refined anisotropically. All calculations were carried out using the SHELX-76 program. For 2928 unique observed reflections [$I > 2\sigma(I)$] the final $R = 0.036$, $R_w = 0.042$, and GOF = 1.4. Full details of the structure determination are available as supplementary material. X-ray crystal data for **2e**: Data collected at 22 °C; $C_{30}H_{27}Co_2O_6P$, fw = 632.38, space group $P2_1/n$, $a = 9.352$ (2) Å, $b = 20.174$ (4) Å, $c = 31.646$ (5) Å, $V = 5925.8$ Å^3, $Z = 8$, $D_c = 1.418$ g cm^3, $F(000) = 2592$, λ(Mo Kα) = 0.71069 Å, μ(Mo Kα), = 12.1 cm^{-1}. Cell dimensions and intensities of 10387 reflections ($2\theta_{max} = 50°$) were measured. The structure was solved by the heavy-atom method, and all non-hydrogen atoms were refined anisotropically. All calculations were carried out using the SHELX-76 program. For 3168 unique observed reflections [$I > 2\sigma(I)$] the final $R = 0.052$, $R_w = 0.048$, and GOR = 1.2. Only one of the two virtually identical independent molecules in the asymmetric unit is shown in the ORTEP diagram. Only the Co, P, and O atoms were refined anisotropically; all the C atoms were refined isotropically. Full details of the structure determination are available as supplementary material.

Acknowledgment. We are grateful for support provided by the National Institutes of Health (Grant GM 34799) and the Petroleum Research Fund, administered by the American Chemical Society. We thank Profs. Bing Fung and Fritz Schmitz for assistance with the spin saturation transfer and NOE experiments and Pressure Chemical Co. for a gift of cobalt carbonyl.

Registry No. **2a**, 141610-08-4; **2b** (isomer 1), 118576-64-0; **2b** (isomer 2), 118628-34-5; **2c** (isomer 1), 118576-65-1; **2c** (isomer 2), 118628-35-6; **2d**, 141527-15-3; **2e**, 118576-66-2; **2f** (isomer 1), 141527-16-4; **2f** (isomer 2), 141610-20-0; **2g** (isomer 1), 118710-59-1; **2g** (isomer 2), 118576-68-4; **2h**, 118576-67-3; **2i**, 141527-17-5; **3a**, 141527-19-7; *anti*-**3b**, 141527-21-1; *syn*-**3b**, 141610-10-8; *anti*-**3c**, 141527-23-3; *syn*-**3c**, 141610-12-0; *anti*-**3d**, 141527-25-5; *anti*-**3e**, 141527-27-7; *anti*-**3f**, 141527-29-9; *syn*-**3f**, 141610-14-2; *anti*-**3g**, 141527-31-3; *syn*-**3g**, 141610-16-4; *anti*-**3h**, 141527-33-5; **3i**, 141527-35-7; **4b**, 141527-36-8; **4b′**, 141610-17-5; **4c**, 141527-37-9; **4c′**, 141610-18-6; **4d**, 141527-39-1; **4e**, 141527-40-4; **4g**, 141527-38-0; **4g′**, 141610-19-7; **4h**, 141527-41-5.

Supplementary Material Available: Tables of complete X-ray crystal data, refinement parameters, positional parameters, and bond lengths and angles for **4b** and **2e** (21 pages). Ordering information is given on any current masthead page.

OM910764A

Lewis-Acid-Promoted Decarbonylation of Coordinated Carbon Dioxide: Reactions of (η^5-MeC_5H_4)$_2$Nb(η^2-CO_2)CH_2SiMe_3 with Lewis Acids

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Received January 13, 1992

The interaction of $Cp'_2Nb(\eta^2\text{-}CO_2)CH_2SiMe_3$ (**1**; $Cp' = \eta^5\text{-}MeC_5H_4$) with several Lewis acids has been studied and found to result in facile decarbonylation of **1**; the Nb-containing products depend markedly on the Lewis acid partner. Reaction of **1** with $LiPF_6$ or $BF_3 \cdot Et_2O$ causes both decarbonylation and deoxygenation, producing $[Cp'_2Nb(F)CH_2SiMe_3]Z$ [$Z = PF_6^-$ (**3**), BF_4^- (**6**)], which have been characterized spectroscopically and (for **3**) by X-ray diffraction; **3** is also produced in the reaction of the oxo derivative $Cp'_2Nb(O)CH_2SiMe_3$ (**2**) with $LiPF_6$ or $BF_3 \cdot Et_2O$. **1** reacts with $ZnCl_2$ first to form an adduct, $Cp'_2Nb(CO)_2CH_2SiMe_3 \cdot ZnCl_2$ (**7**), which based on IR and NMR data appears to have a novel μ-CO_2 unit bridging Nb and Zn. Complex **7** is unstable, decomposing with CO loss to form $[Cp'_2Nb(CH_2SiMe_3)O \cdot ZnCl_2]_2$ (**8**), an adduct of $ZnCl_2$ with the oxo species **2**, which has been characterized crystallographically; **8** is also produced from **2** and $ZnCl_2$. Reaction of **1** with $HgCl_2$ rapidly produces an incompletely characterized product **10**, which has been both decarbonylated and dealkylated. Although $CdCl_2$ does not react with **1** under comparable conditions, Me_3SiCl reacts rapidly with **1** to produce $Cp'_2Nb(O)Cl$ (**11**), resulting from decarbonylation and dealkylation; the structure of **11** has been established by X-ray diffraction.

Introduction

Expanding interest in transition metal-mediated chemical[1] and electrochemical[2] transformations of carbon dioxide has stimulated efforts to elucidate the reactivity of coordinated CO_2.[3] In this context, we reported recently the first example of photoinduced CO_2 disproportionation in the complex $Cp_2Mo(\eta^2\text{-}CO_2)$[4] and its dark reactions with electrophilic agents[5] and transition metal hydrides[6] which

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[1] Reviews: (a) Inoue, S.; Yamazaki, Y. *Organic and Bio-organic Chemistry of Carbon Dioxide*; Kodansha Ltd.: Tokyo, 1982; Chapter 3. (b) Eisenberg, R.; Hendrickson, D. E. *Adv. Catal.* **1979**, *28*, 79. (c) Darensbourg, D.; Kudaroski, R. A. *Adv. Organometal. Chem.* **1983**, *22*, 129; (d) Walther, D. *Coord. Chem. Rev.* **1987**, *79*, 135. (e) Kolomnikov, I. S.; Lysyak, T. V. *Russ. Chem. Rev.* **1990**, *59*, 344. (f) Behr, A. *Carbon Dioxide Activation by Metal Complexes*; VCH: Weinheim, FRG, 1988.

[2] Reviews: ref 1e. *Catalytic Activation of Carbon Dioxide*; ACS Symposium Series No. 363; Ayers, W. M., Ed.; American Chemical Society: Washington, DC, 1988; Chapters 5 and 6.

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[4] Belmore, K. A.; Vanderpool, R. A.; Tsai, J.-C.; Khan, M. A.; Nicholas, K. M. *J. Am. Chem. Soc.* **1988**, *110*, 2004.

