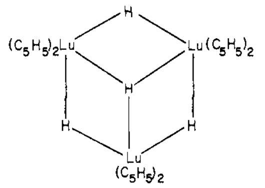

Figure 2. Proposed structure for the $[(C_5H_5)_2LuH]_3H^-$ anion.

peratures of at least 75 °C for 18 h in toluene to completely decompose, and under these conditions a complex mixture of products is formed. In order to examine a lower temperature β-hydrogen elimination reaction for lutetium, we attempted the preparation of $(C_5H_5)_2Lu(t\text{-}C_4H_9)(OEt_2)$. We anticipated that diethyl ether derivatives such as $(C_5H_5)_2Lu(t\text{-}C_4H_9)(OEt_2)$ and/or $(C_5H_5)_2Lu(t\text{-}C_4H_9)(Cl)Li(OEt_2)_2$ would be less strongly solvated and would more readily dissociate diethyl ether to provide a free coordination site for β-hydrogen elimination. Indeed, when $LiC(CH_3)_3$ is reacted with $(C_5H_5)_2LuCl$ in diethyl ether (rather than in THF), the toluene-extracted product is unstable at ambient temperature, depositing a fine white precipitate over a 24-h period.[35] The instability of the *tert*-butyl product(s) complicates characterization and precludes rigorous elimination of LiCl. Consequently, this β-hydrogen elimination also occurs in the presence of LiCl.

The toluene insoluble β-hydrogen elimination product obtained in this way, **4**, readily dissolves in THF (in contrast to the lutetium hydride formed by hydrogenolysis,[4,5] $[(C_5H_5)_2LuH(THF)]_2$, **5**, which is only sparingly soluble in hot THF) and displays a broad IR absorption at 1205 cm^{-1} (cf. ν_{Lu-H} 1350 cm^{-1} for **5**). Deuterolysis of **4** generated 0.8 mol of HD/mol of lutetium and, a CH_3I decomposition reaction generated a surprising 115% yield of CH_4 (vide infra). A complete elemental analysis was obtained on **4**, including analysis for Li and Cl since LiCl was present during the synthesis. The analytical data for Lu, C, and H were consistent with and could have been mistaken for $[(C_5H_5)_2LuH(THF)]_x$.[36] However, lithium was also found in the sample (but not chloride), suggesting a formula of the type $\{[(C_5H_5)_2LuH]_3H\}\{Li(THF)_3\}$.[37]

White needle-like crystals of **4** were obtained by slow diffusion of pentane into a hexane/THF solution and analyzed by X-ray diffraction. Although an adequate data set was obtained, structure solution has not yet been possible.

However, the ^1H NMR spectrum of **4** and the known structure of **3** allow a reasonable structure to be postulated. The 270-MHz ^1H NMR spectrum of **4** exhibits four resonances: two resonances located at δ 3.61 and 1.77 which are assigned to THF in **4**, a singlet at δ 5.83, and a doublet centered at δ 3.93 (J = 7.8 Hz). Although the integrated intensities of the latter two signals (10:1) are appropriate for their assignment as cyclopentadienyl and hydride resonances, respectively, the observed splitting of the hydride signal is unexplainable by Lu-H coupling (for Lu, $I = {}^7/_2$). Therefore, the splitting must be due to a magnetically inequivalent hydride which is not resolved at 270 MHz. The problem was solved by examination of the 500-MHz ^1H NMR spectrum of **4**. At the higher magnetic field, a quartet centered at δ 1.83 is resolved from the β protons of THF (resonating at δ 1.77). This signal is assigned to the postulated inequivalent hydride, based on its coupling constant (J_{HH} = 7.8 Hz) and proton-decoupling experiments. This information together with the knowledge that the cyclopentadienyl rings are equivalent (confirmed by ^{13}C NMR data[38]) allows the structure illustrated in Figure 2 to be proposed for **4**.

Complexes **3** and **4** represent the first trimetallic organolanthanides as well as the first organolanthanide polyhydrides. The synthesis and structural characterization of such species clearly demonstrate that a much more diverse chemistry is available to the lanthanides than has previously been known. Additional syntheses of other classes of lanthanide hydrides,[39] the reaction chemistry of these trimers and the previously reported dimers,[4,5] and the relationship, if any, of these hydrides to the interstitial metallic systems are under investigation.

