Notes

Electrophilic Attack on the Carbon Terminus of a Niobium-Bound Formaldehyde Ligand

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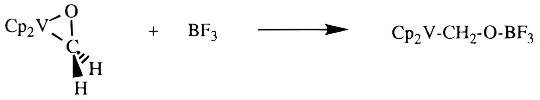
*Summary: The niobocene formaldehyde complex $Cp'_2Nb(Cl)(\eta^2\text{-}CH_2O)$ (**1**, $Cp' = \eta^5\text{-}C_5H_4SiMe_3$) reacts with $[Ph_3C][BF_4]$ to give an alkoxide (**2**) of formula $[Cp'_2Nb(Cl)(OCH_2CPh_3)][BF_4]$ and with $HBF_4{\cdot}OEt_2$ to give analogue **4** ($[Cp'_2Nb(Cl)(OMe)][BF_4]$); these processes constitute examples of electrophilic attack on the formaldehyde carbon, instead of the more typical addition at oxygen. Compound **2** is hydrolyzed to $Cp'_2Nb(Cl)(OBF_3)$ (**3**), a Lewis acid adduct of the corresponding metal oxide; both **2** and **3** have been characterized by X-ray crystallography.*

It is well established that metal−formaldehyde complexes are important models for the catalytic reduction of carbon monoxide.[2,3] Their chemistry has been proposed to involve any of three important chemical processes, these being scission of the C═O bond to make metal−methylene and metal−oxide compounds, C−H scission to make hydrido−formyl isomers, and formation of bimolecular compounds with bridging formaldehyde ($M-CH_2-O-M'$). The first of these has been inferred from Gladysz' observation of the microscopic reverse process, formation of a formaldehyde ligand from a rhenium methylidene and PhIO.[4] The C−H activation is a unimolecular process that has been observed directly.[5] Finally, the conversion of η^2-formaldehyde complexes into bimetallic bridged species requires the addition of a second metal center, and this has been seen to involve attack of the added electrophile on the formaldehyde oxygen; this also activates the system toward insertion of, e.g., carbon monoxide, and thus facilitates carbon−carbon bond formation.[6] We have recently described the chemistry of a niobium formaldehyde complex, $Cp'_2Nb(Cl)(\eta^2\text{-}CH_2O)$ (**1**, $Cp' = \eta^5\text{-}C_5H_4SiMe_3$), and noted that this compound may be reduced (with loss of chloride) to the Nb(IV) derivative $Cp'_2Nb(\eta^2\text{-}CH_2O)$.[7] This latter compound was shown to engage in a hydrogen-bonding interaction with alcohols, but no such interaction was obvious for the starting Nb(V) compound. Earlier, Floriani and co-workers had shown that a vanadium analogue added a variety of Lewis acids at the formaldehyde oxygen (eq 1);[6c] the Lewis acids included alkyl fluorosulfonates, acid chlorides, boron trifluoride, and titanium(IV) chloride. Herein we describe related reactions between **1** and electrophiles, which are seen to involve an unusual regiochemical preference.



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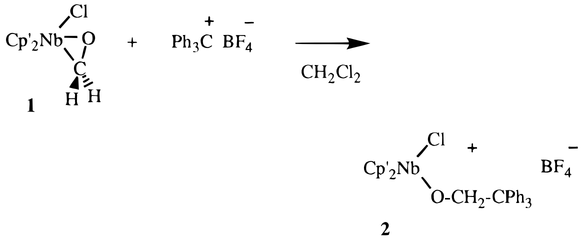
The reaction of equimolar amounts of $[Ph_3C][BF_4]$ and **1** (which has the O-inside geometry shown in eq 2)[7] was carried out in dichloromethane, the solvent removed,



(2)

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(1) (a) Wesleyan University. (b) Indiana University. (c) University of Minnesota.