[5] Tsai, J.-C.; Khan, M.; Nicholas, K. M. *Organometallics* **1989**, *8*, 2967.

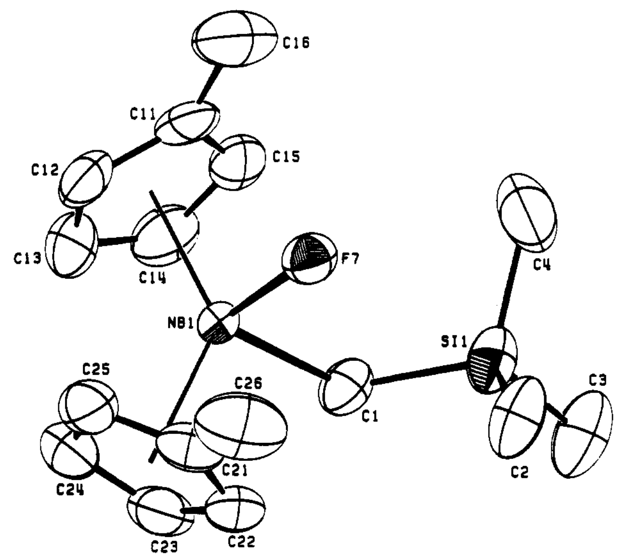


Figure 1. ORTEP diagram for [(MeCp)$_2$Nb(F)CH$_2$SiMe$_3$]PF$_6$ (3, cation only).

ultimately produce cationic carbonyl complexes with formal transfer of oxide from coordinated CO$_2$ to the electrophilic agent.

We have also initiated studies directed toward modeling CO$_2$ insertion reactions into M–C bonds using Cp′$_2$Nb(η^2-CO$_2$)CH$_2$SiMe$_3$ (1, Cp′ = η^5-MeC$_5$H$_4$), the only established example of a complex containing *both* CO$_2$ and alkyl ligands. Unexpectedly, 1 was found to undergo smooth *decarbonylation* rather than *insertion* when heated at 60 °C or irradiated at −20 °C, producing the new *oxo–alkyl* complex Cp′$_2$Nb(O)CH$_2$SiMe$_3$ (2) (eq 1).[7] In continuing

$$\underset{1}{\mathrm{Cp'_2Nb(\eta^2\text{-}CO_2)CH_2SiMe_3}} \xrightarrow{\Delta \text{ or } h\nu} \underset{2}{\mathrm{Cp'_2Nb(O)CH_2SiMe_3}} + \mathrm{CO} \quad (1)$$

efforts to promote migratory insertion reactions of 1, we have examined its interaction with of a variety of Lewis acids, reagents which have been shown previously to facilitate migratory insertions of alkyl metal *carbonyl* (L$_n$M(CO)R) complexes.[8]

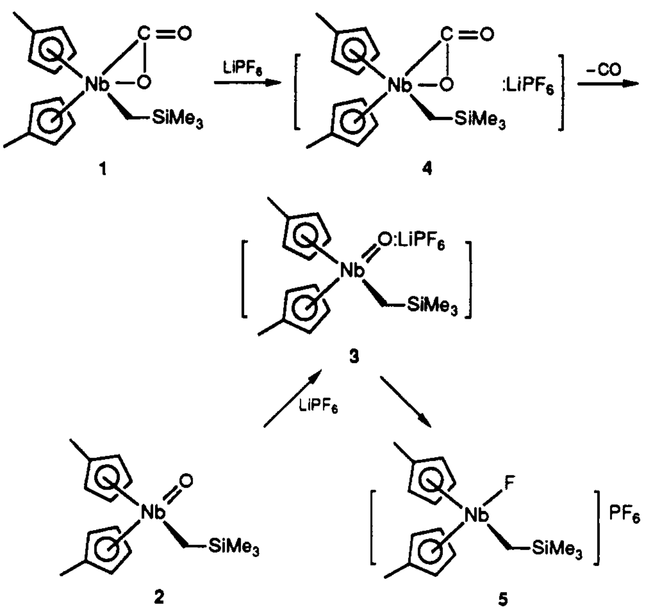
Results and Discussion

Reaction of Cp′$_2$Nb(CO$_2$)CH$_2$SiMe$_3$ (1) with LiPF$_6$ and BF$_3$·OEt$_2$. The addition of excess LiPF$_6$ to a dichloromethane solution of Cp′$_2$Nb(CO$_2$)CH$_2$SiMe$_3$ (1) at room temperature causes a rapid color change from colorless to light yellow. The yellow microcrystalline product 3 was isolated (75% yield) by concentrating the reaction solution and cooling to −10 °C. Compound 3 has been identified as the ionic complex [Cp′$_2$Nb(F)CH$_2$SiMe$_3$]PF$_6$ (eq 2); the fate of the CO$_2$-derived oxygen atom was not

$$\mathrm{Cp'_2Nb(\eta^2\text{-}CO_2)CH_2SiMe_3} + \mathrm{LiPF_6} \rightarrow \underset{3}{\mathrm{[Cp'_2Nb(F)CH_2SiMe_3]PF_6}} + \mathrm{CO} \quad (2)$$

determined. The ^{1}H NMR spectrum of 3 shows singlets at 2.14 ppm, assigned to the methyl protons of the methylcyclopentadienyl ligand, and at 3.55 and 0.14 ppm due to the methylene and methyl protons of the CH$_2$SiMe$_3$ group, respectively; the proton resonances of the methylcyclopentadienyl ring appear as multiplets at 6.65, 6.59, 6.55, and 6.48 ppm, indicating the absence of a vertical symmetry plane. The large downfield shift of the MeC$_5$H$_4$ and CH$_2$SiMe$_3$ resonances in 3 relative to 1 reflects the electron-deficient environment of the former. The FAB mass spectrum of 3 exhibited a prominent peak corresponding to the cationic [Cp′$_2$Nb(F)CH$_2$SiMe$_3$] fragment. An X-ray crystal structure determination confirmed the assigned structure. The ORTEP diagram for 3 is shown in Figure 1; PF$_6^-$ was disordered and hence is omitted for clarity. The basic pseudotetrahedral geometry of 3 is typical of Cp$_2$MXY complexes, with the observed bond lengths and angles being unexceptional. To our knowledge, the structure of 3 provides the first crystallographically determined Cp$_2$Nb–F bond length (1.910 (2) Å). The Nb–CH$_2$SiMe$_3$ distance in 3 (2.200 (4) Å) is slightly but significantly shorter than in the oxo derivative 2 (2.246 (4) Å[7]) and the ZnCl$_2$ adduct of 2 (2.244 (3) Å, vide infra).

