3426 *Organometallics* **2002,** *21,* 3426−3433

Reactions of a Triazacyclononane-Supported Tantalum−Lithium Bridging Alkylidene with Organic Substrates

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Received February 28, 2002

The reactivity of a range of electrophilic organic substrates with a heterobimetallic tantalum−lithium bridging alkylidene [$(Me_3SiCH_2)(ArN{=})Ta(\mu\text{-}CHSiMe_3)(\mu\text{-}\eta_1{:}\eta_3\text{-}{}^iPr_2\text{-tacn})Li$, **3**] is presented. Proton sources of widely varying acidity react to protonate the alkylidene ligand, leading to an interesting tantalum−lithium bridging hydride complex in the case of H_2. The alkylidene **3** undergoes a series of insertion reactions with unsaturated substrates, such as acetonitrile, carbon monoxide, and carbon disulfide; it also reacts with an acid chloride to yield a tantalum enolate species featuring return of the ${}^iPr_2\text{-tacn}^-$ ligand to a tridentate coordination mode. The incorporated lithium in **3** played an important role, at least structurally, in the chemistry observed.

Introduction

The use of 1,4,7-triazacyclononane (tacn) as a ligand in coordination chemistry has been well explored over the past few decades, with numerous reports appearing recently.[1−15] Two main features make this nine-membered macrocycle a useful ligand. First, its three nitrogen atoms provide for tridentate, facial coordination to a metal center. Second, the choice of substituents on each nitrogen atom allows for tuning of the steric bulk and electronic properties of these ligands. Despite the preponderance of complexes displaying the former feature, there are examples of species where tacn ligands exhibit fluxionality in solution due to partial dissociation of the ligand. In this way, tacn can transiently function as a bidentate or a monodentate ligand by dissociation of one or two nitrogen atoms, respectively (Figure 1). In fact, in rare cases, complexes of this type have been isolated and characterized crystallographically, showing the existence of monodentate[12] and bidentate[16−24] tacn coordination in the solid state. In general, it appears that the coordination mode of tacn is strongly influenced by the electronic environment of the metal center. The possibility that tacn may function as a hemilabile ligand[25] in catalytic reactivity is, therefore, a further inducement to its study.

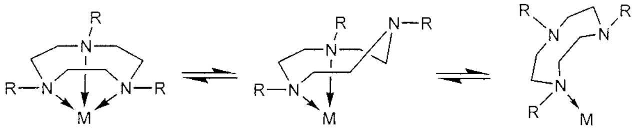

Figure 1. Fluxionality in tacn compounds caused by release and recoordination of nitrogen atoms of the tacn.

Transition metal alkylidenes ($L_nM{=}CR_2$) are useful reagents in an ever-widening range of stoichiometric and catalytic transformations.[26−28] Nucleophilic (Schrock)

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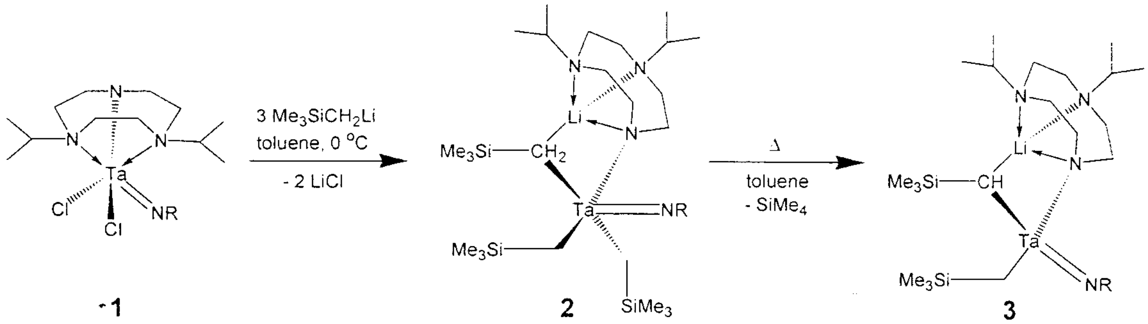
10.1021/om020175c CCC: $22.00
Publication on Web 07/02/2002

Scheme 1



alkylidenes are well studied, and these compounds react with a wide variety of electrophilic sources, ranging from reactive acid chlorides to relatively inert acetylenes.[29−31] Some useful catalytic applications of alkylidenes include ring-opening metathetical polymerization (ROMP), acetylene polymerization, and olefin metathesis. These catalytic reactions, along with an array of useful stoichiometric reactions, allow alkylidene complexes to be employed to great effect in organic synthesis.

A number of monometallic tantalum alkylidenes have been synthesized, and their reactivity has been explored in detail.[32−51] Recently, we reported the synthesis of a tantalum−lithium bridging alkylidene supported by an anionic triazacyclononane ligand (**3**, Scheme 1).[52] In our initial studies of its reactivity, we found that insertion of CO yielded a tantalum−lithium ketene, while double-bond metathesis led to the generation of a tantalum−lithium oxo complex.[53] Additionally, through salt metathesis routes, the lithium ion in **3** could be replaced by other transition metals, such as rhodium and iron.[53] Here we describe the reactivity of **3** with a wide range of organic substrates. To understand the reactivity of this heterobimetallic tantalum−lithium alkylidene species, stoichiometric reactions with a number of electrophilic organic substrates were investigated as a means of gauging the interaction between the two metal centers in this complex. The results are presented in comparison to similar reactions with monometallic tantalum alkylidenes.

