Tetrahedral Lewis Base Adducts of an Acyl. Preparation and X-ray Structure of the Pyridine Adduct $(\eta^5\text{-}C_5Me_5)Cl_3Ta[\eta^2\text{-}OC(SiMe_3)(NC_5H_5)]$

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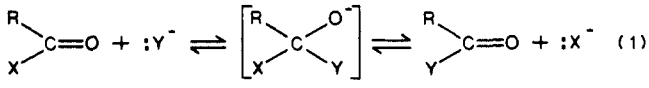
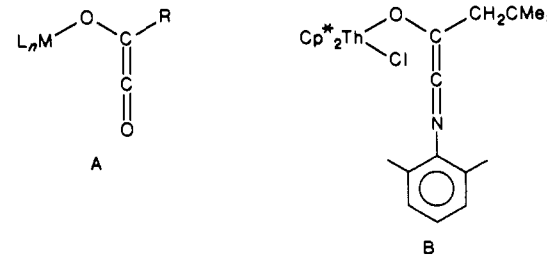
Numerous reactions of the carbonyl group involve nucleophilic attack at the carbon center, as in acyl substitutions (eq 1).[1]



(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 pyridine-catalyzed 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 reactivity[4] 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,[4i] 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 for these ketene intermediates has recently been obtained with the characterization of an analogous ketenimine complex (B, Cp* = η^5-C_5Me_5).[4h] We recently described a tantalum silaacyl



A B

complex, $Cp^*Cl_3Ta(\eta^2\text{-}COSiMe_3)$ (**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 "acyl-coupling" processes.

Addition of pyridine to a pentane solution of **1**[7] resulted in formation of an orange-yellow complex, **2**. The ^{1}H NMR spectrum and elemental analysis were consistent with a 1:1 adduct of **1** and pyridine.[8] Reaction of $Cp^*Cl_3Ta(\eta^2\text{-}^{13}COSiMe_3)$ (**1**-^{13}C) with pyridine proceeded to **2**-^{13}C with replacement of the silaacyl ^{13}C 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**-^{13}C, indicates considerable reduction of the C–O bond. For comparison, the analogous stretches reported for the acetone complex $Cp^*Me_2Ta(\eta^2\text{-}OCMe_2)$ are at 1200 and 1180 cm^{-1}, respectively.[4j]

The crystal structure[9] (Figure 1) shows that **2** is $Cp^*Cl_3Ta[\eta^2\text{-}OC(SiMe_3)(NC_5H_5)]$, a product of pyridine attack at the

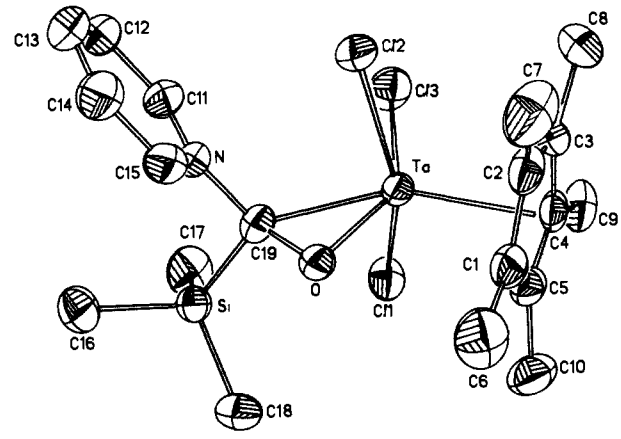


Figure 1. Molecular structure and labeling scheme for $(\eta^5\text{-}C_5Me_5)Cl_3Ta[\eta^2\text{-}OC(SiMe_3)(NC_5H_5)]$, 40% thermal ellipsoids. Ta–C_5 centroid (CNT), 2.171 (5); Ta–Cl(1), 2.439 (2); Ta–Cl(2), 2.447 (1); Ta–Cl(3), 2.469 (2); Ta–O, 1.945 (3); Ta–C(19), 2.214 (5); O–C(19), 1.416 (6); N–C(19), 1.493 (6); Si–C(19) = 1.925 (6) Å. CNT–Ta–Cl(1), 102.3 (2)°; CNT–Ta–Cl(2), 101.8 (2)°; CNT–Ta–Cl(3), 113.0 (2)°; CNT–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(1)–Ta–C(19), 81.2 (1)°; Cl(2)–Ta–C(19), 85.0 (1)°; Cl(3)–Ta–C(19), 100.4 (1)°; O–Ta–C(19), 39.1 (2)°; Ta–O–C(19), 80.7 (3)°; Ta–C(19)–O, 60.1 (2)°; Ta–C(19)–N, 117.2 (4)°; O–C(19)–N, 110.7 (4)°; O–C(19)–Si, 114.5 (3)°; N–C(19)–Si, 109.1 (3)°.