Scheme I



Given the previously demonstrated tendency for 1 to decarbonylate upon heating[7] and the O-centered attack of electrophiles on the isoelectronic Mo analogue, we suspected that the oxo–alkyl derivative Cp′$_2$Nb(O)-CH$_2$SiMe$_3$ (2) or a Lewis acid adduct of 2 was an intermediate in eq 2. Indeed, the interaction of 2 with LiPF$_6$ under identical conditions also gives 3 (62%), supporting this hypothesis. Further insight into the reaction pathway was provided by monitoring the 1/LiPF$_6$ reaction at −30–40 °C by ^{1}H NMR and IR. Under these conditions, the Cp′-H NMR absorptions of 1 at 5.11, 5.21, and 5.98 ppm are replaced by a set of resonances at lower field (6.44, 6.31, 6.25, and 6.18 ppm), consistent with the formation of a 1:LiPF$_6$ adduct (4) in which the electron density around the metal is reduced through the coordination of 1 to Li$^+$ or PF$_5$ (presumably through the oxygen(s) of the CO$_2$ ligand). The IR spectrum of 4 (generated from 1 at −40 °C) exhibited a prominent absorption at 1677 cm^{-1}, reduced significantly from ν(C=O) of 1, which suggests Li–O coordination of a μ-CO$_2$ ligand rather than a Nb-(CO)(OLi)$^+$ species. The intermediate 4 is only stable at −30 °C for 2 h, readily decomposing to 3 with liberation of carbon monoxide. The formation of free carbon monoxide in the reaction was confirmed during ^{13}C NMR

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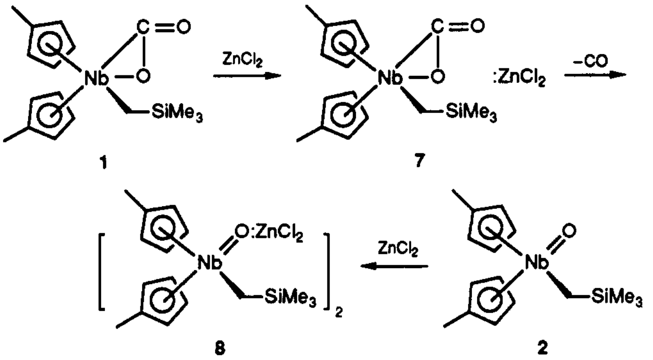
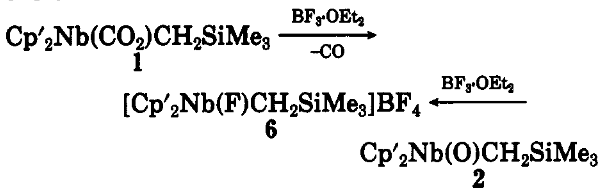
Scheme II



monitoring of the reaction of $Cp'_2Nb(^{13}CO_2)CH_2SiMe_3$ with $LiPF_6$ whereupon a prominent peak at 185 ppm (^{13}CO)[9] was observed. Significantly, intermediate 4 was not detected during parallel ^1H NMR monitoring of the reaction of oxo complex 3 with $LiPF_6$, further supporting the conclusion that 4 is an adduct of 1. The rapid conversion of metal–oxo compounds to metal halides by the action of Lewis acid halides has been observed previously.[10] Thus, the reaction of 1 with $LiPF_6$ is believed to proceed by initial formation of adduct 4 (Scheme I), followed by decarbonylation to the oxo adduct 5 (undetected), which reacts further to give product 3.

The reaction of 1 with $BF_3{\cdot}OEt_2$ in methylene chloride (carried out in an NMR tube) at room temperature was found to produce the analogous tetrafluoroborate salt $[Cp'_2Nb(F)CH_2SiMe_3]BF_4$ (6, eq 3). The ^1H NMR



$$\underset{1}{Cp'_2Nb(CO_2)CH_2SiMe_3} \xrightarrow[-CO]{BF_3{\cdot}OEt_2} \underset{2}{Cp'_2Nb(O)CH_2SiMe_3} \xrightarrow{BF_3{\cdot}OEt_2} \underset{6}{[Cp'_2Nb(F)CH_2SiMe_3]BF_4} \quad (3)$$

spectrum of 6 was identical to that of 3; the presence of the BF_4^- ion in 6 was confirmed by its ^{19}F NMR spectrum, which exhibited a characteristic peak at −147 ppm.[11] The interaction of 3 with $BF_3{\cdot}OEt_2$ in CH_2Cl_2 also was found to produce 6 at room temperature.

Reaction of 1 with $ZnCl_2$. The reaction of 1 with a suspension of anhydrous $ZnCl_2$ in dichloromethane at room temperature resulted in the formation of a pale yellow 1:1 adduct 7 which was isolated by rapid precipitation with hexane (Scheme II). The indicated 1:1 composition for 7 was supported by elemental analysis, although the instability of 7 (vide infra) prevented acquisition of completely satisfactory microanalytical data. The infrared spectrum of 7 exhibits a C=O stretching absorption (1609 cm^{-1}) of significantly reduced energy relative to the starting CO_2 complex 1 (1709 cm^{-1}). The presence of the CO_2 moiety in the adduct 7 was further verified by comparison of its IR spectum with the corresponding product from $Cp'_2Nb(^{13}CO_2)CH_2SiMe_3$ and $ZnCl_2$. The ^{13}C-labeled product 7* shows the appropriate isotopic red shift of the $M-CO_2$ stretching absorption from 1609 to 1563 cm^{-1}. The ^1H and ^{13}C NMR spectra of 7 are very similar to those of 1 except that the resonances of the MeCp ligands are shifted slightly downfield. Three potential binding sites for the $ZnCl_2$ in adduct 7 should be considered: the oxygen(s) of the CO_2 ligand, the niobium, and the MeCp π-electron system. Although this issue could best be addressed by an X-ray structure determination, efforts to obtain crystals of 7 always resulted in decomposition (vide infra). The substantial IR shift in $\nu(M-CO_2)$ in going from 1 to 7, the modest NMR chemical shift differences, and the formally d^0 nature of 1[12] are most consistent with interaction of $ZnCl_2$ with the oxygen(s) of the CO_2 ligand. This conclusion also best accounts for the subsequent chemistry observed for 7 (vide infra) and more generally for the reactions of 1 with other Lewis acids which also result in decarbonylation. Product 7 thus may be added to the growing number of bimetallic μ-CO_2 complexes.[3b–e,13] Additionally, a $ZnBr_2$ adduct (μ_2-O,O) of a cluster μ_3-CO_2 complex has been reported by Caulton and co-workers recently.[14]

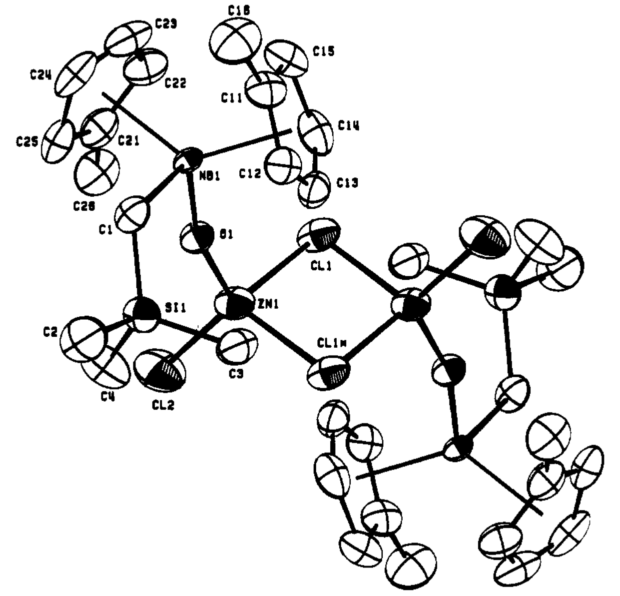


Figure 2. ORTEP diagram for $[(MeCp)_2Nb(CH_2SiMe_3)O{\cdot}ZnCl_2]_2$ (8).