Experimental Section

General Considerations. Standard Schlenk-line and glovebox techniques were used throughout. Pentane, diethyl ether, and toluene were passed through a column of activated alumina and degassed with argon. Octane was distilled from sodium/benzophenone ketyl under nitrogen. Acetonitrile was refluxed over sodium and distilled under nitrogen. Pyridinium chloride, 2,4,6-trimethylphenol, *p*-toluoyl chloride, and carbon disulfide were purchased from Aldrich and used as received. Hydrogen (99.99%) and carbon monoxide (99.50%) were purchased from Airgas and Matheson, respectively, and used as received. The bridging alkyl **2** and alkylidene **3** were synthesized as detailed previously.[52] C_6D_6 and C_7D_8 were vacuum transferred from sodium/benzophenone. Melting points were determined in sealed capillary tubes under nitrogen and are uncorrected. ^{1}H, ^{7}Li, and ^{13}C{^{1}H} NMR spectra were recorded in C_6D_6 at ambient temperature on a Bruker DRX-500 spectrometer, unless otherwise specified. ^{1}H NMR chemical shifts are given relative to C_6D_5H (δ 7.16) and $C_6D_5CD_2H$ (δ 2.09). ^{7}Li NMR spectra are relative to an external LiCl (3 M in D_2O) standard (0.00 ppm). ^{13}C NMR chemical shifts are relative to C_6D_6 (δ 128.39) and C_7D_8 (δ 20.4). IR samples were prepared as Nujol mulls and taken between KBr plates. Elemental analyses were determined by the Microanalytical Laboratory of the College of Chemistry, University of California, Berkeley. Single-crystal X-ray structure determinations were performed at CHEXRAY, University of California, Berkeley.

(Me_3SiCH_2)$_2$(ArN=)Ta(μ-2,4,6-$Me_3C_6H_2O$)(μ-η_1:η_3-^{i}Pr$_2$-tacn)Li (4). A solution of 2,4,6-trimethylphenol (55 mg, 0.40 mmol) in toluene (20 mL) was added to a solution of **3** (300 mg, 0.400 mmol) in toluene (30 mL), and the mixture was stirred for 1 h at ambient temperature. After the removal of solvent under vacuum, pentane was added (30 mL) and the solvent was again removed in vacuo, eliminating residual

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toluene. The solid was then extracted into diethyl ether (20 mL) and filtered, and the solvent was removed under vacuum to give a pale yellow solid (276 mg, 78%): mp 155−157 °C; ^{1}H NMR δ 7.258 (d, 2H, 8 Hz), 6.980 (t, 1H, 8 Hz), 6.840 (s, 2H), 4.486 (sept, 2H, 7 Hz), 4.03 (mult, 2H), 2.93 (mult, 2H), 2.780 (sept, 2H, 7 Hz), 2.496 (s, 6H), 2.43 (mult, 2H), 2.192 (s, 3H), 2.14 (mult, 4H), 1.85 (mult, 2H), 1.501 (d, 12H, 7 Hz), 0.519 (d, 2H, 13 Hz), 0.471 (d, 6H, 7 Hz), 0.450 (d, 6H, 7 Hz), 0.375 (s, 18H), 0.175 (d, 2H, 13 Hz); ^{7}Li NMR δ 1.775; ^{13}C NMR δ 158.7, 153.2, 144.4, 129.7, 128.5, 125.9, 122.9, 122.4, 56.8, 54.1, 51.6, 44.5, 27.6, 25.5, 22.5, 21.9, 20.6, 18.8, 13.8, 4.5; IR 1587 (w), 1432 (s), 1346 (s), 1309 (m), 1294 (m), 1253 (m), 1240 (s), 1226 (s), 1158 (m), 1147 (w), 1115 (w), 1104 (w), 1081 (w), 1065 (w), 1046 (w), 1020 (w), 989 (w), 958 (m), 935 (m), 876 (w), 848 (s), 813 (s), 753 (m), 727 (m), 672 (w), 605 (w). Anal. Calcd for $C_{41}H_{76}LiN_4OSi_2Ta$: C, 55.64; H, 8.65; N, 6.33. Found: C, 55.10; H, 8.12; N, 6.15.

(Me$_3$SiCH$_2$)$_2$(ArN═)(η_1-^{i}Pr$_2$-tacn)Ta (5). A reaction flask was charged with pyridinium chloride (69 mg, 0.60 mmol) and toluene (60 mL), forming a white suspension. A solution of **2** (500 mg, 0.597 mmol) in toluene (20 mL) was added, and the mixture was stirred for 14 h at ambient temperature. After removal of solvent under vacuum, pentane (50 mL) was added, and after stirring, the volatile materials were again removed in vacuo. The yellow oil was then extracted with pentane (60 mL) and filtered to remove lithium chloride. The clear yellow extract was pumped down to an oil under vacuum (373 mg, 84%): ^{1}H NMR δ 7.239 (d, 2H, 8 Hz), 7.030 (t, 1H, 8 Hz), 4.465 (br, 4H), 4.236 (sept, 2H, 7 Hz), 2.87 (mult, 4H), 2.802 (sept, 2H, 7 Hz), 2.224 (s, 4H), 1.446 (d, 12H, 7 Hz), 0.871 (d, 12H, 7 Hz), 0.768 (d, 2H, 12 Hz), 0.579 (d, 2H, 12 Hz), 0.219 (s, 18H); ^{13}C NMR δ 153.5, 142.5, 122.7, 122.6, 64.8, 58.3, 55.4, 52.2, 28.4, 24.5, 18.3, 3.2; IR 1432 (s), 1351 (s), 1296 (w), 1257 (m), 1245 (m), 1167 (w), 1114 (w), 1094 (w), 1046 (w), 1006 (w), 989 (w), 931 (w), 917 (w), 848 (s), 828 (m), 797 (w), 751 (m), 702 (w), 686 (w). Anal. Calcd for $C_{32}H_{65}N_4Si_2Ta$: C, 51.73; H, 8.82; N, 7.54. Found: C, 51.77; H, 8.85; N, 7.43.

