

were obtained. Anal. Calcd for $C_{18}H_{18}Ru_2$: C, 49.53; H, 4.15; Ru, 46.31; M_r , 436.46. Found: C, 49.38; H, 4.04; Ru, 46.20.

Acknowledgment. We wish to thank Dr. A. Schwenk for the ^{103}Rh NMR measurements at 2.8 MHz and Prof. G. M. Sheldrick for his help in solving the structure of 1. We are further grateful to Dr. U. Kölle for supplying a sample of C_5Me_5CoCOT and to BASF, Ludwigshafen, for a generous gift of cyclooctatetraene. This work was supported by the Swiss National Science Foundation (2.165-0.83, 2.689-0.80, and 2.426-0.82).

Registry No. 1, 80951-04-8; 2, 80967-94-8; 3, 104715-97-1; 4, 104715-99-3; 5, 104716-01-0; 6, 104716-03-2; 7, 104716-05-4; 8,

104716-06-5; 9, 104738-02-5; 10 (isomer A), 104716-07-6; 10 (isomer B), 104716-08-7; 11, 104716-09-8; 12, 104760-97-6; 13, 104716-10-1; 14, 104716-12-3; 15, 104760-98-7; 16, 104716-13-4; 17, 104716-15-6; 18, 104716-17-8; 19, 104738-04-7; 20, 104738-05-8; $[C_5Me_5RhCl]_2$, 12354-85-7; $[C_5Me_5IrCl]_2$, 12354-84-6; $CpCo(COT)$, 12110-49-5; $CpRh(COT)$, 55480-71-2; $[CpRu(CH_3CN)_3]PF_6$, 80049-61-2; $[(C_2H_4)_2RhCl]_2$, 12081-16-2; $[CpRh(COT)RnCl]_2$, 104716-18-9; $Mg(Ind)_2$, 53042-25-4; Hmbz, 87-85-4; $[CIRh(COT)RhCl]_n$, 98092-07-0; C_5Me_5CoCOT , 78063-03-3; $[(CO)_2RhCl]_2$, 14523-22-9.

Supplementary Material Available: Tables of bond angles, anisotropic temperature factors, and hydrogen coordinates (19 pages); listings of structure factor amplitudes (99 pages). Ordering information is given on any current masthead page.

Metal-Formaldehyde Chemistry: Metal-Promoted Elementary Transformations of Formaldehyde

Sandro Gambarotta,[†] Carlo Floriani,^{*†} Angiola Chiesi-Villa,[§] and Carlo Guastini[§]

Chemistry Department, Columbia University, New York, New York, 10027, and Istituto di Strutturistica Chimica, Centro di Studio per la Strutturistica Diffattometrica del CNR, Università di Parma, 43100 Parma, Italy

Received March 19, 1986

Paraformaldehyde reacts with vanadocene, cp_2V (I; $cp = \eta^5-C_5H_5$), in a toluene solution to form $[cp_2V(\eta^2-CH_2O)]$ (II). The bonding mode of formaldehyde was determined by an X-ray analysis [$V-C = 2.092$ (8) Å, $V-O = 1.955$ (5) Å, and $C-O = 1.353$ (10) Å]. The formation of II occurred with simultaneous generation of a significant amount of HCOOMe, as a consequence of the fact that II can react further with paraformaldehyde to form HCOOMe. Disproportionation of CH_2O to HCOOMe was observed when the CH_2O ligand was removed from II by using carbon monoxide. Oxymethylene ligands containing a vanadium-carbon σ bond have been formed by reacting complex II with Lewis acids and alkylating agents. Lewis acids, like BF_3 or $TiCl_4$, or alkylating agents, such as Et_3OBF_4 or $MeSO_3F$, gave very unstable oxymethylene compounds which underwent homolytic fission of one $V-C$ σ bond. Stable oxymethylene compounds were isolated when the alkylation of II was carried out by using acyl halides $MeCOCl$ and $PhCOCl$. Compounds isolated in crystalline forms were $[cp_2V(Cl)(OC(O)Me)]$ (VI; $\nu(CO) = 1710$ cm^{-1}) and $[cp_2V(Cl)(OC(O)OPh)]$ (VII; $\nu(CO) = 1690$ cm^{-1}). The ionization of the $V-Cl$ bond in VI and VII allowed the second oxygen to bind vanadium forming metallacycles $[cp_2V(CH_2-O-C(O)-Me)](BPh_4)$ (VIII) and $[cp_2V(CH_2-O-C(O)-Ph)](BPh_4)$ (IX). The CO stretching band is significantly lowered, to 1605 cm^{-1} in VIII and to 1600 cm^{-1} in IX. An important lengthening of the $V-C$ and $C-O$ bond distances accompanying the acylation of formaldehyde [$V-C = 2.159$ (4) Å and $C-O = 1.474$ (5) Å in complex VIII; $V-C = 2.170$ (7) Å, and $C-O = 1.481$ (8) Å in complex IX] was observed. Complexes VIII and IX did not react or only slightly reacted with CO , inducing homolytic cleavage of the $V-C$ bond and forming $[cp_2V(CO)_2]^+$. Nickel(0)-phosphine complexes $[Ni(PR_3)_4]$ ($R = n-Bu$, XV; $R = Ph$, XVI) and $[Ni(PPh_3)_2(C_2H_4)]$ (XVII) promoted decomposition of formaldehyde to CO and H_2 , and they formed $[Ni(PR_3)_3(CO)]$ (XVIII and XIX) and $[Ni(PPh_3)_2(CO)_2]$ (XX), respectively. Reaction of these complexes was stoichiometric, but for XVII the reaction was slightly catalytic when carried out in vacuo. A titanium(III) complex, $[cpTi(Cl)_2(THF)_{1.5}]$ (XXI), was able to promote the deoxygenation of formaldehyde to ethylene, while titanium is converted into different oxo complexes, namely, $[cpTi(Cl)_2(\mu-O)]$ (XXII) and $[cpTi(Cl)(\mu-O)]_4$ (XXIII). Suggestions are given on the organometallic precursors leading to the deoxygenation of formaldehyde. Crystallographic details for complex II: space group $C2/c$ (monoclinic); $a = 13.634$ (3) Å, $b = 6.812$ (1) Å, $c = 20.528$ (4) Å, $\beta = 103.24$ (2)°; $V = 1855.9$ (6) Å³; $Z = 8$; $D_{calcd} = 1.51$ g cm^{-3} . The final R factor was 0.050 ($R_w = 0.051$) for 820 observed reflections. Crystallographic details for complex VIII: space group $P\bar{1}$ (triclinic); $a = 14.542$ (4) Å, $b = 11.108$ (4) Å, $c = 10.019$ (3) Å, $\alpha = 103.51$ (3)°, $\beta = 90.59$ (3)°, $\gamma = 110.39$ (3)°; $V = 1467.5$ (9) Å³; $Z = 2$; $D_{calcd} = 1.30$ g cm^{-3} . The final R factor was 0.057 ($R_w = 0.064$) for 2949 observed reflections. Crystallographic details for complex IX: space group Cc (monoclinic); $a = 11.233$ (1) Å, $b = 16.748$ (1) Å, $c = 17.475$ (1) Å, $\beta = 95.57$ (1)°; $V = 3272.1$ (4) Å³; $Z = 4$; $D_{calcd} = 1.29$ g cm^{-3} . The final R factor was 0.037 ($R_w = 0.039$) for 1789 observed reflections.

Introduction

The $[M(CH_2O)]$ functionality has an unquestionable role in carbon monoxide hydrogenation promoted either by homogeneous or heterogeneous catalysts.¹ Full understanding of the chemistry of such a functionality requires,

of course, syntheses of the $[M(CH_2O)]$ and $[M_2(\mu-CH_2O)]$ units and exploration of their chemistry. A number of significant issues related to this problem are listed below.

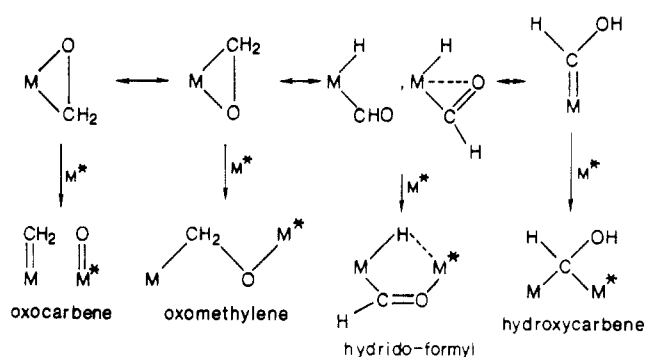
(1) Tkatchenko, I. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 8, Chapter 50.3, pp 102-115. Sneed, R. P. A. *Ibid.*, Chapter 50.2, pp 40-48. Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* 1982, 21, 117-130. Muettterties, E. L.; Stein, J. *Chem. Rev.* 1979, 79, 479-490. Eisenberg, R.; Hendriksen, D. E. *Adv. Catal.* 1979, 28, 79-172. Rofer-De Poorter, C. K. *Chem. Rev.* 1981, 81, 447-474. Beckborow, J. R.; Daroda, R. J.; Wilkinson, G. *Coord. Chem. Rev.* 1982, 43, 17-38.

[†] Columbia University.