(2) (a) Henrici-Olivé, G.; Olivé, S. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 136−141. (b) Numan, J. G.; Bogdan, C. E.; Klier, K.; Smith, K. J.; Young, C.-W.; Herman, R. G. *J. Catal.* **1988**, *113*, 410−433. (c) Mitchell, W. J.; Xie, J.; Jachimowski, T. A.; Weinberg, W. H. *J. Am. Chem. Soc.* **1995**, *117*, 2606−2617.

(3) (a) Dombek, B. D. *J. Am. Chem. Soc.* **1980**, *102*, 6855−6857. (b) Dombek, B. D. *J. Chem. Educ.* **1986**, *63*, 210−212. (c) Ishino, M.; Tamura, M.; Deguchi, T.; Nakamura, S. *J. Catal.* **1987**, *105*, 478−482. (d) Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121−127. (e) Maatta, E. A.; Marks, T. J. *J. Am. Chem. Soc.* **1983**, *103*, 3576−3578.

(4) Buhro, W. E.; Georgiou, S.; Fernandez, J. M.; Patton, A. T.; Strouse, C. E.; Gladysz, J. A. *Organometallics* **1985**, *5*, 956−965.

(5) (a) Erker, G.; Kropp, K.; Krüger, C.; Chiang, A.-P. *Chem. Ber.* **1982**, *115*, 2447−2460. (b) Adams, H.; Bailey, N. A.; Gautlett, J. T.; Winter, M. J.; Woodward, S. *J. Chem. Soc., Dalton Trans.* **1991**, 2217−2221. (c) Bianchini, C.; Meli, A. *Organometallics* **1985**, *4*, 1537−1542. (d) Brown, K. L.; Clark, G. R.; Headford, C. E. L.; Marsden, K.; Roper, W. R. *J. Am. Chem. Soc.* **1979**, *101*, 503−505. (e) Thorn, D. L. *Organometallics* **1982**, *1*, 197−204.

(6) (a) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1983**, *105*, 1690−1691. (b) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1982**, *104*, 2019−2020. (c) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Organometallics* **1986**, *5*, 2425−2433. (d) Berke, H.; Bankhardt, W.; Huttner, G.; v. Seyerl, J.; Zsolnai, L. *Chem. Ber.* **1981**, *114*, 2754−2768. (e) Berke, H.; Huttner, G.; Weiler, G.; Zsolnai, L. *J. Organomet. Chem.* **1981**, *219*, 353−362. (f) Bendix, M.; Grehl, M.; Frohlich, R.; Erker, G. *Organometallics* **1994**, *13*, 3366−3369. (g) Gibson, D. H.; Franco, J. O.; Sleadd, B. A.; Naing, W.; Mashuta, M. S.; Richardson, J. F. *Organometallics* **1994**, *13*, 4570−4577. (h) Ashkam, F. R.; Carroll, K. M.; Briggs, P. M.; Rheingold, A. L.; Haggerty, B. S. *Organometallics* **1994**, *13*, 2139−2141. (i) Erker, G.; Bendix, M.; Petrenz, R. *Organometallics* **1994**, *13*, 456−461.

(7) Thiyagarajan, B.; Michalczyk, L.; Bollinger, J. C.; Huffman, J. C.; Bruno, J. W. *Organometallics* **1996**, *15*, 1989−1999.

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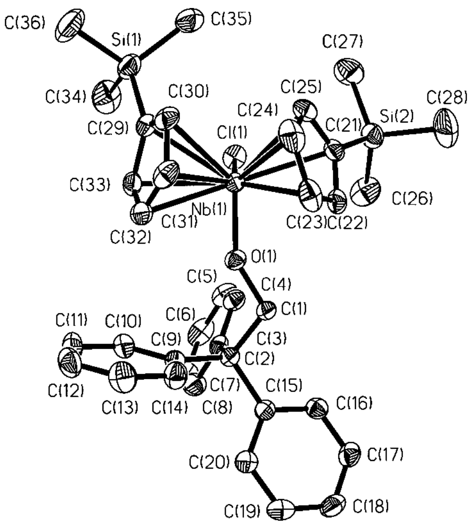


Figure 1. ORTEP representation of the structure of **2** with a view approximately along the Nb−Cl bond.