Acknowledgment. For support of this research we thank the Division of Basic Energy Sciences of the Department of Energy (W.J.E., J.H.M., A.L.W.) and the National Science Foundation (J.L.A., W.E.H.). We also thank Bell Laboratories for a fellowship (A.L.W.) under the Bell Laboratories Graduate Research Program for Women and the Camille and Henry Dreyfus Foundation for a Teacher-Scholar Grant (W.J.E.). The high-field NMR instruments used in this study were funded in part by the NSF Chemical Instrumentation Program and the National Cancer Institute.

Registry No. 1, 78683-33-7; **2**, 80642-71-3; **3**, 80795-37-5; **4**, 80795-38-6; $(C_5H_5)_2LuCl$, 76207-13-1; $(C_5H_5)_2ErCl$, 53224-35-4; $LiC(CH_3)_3$, 594-19-4; LiCl, 7447-41-8; $t\text{-}C_4H_9Li$, 109-72-8.

Supplementary Material Available: Tables of bond distances and angles, final fractional coordinates, and thermal parameter (24 pages). Ordering information is given on any current masthead page.

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[35] In a typical synthesis, $LiC(CH_3)_3$ (0.1858 g, 2.9 mmol) in pentane (15 mL) was slowly dripped into a magnetically stirred solution of $(C_5H_5)_2LuCl$ (0.988 g, 2.9 mmol) in $(C_2H_5)_2O$ (40 mL) maintained at −78 °C. The solution was allowed to slowly warm to room temperature with stirring over 12 h and stirred for several additional hours. The solvent is removed in vacuo and the residue extracted with toluene to yield a clear light gold solution. If the solution is then stirred at room temperature for 24 h, a fine white precipitate deposits which can be isolated by filtration and extracted into THF. Removal of THF by rotary evaporation yields a free-flowing white microcrystalline powder (0.14 g, 0.12 mmol, 12%). At this point, the powder is often pure by ^1H NMR spectroscopy. In some cases, however, subsequent recrystallization is necessary to obtain a pure product.

[36] Anal. Calcd for $LuC_{14}H_{19}O$: Lu, 46.26; C, 44.46; H, 5.06. Found: Lu, 46.42; C, 44.19; H, 4.81.

[37] Anal. Calcd for $Lu_3C_{42}H_{58}O_3Li$: Lu, 45.99; C, 44.20; H, 5.11; Li, 0.61; O, 4.21. Found: Lu, 46.42; C, 44.19; H, 4.81; Li, 0.51; O, 4.07 (by difference). This complex also is subject to desolvation, which is perhaps why a trisolvated complex rather than the expected tetrasolvate is indicated by the elemental analysis.

[38] $^{13}C\{^1H\}$ NMR of **4** (C_4D_8O): δ 105.45 (s).

[39] The reaction of $(C_5H_5)_2LuCl$ with NaH has recently been reported to form $(C_5H_5)_2LuH(THF)$.[6] The IR and ^1H NMR spectra of the product do not agree with our data on **4** or **5**[4,5] and also do not agree with the simple structure proposed in that paper. This complex may represent yet another class of lanthanide hydrides.

[40] **Note Added in Proof**: Recent crystallographic results on **4** verify the structure shown in Figure 2.

Unsymmetrical Introduction of Two Functional Groups into Cyclodextrin. Combination Specificity by Use of *N*-Benzyl-*N*-methylaniline *N*-Oxide Cap

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In cyclodextrin chemistry several modification techniques have been exploited to introduce a substituent directly onto the primary or secondary position.[1] This direct functionalization may be extended even to disubstitution and trisubstitution,[2] although separation of the desired product from a crude mixture seems to be somewhat laborious. More recently, regiocontrol of the capping position via capped cyclodextrins[3] has also been achieved, giving

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[1] For example: (a) Emert, J.; Breslow, R. *J. Am. Chem. Soc.* **1975**, *97*, 670. (b) Iwakura, Y.; Ueno, K.; Toda, F.; Onozuka, S.; Hattori, K.; Bender, M. L. *Ibid.* **1975**, *97*, 4432. (c) Tabushi, I.; Shimidzu, N.; Sugimoto, T.; Shiodzuka, M.; Yamamura, K. *Ibid.* **1977**, *99*, 7100.