Complex 7 was found to be unstable in solution, gradually decomposing to a new compound 8 (90% yield) with loss of CO. The latter was determined by ^{13}C NMR monitoring of the transformation of 7* (* = $^{13}CO_2$) to 8 which was accompanied by the appearance of the resonance for ^{13}CO at 185 ppm. The decarbonylated product 8, which also can be prepared independently in high yield

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[11] Dungan, C. H.; Van Wazer, J. R. *Compilation of Reported ^{19}F-NMR Chemical Shifts*; Wiley-Interscience: New York, 1970.

[12] The Nb(V, d^0) formulaton considers the CO_2 ligand as CO_2^{2-}. The fact that 1 is colorless, relatively air stable, and has a long η^2-C–O bond length[19] supports this formulation; recent electrochemical studies, however, have found that 1 undergoes irreversible electrochemical oxidation with CO_2 evolution (Nicholas, K. M.; DuBois, D. Unpublished results, 1991).

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from $Cp'_2Nb(O)CH_2SiMe_3$ (**3**) and $ZnCl_2$, shows little difference from **2** in its IR, ^1H NMR, and ^{13}C NMR spectra; the Nb=O stretching frequency exhibits a small red shift from 837 cm^{-1} in **2** to 828 cm^{-1} in **8**; all the proton resonances in the ^1H NMR spectrum of **8** shift slightly downfield ($\Delta\delta$ = 0.1–0.5 ppm) compared to that of **2**. The structure of **8** was established by X-ray diffraction (Figure 2) and consists of a centrosymmetric dimeric structure with a Zn_2Cl_4 unit bridging two $Cp'_2Nb(O)R$ fragments through a Nb–O–Zn linkage. Complex **8** constitutes one of the few structurally characterized Lewis acid adducts of a metal–oxo compound,[15] and hence, a few features should be noted. Coordination of Zn to the Nb=O unit causes a slight elongation (0.05 Å) of the Nb–O bond compared to that in **2** and no significant change in the Nb–C(1) length or the O–Nb–C(1) angle. The Nb–O–Zn linkage is decidedly bent but within the range observed in the few previous structures (158–175°).

Reactions of 1 with $HgCl_2$ and Me_3SiCl. Treatment of **1** with $HgCl_2$ in dichloromethane or diethyl ether at room temperature produces a red precipitate immediately which can be isolated by filtration and purified by slow crystallization from acetone/hexane. The product is not soluble in toluene, THF, hexane, or halogenated solvents. The ^1H NMR spectrum of **10** in acetone-d_6 exhibits a group of peaks assigned to the protons of the MeCp group in the region 6.1–6.5 ppm, which are slightly downfield from those of the $Cp'_2NbR(O)\cdot nZnCl_2$ adducts **8** and **9**, but no resonances associated with the CH_2SiMe_3 group were present. Elemental analysis suggested an approximate composition of $Cp'_2Cl_8Hg_2NbO$. Suitable crystals of **10** were obtained for X-ray diffraction after a long crystallization period (ca. 1 month), but final determination of the crystal structure was complicated by an apparent disorder problem. Nonetheless, the presence of $Cp'_2Nb(Cl)–O$ units were clearly present, indicating that **10** is chemically and structurally related to the oxo adducts **8** and **9** formed with $ZnCl_2$, minus the CH_2SiMe_3 unit. We presume that $HgCl_2$, acting as the other Lewis acids, first binds to the CO_2 ligand, inducing decarbonylation, followed by electrophilic cleavage of the $Nb–CH_2SiMe_3$ bond, a well-precedented reaction of metal alkyls with HgX_2.[16]

Given the facile reactions of CO_2 complex **1** with the acids $ZnCl_2$ and $HgCl_2$, we were suprised to find that no reaction occurred when **1** was stirred with a suspension of $CdCl_2$ in CH_2Cl_2 at room temperature for 2 days. We have no convincing explanation for these differences in reactivity but suspect that it may, in part, reflect differences in the limited solubilities of the three salts in the solvents employed.

Finally, the reaction of **1** with Me_3SiCl was found to proceed rapidly, even at −80 °C. The toluene-soluble, Nb-containing product proved to be $Cp'_2Nb(O)Cl$ (**11**, eq 4), which was isolated in 52% yield; no intermediate

$$\underset{\mathbf{1}}{Cp'_2Nb(\eta^2\text{-}CO_2)CH_2SiMe_3} \xrightarrow{Me_3SiCl} \underset{\mathbf{11}}{Cp'_2Nb(O)Cl} + CO \qquad (4)$$

species could be detected by NMR monitoring at −80 °C in THF-d_8. The identity of **11** was established by comparison of its spectroscopic properties with those reported previously,[17] and its structure (Figure 3) was determined by X-ray diffraction for comparison with the related compounds **1**, **2**, **3**, **8**, and **9**. The structure of **11** is unexceptional, with the observed bond lengths and angles being typical of those found in other Cp_2NbXY derivatives. However, it is interesting to note that the Nb–O distance in **11** (1.738 (5) Å) is identical to that in the oxo–alkyl derivative **2** (1.741 (3) Å) but somewhat shorter than that found in the $ZnCl_2$ adduct **8** (1.790 (5) Å). The Si-containing byproduct(s) formed in the reaction was not identified. The reaction of **1** with Me_3SiCl thus induces both decarbonylation and dealkylation as was the case for the reaction of **1** with $HgCl_2$.

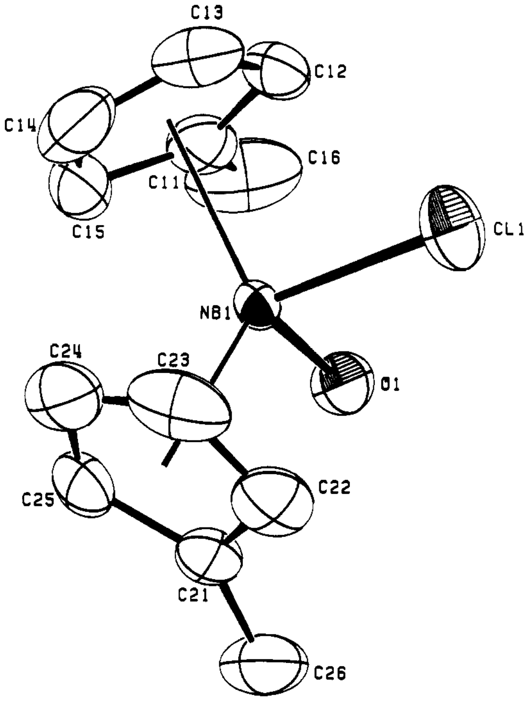

Figure 3. ORTEP diagram for $(MeCp)_2Nb(O)Cl$ (**11**).

