and decamethylferrocene were purchased from Aldrich and Strem, respectively, and were used without further purification.

Cyclic Voltammetry. Cyclic voltammetry was performed with a BAS-100 electrochemical analyzer employing a Pt-disk working electrode and, in the same compartment, a Pt-wire counter electrode. The solvent was THF with 0.15 M tetrabutylammonium perchlorate. The reference electrode (saturated NaCl–SCE) was immersed in a reservoir of solvent and electrolyte that was isolated from the working compartment by a cracked-glass junction designed to minimize solution transfer. The cell was oven-dried and cooled under a stream of argon prior to each use. An argon atmosphere was maintained over the working solution at all times.

Cyclic voltammograms were obtained at low substrate concentrations, typically 5×10^{-4} M, to minimize the *iR* drop error inherent in a low-conductivity nonaqueous medium. Low substrate concentrations were required to minimize fouling of the working electrode. All peak potentials are reported relative to ferrocene (the Cp_2Fe/Cp_2Fe^+ couple is taken to have $E^{\circ\prime}$ equal to +0.31 V).[11]

Preparation of $Cp_2Fe^+BF_4^-$. Preparative electrochemistry was performed with a Princeton Applied Research Model 173 potentiostat equipped with a PAR model 179 digital coulometer. The cell was a three-compartment design with a low-porosity frit separating the working solution from the counter electrode compartment. The working electrode was Pt mesh, the counter electrode was nichrome wire, and the reference was saturated NaCl–SCE. An argon atmosphere was maintained over the working solution.

In a typical experiment, 1.0 mmol of ferrocene (0.19 g) in 35 mL of acetonitrile/0.2 M tetrabutylammonium tetrafluoroborate was oxidized until 48.0 C had passed to afford, in theory, 0.50 mmol of ferrocenium tetrafluoroborate. The acetonitrile was removed in vacuo at room temperature to leave a mixture containing $Cp_2Fe^+BF_4^-$, unoxidized ferrocene, and $Bu_4N^+BF^-$.

The integrity of the ferrocenium salt was verified by dissolving the $Cp_2Fe^+BF_4^-/Cp_2Fe/Bu_4N^+BF_4^-$ mixture in 35 mL of acetonitrile and reducing the solution at 0.00 V vs NaCl–SCE until the current ceased to flow. In each of three trials, more than 90% of the calculated charge passed, indicating that most of the expected ferrocenium ion had been present.

Bulk Oxidations with Cp_2Fe^+. To the solid mixture of ferrocenium tetrafluoroborate, ferrocene, and electrolyte salt was added 4 mL of THF, and the solution was stirred under an argon atmosphere until most of the solids had dissolved. Then 1 mL of a THF solution containing the metal complex (0.25 M based on nickel) was added dropwise at room temperature. This solution was stirred for 15 min before being quenched with 2 mL of water. The organic layer and the water layer were then separated, and the organic layer was analyzed for products. For the oxidation of the two acylate complexes, products and yields are given in Table II. For the I_2 oxidation of the acyl(allyl)nickel complex **3**, the yields are as follows: 1-octen-4-one (**4**), 81%; 2-octen-4-one, 8%; 5-hydroxy-5-allyl-6-decanone, 11%. For the Cp_2Fe^+ oxidation of the acyl(allyl)nickel complex **3**, the yields are as follows: 1-octen-4-one (**4**), 80%; 2-octen-4-one, 7%; 5-hydroxy-5-allyl-6-decanone, 13%.

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Note Added in Proof. After this manuscript was accepted, a paper appeared (Mitsudo, T.; Ishihara, A.; Suzuki, T.; Watanabe, Y. *Organometallics* **1990**, *9*, 1357) which showed that the reaction between I_2 and the corresponding iron acylate complex generates an anionic acyldiiodotricarbonyliron complex.

Structure of a Trinuclear Zr_2Al μ-Ketone Complex with a Bridging Trigonal-Bipyramidal Methyl Group†

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Summary: The reaction of a zirconocene acyl chloride with 0.5 equiv of trimethylaluminum results in the formation of the trinuclear Zr_2Al complex $[Cp_2Zr(\eta^2(C,O)\text{-}OC(CH_3)_2]_2(\mu\text{-}AlMe_2)(\mu\text{-}Me)$, which contains a trigonal-bipyramidal bridging methyl group. The complex crystallizes in the monoclinic system, in space group $P2_1/n$ (C^5_{2h}, No. 14), with a = 10.574 (1) Å, b = 16.456 (2) Å, c = 16.763 (2) Å, β = 103.71 (1)°, V = 2833.6 (9) Å^3, and Z = 4. This is one of the few structures that contains a bridging methyl group with a near-trigonal-bipyramidal structure in which the metals occupy the axial positions and the three hydrogen atoms are in the equatorial plane.