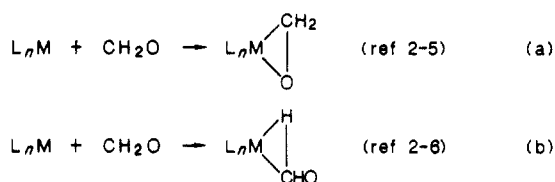
[‡] To whom correspondence should be addressed at ICMA, Université de Lausanne, Place du Château 3, CH-1005 Lausanne, Switzerland.

[§] Università di Parma.

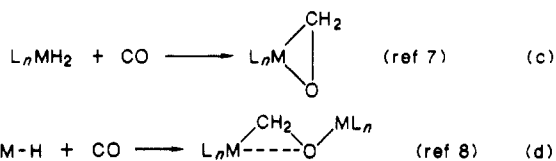
Scheme I



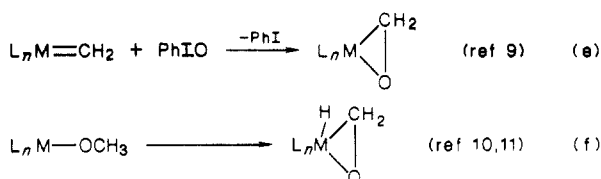
(i) The Synthesis of $[M(\text{CH}_2\text{O})]$ and $[M_2(\mu\text{-CH}_2\text{O})]$ Functionalities. The reaction of formaldehyde with transition-metal complexes seems to be the simplest approach to these units. However, these reactions can lead to results other than the formation of the $[M(\text{CH}_2\text{O})]$ functionality. Among the most interesting possibilities, two are provided by reactions a and b. Reaction of carbon



monoxide with M-H bonds to produce $[M(\text{CH}_2\text{O})]$ units (reactions c and d) seems to be driven by the oxophilicity of the metal center. Some unconventional syntheses,



related to the proposed synthesis of the $[M(\text{CH}_2\text{O})]$ unit in catalytic systems, have been reported.



(2) Brown, K. L.; Clark, G. R.; Headford, C. E. L.; Marsden, K.; Roper, W. R. *J. Am. Chem. Soc.* **1979**, *101*, 503-505.

(3) (a) Berke, H.; Bankhardt, W.; Huttner, G.; v. Seyerl, J.; Zsolnai, L. *Chem. Ber.* **1981**, *114*, 2754-2768. Berke, H.; Huttner, G.; Weiler, G.; Zsolnai, L. *J. Organomet. Chem.* **1981**, *219*, 353-362. (b) Berke, H.; Birk, R.; Huttner, G.; Zsolnai, L. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1984**, *39B*, 1380-1388.

(4) Head, R. A. *J. Chem. Soc., Dalton Trans.* **1982**, 1637-1639.

(5) (a) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1985**, *107*, 2985-2986. (b) Herberich, G. E.; Okuda, J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 402.

(6) Thorn, D. L. *Organometallics* **1982**, *1*, 197-204.

(7) Kropp, K.; Skibbe, V.; Erker, G.; Kruger, C. *J. Am. Chem. Soc.* **1983**, *105*, 3353-3354.

(8) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1983**, *105*, 1690-1691.

(9) Buhro, W. E.; Patton, A. T.; Strouse, C. E.; Gladysz, J. A.; McCormick, F. B.; Etter, M. C. *J. Am. Chem. Soc.* **1983**, *105*, 1056-1058.

(10) (a) Chaudret, B. N.; Cole-Hamilton, D. J.; Nohr, R. S.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1977**, 1546-1557. (b) Green, M. L. H.; Parkin, G.; Moynihan, K. J.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1984**, 1540.

(11) Barger, P. T.; Bercaw, J. E. *Organometallics* **1984**, *3*, 278-284. Erker, G. *Acc. Chem. Res.* **1984**, *17*, 103-109. Wolczanski, P. T.; Bercaw, J. E. *Ibid.* **1980**, *13*, 12-127. Sweet, J. R.; Graham, W. A. G. *J. Am. Chem. Soc.* **1982**, *104*, 2811-2815. Moloy, K. G.; Marks, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 7051-7064. Barger, P. T.; Santarsiero, B. D.; Armantrout, J. Bercaw, J. E. *Ibid.* **1984**, *106*, 5178-5186.

(ii) Identification of the Various Forms Which the $[M(\text{CH}_2\text{O})]$ Unit Can Take When Bonded to a Mononuclear or a Binuclear Structure and the Relationship Existing between Such Forms.¹¹ The most relevant in the context of carbon monoxide reduction are presented in Scheme I. A few of these functionalities, and their relationships, are of current interest of research.¹ Transformations of CH_2O leading to the generation and interconversion of the forms presented in Scheme I involve the C-H bond cleavage, the partial or complete cleavage of the $>\text{C}=\text{O}$ bond, and the rearrangement of each form upon addition of a second reactive site, M^* . The conversion of the $\eta^2\text{-CH}_2\text{O}$ formaldehyde form into the bridging oxymethylene ligand containing a M-C σ bond is a fundamental step for achieving the transformation of a C_1 into a C_2 fragment via insertion reactions.

The present report deals with the coordination of formaldehyde to vanadocene in the $\eta^2\text{-C}_2\text{O}$ form, its conversion into oxymethylene ligands by the action of Lewis acids, and the reaction of oxymethylene derivatives containing M-C σ bonds with carbon monoxide. In addition, the Ni(0)-promoted decomposition of formaldehyde to CO and H_2 and the deoxygenation of formaldehyde to ethylene using a titanium(III) complex are reported.

Some of the results here on vanadocene have been the subject of a communication.¹²

Experimental Section

All the reactions described were carried out under an atmosphere of purified nitrogen. Solvents were purified by standard methods. Paraformaldehyde was obtained from Aldrich and was used without further purification after being degassed in vacuo for a few hours. The presence of traces of moisture is inevitable. Vanadocene, cp_2V^{13} ($\text{cp} = \eta^5\text{-C}_5\text{H}_5$), dichloromonocyclopentadienyltitanium(III), $[\text{cpTi}(\text{Cl})_2(\text{THF})_{1.5}]$,¹⁴ $[\text{Ni}(\text{PPh}_3)_4]$,^{15a} $[\text{Ni}(\text{P-}n\text{-Bu}_3)_4]$,^{15a} $[\text{Ni}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)]$ ^{15b} were prepared as previously reported. IR spectra were recorded with a Perkin-Elmer 283 spectrophotometer. The magnetic susceptibility was determined by the Faraday method.

Synthesis of $\text{cp}_2\text{V}(\text{CH}_2\text{O})$ (II). A toluene (150-mL) solution of vanadocene (7.32 g, 40.4 mmol) was stirred with paraformaldehyde (1.5 g) for 2 days. 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 left 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) were highly air-sensitive. Anal. Calcd for $\text{cp}_2\text{V}(\text{CH}_2\text{O})$, $\text{C}_{11}\text{H}_{12}\text{OV}$: C, 62.57; H, 5.73. Found: C, 62.75; H, 5.78; M_r , 211 (mass spectrum). The IR spectrum (Nujol) showed a strong C-O band at 1160 cm^{-1} . $[\text{cp}_2\text{V}(\text{CH}_2\text{O})]$ is a thermally labile complex. The toluene solution from which complex II was crystallized contained a significant amount of HCOOMe . A toluene solution of complex II did not form any HCOOMe on standing for a long time. A THF solution (30 mL) of $[\text{cp}_2\text{V}(\text{CH}_2\text{O})]$ (0.21 g, 0.99 mmol) was reacted with iodine (0.30 g, 1.18 mmol) to give cp_2VI_2 ¹⁶ and paraformaldehyde. $\mu_{\text{eff}} = 1.71 \mu_B$ at 294 K.

Reaction of Complex II with Carbon Monoxide. A toluene solution (30 mL) of complex II (0.60 g) was reacted with carbon monoxide at atmospheric pressure. The solution showed after a few minutes a very weak band at 1881 cm^{-1} (complex III). The

(12) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1982**, *104*, 2019-2020.

(13) Fischer, E. O.; Vigoureux, S. *Chem. Ber.* **1958**, *91*, 2205-2212.

(14) Coutts, R. S. P.; Martin, R. L.; Wailes, P. C. *Aust. J. Chem.* **1971**, *24*, 2533-2540. Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1983**, *105*, 7295-7301.

(15) (a) Ittel, S. D. *Inorg. Synth.* **1977**, *17*, 117-124. (b) Wilke, G.; Herrmann, G. *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 549-550. (c) Aresta, M.; Nobile, C. F.; Sacco, A. *Inorg. Chim. Acta* **1975**, *12*, 167-168.

(16) Pasquali, M.; Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1981**, *20*, 165-171.

solution was left standing under CO overnight. The color became yellow-brown, while no solid was formed. The IR spectrum of the solution showed a significant increase in the band at 1881 cm^{-1} . The new band at 1730 cm^{-1} , which is due to HCOOMe, continued to increase during the 2 days the solution was left under CO. The presence of HCOOMe was verified by GLC and MS.

Disproportionation of Formaldehyde Promoted by Complexes II and III. To a toluene solution (60 mL) of complex II (0.55 g) was added paraformaldehyde (5.0 g). The suspension was stirred for days and showed a steady increase in HCOOMe to the maximum ratio of 1 mol of HCOOMe/mol of complex II.