In summary, the reaction of $Cp'_2Nb(\eta^2\text{-}CO_2)CH_2SiMe_3$ (**1**; Cp′ = MeC_5H_4) with several Lewis acids results in its facile decarbonylation. With most of the acids tested, reactions proceeded rapidly at or below room temperature. This should be contrasted with the pure thermal decarbonylation of **1** which requires several hours in refluxing THF.[7] The Nb-containing products depend markedly on the Lewis acid partner. With $LiPF_6$ or $BF_3\cdot Et_2O$, both decarbonylation and deoxygenation result to produce $[Cp'_2Nb(F)CH_2SiMe_3]Z$ (**2**; Z = PF_6^-, BF_4^-). Complex **1** reacts with $ZnCl_2$ first to form an adduct $Cp'_2Nb(CO_2)CH_2SiMe_3\cdot ZnCl_2$ (**7**) which appears to have a novel μ-CO_2 unit bridging Nb and Zn. Complex **7** decomposes with CO loss to form $[Cp'_2Nb(CH_2SiMe_3)O\cdot ZnCl_2]_2$ (**8**), a novel adduct of an oxo compound and the Lewis acid. Reaction of **1** with $HgCl_2$ rapidly produces an incompletely characterized product **9** which is both decarbonylated and dealkylated. Although $CdCl_2$ does not react with **1** under comparable conditions, Me_3SiCl reacts rapidly with **1** to produce $Cp'_2Nb(O)Cl$ (**10**), resulting from decarbonylation and dealkylation.

Generally, these reactions appear to proceed via initial interaction of the Lewis acid with the oxygen(s) of the ligated CO_2. This feature indicates a nucleophilic character

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Table I. Crystal Data for 3, 8, and 11

compd	3	8	11
formula	$C_{16}H_{25}F_7NbPSi$	$C_{32}H_{50}Cl_4Nb_2Si_2O_2Zn_2$	$C_{12}H_{14}ClNbO$
mol wt, g mol^{-1}	502.2	981.3	302.6
temp, °C	22	22	22
a, Å; α, deg	9.525 (3)	9.516 (3); 83.43 (2)	8.594 (3)
b, Å; β, deg	10.310 (4)	9.822 (4); 85.68 (2)	12.629 (4); 110.16 (2)
c, Å; γ, deg	20.996 (6)	12.150 (4); 63.63 (2)	11.538 (4)
V, $Å^3$	2061.9	1010.4	1175.5
space group	$P2_12_12_1$	$P1$	$P2_1/n$
Z	4	1	4
density, g cm^{-3}	1.618	1.613	1.710
μ(MoKα), cm^{-1}	7.5	20.9	11.9
F(000)	1016	492	608
data collectn range, deg	3–50	3–53	3–54
total reflns measd	3607	4162	2699
reflns used [$I > 2\sigma(I)$]	3018	3490	2288
R^a	0.029	0.027	0.023
$R_w{}^b$	0.032	0.037	0.033
GOF[c]	1.7	2.4	2.0
largest shift/esd, final cycle	0.2	0.3	0.1
ρ_{max} final diff map, e/$Å^3$	0.55	0.65	0.35

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2]^{1/2}$. [c] $GOF = [\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$.

Table II. Atomic Coordinates for the Non-Hydrogen Atoms of 3

atom	x	y	z
Nb(1)	0.38140 (3)	−0.10375 (3)	0.62908 (2)
P(1)	0.41539 (12)	−0.02642 (13)	0.34291 (6)
Si(1)	0.68007 (12)	0.03528 (14)	0.56710 (6)
F(7)	0.4335 (2)	0.0469 (2)	0.6764 (1)
F(1)	0.5332 (4)	−0.0163 (4)	0.3940 (2)
F(2)	0.3016 (4)	−0.0473 (4)	0.2892 (2)
F(3)	0.3614 (6)	−0.1451 (6)	0.3860 (3)
F(4)	0.5079 (5)	−0.1315 (6)	0.3031 (3)
F(5)	0.4671 (7)	0.0843 (6)	0.3001 (3)
F(6)	0.3414 (7)	0.0719 (7)	0.3853 (4)
F(3′)	0.2734 (7)	−0.0347 (8)	0.3856 (4)
F(4′)	0.4329 (9)	−0.1705 (9)	0.3423 (6)
F(5′)	0.5443 (8)	−0.0012 (9)	0.3035 (5)
F(6′)	0.3883 (8)	0.1230 (6)	0.3409 (5)
C(1)	0.5485 (4)	−0.1037 (4)	0.5568 (2)
C(2)	0.7643 (5)	0.0373 (5)	0.6461 (3)
C(3)	0.8178 (5)	0.0028 (6)	0.5060 (3)
C(4)	0.5988 (6)	0.1941 (5)	0.5503 (3)
C(11)	0.1903 (4)	0.0518 (4)	0.6059 (2)
C(12)	0.1333 (3)	−0.0677 (4)	0.6265 (2)
C(13)	0.1618 (4)	−0.1622 (5)	0.5803 (3)
C(14)	0.2424 (4)	−0.1062 (5)	0.5329 (2)
C(15)	0.2622 (4)	0.0247 (4)	0.5483 (2)
C(16)	0.1790 (5)	0.1798 (5)	0.6369 (3)
C(21)	0.4666 (4)	−0.1969 (4)	0.7300 (2)
C(22)	0.5521 (4)	−0.2448 (4)	0.6814 (2)
C(23)	0.4701 (4)	−0.3213 (4)	0.6400 (2)
C(24)	0.3343 (4)	−0.3211 (4)	0.6638 (3)
C(25)	0.3288 (4)	−0.2410 (4)	0.7174 (2)
C(26)	0.5112 (6)	−0.1144 (5)	0.7840 (3)

for coordinated CO_2 in 1 as has been observed in the chemistry of the isoelectronic and isolobal η^2-CO_2 complex $Cp_2Mo(CO_2)$[5] and some η^1-complexes.[3] Although most of these reactions ultimately result in CO_2 splitting, reactions of electrophiles with the Mo complex proceed with O-transfer to the electrophile and binding of CO to the metal, whereas the corresponding reactions with Nb derivative 1 result in dissociation of CO and retention of the Nb–O linkage, consistent with the greater oxophilicity of the earlier metal niobium. The reluctance of 1 to undergo migratory insertion probably reflects both the energetic accessibility of the decarbonylation pathways (forming a strong Nb–O bond) and the relatively strong Nb–CH_2SiMe_3 bond.[18] We are presently evaluating the importance of the latter factor in a study of a series of $Cp'_2Nb(\eta^2\text{-}CO_2)R$ compounds in which the alkyl group is systematically varied.

Experimental Section

General Methods. All reactions were performed under a dry oxygen-free nitrogen or carbon dioxide atmosphere using standard Schlenk and vacuum line techniques. Glassware was oven-dried at 120 °C overnight prior to use. Solvents were purified and dried by refluxing over drying agents for 2 h prior to distillation (hexane, ether, THF, and toluene were distilled from sodium/benzophenone; dichloromethane was distilled from calcium hydride). The Lewis acids $LiPF_6$, BF_3·OEt_2, $ZnCl_2$, $HgCl_2$, and $ClSiMe_3$ were obtained commercially. $Cp'_2Nb(\eta^2\text{-}CO_2)CH_2SiMe_3$ (1) was prepared as described previously.[19] $Cp'_2Nb(^{13}CO_2)CH_2SiMe_3$ was prepared by using a $^{13}CO_2$ atmosphere (99.5% pure, from ICON Services Inc.) during the final step in preparing 1.

