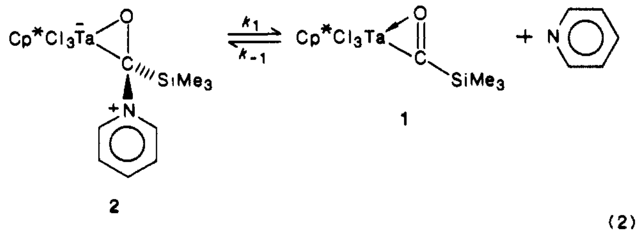
J. Am. Chem. Soc. 1986, 108, 5356-5357

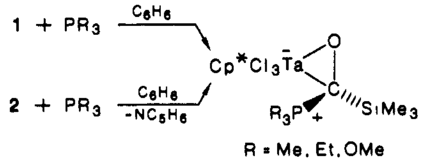
carbonyl carbon of **1**. This complexation results in reduction of the C–O bond order, as seen from comparison of the C(19)–O distance, 1.416 (6) Å, with the C–O distance in the silaacyl $Cp_2Zr(\eta^2\text{-}COSiMe_3)Cl$, 1.244 (3) Å.[10] Distances and angles about C(19) are typical for saturated carbon.[11] 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)

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.

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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) $Å^3$, $Z = 4$, 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 ($4° \leq 2\theta \leq 48°$), 3739 were unique ($R_{int} = 1.8\%$), and 3029 with $F_o \geq 5\sigma(F_o)$ 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).

[10] Tilley, T. D. *J. Am. Chem. Soc.* **1985**, *107*, 4084.

[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.

[12] (a) Messerle, L. W.; Jennische, P.; Schrock, R. R.; Stucky, G. *J. Am. Chem. Soc.* **1980**, *102*, 6744. (b) Churchill, M. R.; Youngs, W. J. *Ibid.* **1979**, *101*, 6462.

[13] (a) Bambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1982**, *104*, 2019. (b) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1985**, *107*, 2985.

[14] (a) Bürgi, H. B.; Dunitz, J. D.; Shefter, E. *J. Am. Chem. Soc.* **1973**, *95*, 5065. (b) Dunitz, J. D. *X-ray Analysis and the Structure of Organic Molecules*; Cornell University Press: Ithaca, 1979; p 366. (c) Birnbaum, G. I. *J. Am. Chem. Soc.* **1974**, *96*, 6165.

[15] (a) Raston, C. L.; Rowbottom, G. L.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1981**, 1389. (b) Tominaga, Y.; Kobayashi, G.; Tamura, C.; Sato, S.; Hata, T. *Acta Crystallogr., Sect. B* **1979**, *35*, 2443.

[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

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[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.

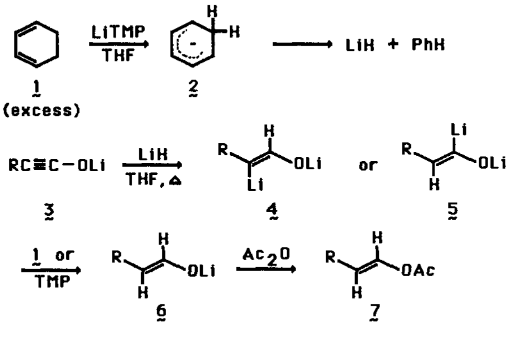
[3] Although we have previously used Schollkopf's term "alkynolate"[4] to describe this species, "ynolate" seems more consistent with the well established terminology used for the related "enolate" and "ynamine" species.

[4] Hoppe, I.; Schollkopf, U. *Liebigs Ann. Chem.* **1979**, 219.

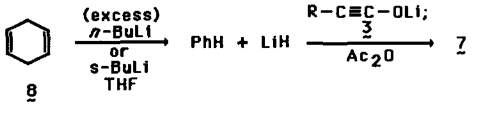
[5] (a) Hofmann, J. E.; Argabright, P. A.; Schriesheim, A. *Tetrahedron Lett.* **1964**, 1005. (b) Wideman, L. G., *J. Org. Chem.* **1970**, *35*, 1698. (c) Atkins, P. J.; Gold, V.; Wassef, W. N. *J. Chem. Soc., Perkin Trans. 2* **1983**, 1197. (d) Rabideau, P. W.; Huser, D. L. *J. Org. Chem.* **1983**, *48*, 4266.