A toluene solution (50 mL) of vanadocene (1.40 g) was reacted for 2 h with carbon monoxide to form $[\text{cp}_2\text{V}(\text{CO})]$ (III),¹⁷ then paraformaldehyde was added (0.4 g), and the resulting suspension was left stirring. Four hours later the IR spectrum showed the only presence of $[\text{cp}_2\text{V}(\text{CO})]$ (1881 cm^{-1}). HCOOMe was detected after 24 h by IR and its content steadily increased, but the reaction never became catalytic. The presence of methylformate was confirmed by MS and GLC.

Reactions of II with Alkylating Agents and Carbon Monoxide. (a) $\text{CH}_3\text{SO}_3\text{F}$. A THF solution (30 mL) of II (1.12 g) was reacted at -10°C with a THF solution (10 mL) of $\text{CH}_3\text{SO}_3\text{F}$ (0.45 mL). A black solid formed suddenly, as the mother liquor became nearly colorless. The suspension was stirred, and its temperature was allowed to rise to 20°C which caused the solid to dissolve, giving a deep blue solution, which was subsequently cooled to -50°C . A black microcrystalline solid formed (0.94 g; IV, R = Me). The thermal instability of the solid and its high sensitivity to oxygen prevented any analytical determination of the solid. After exposure of a THF solution of solid (IV, R = Me) to carbon monoxide, $[\text{cp}_2\text{V}(\text{CO})_2]^+$ was detected in solution. IV was left at room temperature in THF to dissolve and decompose. The presence of significant amounts of dimethylether in solution was confirmed by MS. A related amount of Me_2O was found in the solution which underwent carbonylation.

(b) Et_2OBF_4 . A Et_2O (50-mL) suspension of complex II (0.5 g, 2.76 mmol) was reacted with freshly prepared Et_2OBF_4 (0.4 g, 2.106 mmol). The reaction was carried out at -30°C . A solid formed after 10 h and was collected (0.61 g). When the solid was suspended in THF and exposed to a carbon monoxide atmosphere, $[\text{cp}_2\text{V}(\text{CO})_2](\text{BF}_4)$ (0.35 g) formed. Anal. Calcd for $\text{C}_{12}\text{H}_{10}\text{BF}_4\text{O}_2\text{V}$: C, 44.47; H, 3.11; F, 23.47. Found: C, 44.46; H, 3.22; F, 23.95.

Reaction of Complex II with Acetyl Chloride and Benzoyl Chloride. Complexes VI and VII. A toluene solution (50 mL) of complex II (0.91 g, 4.31 mmol) was reacted with freshly distilled PhCOCl (0.5 mL, 4.31 mmol). In a few seconds a light green crystalline solid precipitated from the solution (0.86 g, 70.9%). Anal. Calcd for $\text{cp}_2\text{V}(\text{CH}_2\text{O}_2\text{CPh})(\text{Cl})$, $\text{C}_{18}\text{H}_{17}\text{O}_2\text{ClV}$: C, 61.45; H, 4.87; Cl, 10.09. Found: C, 60.47; H, 5.18; Cl, 11.16. IR (Nujol): $\nu(\text{CO})$ 1690 cm^{-1} . Complex VII in toluene and DMF showed no reaction with CO at atmospheric pressure and room temperature, even after exposure to CO for 3 days.

Reaction of II with acetyl chloride, carried out following the same procedure, gave a crystalline solid complex, $[\text{cp}_2\text{V}(\text{CH}_2\text{O}_2\text{CMe})(\text{Cl})]$ (VI). Anal. Calcd for $\text{C}_{13}\text{H}_{15}\text{O}_2\text{ClV}$: C, 53.88; H, 5.22; Cl, 12.24. Found: C, 52.99; H, 5.73; Cl, 12.76. IR (Nujol) $\nu(\text{CO})$ 1710 cm^{-1} .

Synthesis of $[\text{cp}_2\text{V}(\eta^2\text{-CH}_2\text{O}_2\text{CR})](\text{BPh}_4)$ (VIII, R = Me, and IX, R = Ph). NaBPh_4 (0.60 g, 1.75 mmol) was added to a THF solution (50 mL) of complex VII. The resulting solution was left standing overnight. A deep blue crystalline solid formed (0.35 g). Anal. Calcd for $\text{C}_{42}\text{H}_{37}\text{BO}_2\text{V}$ (IX): C, 79.36; H, 5.87. Found: C, 78.97; H, 5.89. The IR spectrum showed a strong $\nu(\text{CO})$ (Nujol) at 1600 cm^{-1} . The same procedure was adopted for the synthesis of VIII. Anal. Calcd for $\text{C}_{37}\text{H}_{35}\text{BO}_2\text{V}$: C, 77.48; H, 6.16. Found: C, 76.44; H, 6.03. IR (Nujol): $\nu(\text{CO})$ 1605 cm^{-1} (vs). A THF suspension of VI was left stirring under 1 atm of carbon monoxide for 3 days. The IR spectrum showed only traces of $[\text{cp}_2\text{V}(\text{CO})_2]^+[\text{BPh}_4]^-$.

Reaction of Complex II with Lewis Acids and Carbon Monoxide. (a) BF_3 . A toluene solution (50 mL) of complex II (0.54 g) was reacted with gaseous BF_3 at -60°C . The solution

became violet, and a deep-violet solid formed. The suspension was warmed up to room temperature. The microcrystalline solid (0.66 g; X) proved to be so reactive that it was impossible to obtain analytical data for it. This solid was suspended in THF (50 mL) and reacted with carbon monoxide for 2 days at room temperature. An orange crystalline solid was formed, which had an IR spectrum identical with that of $[\text{cp}_2\text{V}(\text{CO})_2]^+$.¹⁷ Anal. Calcd for $[\text{cp}_2\text{V}(\text{CO})_2](\text{CH}_3\text{OBF}_3)$ (XI), $\text{C}_{13}\text{H}_{13}\text{BF}_3\text{O}_3\text{V}$: C, 46.45; H, 3.90; F, 17.27. Found: C, 45.15; H, 3.36; F, 18.61.

(b) TiCl_4 . A toluene solution (50 mL) of complex II (0.4 g, 1.90 mmol) was reacted at -60°C with a toluene (25 mL) solution of TiCl_4 (0.18 g, 0.95 mmol). A small amount of solid was filtered out which we were unable to identify. The resulting solution on standing gave green crystals, while the solution became deep blue (0.30 g). Anal. Calcd for $[\text{cp}_2\text{V}(\text{CH}_2\text{O})_2(\text{TiCl}_4)]$ (XII); $\text{C}_{22}\text{H}_{24}\text{Cl}_4\text{O}_2\text{TiV}_2$: C, 43.15; H, 3.95; Cl, 23.18. Found: C, 42.15; H, 4.57; Cl, 23.66. A small amount of $[\text{cp}_2\text{V}(\text{Cl})]$ was found in the mother liquor.

A THF solution (30 mL) of complex XII (0.26 g) was exposed to carbon monoxide for 1 day. No carbonyl was detected in solution by IR.

Reaction of $[\text{Ni}(\text{R}_3\text{P})_4]$ with Paraformaldehyde (R = *n*-Bu, Ph). A toluene solution (50 mL) of $[\text{Ni}(\textit{n}\text{-Bu}_3\text{P})_4]$ (XV; 0.80 g) was kept under nitrogen atmosphere to form the corresponding N_2 complex $[\nu(\text{N}=\text{N}) = 2063 \text{ cm}^{-1}]$.^{15c} A large excess of paraformaldehyde (2.0 g) was added. The color of the solution changed in a few minutes from deep red to yellow. A strong CO band from $[\text{Ni}(\textit{n}\text{-Bu}_3\text{P})_3\text{CO}]$ (XVIII) at 1910 cm^{-1} (toluene) appeared. The reaction produced H_2 which was identified by GC and corresponds to approximately 1 mol of H_2 /mol of complex. Carbon monoxide was absent. The NMR of the solution did not show the presence of any Ni-H unit. The solution was reacted with carbon monoxide and showed two strong CO bands (toluene) at 1990 and 1925 cm^{-1} for $[\text{Ni}(\textit{n}\text{-Bu}_3\text{P})_2(\text{CO})_2]$.¹⁸ Analogous results have been obtained by reacting $[\text{Ni}(\text{PPh}_3)_4]$ (XVI) with paraformaldehyde either in a stoichiometric amount or in a large excess. The reaction produced $[\text{Ni}(\text{PPh}_3)_3(\text{CO})]$ [XIX; $\nu(\text{CO}) = 1928 \text{ cm}^{-1}$ (toluene)], which via addition of CO gave the dicarbonyl $[\text{Ni}(\text{PPh}_3)_2(\text{CO})_2]$ [XX; $\nu(\text{CO}) = 2000$ and 1940 cm^{-1} (toluene)]. The reaction produced H_2 gas exclusively and no free carbon monoxide. In a gas-volumetric experiment at 24°C in toluene the amount of H_2 found was 0.97 mol/mol of Ni complex. Complexes $[\text{Ni}(\text{PR}_3)_4]$ (R = *n*-Bu, Ph) react with neither HCOOMe nor *s*-trioxane. Their reaction with paraformaldehyde was carried out in a carbon dioxide atmosphere in an attempt to trap a Ni-H species. The results were exactly the same as above. The reaction was carried out in EtOH with the same purpose, but the amount of H_2 evolved was always 1 mol/mol of complex.