NMR spectra were recorded on a Varian XL-300 FT-NMR spectrometer; ^1H NMR spectra are referenced relative to TMS and ^{19}F NMR spectra relative to CF_3Cl. IR spectra were recorded on a Bio-rad FT-IR spectrometer. Mass (FAB) spectra were recorded on a VG ZAB-E or Kratos HRMS-25 mass spectrometer.

Reaction of $Cp'_2Nb(\eta^2\text{-}CO_2)CH_2SiMe_3$ (1) with $LiPF_6$: $[Cp'_2Nb(F)CH_2SiMe_3]PF_6$ (3). Excess $LiPF_6$ (ca. 0.3 mmol) was added as a solid to a stirred dichloromethane (10 mL) solution of 1 (38 mg, 0.10 mmol) at room temperature. The reaction was completed in 5 min as indicated by a color change from colorless to light yellow. Filtration, concentration of the filtrate to 5 mL, and addition of 3 mL of hexane gave yellow crystals of 3 (75% based on 1) upon cooling at −10 °C. IR (KBr pellet, cm^{-1}) ν 3127 (m), 2962 (m), 2934 (m), 1496 (s), 1455 (s), 1382 (s), 1260 (s), 894 (m), 832 (vs), 741 (s), 558 (s); ^1H NMR (300 MHz, $CDCl_3$) δ 6.65 (m, 2 H, Cp), 6.59 (m, 2 H, Cp), 6.55 (m, 2 H, Cp), 6.48 (m, 2 H, Cp), 3.55 (s, 2 H, CH_2Si), 2.17 (d, 6 H, CH_3Cp), 0.14 (s, 9 H, $Si(CH_3)_3$); ^{19}F NMR ($CDCl_3$) δ 72.6 (d, $J_{P\text{-}F}$ = 709 Hz); MS (FAB) *m/e* (rel intensity) 357.2 ($M^+ - PF_6$, 80), 338.2 ($M^+ - F - PF_6$, 14), 270.1 ($M^+ - CH_2SiMe_3 - PF_6$, 12), 250.1 ($M^+ - F - CH_2SiMe_3 - PF_6$, 19).

The reaction of 1 with $LiPF_6$ was monitored by ^1H NMR. A solution of 1 (5.0 mg, 0.013 mmol) in 0.50 mL of $CDCl_3$ was added to a 5-mm NMR tube and the solution cooled to −30 °C. After the addition of approximately 1 equiv of $LiPF_6$, the ^1H NMR spectrum of the mixture was recorded. ^1H NMR (300 MHz, $CDCl_3$ at −30 °C for intermediate 4) δ 6.44 (m, 2 H, Cp), 6.31 (m, 2 H, Cp), 6.25 (m, 2 H, Cp), 6.18 (m, 2 H, Cp), 2.48 (s, 2 H, CH_2Si), 2.21 (s, 6 H, CH_3Cp), 0.10 (s, 9 H, $Si(CH_3)_3$). Compound 4 was largely converted to salt 3 within minutes above −30 °C.

Reaction of $Cp'_2Nb(O)CH_2SiMe_3$ (2) with $LiPF_6$. To a stirred solution of 2 (35 mg, 0.10 mmol) in 10 mL of CH_2Cl_2 was added an excess of solid $LiPF_6$. After the solution was stirred

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Table III. Atomic Coordinates for the Non-Hydrogen Atoms of 8

atom	x	y	z
Nb(1)	0.26850 (2)	0.84433 (2)	0.77401 (2)
Zn(1)	0.49030 (4)	1.03245 (4)	0.86566 (3)
Cl(1)	0.31772 (8)	1.15116 (9)	1.01355 (7)
Cl(2)	0.57636 (12)	1.18082 (12)	0.76515 (10)
Si(1)	0.64956 (9)	0.60347 (9)	0.66755 (7)
O(1)	0.3937 (2)	0.9319 (2)	0.7965 (2)
C(1)	0.4325 (3)	0.6673 (3)	0.6644 (2)
C(2)	0.7419 (4)	0.4656 (4)	0.5600 (3)
C(3)	0.7412 (3)	0.5056 (4)	0.8021 (3)
C(4)	0.6989 (4)	0.7650 (4)	0.6286 (3)
C(11)	0.1931 (3)	0.6465 (3)	0.8732 (3)
C(12)	0.3547 (3)	0.5999 (3)	0.8910 (3)
C(13)	0.3686 (3)	0.7046 (3)	0.9524 (2)
C(14)	0.2203 (4)	0.8194 (3)	0.9709 (3)
C(15)	0.1097 (3)	0.7833 (3)	0.9237 (3)
C(16)	0.1263 (4)	0.5611 (4)	0.8177 (4)
C(21)	0.1268 (3)	1.0999 (3)	0.6694 (3)
C(22)	0.0189 (3)	1.0662 (3)	0.7394 (3)
C(23)	0.0028 (3)	0.9457 (3)	0.6986 (3)
C(24)	0.1071 (4)	0.8967 (3)	0.6102 (3)
C(25)	0.1870 (4)	0.9904 (3)	0.5917 (3)
C(26)	0.1739 (4)	1.2233 (3)	0.6798 (3)

Table IV. Atomic Coordinates for the Non-Hydrogen Atoms of 11

atom	x	y	z
Nb(1)	0.16154 (2)	0.17886 (1)	0.31537 (2)
Cl(1)	0.26428 (9)	0.03765 (5)	0.46557 (6)
O(1)	0.2665 (2)	0.2852 (1)	0.4023 (1)
C(11)	−0.0731 (3)	0.2791 (2)	0.3463 (2)
C(12)	−0.0652 (3)	0.1817 (2)	0.4022 (2)
C(13)	−0.1080 (3)	0.1009 (2)	0.3113 (3)
C(14)	−0.1388 (3)	0.1486 (3)	0.2001 (3)
C(15)	−0.1081 (3)	0.2573 (3)	0.2202 (2)
C(16)	−0.0460 (4)	0.3834 (2)	0.4073 (4)
C(21)	0.3700 (3)	0.2199 (2)	0.2124 (2)
C(22)	0.3919 (3)	0.1151 (2)	0.2509 (3)
C(23)	0.2480 (4)	0.0574 (2)	0.1785 (3)
C(24)	0.1374 (3)	0.1265 (3)	0.1025 (2)
C(25)	0.2074 (3)	0.2279 (2)	0.1261 (2)
C(26)	0.4893 (4)	0.3090 (2)	0.2579 (3)

for 5 min, the color of the mixture had changed from colorless to light yellow. Filtration, concentration of the filtrate to 5 mL, and cooling to −10 °C gave yellow crystals of 3 (62% based on 1).