Bridging ligands serve as structural models for intermediates in ligand-transfer processes.[1] The structural features of such ligands are useful in interpreting the stereochemistry of related transmetalation reactions. We recently reported the structure of a complex that contained a novel trigonal-bipyramidal methyl group bridging two zirconium centers.[2] This structure, the first example of this type of coordination between transition-metal centers, is of considerable interest as a model for transmetalation reactions that proceed with inversion of configuration.[3] Since our initial report, several other structures of complexes exhibiting a linear methyl bridge have been published.[4] In only one of these cases were the hydrogens of

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† Contribution No. 8060.

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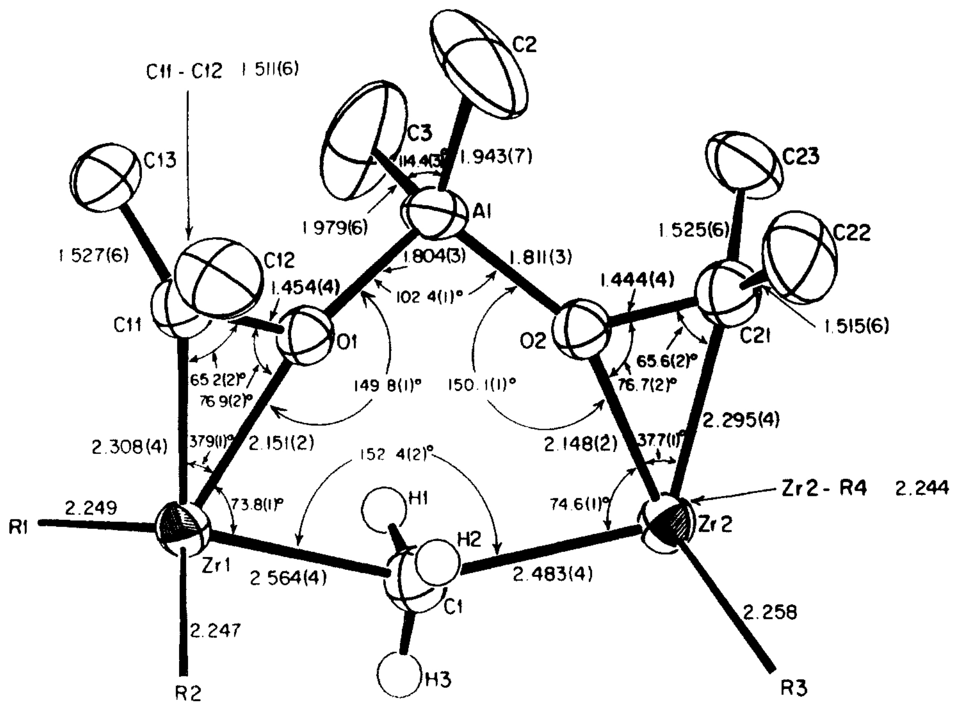
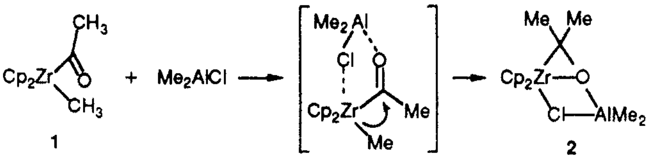


Figure 1. X-ray structure of $[Cp_2Zr(\eta^2(C,O)\text{-}OCMe_2)]_2(\mu\text{-}AlMe_2)(\mu\text{-}CH_3)$ (3c).

the bridging methyl located.[4a] In this case, the μ-methyl group is sp^3-hybridized and its coordination geometry is far from trigonal bipyramidal. In the other structures the geometry about the methyl group could not be determined. Although the hydrogen atom on the μ-CH_3 could not be located in $[CMeC_5H_4U]_2$ (μ-CH_3), the equivalent metal–μ-CH_3 bond distances suggest it has a trigonal-bipyramidal μ-CH_3.[4f] Consequently the structure reported for the earlier bis zirconium complex remains the only confirmed structure containing a trigonal-bipyramidal coordination about carbon.[4,5] We now wish to report an additional example of this very unusual coordination geometry, which suggests that the structure may be more general than anticipated and confirms the structure of the earlier example.