Table 1. Bond Lengths (Å) and Angles (deg) for 2 and 3

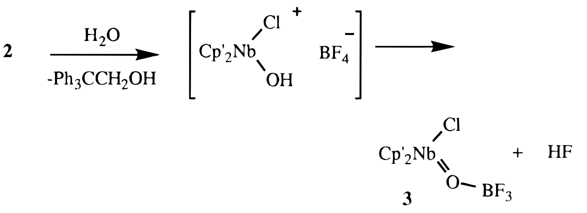
	Compound **2**		
Nb(1)−O(1)	1.8795(14)	Nb(1)−C(33)	2.449(2)
Nb(1)−Cl(1)	2.3880(6)	O(1)−C(1)	1.426(2)
Nb(1)−C(21)	2.499(2)	C(1)−C(2)	1.553(3)
Nb(1)−C(22)	2.470(2)	C(2)−C(3)	1.542(3)
Nb(1)−C(23)	2.407(2)	C(2)−C(9)	1.546(3)
Nb(1)−C(24)	2.413(2)	C(2)−C(15)	1.547(3)
Nb(1)−C(25)	2.407(2)	B(1)−F(1)	1.363(4)
Nb(1)−C(29)	2.494(2)	B(1)−F(2)	1.375(4)
Nb(1)−C(30)	2.433(2)	B(1)−F(3)	1.374(4)
Nb(1)−C(31)	2.384(2)	B(1)−F(4)	1.390(4)
Nb(1)−C(32)	2.444(2)		
Nb(1)−O(1)−C(1)	148.26(12)	F(1)−B(1)−F(2)	111.1(3)
O(1)−C(1)−C(2)	110.7(2)	F(1)−B(1)−F(3)	111.2(3)
C(1)−C(2)−C(3)	112.0(2)	F(1)−B(1)−F(4)	107.9(2)
C(1)−C(2)−C(9)	106.5(2)	F(2)−B(1)−F(3)	108.9(2)
C(1)−C(2)−C(15)	105.8(2)	F(2)−B(1)−F(4)	107.7(3)
Cl(1)−Nb(1)−O(1)	97.00(5)	F(3)−B(1)−F(4)	110.0(2)
	Compound **3**		
Nb(1)−Cl(2)	2.399(4)	Nb(1)−C(18)	2.447(11)
Nb(1)−O(3)	1.830(4)	Nb(1)−C(19)	2.407(16)
Nb(1)−C(8)	2.429(5)	Nb(1)−C(20)	2.430(16)
Nb(1)−C(9)	2.404(27)	Nb(1)−C(21)	2.525(10)
Nb(1)−C(10)	2.442(4)	O(3)−B(7)	1.486(8)
Nb(1)−C(11)	2.443(13)	B(7)−F(4)	1.419(22)
Nb(1)−C(12)	2.444(15)	B(7)−F(5)	1.372(5)
Nb(1)−C(17)	2.499(7)	B(7)−F(6)	1.376(14)
Cl(2)−Nb(1)−O(3)	98.8(3)	F(6)−B(7)−O(3)	108.7(9)
Nb(1) -O(3) -B(7)	167.73(14)	F(4)−B(7)−F(5)	109.4(11)
F(4)−B(7)−O(3)	106.7(11)	F(4)−B(7)−F(6)	108.8(7)
F(5)−B(7)−O(3)	110.5(6)	F(5)−B(7)−F(6)	112.5(11)