Reaction of $Cp'_2Nb(\eta^2\text{-}CO_2)CH_2SiMe_3$ (1) with $BF_3{\cdot}OEt_2$: $[Cp'_2Nb(F)CH_2SiMe_3]BF_4$ (6). To a 0.5-mL solution of 1 (5.0 mg, 0.013 mmol) in $CDCl_3$ was added 1.6 μL (0.013 mmol) of $BF_3{\cdot}OEt_2$ at room temperature. The solution turned light yellow immediately upon shaking. The ^1H NMR and ^{19}F NMR spectra were then recorded, displaying a set of new resonances assigned to $[Cp'_2Nb(F)CH_2SiMe_3]BF_4$ (6). ^1H NMR (300 MHz, $CDCl_3$) δ 6.65 (m, 2 H, Cp), 6.59 (m, 2 H, Cp), 6.55 (m, 2 H, Cp), 6.48 (m, 2 H, Cp), 3.55 (s, 2 H, CH_2Si), 2.17 (d, 6 H, CH_3Cp), 0.14 (s, 9 H, $Si(CH_3)_3$); ^{19}F NMR ($CDCl_3$, relative to CF_3Cl) δ −147 (BF_4^-); MS (FAB) *m/e* (rel intensity) 357.0 ($M^+ - BF_4$, 79), 339.0 ($M^+ - BF_4 - CH_3$, 6), 270.0 ($M^+ - BF_4 - CH_2Si(CH_3)_3$, 64), 250.0 ($M^+ - BF_4 - F - CH_2Si(CH_3)_3$).

Reaction of $Cp'_2Nb(O)CH_2SiMe_3$ (2) with $BF_3{\cdot}OEt_2$. To a 0.5-mL solution of 1 (5.0 mg, 0.013 mmol) in $CDCl_3$ was added 1.8 μL (0.014 mmol) of $BF_3{\cdot}OEt_2$ at room temperature; the solution turned light yellow immediately. The ^1H NMR and ^{19}F NMR spectra were then recorded, displaying identical sets of resonances (for 6) to those produced in the reaction of 1 with $BF_3{\cdot}OEt_2$.

Reaction of 1 with $ZnCl_2$: $Cp'_2Nb(CO_2)CH_2SiMe_3{\cdot}ZnCl_2$ (7). To a solution of 1 (38.2 mg, 0.10 mmol) in 10 mL of dichloromethane was added $ZnCl_2$ solid (13.6 mg, 0.10 mmol). The mixture was stirred for 10 min and then filtered. Addition of hexane to the filtrate at −78 °C precipitated the adduct 7 as a white solid (58%). IR ($CDCl_3$, cm^{-1}) ν 3100 (w), 2927 (vs), 2853 (s), 1715 (s), 1609 (vs), 1493 (w), 1466 (m), 1457 (m), 1389 (w), 1258 (vs), 1246 (m), 1133 (s), 1045 (m), 848 (s), 826 (vs); IR (for $Cp'_2Nb(^{13}CO_2)CH_2SiMe_3{\cdot}ZnCl_2$, $CDCl_3$, cm^{-1}) ν 3105 (w), 2952 (s), 2877 (w), 1664 (m), 1563 (vs), 1495 (w), 1458 (w), 1382 (w), 1246 (s), 1234 (s), 1046 (m), 849 (vs), 826 (vs); ^1H NMR (300 MHz, $CDCl_3$) δ 6.51 (m, 2 H, Cp), 6.12 (m, 2 H, Cp), 5.43 (m, 2 H, Cp), 5.42 (m, 2 H, Cp), 2.17 (s, 2 H, CH_2Si), 1.62 (s, 6 H, CH_3Cp), 0.15 (s, 9 H, $Si(CH_3)_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.6, 120.8, 116.2, 107.6, 98.9, 95.8, 31.9, 14.5, 4.5; MS (FAB) *m/e* (rel intensity) 490.0 ($M^+ - CO$, 8.9), 455.0 ($M^+ - CO - Cl$, 7.2), 355.0 ($M^+ - CO - ZnCl_2$, 58), 339 ($M^+ - CO - ZnCl_2 - CH_3$, 100), 338 ($M^+ - CO_2 - ZnCl_2$, 84). Anal. Calcd (Found): C, 39.4 (40.0); H, 4.8 (5.1). Attempts to obtain X-ray quality crystals of 7 by slow diffusion or evaporation from various solvents resulted in gradual decarbonylation to 8 (90%).

Reaction of 3 with $ZnCl_2$: $[Cp'_2Nb(O)CH_2SiMe_3{\cdot}ZnCl_2]_2$ (8). Oxo complex 3 (35 mg, 0.10 mmol) was dissolved in 10 mL of dichloromethane, and to the stirred solution at room temperature was added $ZnCl_2$ (14 mg, 0.10 mmol); the solution became light yellow within 2 min. After stirring for an additional 10 min, the mixture was filtered, the filtrate was concentrated to 5 mL, and 3 mL of hexane was added. Cooling of the mixture to −10 °C gave light yellow crystals of 8 (90%). IR (KBr, cm^{-1}) ν 3101 (m), 2949 (m), 2892 (w), 1502 (m), 1454 (m), 1407 (w), 1379 (w), 1243 (s), 1032 (w), 931 (m), 855 (s), 828 (vs), 750 (w), 716 (m), 677 (m), 612 (m); ^1H NMR (300 MHz, $CDCl_3$) δ 6.16 (m, 2 H, Cp), 6.12 (m, 2 H, Cp), 5.95 (m, 2 H, Cp), 5.84 (m, 2 H, Cp), 1.20 (s, 2 H, CH_2Si), 2.20 (s, 6 H, CH_3Cp), 0.11 (s, 9 H, $Si(CH_3)_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 117.7, 112.0, 110.5, 109.9, 31.0, 16.5, 3.9; MS (FAB) *m/e* (rel intensity) 807 ($M^+ - 2Cp - CH_3$, 6.1), 490.0 ($M^+ - Cp'_2Nb(O)CH_2SiMe_3{:}ZnCl_2$, 19.5), 452.9 ($M^+ - Cp'_2Nb(O)CH_2SiMe_3{:}ZnCl_2 - Cl$, 19.6), 418.0 ($M^+ - Cp'_2Nb(O)CH_2SiMe_3{:}ZnCl_2 - 2Cl$, 12.3), 355 ($M^+ - Cp'_2Nb(O)CH_2SiMe_3{:}ZnCl_2 - ZnCl_2$, 19.0), 339 ($M^+ - Cp'_2Nb(O)CH_2SiMe_3{:}ZnCl_2 - ZnCl_2 - Me$, 72.2%). Single diamondlike crystals of 8 for X-ray analysis were obtained from hexane/dichloromethane at −10 °C.