(Me$_3$SiCH$_2$)$_2$(ArN═)Ta(μ-H)(μ-η_1:η_3-^{i}Pr$_2$-tacn)Li (6). A 250 mL reaction flask containing **3** (452 mg, 0.603 mmol) dissolved in toluene (50 mL) was frozen solid in a liquid nitrogen bath. The flask was evacuated for 15 min and then refilled with H_2. The taps were closed, and after warming to room temperature, the flask was heated to 65 °C in an oil bath for 23 h. The flask was cooled to room temperature, and the solvent was removed under vacuum over the course of 14 h. Pentane (30 mL) was added, and the volatile materials were again removed under vacuum. The sticky yellow solid was extracted with pentane and filtered to a new flask, removing a white solid. The yellow solution was pumped down to a foamy yellow solid (281 mg, 62%): mp 123−125 °C; ^{1}H NMR (in toluene-d_8, −28 °C) δ 11.03 (q (1:1:1:1), 1H, $^1J_{\mathrm{LiH}} = 14.7$ Hz), 7.177 (d, 2H, 8 Hz), 6.933 (t, 1H, 8 Hz), 4.202 (sept, 2H, 7 Hz), 3.64 (mult, 1H), 3.11 (mult, 1H), 2.95 (mult, 1H), 2.72 (mult, 1H), 2.688 (sept, 1H, 7 Hz), 2.40 (mult, 1H), 2.023 (sept, 1H, 7 Hz), 1.84 (mult, 2H), 1.66 (mult, 1H), 1.57 (mult, 2H), 1.474 (d, 6H, 7 Hz), 1.446 (d, 6H, 7 Hz), 1.35 (mult, 2H), 0.896 (d, 1H, 12 Hz), 0.840 (d, 3H, 7 Hz), 0.582 (s, 9H), 0.544 (d, 3H, 7 Hz), 0.524 (d, 1H, 12 Hz), 0.517 (s, 9H), 0.505 (d, 1H, 12 Hz), 0.472 (d, 3H, 7 Hz), 0.372 (d, 3H, 7 Hz), 0.232 (d, 1H, 12 Hz); ^{7}Li NMR δ 3.627 (d, $^1J_{\mathrm{LiH}} = 14.7$ Hz); ^{13}C NMR (in toluene-d_8, −28 °C) δ 153.9, 142.9, 122.3, 121.1, 53.5, 53.0, 52.7, 51.7, 51.2, 49.1, 46.1, 45.9, 45.3, 45.1, 27.8, 25.8, 24.0, 19.3, 17.1, 15.1, 4.5, 4.2; IR 1430 (s), 1350 (s), 1294 (m), 1260 (m), 1238 (m), 1164 (w), 1147 (w), 1128 (w), 1113 (m), 1005 (m), 1100 (m), 1089 (m), 1078 (m), 1045 (m), 988 (w), 964 (w), 924 (w), 897 (w), 876 (w), 849 (s), 819 (m), 775 (w), 750 (m), 672 (w), 638 (w), 620 (w). Anal. Calcd for $C_{32}H_{66}LiN_4Si_2Ta$: C, 51.18; H, 8.86; N, 7.46. Found: C, 51.57; H, 8.51; N, 7.16.

(Me$_3$SiCH$_2$)(ArN═)Ta[μ-Me$_3$SiCH═C(Me)N](μ-η_1:η_3-^{i}Pr$_2$-tacn)Li (7). A flask was charged with **3** (350 mg, 0.467 mmol) and toluene (40 mL). Acetonitrile (25 μL) was added via syringe. The system was closed and heated to 90 °C for 36 h. The toluene was removed under vacuum, and pentane was added (40 mL). Again, all volatile materials were removed in vacuo, yielding an orange solid. The solid was extracted with diethyl ether (40 mL), and the solution was filtered to another flask. The removal of solvents under vacuum yielded the desired product (281 mg, 76%): mp 78−79 °C; ^{1}H NMR δ 7.302 (d, 2H, 7.5 Hz), 7.011 (t, 1H, 7.5 Hz), 4.506 (sept, 2H, 7 Hz), 3.93 (mult, 1H), 3.854 (s, 1H), 3.33 (mult, 1H), 2.83 (mult, 2H), 2.564 (sept, 1H, 7 Hz), 2.512 (sept, 1H, 7 Hz), 2.43 (mult, 1H), 2.189 (s, 3H), 1.95 (mult, 3H), 1.82 (mult, 2H), 1.71 (mult, 2H), 1.577 (d, 6H, 7 Hz), 1.509 (d, 6H, 7 Hz), 0.874 (d, 3H, 7 Hz), 0.802 (d, 3H, 7 Hz), 0.739 (d, 3H, 7 Hz), 0.550 (d, 3H, 7 Hz), 0.425 (d, 1H, 11 Hz), 0.385 (s, 9H), 0.301 (s, 9H), 0.284 (d, 1H, 11 Hz); ^{7}Li NMR δ 2.699; ^{13}C NMR δ 173.6, 142.2, 121.7, 120.0, 95.9, 63.1, 56.5, 54.8, 54.4, 51.0, 50.2, 47.5, 45.6, 44.2, 44.1, 27.7, 27.3, 24.4, 23.8, 20.7, 18.8, 17.6, 16.2, 2.9, 0.9; IR 1632 (w), 1585 (w), 1525 (m), 1428 (s), 1354 (s), 1315 (s), 1291 (s), 1255 (m), 1242 (s), 1148 (w), 1124 (w), 1114 (w), 1099 (w), 1082 (w), 1071 (w), 1043 (m), 1021 (w), 977 (w), 964 (w), 950 (w), 918 (w), 894 (w), 880 (w), 848 (s), 832 (s), 750 (m), 712 (m), 681 (w), 632 (w). Anal. Calcd for $C_{34}H_{67}N_5Si_2TaLi$: C, 51.69; H, 8.55; N, 8.87. Found: C, 51.96; H, 8.82; N, 8.54.