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(7) (a) Bubbling CO through a green pentane solution of $Cp^*Cl_3TaSiMe_3$[7b] produces an orange solution that upon cooling precipitates reasonably pure **1** as an orange powder. In the solid state **1** is stable for at least 1 day at −45 °C but decomposes within an hour at room temperature. (b) Arnold, J.; Shina, D.; Tilley, T. D.; Arif, A. M. *Organometallics*, in press.

(8) For **2**: yield 92%. Anal. C, H, Cl. ^{1}H NMR (benzene-d_6, 20 °C, 300 MHz) δ 0.16 (s, 9 H, $SiMe_3$), 2.24 (s, 15 H, C_5Me_5), 6.29 (t, 1 H, py), 6.41 (t, 1 H, py), 6.53 (t, 1 H, py), 7.63 (d, 1 H, py), 8.41 (d, 1 H, py).

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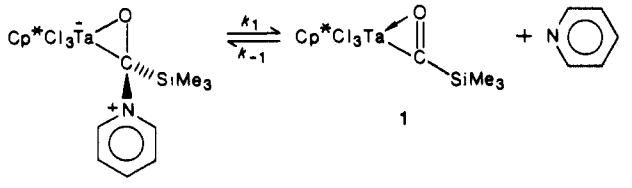
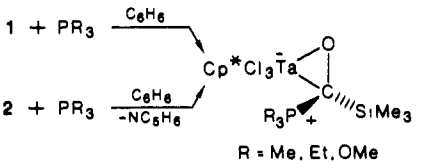
carbonyl carbon of **1**. This complexation results in reduction of the C–O bond order, as seen from comparison of the C(19)–O distance, 1.416 (6) Å, with the C–O distance in the silaacyl $Cp_2Zr(\eta^2\text{-}COSiMe_3)Cl$, 1.244 (3) Å.[10] Distances and angles about C(19) are typical for saturated carbon.[11] The Ta–C(19) distance of 2.214 (5) Å is similar to Ta–C single-bond distances in $Cp^*Ta(CHPh)(CH_2Ph)_2$ (av 2.21 Å),[12a] $Cp^*Cl_2Ta(C_4H_8)$ (2.22 Å),[12b] and $Cp^*Cl_2Ta(C_7H_{12})$ (av 2.20 Å).[12b] Although the η^2-$OC(SiMe_3)(NC_5H_5)$ 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 $Cp_2V(\eta^2\text{-}CH_2O)$, 1.35 Å[13a] and $Cp_2Mo(\eta^2\text{-}CH_2O)$, 1.36 Å[13b]). The structural characterization of organic compounds containing long intramolecular N(amine)···C(carbonyl) interactions[14] 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 NC_5H_5 and $Cp^*Cl_3Ta[\eta^2\text{-}OC(SiMe_3)(NC_5D_5)]$ (by ^1H NMR). Pseudo-first-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 ($k_1 = (6.6 \pm 0.8) \times 10^{-4}$ s^{-1}; toluene-d_8, −15 °C) is consistent with a simple dissociative process (eq 2) and rules out S_N2 displacement.



2 1 (2)

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 ^{13}C 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 $Cp^*Cl_3Ta[\eta^2\text{-}OC(SiMe_3)(PR_3)]$ with structures analogous to **2**[16] (eq 3).



(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.

(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) Å^3, $Z = 4$, D(calcd) = 1.67 g cm^{-3}, $\mu = 52.5$ cm^{-1}, Mo K_α ($\lambda = 0.71073$ Å), 23 °C, Nicolet R3 diffractometer, graphite monochromator, orange crystal (0.23 × 0.23 × 0.23 mm) sealed in glass capillary. Of 4064 reflections collected ($4° \le 2\theta \le 48°$), 3739 were unique ($R_{int} = 1.8\%$), and 3029 with $F_o \ge 5\sigma(F_o)$ were considered observed. Corrections for a 5% linear decay and for absorption (empirical, 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/parameter = 11.9, GOF = 1.297, last cycle $\Delta/\sigma = 0.06$, highest peak = 0.54 e Å^{-3} (1.25 Å from Ta).

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(11) The C–O bond lengths in dimethyl ether and ethanol are 1.41 Å. The C–N bond in methylamine is 1.47 Å. March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1985; p 19.

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(16) The X-ray structure of the PEt_3 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 ynolate[3] 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 solution[2]), was undergoing direct hydride transfer[5] to the ynolate anions **3** (i.e., **2** + **3** → PhH + **4** or **5**). Since decomposition of simple cyclohexadienyl anions to benzene and metal hydrides was known,[6] however, we examined the remote possibility

(1) Smith, Kline & French Postdoctoral Scientist.

(2) Kowalski, C. J.; Haque, M. S. *J. Am. Chem. Soc.* **1986**, *108*, 1325. As a consequence of the method used to prepare ynolate anion solutions for these reductions, they also contained lithium tetramethylpiperidide and tetramethylpiperidine.

(3) Although we have previously used Schollkopf's term "alkynolate"[4] to describe this species, "ynolate" seems more consistent with the well established terminology used for the related "enolate" and "ynamine" species.

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