Reaction of $[\text{Ni}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)]$ (XVII) with Paraformaldehyde. A toluene solution (30 mL) of $[\text{Ni}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)]$ (0.78 g) was reacted with solid paraformaldehyde (1.5 g). The suspension was left stirring for 1 day under vacuum. The IR spectrum of the solution showed two CO bands at 2000 and 1940 cm^{-1} (complex XX). The GC analysis of the gases showed the presence of CO, H_2 , and C_2H_4 . The CO/ H_2 ratio was found to be approximately 5. Decomposition of paraformaldehyde into H_2 and CO occurs only when reaction is carried out in vacuo.

Reaction of $[\text{cpTi}(\text{Cl})_2(\text{THF})_{1.5}]$ with Paraformaldehyde. A toluene suspension (50 mL) of $[\text{cpTi}(\text{Cl})_2(\text{THF})_{1.5}]$ was reacted with solid paraformaldehyde (3.0 g) at room temperature. The solution was heated by boiling, and in a few minutes the violet solid formed by loss of THF from the starting material dissolved, giving a golden yellow solution. The excess of paraformaldehyde was filtered out, and *n*-hexane (30 mL) was added to the resulting solution. The solution was left standing for 2 days and gave a mixture of two highly crystalline solids (0.88 g), which were shown by X-ray analysis to be the known $[\text{cpTi}(\text{Cl})_2\text{O}]$ ¹⁹ and $[\text{cpTi}(\text{Cl})(\text{O})]_4$.²⁰ The only gaseous product detected by GC was ethylene.

(18) Meriwether, L. S.; Fiene, M. L. *J. Am. Chem. Soc.* **1959**, *81*, 4200-4208.

(19) Thewalt, U.; Schomburg, D. *J. Organomet. Chem.* **1977**, *127*, 169-174.

(20) Skapki, A. C.; Troughton, P. G. H. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1970**, *26B*, 716-722.

(17) Fachinetti, G.; Del Nero, S.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1976**, 1046-1049. Calderazzo, F.; Bacciarrelli, S. *Inorg. Chem.* **1963**, *2*, 721-723.

Table I. Experimental Data for the X-ray Diffraction Studies on Crystalline [cp₂V(CH₂O)], [cp₂V(MeCO₂CH₂)BPh₄], and [cp₂V(PhCO₂CH₂)BPh₄]

	II	VIII	IX
mol formula	C ₁₁ H ₁₂ O _V	C ₃₇ H ₃₅ BO ₂ V	C ₄₂ H ₃₇ BO ₂ V
cryst system	monoclinic	triclinic	monoclinic
space group	C2/c [C _{2h} ⁶ ; no. 15]	P $\bar{1}$ [C ₁ ¹ ; no. 2]	Cc [C ₂ ¹ ; no. 9]
cell dims at 295 K			
a, Å	13.634 (3)	14.542 (4)	11.233 (1)
b, Å	6.812 (1)	11.108 (4)	16.748 (1)
c, Å	20.528 (4)	10.019 (3)	17.475 (1)
α , deg	90	103.51 (3)	90
β , deg	103.24 (2)	90.59 (3)	95.57 (1)
γ , deg	90	110.39 (3)	90
V, Å ³	1855.9 (6)	1467.5 (9)	3272.1 (4)
Z	8	2	4
D _{calcd} , g cm ⁻³	1.51	1.30	1.29
mol wt	211.2	573.4	635.5
cryst dims, mm	0.08 × 0.24 × 0.37	0.19 × 0.37 × 0.68	0.18 × 0.39 × 0.74
linear absorptn, cm ⁻¹	9.87	29.7	3.27
diffractometer		Siemens AED	
scan type		$\theta/2\theta$	
scan speed		3–12° θ /min	
scan width		($\theta - 0.5^\circ$) - [$\theta + (0.5 + \Delta\theta)$] ($\Delta\theta = (\lambda_{\alpha 2} - \lambda_{\alpha 1})/\lambda \tan \theta$)	
radiation	Nb-filtered Mo K α ($\lambda = 0.7107$ Å)	Ni-filtered Cu K α ($\lambda = 1.5418$ Å)	Nb-filtered Mo K α ($\lambda = 0.7107$ Å)
reflcn measd	$\pm h, +k, +l$	$\pm h, \pm k, +l$	$\pm h, +k, +l$
2 θ range, deg	6–50	6–120	5–52
std reflcn	231	242	600
	these were measured after every 50 reflctns:	no significant changes in intensity were observed	
unique total data	1626	4182	3330
unique obsd data ($I > 2\sigma$)	820	2949	1789
no. of variables	118	371	412

X-ray Crystallography

The crystals selected for study were mounted in glass capillaries and sealed under nitrogen. Extensive preliminary investigations employing rotation and Weissenberg photographs showed the crystals of complex II to be monoclinic (with systematic absences consistent with the space groups C2/c or Cc) and the crystals of IX to be triclinic. Crystal data and details of the parameters associated with data collection are given in Table I. Lattice constants came from a least-squares refinement of the 2 θ values for 15 reflections having 2 $\theta > 40^\circ$ for complex II and 20 reflections having 2 $\theta > 30^\circ$ and $>70^\circ$ for complexes VIII and IX, respectively.

Data were collected at room temperature on a single-crystal diffractometer. For intensities and background the profile measurement technique was used.²¹ The structure amplitudes were obtained after the usual Lorentz and polarization reduction,²² and the absolute scale was established by the Wilson's method.²³ No correction for absorption was applied.

The function minimized during the least-squares refinement was $\sum w|F|^2$. The weighting scheme used was $w = k/[\sigma^2(F_o) + |g|(F_o^2)]$; k was redetermined after each structure factor calculation and refined by fitting $(|F_o| - |F_c|)^2$ to $[\sigma^2(F_o) + |g|(F_o^2)]/k$. The value for g was that giving the smallest variation of the mean value of $w(|F_o| - |F_c|)^2$ as a function of the magnitude of F_o . Anomalous scattering corrections were included in all structure factor calculations.^{19b} Scattering factors for neutral atoms were taken from ref 24 for V, from ref 25 for O, C, and B, and from ref 26 for H.

Structure Solution and Refinement for Complex II. The E statistic calculated as a function of $\sin \theta$ marginally favored the centric case, $(|E^2 - 1|)$ being equal to 0.92 (≈ 0.97 is the theoretical value accepted for centrosymmetric structures). The

space group C2/c was then assumed and was confirmed by the successful solution and refinement of the crystal structure. The structure was solved by the heavy-atom method, starting from a three-dimensional Patterson map which gave the approximate coordinates for the vanadium and oxygen atoms. The remaining non-hydrogen atoms were located from the subsequent difference Fourier synthesis. Full-matrix least-squares refinement of the scale factor and positional and anisotropic thermal parameters for all 13 non-hydrogen atoms led to convergence with $R_F = 5.0\%$ and $R_{wF} = 5.1\%$ for 820 observed reflections. The 12 hydrogen atoms were readily located in geometrically reasonable regions with electronic density ranging from 0.8 to 0.4 e Å⁻³; these were assigned isotropic thermal parameters of $B = 7.1$ Å² and included in successive calculations but were not refined.

Three further cycles of full-matrix least-squares refinement led to final convergence with $R_F = 4.8\%$, $R_{wF} = 4.9\%$, and $GOF = 0.20$. In the final cycle no parameter shifted by more than 0.3 times its standard deviation, and the values for k and g were 0.2894 and 0.004001, respectively. A final difference Fourier synthesis showed no unexpected features with no peak above the general background.

Structure Solution and Refinement for Complex VIII. The 2949 reflections with $I > 2\sigma(I)$ were used in the structure solution and refinement. The structure was solved by the heavy-atom method and refined to final R and R_w values of 5.7% and 6.4%, respectively. In the initial stages the Ph rings of the anion were considered as idealized rigid groups (D_{6h}). In the final refinement all constraints were removed, and all non-hydrogen atoms were allowed to vary anisotropically. Refinement was continued until shifts in all parameters were less than one estimated standard deviation in the respective parameter. The hydrogen atoms were located from successive difference Fourier syntheses and introduced as fixed contributors with isotropic thermal parameters fixed at 6.3 Å². In the final difference map there were no peaks above the general background. The NO:NV ratio was 2949:371 $\approx 7.9:1$. The values for k and g were 1.0000 and 0.029237, respectively, and the goodness of fit was 0.40.

Structure Solution and Refinement for Complex IX. The E statistic calculated as a function of $\sin \theta$ favored the acentric case, $(|E^2 - 1|)$ being equal to 0.73 (0.74 is the theoretical value accepted for the noncentrosymmetric structures). The space group Cc was then assumed and was confirmed by the successful solution and refinement of the crystal structure. The structure was solved by the heavy-atom method, starting from a three-dimensional Patterson map, which gave the approximate coordinates

(21) Lehmann, M. S.; Larsen, F. K. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffraction, Theor. Gen. Crystallogr.* **1974**, *A30*, 580–584.

(22) Data reduction, structure solution, and refinement were carried out on a Cyber 7600 computer of the Centro di Calcolo dell'Italia Nord-Orientale, using: *SHELX-76 System of Crystallographic Computer Programs*; Sheldrick, G., Eds.; University of Cambridge: Cambridge, England, 1976. Calculation were performed with the financial support of the University of Parma.

(23) Wilson, A. J. C. *Nature (London)* **1942**, *150*, 151–152.