(Me$_3$SiCH$_2$)(ArN═)Ta(μ-η_1:η_3-^{i}Pr$_2$-tacn)[η_2-*C,O*:η_1-*O*-C(O)═CHSiMe$_3$] (8). A solution of **3** (410 mg, 0.547 mmol) in toluene (40 mL) was frozen with liquid nitrogen, and dissolved gases were removed by evacuating the flask for 15 min. The flask was refilled with CO (1 atm) and allowed to warm to room temperature. After stirring for 1 h, the volatiles were removed in vacuo to give an orange oil. Addition and subsequent removal of pentane (40 mL) and residual toluene under vacuum yielded a yellow-orange solid. The product was extracted with octane (20 mL), filtered, and concentrated to 6 mL, whereupon crystal growth commenced at room temperature. Cooling to −40 °C maximized crystallization, and the product (pale orange needles) was isolated by filtration and dried under vacuum (180 mg, 42%): mp 127 °C (dec); ^{1}H NMR δ 7.216 (d, 2H, 7.5 Hz), 6.973 (t, 1H, 7.5 Hz), 5.517 (s, 1H), 4.089 (sept, 2H, 7 Hz), 3.98 (mult, 1H), 2.88 (mult, 1H), 2.80 (mult, 1H), 2.70 (mult, 1H), 2.426 (sept, 1H, 7 Hz), 2.41 (mult, 1H), 2.254 (sept, 1H, 7 Hz), 1.91 (mult, 1H), 1.81 (mult, 4H), 1.74 (mult, 2H), 1.481 (d, 6H, 7 Hz), 1.474 (d, 6H, 7 Hz), 0.796 (d, 1H, 12 Hz), 0.795 (d, 3H, 7 Hz), 0.755 (d, 3H, 7 Hz), 0.591 (d, 1H, 12 Hz), 0.583 (d, 3H, 7 Hz), 0.517 (d, 3H, 7 Hz), 0.505 (s, 9H), 0.475 (s, 9H); ^{7}Li NMR δ 1.874; ^{13}C NMR δ 153.5, 143.0, 122.3, 121.2, 93.5, 54.9, 54.5, 54.1, 53.8, 51.2, 49.4, 47.8, 44.6, 44.4, 28.0, 25.1, 24.1, 19.3, 18.7, 18.0, 17.6, 3.8, 1.7; IR: 1577 (m), 1433 (s), 1368 (s), 1355 (s), 1297 (m), 1254 (w), 1237 (m), 1157 (w), 1124 (w), 1106 (w), 1080 (w), 1043 (w), 1023 (w), 990 (w), 961 (m), 952 (m), 925 (m), 906 (w), 877 (w), 848 (s), 831 (s), 800 (w), 772 (w), 756 (m), 732 (w), 716 (w), 692 (m), 681 (w). Anal. Calcd for: $C_{33}H_{64}LiN_4OSi_2Ta$: C, 51.01; H, 8.30; N, 7.21. Found: C, 50.98; H, 8.29; N, 7.22.

(Me$_3$SiCH$_2$)(ArN═)Ta(η_1:η_1-Me$_3$SiCH═CS$_2$)(μ-η_1:η_3-^{i}Pr$_2$-tacn)Li (9). A flask was charged with **3** (500 mg, 0.667 mmol) and toluene (40 mL). CS_2 (40 μL, 51 mg, 0.66 mmol) was added via syringe. The system was sealed and heated to 85 °C for a period of 14 h, resulting in a red solution. After cooling to room temperature, the solution was filtered and pumped down to a red-orange foamy solid. Pentane (10 mL) was added, and the volatile materials were again removed under vacuum. The solid was then washed with cold pentane (5 mL, −40 °C) and dried under vacuum (236 mg, 43%): mp 158 °C (dec); ^{1}H NMR δ 7.253 (t, 2H, 7.5 Hz), 6.967 (d, 1H, 7.5 Hz), 5.754 (s, 1H), 4.414 (sept, 2H, 7 Hz), 4.09 (mult, 1H), 3.98 (mult, 1H), 2.85 (mult, 2H), 2.660 (sept, 1H, 6.5 Hz), 2.506 (sept, 1H, 6.5 Hz), 2.46 (mult, 1H), 1.97 (mult, 3H), 1.81 (mult, 2H), 1.60 (mult, 2H), 1.543 (d, 6H, 7 Hz), 1.482 (d, 6H, 7 Hz), 0.981 (d, 3H, 6.5 Hz), 0.882 (d, 1H, 8 Hz), 0.868 (d, 1H, 8 Hz), 0.691 (d, 3H, 6.5 Hz), 0.684 (d, 3H, 6.5 Hz), 0.612 (d, 3H, 6.5 Hz), 0.457 (s, 9H), 0.406 (s, 9H); ^{7}Li NMR δ 4.224; ^{13}C NMR δ 154.3, 152.7, 144.8, 122.8, 122.5, 63.2, 56.8, 54.8, 53.7, 53.5, 49.6, 48.5, 47.4, 43.8, 28.5, 25.1, 24.8, 22.7, 20.3, 16.4, 16.3, 14.2, 3.5, 0.6; IR 1586 (w), 1519 (s), 1483 (m), 1429 (s), 1388 (m), 1359 (s), 1345 (s), 1293 (s), 1254 (m), 1240 (s), 1166 (w), 1145 (w), 1125 (w), 1109 (w), 1078 (w), 1044 (w), 1019 (w), 983 (w), 965 (w), 953 (w), 937 (w), 914 (w), 898 (m), 869 (s), 850 (s), 835 (s), 798 (w), 771 (w), 754 (s), 731 (w), 719 (w), 685 (w), 639 (w), 616 (w), 566 (w), 555 (w). Anal. Calcd for $C_{33}H_{64}N_4Si_2S_2TaLi$: C, 48.04; H, 7.82; N, 6.79. Found: C, 47.80; H, 7.86; N, 6.75.

