} (vs). Proposed structures are based on preliminary X-ray analysis results.

[18] Dombek, B. D. *J. Am. Chem. Soc.* **1980**, *102*, 6855–7. *Ibid.* **1979**, *101*, 6466–8.

[19] Fahey, D. R. *J. Am. Chem. Soc.* **1981**, *103*, 136–41.

Modes of β-Silyl Involvement in Solvolysis

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Received November 12, 1981

A β-silicon atom strongly activates the departure of groups under both solvolytic and pyrolytic conditions.[1,2] The overall result is an elimination reaction (eq 1), whose mechanism has at one

$$Me_3SiCH_2CH_2X + ROH \rightarrow CH_2{=}CH_2 + Me_3SiOR + HX \qquad (1)$$

time been considered to involve rate-determining expulsion of a silylenium ion[3,4] or a four-centered transition state with concerted departure of Me_3SiX.[5] Most authors currently subscribe to a

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[1] Jarvie, A. W. P. *Organomet. Chem. Rev., Sect. A* **1970**, *6*, 153–170.

[2] Sommer, L. H.; Whitmore, F. C. *J. Am. Chem. Soc.* **1946**, *68*, 485–487.

[3] We use the term silylenium for electron-deficient positive silicon (R_3Si^+) and siliconium for electron-sufficient positive silicon (R_5Si^+).

[4] Sommer, L. H.; Baughman, G. A. *J. Am. Chem. Soc.* **1961**, *83*, 3346–3347.

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