[2] (a) Boger, J.; Brenner, D. G.; Knowles, J. R. *J. Am. Chem. Soc.* **1979**, *101*, 7630. (b) Boger, J.; Knowles, J. R. *Ibid.* **1979**, *101*, 7631.

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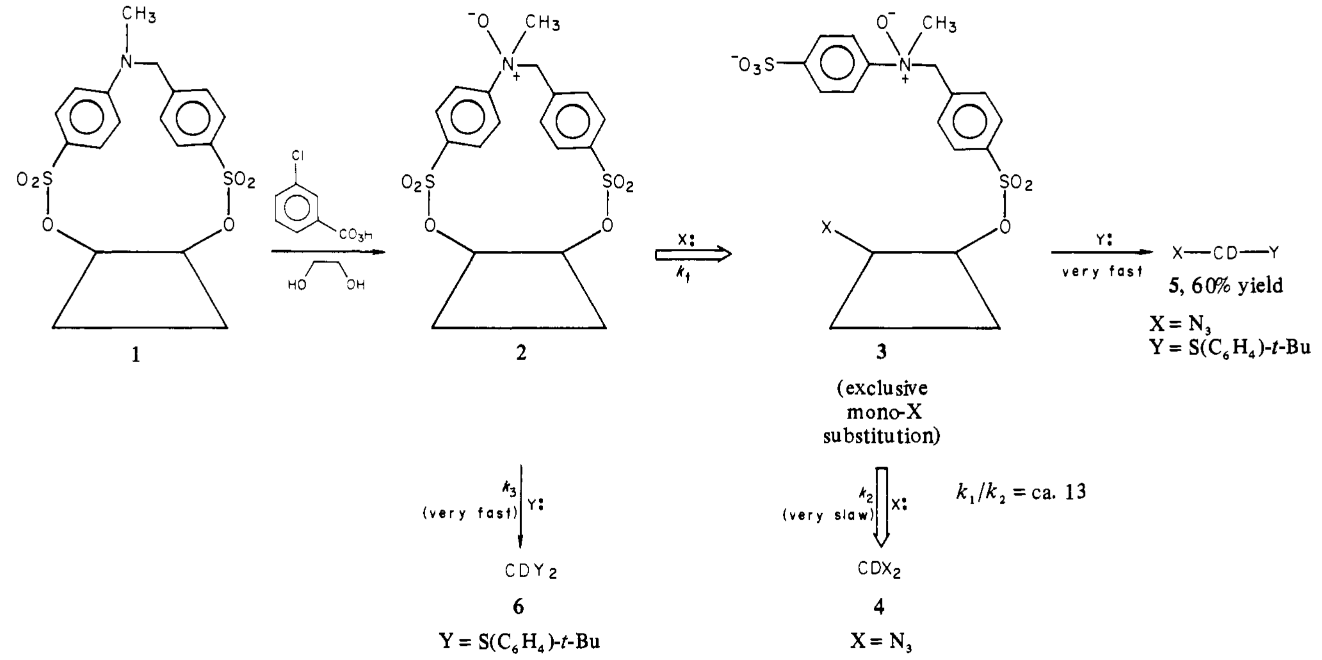
Scheme I



great promise of regiospecific bifunctionalization of cyclodextrin with two identical groups.

However, for further sophistication of enzyeme models by the use of cyclodextrins (CD) it is necessary and important to functionalize cyclodextrins with two *different* functional groups X and Y. Treatment of an appropriate symmetrical cap with a mixture of two nucleophiles X and Y would lead to a 1:2:1 statistical mixture of CDX_2, CDXY, and CDY_2. The probable similarity in physical properties of these three compounds should make the isolation yield of CDXY extremely poor.

In this communication we report a novel capped cyclodextrin, *N*-benzyl-*N*-methylaniline-*p*,*p*′-disulfonate *N*-oxide cap (**2**),[4a] in which the capping moiety has for the first time enabled us to afford "combination selectivity" in the preparation of CDXY (**5**) in an excellent yield (see Scheme I). This flamingo-type capping is a new synthetic strategy in cyclodextrin functionalization.