Table 2. Crystallographic Data for 2 and 3

	2	**3**
formula	$C_{37}H_{44}BClF_4NbOSi_2$	$C_{16}H_{26}BClF_3NbOSi_2\cdot{}^1/_2CH_2Cl_2$
fw	882.42	529.19
cryst dimens, mm	0.45 × 0.30 × 0.22	0.26 × 0.20 × 0.09
space group	$P\bar{1}$	$Pc2_1n$
cell dimens		
T, °C	−100	−165
a, Å	11.6341(1)	18.370(2)
b, Å	14.4184(1)	28.427(4)
c, Å	14.7618(1)	8.723(1)
α, deg	61.924(1)	90
β, deg	72.114(1)	90
γ, deg	81.081(1)	90
Z (molecules/cell)	2	8
V, $Å^3$	2079.07(3)	4555.01
d(calcd), g cm^{-3}	1.410	1.543
wavelength, Å	0.710 73	0.710 69
linear abs coeff, mm^{-1}	0.650	0.8739
R	0.0727	0.0588
R_w	0.0290	0.0481

and the residue treated with ether. This yielded a light yellow solid that was collected by filtration; there was little or no organic byproduct observed, and the niobium-containing product **2** was determined to be an adduct of **1** and the triphenylcarbenium ion (eq 2). The ^{1}H NMR signal for the formaldehyde-derived methylene group in **2** appeared at 5.66 ppm ($CDCl_3$), whereas **1** exhibited a formaldehyde resonance at 3.55 ppm. From this it may be inferred that product formation led to a considerable deshielding of the formaldehyde protons. This did not constitute unambiguous proof of the structure, so X-ray data were sought. Compound **2** was crystallized from cold chloroform, from which it formed nearly colorless cubes. These diffracted well, and the structure is depicted in Figure 1; key bond lengths and angles are collected in Table 1, crystallographic parameters are in Table 2, and a complete summary of the crystallographic determination is available as Supporting Information. The structure is presented with a view approximately along the Nb−Cl bond so as to emphasize the alkoxide formed from formaldehyde and the triphenylcarbenium ion. The cation adopts a bent metallocene structure, and the unit cell contains the BF_4^- counterion and a molecule of $CHCl_3$. The Nb−O bond length is 1.8795(14) Å, and the Nb−O−C angle is 148.26(12)°; this may be the result of multiple Nb−O bond character, but it has been shown that large angles at oxygen may also be due to steric factors.[8] Although the formaldehyde hydrogens were not located, the large Nb−O−C angle and a reaction discussed below confirm that the reaction occurred at the formaldehyde carbon.

Compound **2** was not extremely sensitive toward air, so we allowed $CDCl_3$ solutions to stand open for ca. 24 h to probe the stability of the cationic alkoxide. At the end of this period, **2** had decomposed completely to a diamagnetic niobium-containing product **3** and the known[9] alcohol Ph_3CCH_2OH (eq 3); the latter was identified by ^{1}H NMR and GC-MS studies. Compound **3** exhibited four resonances for the Cp′ ligands and one for the $SiMe_3$ groups, but this was not sufficient to identify it. As such, the compound was crystallized from methylene chloride, from which it formed yellow cubes. Crystallographic analysis of **3** revealed the structure depicted in Figure 2; crystal data are in Table 2, and key bond lengths and angles are in Table 1. The unit cell contains four CH_2Cl_2 molecules and eight molecules of **3**, and **3** is best described as an adduct between the



(3)

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[8] Steffey, B. D.; Fanwick, P. E.; Rothwell, I. P. *Polyhedron* **1990**, *9*, 963−972.

[9] (a) Lee, K. I.; Okamoto, Y. *J. Org. Chem.* **1976**, *41*, 1552−1555. (b) Ferguson, G.; Glidewell, C.; Zakaria, C. M. *Acta Crystallogr. C* **1994**, *C50*, 928−931.