As previously reported,[6] zirconium ketone complexes are formed in the reaction between methyl–acyl complexes 1 and dialkylaluminum chloride reagents. These reactions occur via the migration of an alkyl group to a cis-acyl ligand to form a zirconocene ketone complex (eq 1).

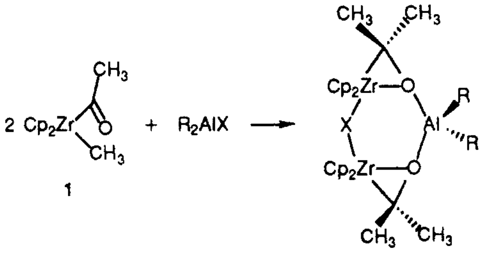


(1)

Mechanistic studies established that this ligand transformation is intramolecular and that the coupling is facilitated by the alkylaluminum reagents.[7]

Results and Discussion

During the course of the study of the mechanism of the interaction of alkylaluminum reagents with zirconocene acyls, we observed that the trinuclear Zr_2Al briding ketone complexes 3 are formed (eq 2) when the reaction was carried out in the presence of excess 1. In the presence of dialkylaluminum chloride reagents (R_2AlCl, R = iBu, Me), complexes **3a**,**b** with bridging chloride ligands are formed; in the presence of trimethylaluminum, complex **3c** with a bridging methyl group is formed. The bridging chloride complex **3a** can also be formed by heating a benzene solution of the ketone complex **2** and pyridine to 60 °C for 1 h.[8] The ketone complexes **3** are considerably more stable than the ZrAl ketone complexes **2**. The ketone complexes **2** are unstable above 25 °C, while no significant decomposition of **3a** was observed after heating in toluene at 80 °C for 12 h.



(2)

3a: R = Me, X = Cl
b: R = iBu, X = Cl
c: R = Me, X = Me

The spectral and analytical data suggested that these ketone complexes were closely related to the trinuclear Zr_2Al bridging ketene complexes that we have described in detail elsewhere.[2] An X-ray crystal structure of the bridging methyl derivative **3c**, prepared from the methyl–acyl complex and 0.5 equiv of Me_3Al, is presented in Figure 1. This molecule consists of two zirconocene ketone complexes bridged by a methyl group and a dimethylaluminum center. The most unusual feature of this compound is the geometry of the bridging methyl ligand. The methyl group is very nearly planar, with the methyl carbon being sp^2-hybridized in a trigonal-bipyramidal coordina-

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[8] The pyridine adduct[7] of ketone complex **2** is an intermediate in this reaction.

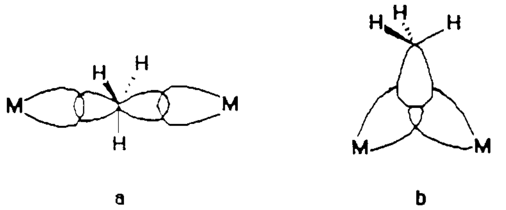
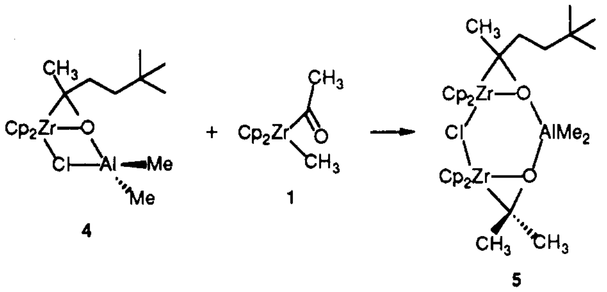


Figure 2. Orbital overlap representation of bonding modes associated with a bridging methyl ligand.

tion geometry with the zirconium centers occupying the apical positions.[9] The important structural features of this complex (**3c**) are almost identical with those found for the related ketene complex. The Zr–C–Zr angle is 147.8 (3)° for the ketene complex and 152.5 (2)° for the ketone structure. In neither case is the methyl group symmetrically bound. The two Zr–C bond distances for the ketene complex are 2.559 (7) and 2.456 (7) Å and are 2.564 (4) and 2.483 (4) Å in the ketone complex reported here. We previously offered a simplified molecular orbital bonding scheme (Figure 2a) for this type of bridging arrangement as one involving an electon-deficient three-center–two-electron bond utilizing a carbon p orbital. This contrasts with the more common bonding description offered for the majority of bridging alkyl ligands as shown in Figure 2b.