N-Benzyl-*N*-methylaniline-*p*,*p*′-disulfonate capped-β-CD (**1**), prepared by the treatment of *N*-benzyl-*N*-methylaniline-*p*,*p*′-disulfonyl chloride[4b] with β-CD in dry pyridine, was purified by reprecipitation (overall yield, 20%). Further purification was carried out by silica gel column chromatography (CH_3CN–H_2O, 5:1) and the purity of *N*-cap **1** was ascertained by HPLC. An NMR spectrum of **1** showed the characteristic absorptions of protons of the capping moiety: (Me_2SO-d_6) δ centered at 7.10 (d, 2 H, aromatic H ortho to NMe, *J* = 9 Hz), 7.9, 7.8 (6 H, other aromatic H), 5.1 (7 H, C_1H), 4.8–3.5 (C_2, C_3, C_6–OH, other H). Anal. Calcd for $C_{56}H_{81}O_{39}NS_2\cdot 3H_2O$ (**1**): C, 44.53; H, 5.81; N, 0.927. Found: C, 44.59; H, 6.17; N, 1.12. Further structural determination of **1** was made by converting **1** to CD[S(C_6H_4)-*t*-Bu]$_2$ (**6**)[5] or CD(N_3)$_2$ (**4**) (vide infra), which was identical with those independently prepared from diphenylmethane capped-β-CD according to NMR spectrometry,[5] TLC, and/or HPLC. The *N*-capped-β-CD (**1**) thus prepared was treated with an excess amount of *m*-ClPBA in ethylene glycol at 0 °C for 3 h and purified by reprecipitation (83%) to afford the corresponding *N*-oxide **2** (flamingo cap), whose NMR spectrum showed the characteristics downfield shift of the aromatic protons ortho to the N→O (δ from 7.1 to 7.4) compared with **1**. The UV spectrum of **2**, exhibiting only a small shoulder at ~300 nm (sh), compared with **1** (290–310 nm, $\epsilon \leq 940$) strongly supported aryl-N→O chromophore. Moreover, treatment of **1** or **2** with KI in DMF gave diiodo-β-CD identical with authentic diiodide[6] (R_f 0.5, *n*-PrOH–AcOEt–H_2O–25% NH_3 = 5:2:3:1), strongly supporting **1** and **2** as having the cap structure of a disulfonate linkage.

Table I

reaction period of X treatment (26 °C), h	product ratio		
	β-CDX_2 (**4**)	β-CDXY (**5**)	β-CDY_2 (**6**)
4	0	74 ± 5	26 ± 5
7	~0	86 ± 4	14 ± 4
12	10 ± 3	79 ± 3	11 ± 3

The "combination specific" preparation of CDXY (**5**) was very simple, i.e., two reactants, X and then Y, each in an excess amount, were applied consecutively to the *N*-oxide **2** in water without isolation of any intermediate. Thus, treatment of **2** with NaN_3 (320 equiv, 7 h) followed by sodium *p-tert*-butylthiophenolate (30 equiv, 12 h) treatment at 26 °C under nitrogen, gave β-cd-(N_3)[S(C_6H_4)-*t*-Bu] (**5**) in a 59% *analytical* yield. The product was contaminated by only a small amount of the symmetrically disubstituted product β-CD[S(C_6H_4)-*t*-Bu]$_2$ (**6**, 9.6% analytical yield) (Scheme I) based on the HPLC determination through μ-Bondapak CH (CH_3CN–H_2O, 4:1). The product ratio, **4**:**5**:**6**, was ~0:86:14 (Table I). Purification of **5** was achieved by silica gel column chromatography, and pure **5** exhibited a characteristic ν_{N_3} at 2080 cm^{-1} and a satisfactory ^{1}H NMR spectrum [(Me_2SO-d_6) δ 7.54 (4 H, aromatic H), 5.10 (7 H, C_1–H), 3.4–4.2 (C_2, C_3, C_6–OH, other H), 1.48 (9 H, *t*-Bu)] strongly supporting successful unsymmetrical disubstitution. The distribution ratio,