$(Me_3SiCH_2)(ArN{=})(\eta_3\text{-}^iPr_2\text{-tacn})[Me_3SiCH{=}C(4\text{-Me-}C_6H_4)O]Ta$ (10). A small flask was charged with **3** (312 mg, 0.416 mmol) and toluene (40 mL), and *p*-toluoyl chloride (55 μL, 0.416 mmol) was added via syringe, causing the solution to darken to a deep orange color. After stirring for 2 h at ambient temperature, the solution was filtered in order to remove liberated lithium chloride. The toluene was removed under vacuum, and the solution was thrice treated with pentane (30 mL) and pumped down to a solid, yielding a pale orange solid. The solid was extracted with pentane (25 mL) and was filtered to another flask. The solution was concentrated to 3 mL in vacuo and slowly cooled to −40 °C, resulting in the formation of pale yellow crystals. The product was isolated by filtration and dried under vacuum (244 mg, 68%): mp 159−162 °C; ^{1}H NMR δ 7.444 (d, 2H, 8 Hz), 7.307 (d, 2H, 7.5 Hz), 6.985 (d, 2H, 7.5 Hz), 6.979 (t, 1H, 8 Hz), 5.079 (s, 1H), 4.62 (br, 2H), 4.29 (mult, 1H), 3.81 (mult, 1H), 3.162 (sept, 1H, 6 Hz), 2.982 (sept, 1H, 6 Hz), 2.86 (mult, 1H), 2.65 (mult, 2H), 2.54 (mult, 1H), 2.25 (mult, 1H), 2.15 (mult, 1H), 2.10 (s, 3H), 1.88 (mult, 1H), 1.72 (mult, 2H), 1.59 (mult, 1H), 1.550 (d, 12H, 6 Hz), 1.005 (d, 3H, 6 Hz), 0.92 (br, 6H), 0.695 (s, 1H, 7.5 Hz), 0.610 (s, 1H, 7.5 Hz), 0.604 (d, 3H, 6 Hz), 0.370 (s, 9H), 0.113 (s, 9H); ^{13}C NMR δ 171.5 (C), 152.0 (C), 146.6 (C), 140.4 (C), 137.3 (C), 129.1 (CH), 128.3 (CH), 122.9 (CH), 122.8 (CH), 100.4 (CH), 58.7 (CH_2), 55.6 (CH), 55.5 (CH_2), 55.4 (CH), 55.3 (CH_2), 53.4 (CH), 52.5 (CH_2), 50.7 (CH_2), 50.4 (CH_2), 49.1 (CH_2), 27.0 (CH_3), 26.6 (CH_3), 21.1 (CH_3), 19.8 (CH_3), 17.7 (CH_3), 17.3 (CH_3), 3.6 (CH_3), 1.2 (CH_3); IR 1904 (w), 1611 (w), 1578 (s), 1506 (w), 1489 (w), 1431 (s), 1344 (s), 1306 (s), 1292 (s), 1245 (m), 1173 (s), 1156 (m), 1107 (s), 1073 (m), 1044 (m), 1021 (w), 982 (w), 953 (m), 906 (w), 881 (s), 841 (s), 830 (s), 755 (m), 738 (m), 717 (m), 660 (m), 608 (w). Anal. Calcd for $C_{40}H_{71}N_4OSi_2Ta$: C, 55.79; H, 8.31; N, 6.51. Found: C, 55.54; H, 8.40; N, 6.27.

X-ray Crystallography. A summary of crystal data and collection parameters for the crystal structures of **8** and **10** are given in Table 1. Details of individual data collection and solution are given below. ORTEP diagrams were created using the ORTEP-3 software package.[54] For each sample, a crystal was mounted on a glass capillary using Paratone-N hydrocarbon oil. The crystal was transferred to a Siemens SMART[55] diffractometer/CCD area detector, centered in the X-ray beam, and cooled using a nitrogen-flow low-temperature apparatus that had been previously calibrated by a thermocouple placed at the same position as the crystal. A least-squares refinement on data from 60 sample frames allowed determination of cell constants and the orientation matrix. An arbitrary hemisphere of data was collected using 0.3° ω-scans, and the data were integrated by the program SAINT.[56] The final unit cell parameters were determined by least-squares analysis of the reflections with $I > 10\sigma(I)$. Data analysis using Siemens XPREP[57] determined the space group. The data were corrected for Lorentz and polarization effects, but no correction for crystal decay was applied. Equivalent reflections were averaged, and the structure was solved by direct methods[58] and expanded using Fourier techniques,[59] all within the teXsan[60] software package. Hydrogen atoms were included as fixed atoms but not refined. The weighting schemes were based on counting statistics and included a factor ($p = 0.030$) to reduce the weight of intense reflections. The analytical forms of the scattering factor tables for the neutral atoms were used,[61] and all scattering factors were corrected for both the real and imaginary components of anomalous dispersion.[62]