0002-7863/86/1508-5356$01.50/0

Scheme I



that relatively unreactive LiH[7] might be the active reducing species in these reactions. Treating a THF solution of 1,4-cyclohexadiene (**8**) with excess *sec*- or *n*-butyllithium at low temperature under nitrogen produced LiH as a suspended white solid after warming to room temperature (eq 1).[8] NMR analysis of the liquid phase

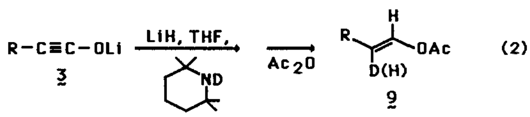


(1)

showed a singlet for benzene but no peak for starting diene or the cyclohexadienyl anion **2**. The solid LiH (always under nitrogen) could be rinsed free of the original liquid phase (using dry THF) without affecting its subsequent reactivity.

When such cyclohexadiene-free LiH was heated at reflux with a solution of ynolate anion **3** (R = CH_2CH_2Ph), reduction to the enolate anion **6** occurred exactly as in the reductive homologation procedure employing excess 1,3-cyclohexadiene.[2] An acetic anhydride quench afforded the same *E*-enol acetate product (**7**, R = CH_2CH_2Ph) in 65% yield. LiH itself, therefore, had indeed reduced the ynolate anion. Excess lithium tetramethylpiperidide and 1,3-cyclohexadiene, in THF at room temperature, also afforded diene-free LiH which effected this same reduction. Since precipitates were similarly observed under the diene-rich conditions originally used in the reductive homologation procedure,[2] it appears likely that LiH was the reducing agent in those cases as well. On exposure to air, a suspension of LiH (prepared as in eq 1) lost this ability to reduce ynolate anions. An interfering surface oxidation of the LiH is suggested, which explains the fact that commercial LiH would not reduce ynolate anion **3** (R = CH_2CH_2Ph). Ashby has similarly observed reactions for which commercial LiH was ineffective but which did occur using LiH generated in situ by hydrogenation of *tert*-butyllithium.[9]

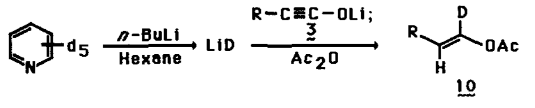
In order to determine the regiochemistry of hydride addition, attempts were made under the diene-free conditions of eq 1 to trap intermediate **4** or **5** with chlorotrimethylsilane;[10] only the silyl enol ether corresponding to **7** (R = CH_2CH_2Ph) was obtained, however. Protonation of the dianion intermediate had occurred but not by the THF solvent (as shown by a later experiment in THF-d_8). Tetramethylpiperidine was then investigated as a possible proton source remaining from the ynolate anion formation.[2] Lithium tetramethylpiperidide was treated with an equivalent of methanol-*d*, and the resulting solution of N-deuterated piperidine was added (in 5-fold excess) to a solution of ynolate anion **3**. This mixture was then heated at reflux with LiH (from 1,4-cyclohexadiene and *n*-butyllithium) and quenched after cooling with acetic anhydride (eq 2). Obtained was the enol-



(2)

acetate **9** (R = CH_2CH_2Ph), the 2-position of which had about 50% incorporation of deuterium.[11] This strongly suggests that the intermediate in these ynolate anion reductions is the dianion **4**, which can effectively be C-protonated by tetramethylpiperidine in the reaction medium.

As a more direct probe, LiD was prepared by modification of a 2,6-dibutylpyridine synthesis;[12] thus pyridine-d_5 was heated with 3 equiv of *n*-butyllithium in hexane to afford a reddish suspension of LiD (eq 3). A solution of ynolate anion **3** in THF was added,



(3)

and after another hour at reflux the mixture was cooled and quenched with acetic anhydride. The product enol acetate **10** was completely deuterated at the 1-position,[13] again supporting the intermediacy of dianion **4** in these reductions. In addition, the *Z* isomer of enolate anion **6** (R = Ph), generated from the enol acetate,[14] was shown not to isomerize during reduction of the corresponding ynolate **3** (R = Ph). (*Z*)-Enolate cannot be an intermediate in the reduction, therefore, since ynolate **3** (and in fact all but one of the ynolates studied thus far[2]) affords exclusively the (*E*)-enol acetate product **7**. Direct formation of (*E*)-enolate, assuming that C-protonation of dianion **4** occurs with retention of configuration, requires the overall geometry (if not exact structure of dianion **4** to be as shown in Scheme I.