(24) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV: (a) p 99; (b) p 149.

(25) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffraction, Theor. Gen. Crystallogr.* **1968**, *A24*, 321–324.

(26) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175–3187.

Table II. Fractional Atomic Coordinates ($\times 10^4$) with Estimated Standard Deviations in Parentheses for Complex II

atom	x/a	y/b	z/c
V	2160 (1)	2010 (2)	1314 (1)
O1	2216 (4)	-782 (7)	1540 (3)
C1	1183 (7)	4464 (14)	1556 (5)
C2	922 (7)	2733 (19)	1852 (5)
C3	502 (7)	1456 (15)	1343 (8)
C4	496 (6)	2339 (15)	753 (5)
C5	899 (5)	4159 (13)	860 (4)
C6	3600 (6)	3214 (16)	1970 (1)
C7	3227 (6)	4607 (13)	1488 (5)
C8	3217 (6)	3856 (20)	871 (5)
C9	3628 (7)	2002 (20)	964 (6)
C10	3869 (6)	1625 (15)	1655 (6)
C11	2057 (9)	-763 (12)	865 (4)

Table III. Fractional Atomic Coordinates ($\times 10^4$) with Estimated Standard Deviations in Parentheses for Complex VIII

atom	x/a	y/b	z/c
V	2366 (0)	129 (1)	1641 (1)
O1	3511 (2)	1186 (2)	708 (3)
O2	3666 (2)	2962 (2)	2373 (3)
C1	1584 (4)	-228 (7)	-491 (6)
C2	1503 (3)	909 (6)	352 (5)
C3	933 (3)	533 (5)	1402 (5)
C4	667 (4)	-790 (7)	1243 (8)
C5	1097 (5)	-1274 (6)	32 (8)
C6	3552 (5)	133 (6)	3093 (6)
C7	2649 (5)	-296 (5)	3678 (5)
C8	2063 (5)	-1490 (5)	2796 (6)
C9	2540 (8)	-1832 (6)	1709 (7)
C10	3469 (6)	-854 (8)	1873 (6)
C11	2795 (3)	2135 (4)	2910 (4)
C12	3920 (3)	2385 (4)	1257 (4)
C13	4729 (3)	3245 (4)	659 (5)
B	2202 (2)	4248 (3)	7279 (4)
C21	3011 (2)	3509 (3)	6995 (3)
C22	2842 (3)	2316 (3)	7354 (4)
C23	3518 (3)	1668 (4)	7186 (4)
C24	4384 (3)	2201 (4)	6642 (4)
C25	4570 (3)	3361 (4)	6277 (4)
C26	3894 (2)	3997 (3)	6442 (3)
C31	1170 (2)	3421 (3)	6273 (3)
C32	476 (2)	4024 (3)	6144 (4)
C33	-387 (3)	3410 (4)	5295 (5)
C34	-630 (3)	2122 (5)	4517 (4)
C35	19 (3)	1487 (4)	4611 (4)
C36	895 (2)	2131 (3)	5469 (4)
C41	1998 (2)	4401 (3)	8918 (3)
C42	2765 (2)	4724 (3)	9937 (4)
C43	2637 (3)	4895 (4)	11319 (4)
C44	1717 (3)	4728 (4)	11759 (4)
C45	938 (3)	4407 (4)	10795 (4)
C46	1077 (2)	4254 (4)	9400 (4)
C51	2661 (2)	5725 (3)	6957 (3)
C52	3008 (3)	6916 (3)	7960 (4)
C53	3429 (3)	8138 (3)	7622 (5)
C54	3510 (3)	8192 (3)	6291 (5)
C55	3165 (2)	7021 (3)	5256 (4)
C56	2749 (2)	5822 (3)	5609 (4)

for the vanadium and oxygen atoms. The remaining non-hydrogen atoms were located from a series of difference Fourier synthesis, each being phased by an increasing number of atoms. Full-matrix least-squares refinement of the scale factor and positional and anisotropic thermal parameters for all non-hydrogen atoms led to convergence with $R_F = 4.8\%$ and $R_{wF} = 5.2\%$ for 1789 observed reflections. Hydrogen atoms were now located in a difference Fourier map and included in calculations as fixed contributors ($B = 6.3 \text{ \AA}^2$). Three further cycles of full-matrix least-squares refinement led to final convergence with $R_F = 3.7\%$, $R_{wF} = 3.9\%$, and $GOF = 0.37$. For confirmation of the choice of hand for the dissymmetric space group, the model was inverted and converged. Final agreement factors of $R_F = 3.9\%$ and $R_{wF} = 4.2\%$ indicated

Table IV. Fractional Atomic Coordinates ($\times 10^4$) with Estimated Standard Deviations in Parentheses for Complex IX

atom	x/a	y/b	z/c
V	0 (1)	1245 (1)	2500 (1)
O1	-297 (4)	2398 (2)	2139 (3)
O2	-372 (4)	2738 (2)	3359 (3)
C1	1607 (6)	476 (4)	2351 (5)
C2	1733 (6)	1153 (5)	1931 (4)
C3	1885 (6)	1758 (4)	2439 (7)
C4	1826 (6)	1489 (7)	3167 (6)
C5	1629 (6)	645 (6)	3112 (5)
C6	-1622 (7)	508 (5)	2767 (5)
C7	-882 (6)	13 (4)	2393 (5)
C8	-810 (6)	303 (4)	1649 (4)
C9	-1479 (9)	981 (5)	1561 (6)
C10	-2012 (7)	1109 (5)	2245 (9)
C11	-492 (6)	1873 (4)	3509 (4)
C12	-305 (5)	2918 (4)	2646 (4)
C13	-212 (5)	3772 (3)	2465 (5)
C14	-532 (6)	4335 (4)	2962 (5)
C15	-433 (7)	5146 (5)	2750 (7)
C16	36 (8)	5333 (5)	2074 (8)
C17	327 (8)	4773 (5)	1582 (5)
C18	195 (7)	3967 (4)	1758 (5)
B	668 (6)	2009 (4)	-790 (4)
C21	1379 (3)	1201 (2)	-410 (2)
C22	751 (3)	539 (2)	-178 (2)
C23	1370 (3)	-135 (2)	113 (2)
C24	2617 (3)	-146 (2)	172 (2)
C25	3246 (3)	516 (2)	-59 (2)
C26	2626 (3)	1189 (2)	-350 (2)
C31	-744 (2)	2035 (2)	-556 (2)
C32	-1073 (2)	2563 (2)	4 (2)
C33	-2244 (2)	2566 (2)	206 (2)
C34	-3087 (2)	2041 (2)	-152 (2)
C35	-2759 (2)	1513 (2)	-713 (2)
C36	-1587 (2)	1511 (2)	-915 (2)
C41	1355 (4)	2853 (2)	-470 (2)
C42	1145 (4)	3548 (2)	-901 (2)
C43	1650 (4)	4269 (2)	-634 (2)
C44	2364 (4)	4295 (2)	65 (2)
C45	2574 (4)	3599 (2)	496 (2)
C46	2070 (4)	2878 (2)	229 (2)
C51	645 (5)	1997 (2)	-1751 (2)
C52	1577 (5)	1649 (2)	-2106 (2)
C53	1563 (5)	1667 (2)	-2905 (2)
C54	617 (5)	2034 (2)	-3348 (2)
C55	-315 (5)	2382 (2)	-2993 (2)
C56	-300 (5)	2363 (2)	-2194 (2)

the previous choice to be the correct one. In the final cycle no parameter shifted by more than 0.3 times its standard deviation, and the values for k and g were 0.3307 and 0.003354, respectively. A final difference Fourier synthesis showed no unexpected features with no peak above the general background. During all the refinement the phenyl rings of the BPh_4^- anion were treated as idealized rigid groups.²²

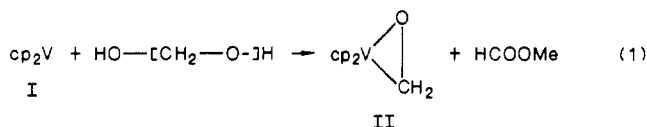
Final atomic coordinates are listed in Tables II-IV, and thermal parameters are given in Tables SIV-SVI.²⁷

Results and Discussion

Paraformaldehyde has been used as a source of monomeric formaldehyde in reactions with metal complexes, on the assumption that it can provide some free formaldehyde in solution of organic solvent. A major problem in these reactions is to limit the degree of hydration of formaldehyde, since hydration can promote hydrolysis of the complexes.

Vanadocene, cp_2V ($\text{cp} = \eta^5\text{-C}_5\text{H}_5$), reacted with a toluene suspension of paraformaldehyde giving a deep-green solution from which II was crystallized. The solution contained a significant amount of HCOOMe (vide infra).

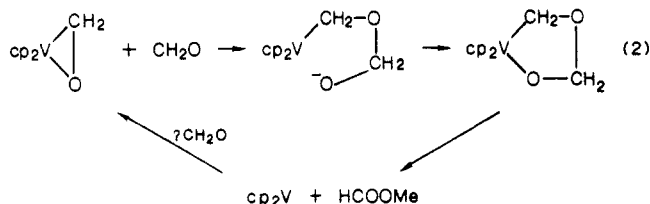
(27) See paragraph at the end of the paper regarding supplementary material.