This new, rather unusual bonding geometry has interesting implications for interpreting the stereochemistry of the transmetalation reactions between electrophilic metal centers and the racemization of Grignard and alkyllithium reagents. The similar methyl structures that are obtained from two different complexes confirms that the original structure, which was based on locating hydrogen atoms by X-ray diffraction methods, was correct and suggests that the subtle structural features of this type of bridging structure are not the result of crystal-packing forces.

Mechanism. On the basis of our earlier studies on the formation of the ketone complexes **2**,[4,5] the most likely mechanism for the formation of the trinuclear ketone complexes **3** is one involving initial formation of the ketone complex **2** followed by a bimolecular reaction between **2** and another molecule of the acyl **1**. Support for this hypothesis was provided by treating the ketone complex **4** with the methyl acyl **1** to give the trinuclear ketone complex **5** (eq 3).



(3)

Significantly, none of the symmetric ketone complex **3a** is formed in this reaction, implying that there is not a competitive dissociation of R_2AlCl from **4** prior to reaction with **1**. A remarkable implication of these results is that the ketone complexes **2** are sufficiently Lewis acidic to induce the coupling of the acyl and alkyl ligands of **1**.

In summary, we have shown that the reaction of zirconium acyl ligands and alkylaluminum reagents is a general route to alkylaluminum adducts of zirconium ketone complexes. By appropriate choice of the aluminum reagent and stoichiometry of the reaction, both 1:1 aluminum adducts and 2:1 adducts can be prepared. The 2:1 adduct contains a trigonal-bipyramidal methyl bridge.

Experimental Section

General Procedures. All manipulations were carried out under argon with use of standard Schlenk techniques or in a nitrogen-filled glovebox equipped with a −40 °C freezer. Argon was purified by passage through columns of Chemalog RS-11 catalyst and Linde 4-Å molecular sieves. Toluene, benzene, diethyl ether, pentane, THF, and hexane, including NMR solvents, were stirred over CaH_2 and transferred onto sodium benzophenone ketyl. Solvents dried in this manner were vacuum-transferred and stored under argon in flasks equipped with Teflon Kontes valves. The acyl complexes **1a–e**[10] and **3**, and **3**-d_6-^{13}C[11] and the ketone complex **2a**[7] were prepared by literature procedures. $AlMe_3$ was used as the neat compound (Alfa) or as 2 M solutions in toluene (Aldrich). Et_3Al, $AlMe_2Cl$, diisobutylaluminum chloride, and diisobutylaluminum hydride were obtained neat from Texas Alkyls and were used without further purification. Mesitylene was dried over calcium hydride, vacuum-transferred, and stored in the drybox. ^1H NMR spectra were recorded in C_6D_6, $CDCl_3$, or C_7D_8 with residual protio solvent resonances as an internal reference on Varian EM-390, JEOL FX-90Q, JEOL GX-400, and Bruker WM-500 spectrometers. ^{13}C NMR spectra were obtained on the JEOL instruments. IR spectra were recorded as Nujol mulls or in solution in C_6D_6 on a Beckman IR-4240 or Shimadzu IR-435 instrument. Elemental analyses were performed at the California Institute of Technology Analytical Facility, Dornis and Kolbe Microanalytical Laboratory, or MicAnal Laboratories. All reactions were carried out at room temperature unless otherwise indicated.