Table 1. Crystal Data and Collection Parameters

	8	**10**
formula	$C_{33}H_{64}LiN_4OSi_2Ta$	$C_{33}H_{71}N_4OSi_2Ta$
fw	776.95	861.15
space group	*Pbca* (#61)	$P\bar{1}$ (#2)
temperature (°C)	−107	−117
a (Å)	17.1859(3)	10.345(2)
b (Å)	19.2859(3)	10.809(2)
c (Å)	24.3778(4)	21.829(5)
α (deg)	90	79.567(3)
β (deg)	90	80.290(4)
γ (deg)	90	67.108(3)
V (Å^3)	8079.9(2)	2198.3(8)
Z	8	2
density$_{calc}$ (g/cm^3)	1.277	1.301
diffractometer	Siemens SMART	Siemens SMART
radiation	Mo Kα (λ = 0.71069 Å)	Mo Kα (λ = 0.71069 Å)
monochromator	graphite	graphite
detector	CCD area detector	CCD area detector
scan type, width	ω, 0.3°	ω, 0.3°
scan speed	10.0 s/frame	20.0 s/frame
no. of reflns measd	hemisphere	hemisphere
2θ range (deg)	3−46.4	3−46.5
μ (cm^{-1})	28.03	25.83
T_{max}, T_{min}	0.72, 0.51	0.907, 0.447
cryst dimens (mm)	0.17 × 0.17 × 0.16	0.17 × 0.11 × 0.04
no. of reflns measd	33 010	10 049
no. of unique reflns	6371	6151
no. of observations	3179	4439
no. of params	378	220
R, R_w, R_{all}	0.025; 0.028; 0.060	0.109; 0.154; 0.139
GOF	0.79	4.07

Compound 8. X-ray quality crystals were grown from a saturated octane solution that was cooled to −40 °C. One isopropyl group exhibited rotational disorder with a methyl group occupying each of two positions in a 2:1 ratio. The final cycle of full-matrix least squares refinement [minimizing the quantity $\sum w(|F_o| - |F_c|)^2$, where *w* is the weight of a given observation] was based on 3179 observed reflections [$I > 3.00\sigma(I)$] and 378 variable parameters and converged with final residuals:[27] $R = 0.025$, $R_w = 0.028$, and GOF = 0.79.

Compound 10. X-ray quality crystals were grown by slow cooling of pentane to −40 °C. One trimethylsilyl group was rotationally disordered in the typical fashion and modeled as six carbon atoms of 50% occupancy. The final cycle of full-matrix least squares refinement [minimizing the quantity $\sum w(|F_o| - |F_c|)^2$, where *w* is the weight of a given observation] was based on 4439 observed reflections [$I > 3.00\sigma(I)$] and 220 variable parameters and converged yielding final residuals:[27] $R = 0.109$, $R_w = 0.154$, and GOF = 4.07.

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cam-

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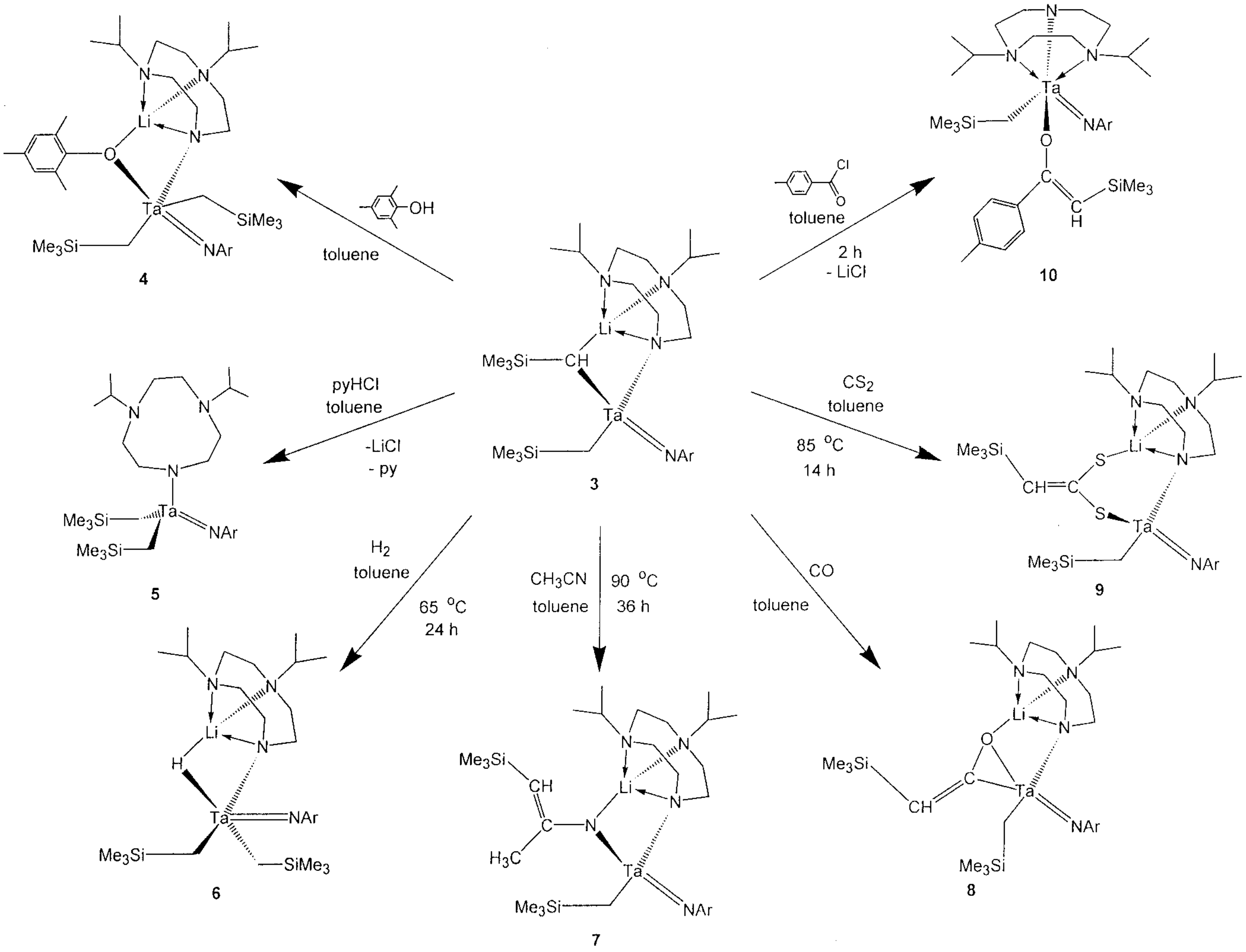
Scheme 2



bridge, CB2 1EZ [fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk].

