Tetrahedral Lewis Base Adducts of an Acyl. Preparation and X-ray Structure of the Pyridine Adduct $(\eta^5 - C_5 Me_5) Cl_3 Ta[\eta^2 - OC(SiMe_3)(NC_5 H_5)]$

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Numerous reactions of the carbonyl group involve nucleophilic attack at the carbon center, as in acyl substitutions (eq 1).¹

$$\begin{array}{c} R \\ x \\ \end{array} c = 0 + : Y^{-} \rightleftharpoons \begin{bmatrix} R \\ x \\ \end{array} c \begin{pmatrix} 0^{-} \\ y \\ \end{bmatrix} \rightleftharpoons \begin{array}{c} R \\ y \\ \end{array} c = 0 + : X^{-} \quad (1)$$

Because of the importance of these reactions, attention has focused on the tetrahedral addition intermediate, which has proven difficult to detect.^{1,2} Tetrahedral amine adducts are thought to take part in nucleophilic acyl substitution reactions, such as the pyridinecatalyzed hydrolysis of anhydrides.^{1,3} Here we report the formation and crystal structure of a stable tetrahedral pyridine adduct (2)

 η^2 -Acyl complexes of electropositive d- and f-block metals exhibit electrophilic reactivity⁴ which has been attributed to oxycarbene^{4q} or carbenium ion^{4r} character at the acyl carbon atom. Although η^2 -acyls are known to undergo nucleophilic attack,⁴ their reactivity toward simple Lewis donors is not well documented.5 Some η^2 -acyls couple with carbon monoxide by an unknown process to give ketene derivatives (A).^{4h,6} Structural evidence

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Figure 1. Molecular structure and labeling scheme for $(\eta^5-C_5Me_5)$ - $Cl_3Ta[\eta^2 - OC(SiMe_3)(NC_5H_5)]$, 40% thermal ellipsoids. Ta-C₅ centroid (CNT), 2.171 (5); Ta-Cl(1), 2.439 (2); Ta-Cl(2), 2.447 (1); Ta-Cl(3), $(2)^{\circ}$; $(2)^{\circ}$; Ta-O, 107.5 (2)°; CNT-Ta-C(19), 146.5 (2)°; Cl(1)-Ta-Cl(2), 153.4 (0)°; Cl(1)-Ta-Cl(3), 80.4 (1)°; Cl(2)-Ta-Cl(3), 79.8 (1)°; Cl(1)-Ta-O, 93.0 (1)°; Cl(2)-Ta-O, 90.5 (1)°; Cl(3)-Ta-O, 139.4 (1)°; Cl- $\begin{array}{l} 12-0, 95.0 \ (1)^{\circ}, Cl(2)-12-0, 90.5 \ (1)^{\circ}, Cl(3)-12-0, 139.4 \ (1)^{\circ}, Cl(3)-0, 139.4 \ (1)^{\circ}, Cl($

for these ketene intermediates has recently been obtained with the characterization of an analogous ketenimine complex (B, Cp* = η^5 -C₅Me₅).^{4h} We recently described a tantalum silaacyl



complex, $Cp^*Cl_3Ta(\eta^2 - COSiMe_3)$ (1), that exhibited electrophilic behavior in its reactions with carbon monoxide.⁶ Isolation and characterization of the pyridine adduct of 1 (vide infra) provides evidence for the formation of tetrahedral intermediates in the reactions of η^2 -acyl complexes with Lewis donors and establishes a structural type to be considered as an intermediate in "acylcoupling" processes.

Addition of pyridine to a pentane solution of 1^7 resulted in formation of an orange-yellow complex, 2. The ¹H NMR spectrum and elemental analysis were consistent with a 1:1 adduct of 1 and pyridine.⁸ Reaction of Cp*Cl₃Ta(η^{2-13} COSiMe₃) (1-¹³C) with pyridine proceeded to $2^{-13}C$ with replacement of the silaacyl ¹³C NMR shift (351 ppm) by a peak at 117 ppm. The infrared C-O stretching frequency, assigned as 1039 cm⁻¹ for 2 and 1022 cm^{-1} for 2-¹³C, indicates considerable reduction of the C-O bond. For comparison, the analogous stretches reported for the acetone complex Cp*Me₂Ta(η^2 -OCMe₂) are at 1200 and 1180 cm⁻¹, respectively.4j

The crystal structure⁹ (Figure 1) shows that 2 is Cp*Cl₃Ta- $[\eta^2 - OC(SiMe_3)(NC_5H_5)]$, a product of pyridine attack at the

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carbonyl carbon of 1. This complexation results in reduction of the C-O bond order, as seen from comparison of the C(19)-O distance, 1.416 (6) Å, with the C-O distance in the silaacyl $Cp_2Zr(\eta^2-COSiMe_3)Cl, 1.244$ (3) Å.¹⁰ Distances and angles about C(19) are typical for saturated carbon.¹¹ The Ta-C(19) distance of 2.214 (5) Å is similar to Ta-C single-bond distances in Cp*Ta(CHPh)(CH₂Ph)₂ (av 2.21 Å),^{12a} Cp*Cl₂Ta(C₄H₈) (2.22 Å),^{12b} and Cp*Cl₂Ta(C₇H₁₂) (av 2.20 Å).^{12b} Although the η^2 -OC(SiMe₃)(NC₅H₅) ligand resembles an η^2 -ketone, the spectroscopic data and the bond lengths and angles indicate that it derives no significant contribution from a coordinated O=C< resonance hybrid (cf. C-O distances in Cp₂V(η^2 -CH₂O), 1.35 Å^{13a} and $Cp_2Mo(\eta^2-CH_2O)$, 1.36 Å^{13b}). The structural characterization of organic compounds containing long intramolecular N- $(amine)\cdots C(carbonyl)$ interactions¹⁴ has allowed construction of a reaction coordinate for nucleophilic addition to a carbonyl group.^{14a,b} In the formation of 2, amine addition to 1 is complete, as evidenced by the N-C(19) distance, 1.493 (6) Å, which is in the region expected for an N⁺-C single bond.^{14c,15}