Complex II is paramagnetic with one unpaired electron as expected formally for a vanadium(IV) or for a vanadium(II) with the cp_2VL set of ligands around the metal. The strong C–O stretching vibration for the $\eta^2\text{-H}_2\text{C-O}$ -bonded unit appears at 1160 cm^{-1} . The η^2 -bonding mode of formaldehyde is shown in Figure 1, while the most relevant bond distances and angles for II are listed in Table V. The C–O bond distance [$1.353(10)\text{ \AA}$] is in the range of the other formaldehyde complexes reported thus far: $[\text{Fe}(\text{CO})_2(\text{P}(\text{OMe})_3)_2(\eta^2\text{-CH}_2\text{O})]$,^{3a} $[\text{cpRe}(\text{PPh}_3)(\text{NO})(\eta^2\text{-CH}_2\text{O})]^+$,⁹ $[\text{cp}_2\text{Mo}(\eta^2\text{-CH}_2\text{O})]$,⁵ and $[(\text{cp}_2\text{ZrCl})_2(\text{CH}_2\text{O})]$.⁸ The exception is the osmium complex $[\text{Os}(\text{CO})_2(\text{PPh}_3)_2(\eta^2\text{-CH}_2\text{O})]^2$ which has a much longer C–O bond distance [$1.59(1)\text{ \AA}$]. All these C–O bond distances must be compared with the C–O bond distance [1.225 \AA] in free formaldehyde.²⁸ A common characteristic of the most of the oxophilic metals is that the metal–oxygen bond distance is significantly shorter than the metal–carbon bond distance [$\text{V-C11} = 2.092(8)$ vs. $\text{V-O1} = 1.955(5)\text{ \AA}$], and a similar trend was observed in $[\text{cp}_2\text{Mo}(\eta^2\text{-CH}_2\text{O})]$.⁵

A few examples of organometallic derivatives of vanadium are available for a significant comparison of the corresponding V–C σ bond distances,²⁹ and this leads to the conclusion that the V–C bond in complex II has some double-bond character. A recent example containing a genuine V–C single bond is the complex $[\text{V}(\text{acacen})(\text{CH}_2\text{Ph})_2]$ [acacen = *N,N'*-ethylenebis(acetylacetoniminato) dianion] having a V–C bond distance of $2.156(7)\text{ \AA}$.³⁰

An important facet of the synthesis of II is the presence of HCOOMe in solution. We found that the complex itself does not decompose in toluene giving HCOOMe but promotes the disproportionation of paraformaldehyde to methyl formate. This is a classic reaction which can be achieved by many reagents and particularly by $\text{Al}(\text{OR})_3$ in the Tishchenko form.³¹ The mechanism may or may not have close similarities with that promoted by complexes like II. Two limiting cases can be proposed. The first one (eq 2) involves a head-to-tail dimerization of the



CH_2O unit, a pathway which is highly reminiscent of the disproportionation of the $[\text{M-CHO}]$ functionality^{32a} and which has been postulated by Roper for a ruthenium-promoted transformation of formaldehyde into a methyl and a formate group.^{32b} These groups can be reductively

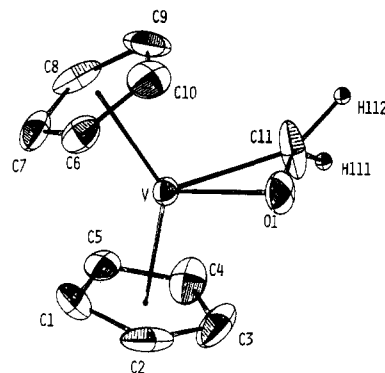
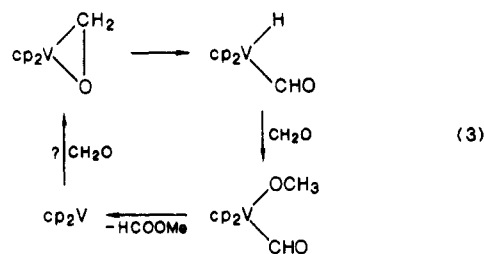


Figure 1. An ORTEP drawing for complex II (30% probability ellipsoids).

Table V. Selected Bond Distances (\AA) and Angles (deg)

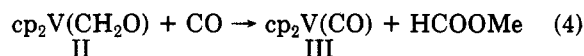
	II	VIII	IX
V–O1	1.955 (5)	2.051 (2)	2.049 (4)
V–C11	2.092 (8)	2.159 (4)	2.170 (7)
V–cp1	1.964 (9)	1.966 (6)	1.955 (7)
V–cp2	1.945 (9)	1.939 (8)	1.951 (8)
O1–C11	1.353 (10)		
O1–C12		1.236 (4)	1.243 (8)
O2–C12		1.280 (5)	1.291 (9)
O2–C11		1.474 (5)	1.481 (8)
C12–C13		1.468 (6)	1.471 (9)
cp1–V–cp2	137.6 (5)	137.1 (3)	134.7 (4)
O1–V–C11	38.9 (3)	76.4 (1)	75.3 (2)
cp1–V–O1	109.9 (3)	105.9 (2)	105.8 (3)
cp1–V–C11	109.5 (4)	105.3 (2)	108.4 (3)
cp2–V–O1	110.8 (3)	107.8 (2)	109.4 (3)
cp2–V–C11	109.5 (4)	107.8 (2)	107.3 (3)

eliminated from the metal-forming methyl formate. The alternative mechanism (eq 3) involves as a key step the very plausible rearrangement of the CH_2O to a metal-hydrido-formyl group.^{2,6,33} Both eq 2 and 3 imply catalytic



activity of II in causing the disproportionation of formaldehyde, which we were not able to demonstrate experimentally. A possible explanation for this might be the amount of water that paraformaldehyde carries which may cause hydrolysis of some intermediates.

A related reaction to (2) and (3) is the formation of HCOOMe when complex II is reacted with carbon monoxide (eq 4). Complex III itself was found to be active



in promoting the disproportionation of paraformaldehyde. The reaction of carbon monoxide with II must free some formaldehyde ligand; free formaldehyde is required for the metal-bonded formaldehyde group to produce HCOOMe. In addition, complex III reacted with paraformaldehyde and released some carbon monoxide, which was detected by GLC. The observed disproportionation involves both free and metal-bonded formaldehyde in a sort of equilibrium between II and III. We would like to add a comment

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

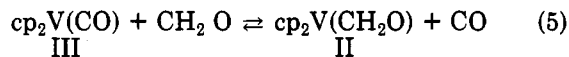
(29) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* 1984, 886–887. Fachinetti, G.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* 1979, 18, 2282–2287.

(30) Gambarotta, S.; Mazzanti, M.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* 1985, 829–830.

(31) March, J. *Advanced Organic Chemistry: Reactions, Mechanisms and Structure*, 3rd ed.; McGraw-Hill: New York, 1985; p 1119.

(32) (a) Casey, C. P.; Andrews, M. A.; McAlister, D. R. *J. Am. Chem. Soc.* 1979, 101, 3371–3373. Casey, C. P.; Neumann, S. M.; Andrews, M. A.; McAlister, D. R. *Pure Appl. Chem.* 1980, 52, 625–633. (b) Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* 1982, 234, C5–C8.

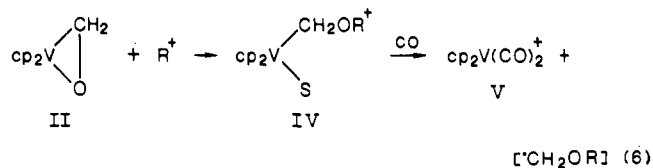
(33) Bianchini, C.; Meli, A. *Organometallics* 1985, 4, 1537–1542.



on the observation that a very common product of syngas chemistry is HCOOMe. The genesis is currently explained by assuming the insertion of carbon monoxide into a metal-OCH₃ group.³⁴ The results outlined above suggest reconsideration of this hypothesis. The formation of HCOOMe may be proof that a catalytic system produces formaldehyde in a preliminary step, which subsequently disproportionates, as the primary product in the hydrogenation of carbon monoxide.

The reaction of carbon monoxide did not afford any interesting transformation of the M-CH₂O functionality, as expected, since it does not contain any M-C σ bonds.³⁵ The transformation of the formaldehyde group into an oxymethylene ligand containing a M-C σ bond was examined next. To this purpose, a number of reaction of II with Lewis acids and alkylating agents were studied.

Mild alkylating agents, like CH₃I, did not react with II. Stronger alkylating reagents, like MeSO₃F and Et₃OBf₄, reacted producing very reactive derivatives. The isolation

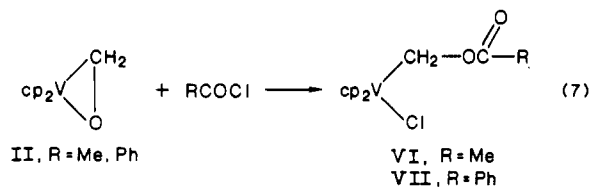


R = Me or Et as [MeSO₃F] or [Et₃OBf₄]; S = solvent molecule.

of complexes IV was almost prevented by their thermal instability and high reactivity. When they are allowed to decompose by warming to room temperature, they give the cp₂V⁺ cation¹⁷ and CH₃OR which are expected products of homolytic fission of the V-C σ bond. Reaction of complexes IV even at low temperature with carbon monoxide gave the same result, except for the fact that the cp₂V⁺ is trapped in the form of the corresponding dicarbonyl V.¹⁷ No insertion of carbon monoxide into the V-C σ bond was observed.