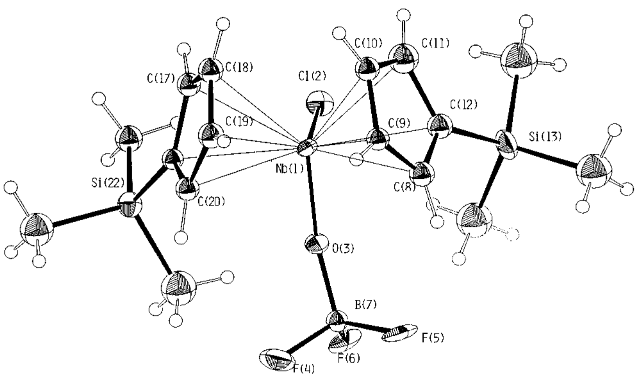
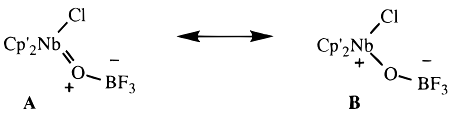


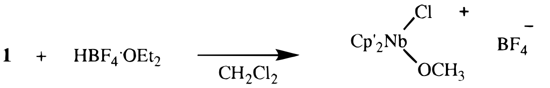
Figure 2. ORTEP representation of the structure of **3**.

known[10] oxide $Cp'_2Nb(Cl)(O)$ and BF_3. Indeed, the direct reaction of the oxide and $BF_3 \cdot OEt_2$ constitutes the preferred synthesis of **3**. In **3** the Nb−O bond length is 1.830(4) Å, and the Nb−O−B angle is 167.73(14)°. For comparison, it may be noted that the Nb═O bond length in $Cp'_2Nb(Me)(O)$ is 1.720(7) Å,[10] the Nb−O bond length in $[Cp_2NbCl]_2O$ is 1.924(9) Å,[11] and the Nb−O bond lengths in the peroxide $Cp_2Nb(Cl)(\eta^2\text{-}O_2)$ are 1.97(1) and 2.00(1) Å.[12] Thus the Nb−O bond length in **3** is intermediate between the ranges seen for double and single bonds. We are inclined to assign some multiple Nb−O bond character in **3** (i.e. nearly equal contributions from resonance forms **A** and **B**), based on the



comparison with the known structures. We propose that the conversion of **2** to **3** proceeds as shown in eq 3. Initial hydrolysis gives rise to the alcohol and the cationic hydroxo−niobium compound. This would be expected to exhibit appreciable acidity, and a reaction with the counterion should yield **3** and hydrogen fluoride. We have been unable to confirm the presence of HF, but there are no fluoride-containing organic byproducts in evidence.

Our initial hypothesis for the regiochemistry seen in eq 2 was based on steric arguments; we suspected that the large trityl cation could not gain access to the formaldehyde oxygen and that this led to the reaction at carbon. To test this, we reacted **1** with $HBF_4 \cdot OEt_2$ with the expectation that the proton source would not be subject to steric constraints. In fact, this reaction (eq 4) led cleanly to the cationic niobium methoxide,



$$\mathbf{1} + HBF_4 \cdot OEt_2 \xrightarrow[CH_2Cl_2]{} [Cp'_2Nb(Cl)(OCH_3)]^+ \; BF_4^- \qquad (4)$$

4

which precipitated as a colorless solid. The spectral data confirm this regiochemistry, since the NMR shows a methyl resonance (which integrates for three protons) at 4.55 ppm ($CDCl_3$) and the IR spectrum shows no evidence for an OH stretch. Hence, it appears that the preference for electrophilic addition to the carbon terminus of the formaldehyde ligand in **1** is not related to steric factors and presumably reflects the strength of the Nb−O bond.