[Cp$_2$Zr(η^2(*C*,*O*)-OCMe$_2$)]$_2$[μ-Al(CH$_2$CHMe$_2$)$_2$](μ-Cl) (3b). The acyl **1** (0.357 g, 1.277 mmol) was dissolved in benzene and cooled to 0 °C. A benzene solution of diisobutylaluminum chloride (0.124 mL, 0.638 mmol) was added slowly via cannula to the acyl solution. The resulting yellow solution was stirred as it was warmed to room temperature and evacuated to dryness. The residue was washed with 6 mL of pentane to give **3b** as a yellow powder (0.308 g, 0.419 mmol, 66%). ^1H NMR (C_6D_6): δ 5.71 (s, 20 H), 2.28 (m, J = 6.6 Hz, 2 H), 1.79 (s, 12 H), 1.31 (d, J = 6.6 Hz, 12 H), 0.30 (d, J = 6.8 Hz, 4 H). ^{13}C NMR (C_6D_6): δ 109.3, 80.3, 33.5, 28.5, 26.4. Anal. Calcd for $C_{34}H_{50}O_2ClAlZr_2$: C, 55.51; H, 6.80; Cl, 4.82. Found: C, 55.35; H, 6.93; Cl, 4.03.

[Cp$_2$Zr(η^2(*C*,*O*)-OCMe$_2$)]$_2$(μ-AlMe$_2$)(μ-CH$_3$) (3c). The acyl complex **1** (0.858 g, 3.06 mmol) was dissolved in a minimum amount of toluene, placed under an atmosphere of CO, and cooled to 0 °C. A toluene solution of $AlMe_3$ (0.138 g, 1.91 mmol) was prepared and cannulated into the acyl solution. The solution was stirred briefly at 0 °C, after which **3c** precipitated as yellow microcrystals. After the solution was cooled at −20 °C for 4 h, the dark yellow supernatant was removed with a cannula and the resulting yellow solid washed with two 10-mL portions of cold toluene to give **3c** as a yellow powder, which was only sparingly soluble in aromatic solvents or THF. A yellow crystal suitable for X-ray analysis was obtained from CD_2Cl_2 by slow cooling in a dewar with 2-propanol in a −50 °C freezer. ^1H NMR (C_6D_6): δ 5.57 (s, 2 H), 1.67 (s, 12 H), −0.37 (s, 6 H), −0.50 (s, 3 H). ^1H NMR (THF): δ 5.86 (s, 20 H), 1.55 (s, 12 H), −0.28 (s, 3 H), −0.88 (s, 6 H). Anal. Calcd for $C_{29}H_{41}O_2AlZr_2$: C, 55.19; H, 6.55. Found: C, 55.22; H, 6.66.

Crystal Parameters: 0.22 × 0.20 × 0.37 mm; $Zr_2AlC_{29}H_{41}O$; fw 631.07; space group $P2_1/n$ (No. 14); a = 10.574 (1) Å; b = 16.456 (2) Å; c = 16.763 (2) Å; β = 103.71 (1)°; V = 2833.6 (9) Å^3; ρ = 1.48 (1) g cm^{-3}; μ = 7.79 cm^{-1} (μr_{max} = 0.188); CAD-4 diffractometer; θ–2θ scan; 2θ from 1° to 50°; 9707 reflections measured;

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[9] The low solubility of the ketone complex **3c** precluded measurement of the C–H coupling constants for the bridging methyl group. However, for the analogous compound containing a trigonal-bipyramidal methyl group between two zirconocene ketene centers,[2] the C–H coupling constants are anomalously high (136 Hz), consistent with an sp^2-hybridized structure in solution.

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4973 independent reflections used in structure solution and refinement (goodness of fit for merging 1.06); 4341 reflections with $F_o^2 > 0$ used in R, which was 0.054 at convergence with most non-hydrogen atoms anisotropic; three hydrogens on bridging methyl group refined, remainder positioned by difference maps or by calculation with C–H = 0.95 Å; refined C–H distances 0.82 (4), 0.94 (4), and 0.88 (4) Å; H–C–H angles 121 (4), 121 (4), and 116 (4)°. The refinement was smooth, and the low values of the final residuals indicates the model is an excellent one. Complete details are given in the supplementary material.

Formation of 3a from 2 and 1. Addition of a benzene-d_6 solution of the alkyl–acyl complex 1 to the ketone complex 2 led to the immediate precipitation of **3a** as a yellow microcrystalline material.