Recent calculations by Houk and Schleyer indicate that LiH should add to acetylene, and yet the authors note that "LiH does not add to unsaturated hydrocarbons under normal conditions...".[15] When 4-octyne was added to a solution of ynolate anion **3** (R = CH_2CH_2Ph) and the mixture was submitted to the LiH reduction conditions, the ynolate anion reduced completely but no reduction of 4-octyne was observed. This suggests that it is the unique nature of the ynolate anion, and not simply the reactive form of LiH present, which accounts for the remarkable addition of LiH to these "acetylenic" intermediates.[16] Ester derived ynolate anions have now played a key role in our normal[17] as well as reductive[2] homologation procedures, and studies investigating other uses of these readily available intermediates are currently under way.

Acknowledgment. We thank our colleague, Dr. Ivan Lantos, who prompted us to seriously consider the LiH possibility and thus initiate these studies in a fruitful manner.

Note Added in Proof. Another preparation of active LiH has recently been reported by Klusener et al.[18]

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(6) (a) Paul, R.; Tchelitcheff, S. *C. R. Hebd. Seances Acad. Sci.* **1954**, *239*, 1222. (b) Bates, R. B.; Gosselink, D. W.; Kaczynski, J. A., *Tetrahedron Lett.* **1967**, 199. (c) Kloosterziel, H.; Van Drunen, J. A. A. *Recl. Trav. Chim. Pays-Bas* **1970**, *89*, 368. (d) Olah, G. A.; Asensio, G.; Mayr, H.; Schleyer, P. *J. Am. Chem. Soc.* **1978**, *100*, 4347. Also see ref 5d.

(7) Brown, C. A. *J. Org. Chem.* **1974**, *39*, 3913.

(8) Careful treatment of this suspension with 2-propanol (at −78 °C) afforded about 0.9 the volume of gas expected based on quantitative conversion of 1,4-cyclohexadiene to LiH.

(9) Ashby, E. C.; Noding, S. A. *J. Org. Chem.* **1980**, *45*, 1041.

(10) Silylation of α-keto dianions analogous to **4** proceeds smoothly; see: Kowalski, C. J.; O'Dowd, M. L.; Burke, M. C.; Fields, K. W. *J. Am. Chem. Soc.* **1980**, *102*, 5411.

(11) The NMR spectrum indicated a 53:47 mixture of **9**-"D" and **9**-"H" (R = CH_2CH_2Ph), as evidenced by a reduction in the intensity of the signals of **9**-"H" at both C-2 [δ 5.44 (dt, *J* = 12.5, 7 Hz, 0.47 H)] and C-1 [δ 7.10 (d, *J* = 12.5 Hz, 0.47 H)] and the presence of a new signal at δ 7.06 (s, 0.53 H) for the C-1 hydrogen of **9**-"D".

(12) Francis, R. F.; Wisener, J. T.; Paul, J. M. *J. Chem. Soc. D* **1971**, 1420.

(13) Important differences in the NMR spectrum of **10** vs. **7** (R = CH_2CH_2Ph) include complete absence in **10** of the δ 7.10 doublet (*J* = 12.5 Hz, 1 H) of the C-1 hydrogen in **7** and collapse of the C-2 signal of **7** at δ 5.44 (dt, *J* = 12.5, 7 Hz, 1 H) into a multiplet at 5.25–5.65 (1 H) in **10**.

(14) Jablonski, R. J.; Snyder, E. I. *J. Am. Chem. Soc.* **1969**, *91*, 4445.

(15) Houk, K. N.; Rondan, N. G.; Schleyer, P. R.; Kaufmann, E.; Clark, T. *J. Am. Chem. Soc.* **1985**, *107*, 2821.

(16) Both diisobutylaluminum hydride and lithium aluminum hydride (suggested by a referee) seem to effect reduction of ynolate anion **3** (R = CH_2CH_2Ph). Quenching to afford either aldehyde or enol acetate products, however, produced complex mixtures which contained only small amounts of the desired products. With additional work, such soluble reducing agents may still prove useful in ynolate reductions.

(17) Kowalski, C. J.; Haque, M. S.; Fields, K. W. *J. Am. Chem. Soc.* **1985**, *107*, 1429.

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