In summary, the Nb(V) formaldehyde complex **1** reacts with a substituted carbenium ion to make a carbon−carbon bond and with a proton source to make a carbon−hydrogen bond. This contrasts with the reaction shown in eq 1, in which a vanadium-bound formaldehyde reacts with BF_3 at oxygen; thus, while the carbenium ion and BF_3 are isoelectronic, they give opposite regiochemistry in reactions with formaldehyde. Gladysz has shown that slippage from η^2-C,O binding to η^1-O binding can activate the aldehyde carbon toward nucleophiles,[13] but the work described here constitutes an example of *electrophilic* attack on the carbon end of a bound formaldehyde.[14] The facile reaction of η^2-complexed aldehydes (or ketones) with electrophiles may be attributed to the extra electron density deposited into the ligand π^* orbital by the electron-rich metal center. Some of this back-bonding electron density must be localized at the carbon center, and this work constitutes a case in which carbon serves as the nucleophile so as to preserve the strong metal−oxygen bond.

Experimental Section

General Considerations. All manipulations involving metal complexes were carried out under an atmosphere of nitrogen which was first passed through activated BTS catalyst and molecular sieves. Standard Schlenk techniques were used to handle solutions,[15] and solids were transferred in a Vacuum Atmospheres Corp. glovebox under purified nitrogen. Solvents toluene, hexane, and ether (J. T. Baker) were distilled from sodium benzophenone ketyl under nitrogen; chloroform and methylene chloride were distilled from P_2O_5. $NbCl_5$ and paraformaldehyde (Aldrich) were commercial materials; the latter was dried in vacuo prior to use. Compound **1** was prepared as described previously,[7] as was $Cp'_2Nb(O)Cl$.[10]

Synthesis of 2. Compound **1** (0.2 g, 0.46 mmol) was dissolved in 20 mL of methylene chloride. To the resulting yellow solution was added 0.15 g (0.46 mmol) of Ph_3CBF_4. The reaction was stirred for 45 min at 25 °C, and the solvent was removed in vacuo. The residue was extracted with 20 mL of diethyl ether, and filtration yielded a light yellow solid (0.28 g, 0.37 mmol, 80.4%). This was dried in vacuo and recrystallized from chloroform at −20 °C. ^1H NMR ($CDCl_3$): 7.32 (m, 11 H, 9 Ph and 2 Cp′), 7.03 (d, 6H, Ph), 6.69 (m, 2H, Cp′), 6.50 (m, 2H, Cp′), 6.37 (m, 2H, Cp′), 5.66 (s, 2H, CH_2O), 0.24 ppm (s, 18 H, SiMe). $^{13}C(CDCl_3)$: 143.7, 139.1, 132.4, 129.1, 128.2, 126.7, 122.2, 121.3, 116.9, 60.1 (CH_2O), and 0.8 (SiMe). IR (Nujol): 1251 (m), 1164 (m), 1052 (br, s), 841 cm^{-1} (s).

Synthesis of 3. Oxide $Cp'_2Nb(O)Cl$ (60 mg, 0.143 mmol) was dissolved in 20 mL of toluene. Under nitrogen, 17 μL of

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[10] Antinolo, A.; de Llarduya, J. M.; Otero, A.; Royo, P.; Lanfredi, A. M. M.; Tripicchio, A. *J. Chem. Soc., Dalton Trans.* **1988**, 2685−2693.

[11] Kirillova, N. I.; Lemenovskii, D. A.; Baukova, T. V.; Struchkov, Yu. T. *Koord. Khim.* **1978**, *3*, 1254−1260.

[12] Bkouche-Waksman, I.; Bois, C.; Sala-Pala, J.; Guerchais, J. E. *J. Organomet. Chem.* **1980**, *195*, 307−315.

[13] (a) Huang, Y.-H.; Gladysz, J. A. *J. Chem. Educ.* **1988**, *65*, 298−303. (b) Agbossou, F.; Ramsden, J. A.; Yo-Hsin, H.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1982**, *11*, 692−701. (c) Klein, D. P.; Gladysz, J. A. *J. Am. Chem. Soc.* **1991**, *114*, 8710−8711. (d) Méndez, N. Q.; Seyler, J. W.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 2323−2334. (e) Garner, C. M.; Mendez, N. Q.; Kowalczyk, J. J.; Fernandez, J. M.; Emerson, K.; Larsen, K. D.; Gladysz, J. A. *J. Am. Chem. Soc.* **1990**, *112*, 5146−5160. (f) Méndez, N. Q.; Arif, A. M.; Gladysz, J. A. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1473−1474. (g) Méndez, N. Q.; Mayne, C. L.; Gladysz, J. A. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1475−1476.