The instability of complexes IV does not come as a surprise, since it is well-known that the alkyl residue can reduce vanadium(IV) to vanadium(III), depending on the nature of the organic residue.³⁶ The structure we propose for IV is justified on the basis of analogous structures (vide infra).

Reactions 7 were carried out by using acyl chlorides, and the results were significantly different in terms of stability of the final compounds in comparison with the products from reaction 6. Complexes VI and VII have been isolated



in a crystalline form. They showed high thermal stability.

(34) Bryndza, H. E. *Organometallics* 1985, 4, 1686-1687. Rees, W. M.; Atwood, J. D. *Ibid.* 1985, 4, 1402-1404.

(35) (a) Basolo, F.; Pearson, R. G. *Mechanisms of Inorganic Reactions*, 2nd ed.; Wiley: New York, 1968; Chapter 7. (b) Parrshall, G. W. *Homogeneous Catalysis*; Wiley-Interscience: New York, 1980; Chapter 5. (c) Heck, R. F. *Organotransition Metal Chemistry*; Academic Press: New York, 1974; Chapter 9. (d) Wojcicki, A. *Adv. Organomet. Chem.* 1973, 11, 87-145; 1974, 12, 31-81. (e) Eisenberg, R.; Hendricksen, D. E. *Adv. Catal.* 1979, 28, 79-172. Calderazzo, F. *Angew. Chem., Int. Ed. Engl.* 1977, 16, 299-311.

(36) Connelly, N. G. in *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 3, Chapter 24, pp 656-663.

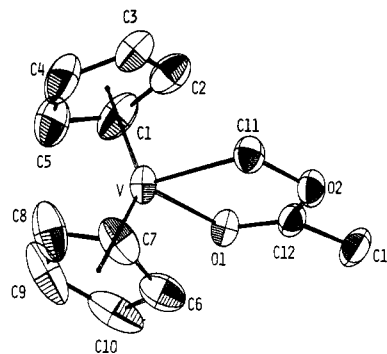


Figure 2. An ORTEP drawing for complex VIII (30% probability ellipsoids).

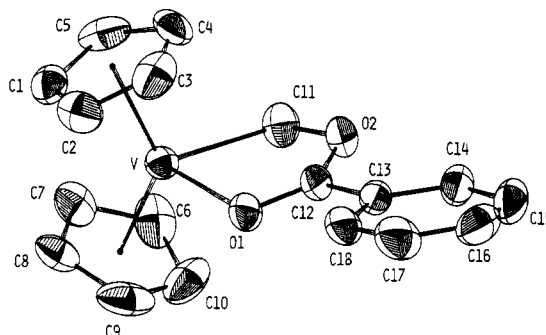
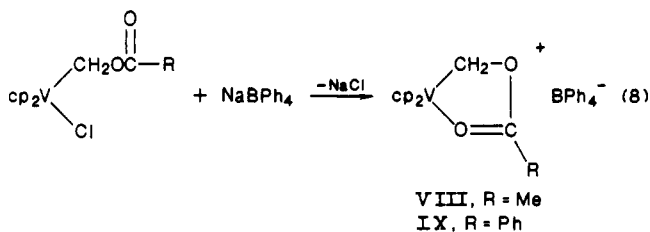


Figure 3. An ORTEP drawing for complex IX (30% probability ellipsoids).

They have one unpaired electron (see Experimental Section). They did not react after exposure for days to carbon monoxide atmosphere. This can be ascribed to the special nature of the (acyloxy)methylene group or to the absence of a vacant coordination site on the metal since the only available orbital is filled by the unpaired electron. We attempted to make a free coordination site on vanadium by removing the Cl⁻ ligand. This attempt was carried out by reacting complexes VI and VII with NaBPh₄. Reaction

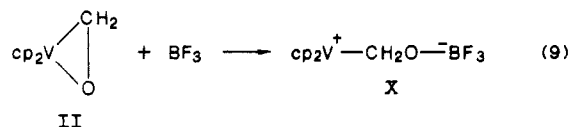


8 did not succeed in providing a free coordination site on the metal, since the (acyloxy)methylene residue can act as a bidentate ligand forming a stable metallacycle. The cationic acyloxymethylene complexes VIII and IX seem more reactive with CO, even if the only detectable species were traces of [cp₂V(CO)₂]⁺.¹⁷ The structures we determined for complexes VIII and IX serve as support for the structure we proposed for complexes IV, VI, and VII as mentioned above. The ORTEP shown for complexes VIII and IX are reported in Figures 2 and 3, while the most relevant bond distances and angles are in Table V. In both complexes the (acyloxy)methylene fragment acts as bidentate ligand for the metal in the equatorial plane. In complex VIII the metallacyclic ring is nearly planar, with a maximum displacement of 0.058 Å for C11. The dihedral angles determined by the metallacycle plane and the cp rings are 21.2 (2) and 20.1 (2)°. In complex VIII the chelation ring shows an envelope conformation, the vanadium atom being displaced by 0.507 (1) Å from the plane through C11, O2, C12, O1 (Table SX), which forms dihe-

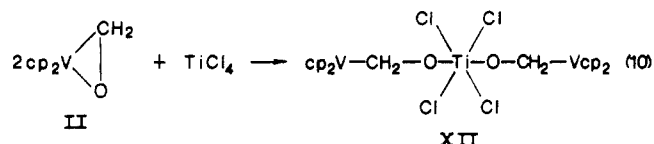
dral angles of 5.6 (3) and 40.3 (3)° with the cyclopentadienyl rings C1...C5 and C6...C10, respectively.

The most significant structural parameters appear in the oxymethylene unit. A significant lengthening of the V-C and V-O bonds is observed moving from complex II to complexes VIII and IX (V-C11 = 2.159 (4) Å in VIII and 2.170 (7) Å in IX vs. 2.092 (8) Å in II; V-O1 = 2.051 (2) Å in VIII and 2.049 (4) Å in IX vs. 1.955 (5) Å in II. The same trend occurs for the C-O bond distance in the oxymethylene unit (C11-O2 = 1.474 (5) Å in VIII and 1.418 (8) Å in IX vs. C11-O1 = 1.353 (10) Å in II. Both C12-O bond distances have significant double-bond character, with the shortest bond between C12-O1. A significant electron delocalization occurs on the C12-O2 unit. This is in agreement with the shift of the CO stretching vibration in the IR spectrum from 1710 to 1605 cm⁻¹ (complex VIII) and from 1690 to 1600 cm⁻¹ (complex IX). It must be emphasized that the acylation of the formaldehyde group produces a V-C σ bond which can, in principle, undergo insertion reactions. (Acyloxy)methylene compounds have been found to insert carbon monoxide in modeling compounds, or they have been proposed as intermediate in the formation of ethylene glycol precursors during the hydrogenation of carbon monoxide catalyzed by Ru carbonyls.³⁷ Such a reaction was unsuccessful in case of the vanadium derivatives discussed in this paper.

Conversion of the formaldehyde into an oxymethylene group was attempted by using different Lewis acids. These reactions succeeded but produced unstable compounds, which did not insert carbon monoxide in the corresponding V-C σ bonds. Reaction of complex X with carbon monoxide,



oxide, whose isolation is extremely difficult, consistently gave [cp₂V(CO)₂]⁺ (V) as [cp₂V(CO)₂](CH₃OBF₃) (XI). A reasonable degree of stability was found for the complex formed from II and TiCl₄. Results presented above on



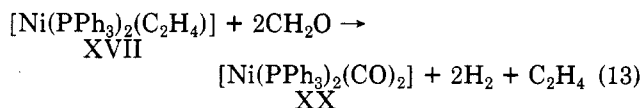
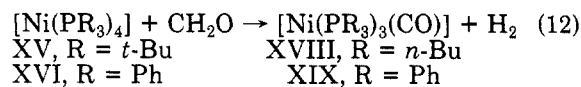
the reaction of alkylating agents and Lewis acids with II, show clearly that attack occurs on the oxygen atom of the CH₂O group regardless of the nature of the Lewis acid, to produce a V-C σ bond.

Decarbonylation of Formaldehyde. A reactive metal site, depending on its oxophilicity and on its oxidation state, can oxidatively add either to the C=O bond or to the C-H bond of formaldehyde. A well-documented reaction for a cationic iridium(I) complex (XIII) is represented in eq 11.⁶ It should also be mentioned that a



rearrangement of the η²-CH₂O formaldehyde group into a hydrido-formyl derivative was observed in [Os(CO)₂(PPh₃)₂(η²-CH₂O)].²

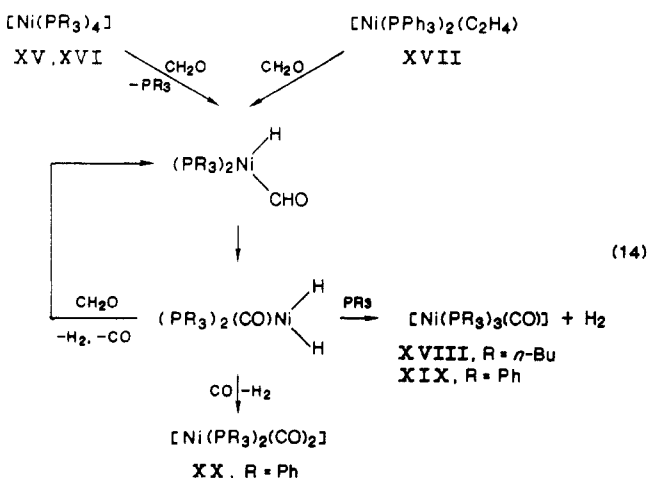
We found that, in related reactions, Ni(0) complexes XV-XVII are able to perform in toluene solution a very fast and quantitative decarbonylation of formaldehyde.