Reaction of 1 with $HgCl_2$. Addition of $HgCl_2$ (27.2 mg, 0.10 mmol) to a stirred diethyl ether solution (10 mL) of 1 (38.2 mg, 0.10 mmol) resulted in the formation of an orange precipitate 10 within a few minutes, which was collected by filtration, washed with THF, and dried in vacuo (60 mg). IR (KBr, cm^{-1}) ν 3095 (m), 2930 (w), 1492 (s), 1451 (m), 1500 (s), 1255 (m), 1028 (2), 853 (vs), 743 (vs), 676 (s), 584 (m); ^1H NMR (300 MHz, acetone-d_6)

Table V. Selected Bond Distances (Å) and Angles (deg) for 3, 8, and 11

3		8		11	
MeCp(1)–Nb	2.110 (3)	MeCp(1)–Nb	2.149 (3)	MeCp(1)–Nb	2.177 (2)
MeCp(2)–Nb	2.106 (4)	MeCp(2)–Nb	2.163 (3)	MeCp(2)–Nb	2.176 (3)
Nb–F	1.910 (2)	Nb–O	1.802 (2)	Nb–O	1.732 (1)
Nb–C(1)	2.199 (4)	Nb–C(1)	2.243 (3)	Nb–Cl	2.431 (1)
		Zn(1)–O(1)	1.908 (2)		
		Zn(1)–Cl(1)	2.369 (1)		
		Zn(1)–Cl(2)	2.187 (1)		
MeCp–Nb–MeCp	132.0 (2)	MeCp–Nb–MeCp	129.7 (1)	MeCp–Nb–MeCp	129.1 (1)
F–Nb–C(1)	99.8 (1)	O(1)–Nb–C(1)	98.5 (1)	O–Nb–Cl	99.6 (1)
		Zn(1)–O(1)–Nb	161.3 (1)		
		O(1)–Zn(1)–Cl(1)	105.9 (1)		
		O(1)–Zn(1)–Cl(2)	120.0 (1)		

Organometallics 1992, *11*, 2613-2622

δ 6.42 (m, 2 H, Cp), 6.25 (m, 2 H, Cp), 6.18 (m, 2 H, Cp), 6.11 (m, 2 H, Cp), 2.12 (s, 6 H, $CpCH_3$). Anal. Calcd (found) for $C_{12}H_{14}Cl_8Hg_2NbO$: C, 15.1 (14.4); H, 1.5 (1.5); Hg, 42.1 (42.2). Single crystals of 10 for X-ray analysis were obtained from acetone/hexane at −10 °C after several weeks.

Reaction of 1 with Me_3SiCl: $Cp'_2Nb(Cl)O$ (11). To a stirred dichloromethane solution of 1 (38.2 mg, 0.10 mmol) was added $ClSiMe_3$ (10.8 mg, 0.10 mmol); the solution became yellow immediately. After the mixture was stirred for 30 min, the solvent was removed at reduced pressure. Trituration of the residue with toluene, followed by cooling of the toluene extracts at −10 °C, gave yellow crystals of $Cp'_2Nb(Cl)O$ (52%) (11). IR (KBr, cm^{-1}) ν 3075 (w), 2922 (w), 1505 (s), 1453 (s), 1359 (m), 1220 (s), 1088 (m), 1023 (vs), 777 (m), 853 (s), 816 (vs), 617 (m); ^1H NMR (300 MHz, $CDCl_3$) δ 6.08 (m, 4 H, Cp), 5.99 (m, 2 H, Cp), 5.96 (m, 2 H, Cp), 2.19 (s, 6 H, Cp); MS (EI, 12 eV, DIP) *m/e* 301.9 (M^+, 24.4), 265.9 ($M^+ - Cl$, 27.7), 223.8 ($M^+ - MeCp$, 100). These data are in agreement with those reported previously.[17]

X-ray Structure Determinations of 3, 8, and 11. Single crystals of 3, 8, and 11 were obtained by recrystallization at reduced temperature as described above. The crystal data for all three compounds were measured on an Enraf-Nonius CAD-4 diffractometer using monochromated Mo Kα radiation (λ = 0.71069 Å). The data were corrected for Lorentz and polarization effects. No absorption corrections was applied since it was judged to be insignificant in all three cases. The atomic scattering factors were taken from the International Tables for X-ray Crystallography, and the structures were solved and refined anisotropically by the full-matrix least-squares method (SHELX-76). For 3, four of the six fluorine atoms of the PF_6^- ion were disordered and each of them was refined with 60% and 40% occupancy at two sites. A summary of the crystal and data collection parameters is provided in Table I, positional parameters are given in Tables II–IV, and bond distances and angles are given in Table V.

Acknowledgment. We are grateful for support provided by the U.S. Department of Energy, Basic Energy Sciences, Chemistry Division (89ER 13997). K.M.N. also acknowledges an AWU Faculty Fellowship supporting a sabbatical stay at the National Renewable Energy Laboratory where (in part) this paper was written.

Supplementary Material Available: Tables of thermal parameters and complete listings of interatomic distances and angles for 3, 8, and 11 (14 pages). Ordering information is given on any current masthead page.

OM9200159

Formation of Substituted Ferracyclopentadiene Complexes by the Reaction of Alkynes with Protonated Diferra-μ-azaallylidene Complexes

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Received December 23, 1991

The dinuclear complexes $[Fe_2\{\mu\text{-}C(H)(CH{=}NHR')\}(CO)_8][BF_4]$ ($R' = Bu^t$, Ph), which possess protonated μ_2,η^1-azaallylidene ligands and are derivatives of the parent methylene complex $Fe_2(\mu\text{-}CH_2)(CO)_8$, react with alkynes ($R^1C{\equiv}CR^2$) to give isomeric hydroxy-imino-ferracyclopentadiene complexes, $Fe_2(\mu\text{-}CR^1CR^2C(OH)C\{C(H){=}NR'\})(CO)_6$, and amino-ferracyclopentadiene complexes, $Fe_2(\mu\text{-}CR^1CR^2CHC\{N(H)R'\})(CO)_6$, with the distribution of products dependent on the alkyne employed. The former were also isolated as their BF_3 adducts $Fe_2(\mu\text{-}CR^1CR^2C(O\text{-}BF_3)C\{C(H){=}NHR'\})(CO)_6$, and two of these latter complexes have been crystallographically characterized. They have a typical ferracyclopentadiene (ferrole) ring with an iminium substituent ($C(H){=}NHR'$) on the α-carbon of the ring, which is hydrogen-bonded though the nitrogen atom to the oxygen substituent on the β-carbon of the ferracyclopentadiene ring, which is in turn coordinated by the BF_3 group. The BF_3 group can be removed by reaction with aqueous base to give the free hydroxy-imino-ferracyclopentadiene complexes. The amino-ferracyclopentadiene complex with $R' = Bu^t$ and $R^1 = R^2 = Ph$ has also been crystallographically characterized. It is a typical ferracyclopentadiene complex with an amino group on the α-carbon. The amino-ferracyclopentadiene complexes are also formed in near quantitative yield by an acid-catalyzed ring contraction of the 2-ferrapyridine complexes $Fe_2(\mu\text{-}CR^1CR^2CHCHNR')(CO)_6$.

Introduction

We recently reported that the protonated azaallylidene complexes **2a,b** result from the addition of $HBF_4{\cdot}Et_2O$ and CO to the 2-ferrapyrrolinone complexes **1a,b**, eq 1.[1] These compounds are derivatives of the well-known complex $Fe_2(\mu\text{-}CH_2)(CO)_8$ (**3**).[2] This latter compound has been

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0276-7333/92/2311-2613$03.00/0