[14] Rosenfeldt, F.; Erker, G. *Tetrahedron Lett.* **1980**, *21*, 1637−1640.

[15] Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley-Interscience: New York, 1986; Chapter 1.

$BF_3{\cdot}OEt_2$ (Aldrich) was added via syringe. The resulting solution was stirred at 25 °C for 12 h and then filtered to remove a yellow solid. Solvent was removed in vacuo to give a yellow oil, which was precipitated from hexane. Yield: 0.030 g, 0.062 mmol, 43%. The compound was crystallized from cold methylene chloride. ^1H NMR ($CDCl_3$): 6.41 (m, 2H, Cp′), 6.77 (m, 2H, Cp′), 6.99 (m, 2H, Cp′), 7.14 (m, 2H, Cp′), 0.35 (s, 18H, SiMe). ^{13}C NMR ($CDCl_3$): 112.4 ppm, 115.7, 129.8, 130.3, 133.7, −0.16 ppm. IR (neat): 3121 (m), 2945 (s), 1415 (m), 1253 (s), 1034 (s, br), 834 cm^{-1} (s, br).

Synthesis of 4. Compound **1** (0.10 g, 0.23 mmol) was dissolved in 50 mL of methylene chloride. Under nitrogen purge, 0.068 mL (0.46 mmol) of $HBF_4{\cdot}OEt_2$ was added via syringe. The resulting suspension was stirred for ca. 30 min at ambient temperature and then concentrated to ca. 5 mL in vacuo. Ether was added to produce a colorless precipitate, which was isolated by filtration and dried in vacuo (0.080 g, 69%). ^1H NMR ($CDCl_3$): 7.51 (m, 2H, Cp′), 6.97 (m, 4H, Cp′), 6.94 (m, 2H, Cp′), 4.55 (s, 3H, Ome), 0.30 ppm (s, 18H, SiMe). IR (Nujol): 1256 (m), 1091 (m), 1040 (br, s), 838 cm^{-1} (s).

Crystallographic Study of 2. This structure was determined at the University of Minnesota by V.G.Y. A crystal was attached to a glass fiber and mounted on the Siemens SMART system. An initial set of cell constants was calculated from reflections harvested from three sets of 30 frames. These were oriented such that orthogonal wedges of reciprocal space were surveyed. Final cell constants were calculated from a set of 5642 strong reflections from the actual data collection. Data were collected using the hemisphere collection technique for θ 1.60−25.03°. The space group $P\bar{1}$ was determined from systematic absences and intensity statistics. A successful direct methods solution was calculated which provided most non-hydrogen atoms. Several full-matrix least squares/difference Fourier cycles were performed which located the remainder of the non-hydrogen atoms; all non-hydrogen atoms were refined with anisotropic displacement parameters, and all hydrogen atoms were placed in idealized positions with individual isotropic parameters. Full details are available as Supporting Information.

Crystallographic Study of 3. This structure was determined by J.C.B. of Indiana University. Details of the methods used have described.[16] The structure was solved using direct methods and Fourier techniques. Hydrogen atoms were fixed at idealized positions during structure refinement. The unit cell contained two distinct molecules of **3**, but these exhibited similar structural parameters; only one such molecule is described in Tables 1 and 2, but full details are available as Supporting Information.

Acknowledgment. We thank the National Science Foundation for support of this work.

Supporting Information Available: Text giving X-ray procedures, ORTEP diagrams, and listings of crystallographic data for **2** and **3** (29 pages). Ordering information is given on any current masthead page.

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[16] Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem*. **1980**, *19*, 2755−2762.