Decarbonylation of formaldehyde in reaction 12 is stoichiometric, as no carbon monoxide was observed in the gas phase. However, when reaction 13 was performed under vacuum, it was possible to detect a significant amount of carbon monoxide, which indicates some catalytic activity of XVII in promoting the decarbonylation of formaldehyde. Complexes XV-XVII seemed unable to promote hydrogen transfer from formaldehyde to a substrate. Ethylene itself is recovered unchanged in reaction 13. In spite of the addition of other hydrogen acceptors to the reaction, such as CO₂, which can react with M-H bonds, molecular hydrogen is formed. In contrast, Rh-promoted hydrogen transfer from formaldehyde to other aldehydes and ketones was observed and reported.³⁸

A recent related investigation deals with the reaction of [Ni(np₃)] (np₃ = tris[2-(diphenylphosphino)ethyl]amine) of formaldehyde. Decarbonylation of CH₂O was observed to form [Ni(np₃)(CO)].³³ As a matter of fact the rigid coordination sphere imposed by the np₃ ligand may affect significantly the action mode of the metal site, as a consequence of the tetracoordination continuously assured by the four donor atoms of the structure. With use of monodentate ligands or a poor coordination sphere around the metal, the formaldehyde decompositions can both occur through a different pathway and rise to the catalytic threshold.

Reactions 12 and 13 involve steps which are closely related to those described for the dehydrogenation of methoxy groups by ruthenium^{10a} and tungsten complexes^{10b} and those involved in the reaction of Ni(np₃) with formaldehyde.³³ This result seems to be in line with the well-known metal-promoted decarbonylation of aldehydes.³⁹ This type of reaction involves as a key step the oxidative addition of the C-H bond to the metal. The



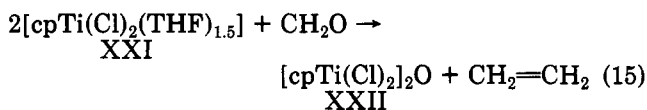
(38) Cook, J.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* 1981, 924-925.

(39) Tsuji, J. *Decarbonylation Reactions using Transition Metal Compounds: Organic Synthesis via Metal Carbonyls*; Wender, I., Pino, P., Eds.; Wiley: New York, 1977; Vol. II, p 595.

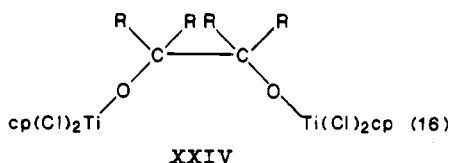
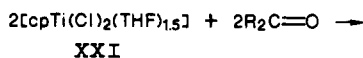
(37) Dombek, B. D. *J. Am. Chem. Soc.* 1980, 102, 6855-6857; 1979, 101, 6466-6468.

proposed pathways take into account the observed poor catalytic decomposition of paraformaldehyde promoted by XVII vs. the stoichiometric result when XV and XVI have been used and the presence of significant amounts of carbon monoxide in the gas phase.

Deoxygenation of Formaldehyde. Carbon-oxygen bond cleavage is a fundamental transformation of the CH_2O fragment which, as emphasized in the introduction, is related to some of the proposed steps in the hydrogenation of carbon monoxide.⁴⁰ We achieved C-O bond cleavage by reacting paraformaldehyde with complex XXI.¹⁴ Reaction 15 was performed in boiling toluene.



Ethylene was the only detectable organic product. The reaction produced two μ -oxo complexes of titanium(IV) which crystallized together. X-ray analysis indicated that the two μ -oxo complexes were $[\text{cpTi}(\text{Cl})_2]_2\text{O}$ (XXII)¹⁹ and $[\text{cpTi}(\text{Cl})(\mu\text{-O})]_4$ (XXIII). Deoxygenation of formaldehyde probably produces XXII exclusively, while XXIII is probably formed from the hydrolysis of XXII. Hydrolysis is unavoidable, since paraformaldehyde always has a certain degree of hydration. It should be mentioned that complex XXI is a well-known free radical type coupling agent with the carbonyl group.⁴¹ In general, however,



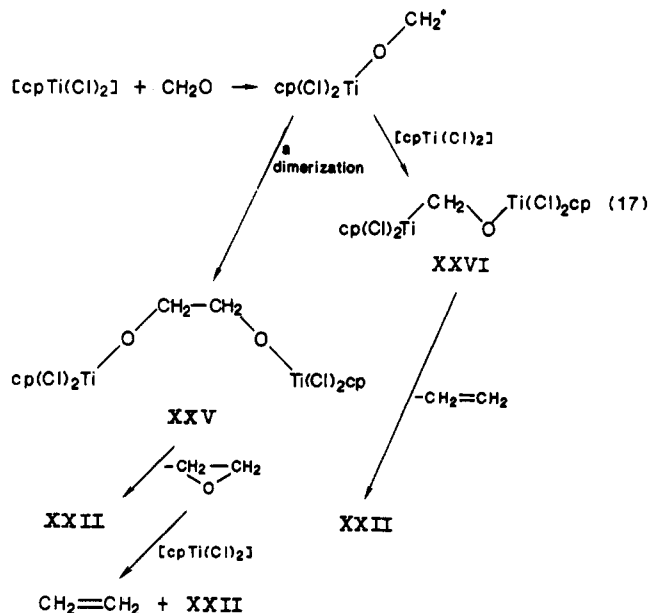
low-valent titanium species produced by the McMurry method promote the deoxygenation of ketones and aldehydes to the corresponding olefins.⁴²

One of the steps proposed in the hydrogenation of carbon monoxide over heterogeneous catalysts is the C-O bond breaking in CO or in CO-derived species.¹ A few experimental results support the currently accepted formation of carbido species from CO, while deoxygenation of CO-derived species has not been considered as a sig-

nificant step leading to the C-O bond scission in a C_1 unit.^{1,2}

The present results seem to suggest that provided there is a metallic system forming CH_2O from H_2 and CO in a preliminary step, the deoxygenation of CH_2O to a formal methylene $[\text{CH}_2]$ is a process occurring under rather mild conditions.

On the basis of the products from reaction 15, there is no single obvious metallorganic precursor of ethylene. Two likely pathways can be invoked (eq 17). It must be



mentioned that the most questionable step in either pathway is the elimination of ethylene oxide from XXIV; the other steps have been observed. The suggested deoxygenation of the oxymethylene bridge in XXV is similar to the observed deoxygenation of formaldehyde⁷ in the complex $[\text{cp}_2\text{Zr}(\text{CH}_2\text{O})]_3$ producing $[\text{cp}_2\text{ZrO}]_3$.⁴³

Registry No. I, 1277-47-0; II, 80737-39-9; III, 53339-41-6; IV, 104114-35-4; V, BF_4 , 79725-54-5; VI, 104114-36-5; VII, 80737-40-2; VIII, 104114-38-7; IX, 80737-42-4; X, 104114-39-8; XI, 104114-40-1; XII, 104114-41-2; XV, 28101-79-3; XVI, 15133-82-1; XVII, 23777-40-4; XVIII, 29020-56-2; XIX, 15376-83-7; XX, 13007-90-4; XXI, 87587-73-3; XXII, 12146-06-4; XXIII, 12171-57-2; $\text{Ni}(\text{N}_2)_4$, 40695-55-4; HCOOMe , 107-31-3; paraformaldehyde, 30525-89-4.

Supplementary Material Available: Hydrogen coordinates (Tables SI-SIII), thermal parameters (Tables SIV-SVI), bond distances and angles (Tables SVII-SIX), and least-squares planes for compounds II, VII, and IX (Table SX) (11 pages); listings of observed and calculated structure factors for compounds II, VIII, and IX (38 pages). Order information is given on any current masthead page.

(40) Brady III, R. C.; Pettit, R. *J. Am. Chem. Soc.* **1980**, *102*, 6181-6182; **1981**, *103*, 1287-1289. Herrmann, W. A.; Plank, J.; Riedel, D.; Ziegler, M. L.; Weidenhammer, K.; Guggolz, E.; Balbach, B. *Ibid.* **1981**, *103*, 63-75.

(41) Coutts, R. S. P.; Wailes, P. C.; Martin, R. L. *J. Organomet. Chem.* **1973**, *50*, 145-151. Huffman, J. C.; Moloy, K. G.; Marsella, J. A.; Caulton, K. G. *J. Am. Chem. Soc.* **1980**, *102*, 3009-3014.

(42) McMurry, J. E. *Acc. Chem. Res.* **1974**, *7*, 281-286. Corey, E. J.; Danheiser, R. L.; Chandrasekaran, S. *J. Org. Chem.* **1976**, *41*, 260-265. McMurry, J. E.; Fleming, M. P.; Kees, K. L.; Krepski, L. R. *J. Org. Chem.* **1978**, *43*, 3255-3266 and references therein.

(43) Fachinetti, G.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1979**, *101*, 1767-1775.