Results and Discussion

To probe the reactivity of the tantalum−lithium alkylidene **3**, we explored reaction pathways commonly observed in traditional monometallic alkylidenes.[27,28] Specifically, the reactions of **3** with proton sources, nitriles, and other unsaturated electrophiles have been investigated as a means of determining the effect of the lithium ion in this compound.

Reaction with Proton Sources. The reaction between **3** and 2,4,6-trimethylphenol proceeded rapidly upon mixing toluene solutions of the two materials, as observed by a color change from deep yellow to nearly colorless. After removal of reaction solvent under vacuum, compound **4** was isolated by extraction with ether and was obtained as a slightly sticky solid in excellent yield. The ^{1}H NMR spectrum showed six independent resonances (all multiplets) for the three pairs of diastereotopic protons of the ethylene bridges in the ^{i}Pr$_2$-tacn$^-$ ligand, consistent with mirror symmetry in the molecule. The two trimethylsilylmethyl ligands were equivalent, showing three resonances (two for the diastereotopic methylene and one for the methyl groups) in a 1:1:9 ratio. On the basis of these data, the structure of **4** was assigned as a bridging aryloxide species, as shown in Scheme 2. The ^{13}C NMR spectrum was rather unremarkable, and the ^{7}Li NMR showed a resonance at 1.775 ppm, shifted upfield from its precursor (**3**, 2.986 ppm), as well as from the corresponding bridging alkyl species (**2**, 2.103 ppm). This is likely a result of the shielding caused by the phenoxy ligand bound to the lithium.[63] Although structural evidence confirming the proposed connectivity is presently lacking, the bridging motif has been identified in a number of related complexes (see below), in which four-coordinate Li is invariably observed. The reactivity seen here is comparable to that of $(Me_3CCH{=})Ta(Me_3CCH_2)_3$, which reacts with 2 equiv of TpOH [Tp = $(C_6H_4)_3C_2HOH$] to yield $(Me_3CCH_2)_3Ta(OTp)_2$.[64] In both cases, the nucleophilic alkylidene moiety is protonated by the weakly acidic alcohol.

The reaction between **3** and pyridinium chloride proceeded slowly in toluene due, no doubt, to the low solubility of the latter in this solvent. After stirring overnight, a quantitative conversion to a new compound (**5**) was observed by ^{1}H NMR spectroscopy (Scheme 2). The spectrum of this species was very distinctive,

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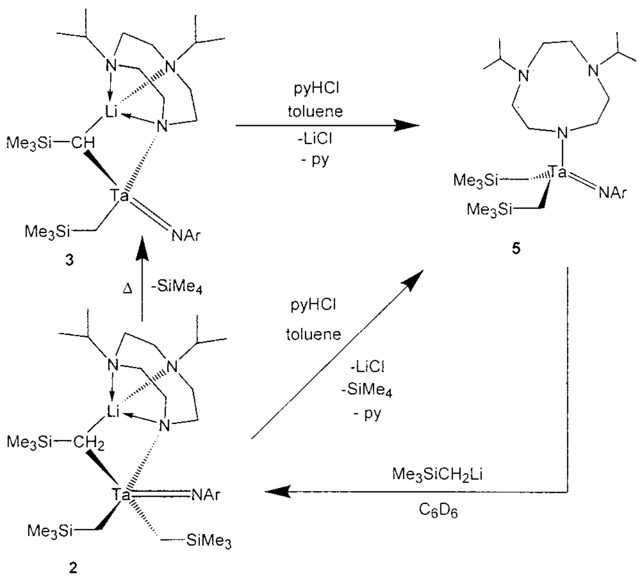
Scheme 3



containing only three resonances for the ethylene bridges of the $^{i}Pr_2$-tacn$^-$ ligand (two multiplets, one singlet). This indicated not only the presence of mirror symmetry but also equilibration of the methylene hydrogens in this ligand. These data suggest a monodentate bonding motif for $^{i}Pr_2$-tacn$^-$ (operating as a simple amide ligand) in this compound. Also, only one isopropyl resonance was observed for the imido group, demonstrating its rapid rotation on the NMR time scale. Additionally, the ^{13}C NMR spectrum showed a set of peaks fully in agreement with the high symmetry exhibited by **5**. Thus, **5** was formulated as the pseudotetrahedral compound $(Me_3SiCH_2)_2(ArN{=})(\eta_1\text{-}{}^{i}Pr_2\text{-tacn})Ta$. The compound was isolated in analytically pure form from pentane as a yellow oil. The reaction of **3** with pyHCl can be compared with that of a traditional alkylidene, as shown by the reaction of $(Me_3CCH{=})Ta(Me_3CCH_2)_3$ with HCl to give $(Me_3CCH_2)_4TaCl$.[32] In contrast to **4**, the chloride ligand departs with the lithium ion, due to the strong driving force provided by the precipitation of lithium chloride.