Rotation about the C(19)-N bond in 2 is slow on the NMR time scale; the five pyridine ring protons remain inequivalent from -75 to 90 °C, where the compound begins to decompose rapidly. Facile pyridine- d_5 exchange with 2 yields free NC₅H₅ and $Cp^*Cl_3Ta[\eta^2-OC(SiMe_3)(NC_5D_5)]$ (by ¹H NMR). Pseudofirst-order kinetic studies with 15-45 equiv of pyridine- d_5 showed the exchange rate to be independent of [pyridine- d_5]. The first-order rate law ($k_1 = (6.6 \pm 0.8) \times 10^{-4} \text{ s}^{-1}$; toluene- d_8 , -15 °C) is consistent with a simple dissociative process (eq 2) and rules out S_N2 displacement.



To investigate the role of tetrahedral intermediates in η^2 -acyl chemistry, we are examining further aspects of the reactivity of 1 toward nucleophiles. No adduct formation could be detected by ¹H or ¹³C NMR upon addition of excess ether (diethyl ether, tetrahydrofuran) to toluene- d_8 solutions of $1^{-13}C$ (-60 to +20 °C). Addition of PR_3 (R = Me, Et, OMe) to 1 or 2, however, gives rise to new compounds of the general formula $Cp^*Cl_3Ta[\eta^2 OC(SiMe_3)(PR_3)$ with structures analogous to 2^{16} (eq 3).



It is remarkable that in the formation of these novel adducts, the carbonyl carbon of 1, rather than the (formally) 16-electron metal center, acts as the more electrophilic site. Hoffmann and co-workers have recently suggested that the electrophilic character of some η^2 -acyl ligands derives from stabilization of the π^*_{CO} level by interaction with an unoccupied metal d-orbital.^{4r} The observed reactivity of 1 might likewise be due to lowering of the π^*_{CO} level, not only by a tantalum d-orbital but additionally by overlap with an acceptor orbital on silicon. We are investigating analogous acyl complexes to elucidate the role of the silyl group in these transformations.¹⁷

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Supplementary Material Available: A listing of bond lengths, bond angles, positional and thermal parameters, and observed and calculated structure factors for 2 (24 pages). Ordering information is given on any current masthead page.

(16) The X-ray structure of the PEt₃ derivative has recently been determined. (17) Arnold, J., work in progress.

Lithium Hydride Addition to Ynolate Anions: The **Mechanism of Reductive Ester Homologation**

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Recently we described a procedure for the reductive homologation of esters,² in which strongly basic solutions of lithium ynolate³ anions 3, upon heating with excess 1,3-cyclohexadiene (1), afforded aldehyde enolate anions 6. Herein we report that LiH (formed in situ) is the actual reducing agent involved, undergoing an unprecedented addition to the ynolate anion triple bond to generate an intermediate α -aldehydo dianion 4 as shown in Scheme I.

Initially it seemed most likely to us that cyclohexadienyl anion (2) (from 1 and lithium tetramethylpiperidide present in the ynolate solution²), was undergoing direct hydride transfer⁵ to the ynolate anions 3 (i.e., $2 + 3 \rightarrow PhH + 4$ or 5). Since decomposition of simple cyclohexadienyl anions to benzene and metal hydrides was known,⁶ however, we examined the remote possibility

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⁽⁹⁾ $C_{19}H_{29}Cl_3NOSiTa:$ monoclinic, $P2_1/n$, a = 10.322 (2) Å, b = 14.503(3) Å, c = 16.289 (3) Å, $\beta = 101.73$ (1)°, V = 2392.2 (7) Å³, Z = 4, D(calcd) = 1.67 g cm⁻³, $\mu = 52.5$ cm⁻¹, Mo K_a ($\lambda = 0.71073$ Å), 23 °C, Nicolet R3 diffractometer, graphite monochromator, orange crystal ($0.23 \times 0.23 \times 0.23$ mm) sealed in glass capillary. Of 4064 reflections collected ($4^{\circ} \le 2\theta \le 48^{\circ}$), 3739 were unique ($R_{int} = 1.8\%$), and 3029 with $F_0 \ge 5\sigma(F_0)$ were considered observed. Corrections for a 5% linear decay and for absorption (empirical, max/min transmission = 0.295/0.230) were anplied to the intensity data max/min transmission = 0.295/0.230) were applied to the intensity data. Heavy atom solution, blocked cascade refinement, non-hydrogen atoms anisotropic, hydrogen atoms isotropic (pyridine hydrogen atoms found and refined, the rest fixed and idealized). $R_F = 2.62\%$, $R_{wF} = 2.72\%$, data/param-The first index and reduced by $R_F = 2.02.6$, $R_W = 2.12.6$, and parameter entry of the set of t

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