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(3) (a) Tabushi, I.; Shimokawa, K.; Shimidzu, N.; Shirakata, H.; Fujita, K. *J. Am. Chem. Soc.* **1976**, *98*, 7855. (b) Tabushi, I.; Fujita, K.; Yuan, L. C. *Tetrahedron Lett.* **1977**, 2503. (c) Breslow, R.; Bovery, P.; Hersh, C. L. *J. Am. Chem. Soc.* **1980**, *102*, 2115. (d) Tabushi, I.; Kuroda, Y.; Yokota, K.; Yuan, L. C. *Ibid.* **1981**, *103*, 711. (e) Tabushi, I.; Yuan, L. C. *Ibid.* **1981**, *103*, 3574. (f) Tabushi, I.; Shimokawa, K.; Fujita, K. *Tetrahedron Lett.* **1977**, 1527. (g) Breslow, R.; Doherty, J. B.; Guillot, G.; Hersh, C. L. *J. Am. Chem. Soc.* **1978**, *100*, 3227. (h) Tabushi, I.; Kuroda, Y.; Shimokawa, K. *Ibid.* **1979**, *101*, 1614. (i) Tabushi, I.; Kuroda, Y.; Mochidzuki, A. *Ibid.* **1980**, *102*, 1152.

(4) (a) This cap is called a "flamingo cap" for simplicity and also in order to describe its unique higher half-of-the-sites reactivity of the *N*-oxide cap **2**, which easily stands on one end as well as on two ends, like a flamingo. (b) Prepared in three steps from sulfanilic acid. Bis(*N*,*N*′-dimethylamide) derivative: mass spectrum 411 *m*/*e*(P^+).

(5) **6** (78% isolation yield from **1**): NMR (Me_2SO-d_6) δ centered at 7.52 (8 H, aromatic proton), 5.10 (7 H, C_1H), 3.4–4.2 (C_2, C_3, C_6–OH, other H), 1.48 (s, 18 H, –CH_3) (HMDS external standard).

(6) Diiodide derived from diphenylmethane capped-β-CD (ref 3a) with KI/DMF.

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 $\mathbf{2} \rightarrow \mathbf{3}$ and $\mathbf{3} \rightarrow \mathbf{4}$, 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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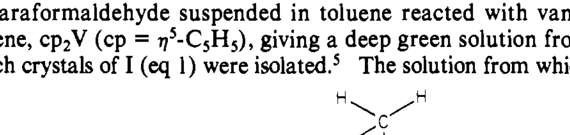
Notwithstanding that the metal–formaldehyde group, M–CH_2O, could play a significant and unexpected role in carbon monoxide reduction,[1] its chemistry is limited to the only formaldehyde complex identified so far, $Os(CO)_2(PPh_3)_2(\eta^2\text{-}CH_2O)$.[2] The very close relationship between formyl, formaldehyde, oxymethylene, and hydroxycarbene derivatives makes the genesis and the chemistry of the M–CH_2O 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_2V ($cp = \eta^5\text{-}C_5H_5$), 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 $Os(CO)_2(PPh_3)_2(\eta^2\text{-}CH_2O)$[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]



I

(1)

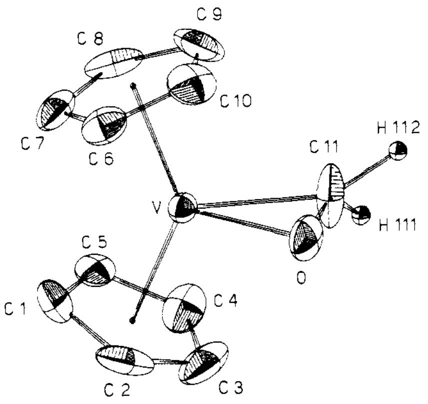
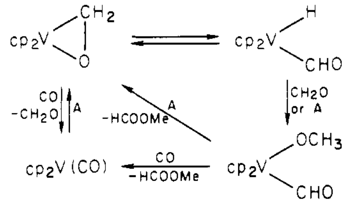


Figure 1. ORTEP drawing of $Cp_2V(CH_2O)$.[8] Selected bond lengths (Å): C11–O = 1.353 (10), V–C11 = 2.092 (8), V–O = 1.955 (5), V–cp$_1$(⊥) = 1.964 (9), V–cp$_2$(⊥) = 1.945 (9) Å.

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 $cp_2V(CH_2O)$, $C_{11}H_{12}OV$: 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_2VI_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 *C2/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 $V(CH_2O)$ 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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