$[Cp_2Zr(\eta^2(C,O)\text{-}OCMe_2)][Cp_2Zr(\eta^2(C,O)\text{-}OC(Me)\text{-}CH_2CH_2CMe_3)](\mu\text{-}AlMe_2)(\mu\text{-}Cl)$ (5). The ketone complex 4[7] and the acyl 1 were dissolved in toluene to give a yellow solution, which was stirred briefly and evacuated to give **5** as a yellow powder (0.276 g, 0.383 mmol, 52%). ^{1}H NMR (C_6D_6): δ 5.86 (s, 5 H), 5.75 (s, 5 H), 5.73 (s, 5 H), 5.69 (s, 5 H), 2.60 (td, ^3J = 12.7 Hz, ^2J = 3.9 Hz, 1 H), 1.75 (s, 3 H), 1.65 (s, 3 H), 1.61 (s, 3 H), 1.39 (td, ^3J = 13.2 Hz, ^2J = 3.9 Hz), 1.27 (td, ^3J = 13.2 Hz, ^2J = 4.6 Hz, 1H), 1.01 (s, 9 H), −0.23 (s, 3 H), −0.28 (s, 3 H). ^{13}C NMR (C_6D_6): δ 110.1, 109.9, 109.7, 109.6, 83.9, 77.9, 42.4, 41.8, 34.5, 33.8, 32.5, 30.6, 30.0.

Acknowledgment. We acknowledge the National Institutes of Health and the National Science Foundation for financial support of this research and the National Science Foundation (Grant No. CHE-83-19039) for financial support of the X-ray facility.

Supplementary Material Available: A complete description of data collection and refinement and tables of crystallographic data, all final positional and thermal parameters, and selected distances and angles (8 pages); a table of observed and calculated structure factors (19 pages). Ordering information is given on any current masthead page.

Hydrolysis of Tetrachloro(pentamethylcyclopentadienyl)niobium(V). Crystal Structure of $[Nb_2(\eta^5\text{-}C_5Me_5)_2Cl_2(\mu_2\text{-}O)(\mu\text{-}Cl)](\mu_2\text{-}O)_2(\mu_3\text{-}O)[Nb(\eta^5\text{-}C_5Me_5)Cl]$

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Sagrario Martinez-Carrera,[‡] and Pascual Royo*[,†]

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Received December 21, 1989

Summary: $NbCp^*Cl_4$ (**1**; Cp* = η^5-C_5Me_5) is directly isolated as a crystalline solid by reacting $NbCl_5$ with $SiMe_3(C_5Me_5)$ in dichloromethane–toluene (3:1). Complex **1** reacts with H_2O in the presence of $NHEt_2$ to give the mononuclear hydroxo complex $NbCp^*Cl_3(OH)$ (**2**), which reacts with **1**, losing HCl to give the μ-oxo complex $[NbCp^*Cl_3]_2(\mu\text{-}O)$ (**3**), also formed by exposure of solid samples of **1** to the ambient atmosphere. **2** also reacts with H_2O in solution to form the μ-oxo hydroxo complex $[NbCp^*Cl_2(OH)]_2(\mu\text{-}O)$ (**4**), which is also formed from **3** by exposure to air. When the dinuclear complex **4** is heated, it yields the trinuclear niobium oxide cluster $Nb_3Cp^*_3(\mu_2\text{-}O)_3(\mu_3\text{-}O)(\mu_2\text{-}Cl)Cl_3$ (**5**). The crystal structure of **5** is reported. The compound crystallizes in the monoclinic space group $P2_1/n$, with $Z = 4$, a = 11.357 (6) Å, b = 19.685 (10) Å, and c = 15.797 (6) Å. Anisotropic refinement of all atoms except hydrogen atoms converged to the residuals R = 0.069 and R_w = 0.030 for 2722 reflections.

The stabilizing[1] effects of the bulky and strong electron donor pentamethylcyclopentadienyl ligand permit us extend the already well-developed chemistry of related early transition metals, whose high oxophilicity[2] gives rise to the reactivity of their derivatives with water and other oxygen sources such as N_2O and CO_2[3] or CO[4] to give complexes containing oxo bridges between two or more metal centers.[5] The hydrolysis of $TaCp^*Cl_4$[6] has been reported to lead to the formation of a mononuclear hydroxo complex and di- and trinuclear (μ-oxo)tantalum derivatives. Here we report a similar hydrolytic behavior for $NbCp^*Cl_4$.

Mono(pentamethylcyclopentadienyl)niobium and -tantalum complexes were first prepared by the reaction of MCl_5 (M = Nb, Ta) with $SnBu^n_3(C_5Me_5)$,[7] the niobium derivative being described as an oily residue. The yields have been optimized by using $SiMe_3(C_5Me_5)$,[8] which is a

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