Interestingly, **5** can also be synthesized by the reaction of the bridging *alkyl* species (**2**) with 1 equiv of pyridinium chloride. In this case, the reaction resulted in the release of both tetramethylsilane and lithium chloride as the reaction proceeded to yield a product spectroscopically identical to that described above (Scheme 3). In accord with this reactivity, addition of $LiCH_2SiMe_3$ to **5** regenerates **2** quantitatively.

The alkylidene ligand in **3** is also converted to an alkyl group when exposed to hydrogen gas at 65 °C in toluene. Heterolysis of H_2 protonates the alkylidene, and the counterion (hydride) is retained in a bridging fashion, bound to the tantalum and lithium atoms (Scheme 2). At room temperature, the ^1H NMR spectrum of this compound (**6**) supports this geometry by showing a ^1H resonance for the hydride at 11.03 ppm as a 1:1:1:1 quartet ($^1J = 14.7$ Hz). This splitting, due to a coupling between H and ^7Li ($S = 3/2$), is matched by the appearance of a doublet with an identical $^1J_{LiH}$ at 3.627 ppm in the ^7Li NMR spectrum (Figure 2). Observation of coupling in lithium hydride species is rare.[65−69] One-bond coupling between lithium and hydrogen nuclei has been reported in two previous cases,[70,71] and the $^1J_{Li-H}$ coupling constant for **6** (14.7 Hz) is somewhat larger than those observed previously (6.4−10.5 Hz).

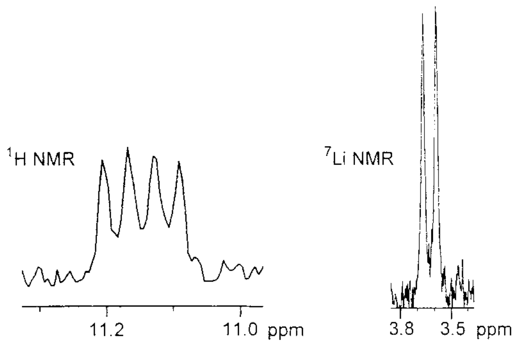


Figure 2. Lithium hydride NMR signals observed at room temperature for **3**.

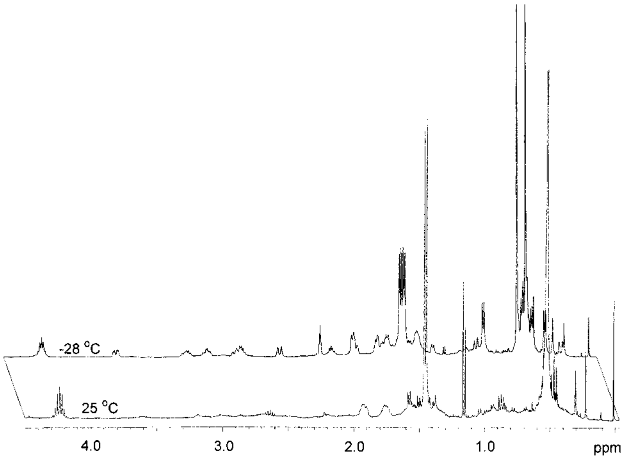


Figure 3. Portion of the ^1H NMR spectra for **3** at 25 °C and −28 °C, showing the enhanced resolution achieved upon cooling.

The remainder of the ^1H NMR spectrum for **6** is broad and uninterpretable at room temperature, indicating fluxionality in this compound. Upon cooling to −28 °C, the spectrum sharpened considerably (Figure 3), with the resonances being indicative of an asymmetric species with inequivalent trimethylsilylmethyl ligands. This is consistent with a square pyramidal coordination sphere in which the imido ligand is axial and the two alkyl ligands are oriented in a *cis* fashion. The fluxionality in **6** observed at room temperature can be attributed to equilibrium between this square pyramidal structure and a trigonal bipyramidal arrangement. The hydride **6** was isolated as a pale yellow solid and is stable for weeks as a solid, but slowly decomposes to an intractable product in solution.

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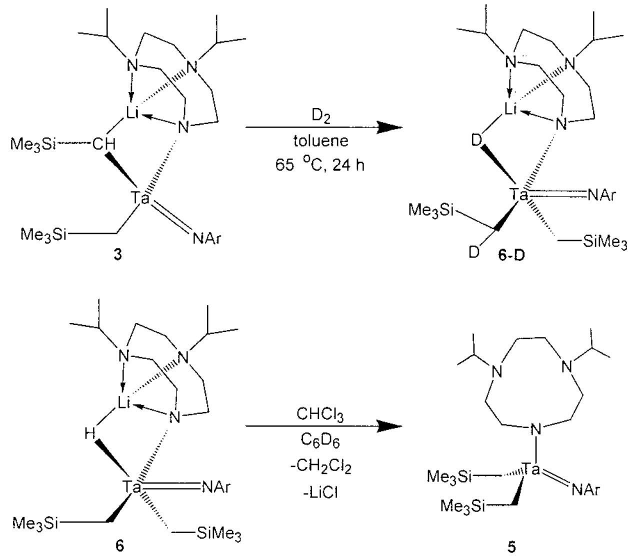
Scheme 4



Further evidence for the formation of this product was obtained by repeating the reaction with D_2. Under these conditions, the resonance at 11.03 ppm in the ^{1}H NMR spectrum was absent, and the ^{7}Li NMR signal was broadened due to coupling from the quadrupolar deuteride ($S = 1$). In the ^{2}H NMR spectrum of **6-D**, resonances appeared at 11.03 (br, s) and 0.52 (br, d) due to the bridging deuteride and the $CDHSiMe_3$ group, respectively (Scheme 4).

Reaction of **6** with chloroform in C_6D_6 proceeds slowly to form a product spectroscopically identical to **5**, with concomitant formation of dichloromethane and LiCl (Scheme 4). This contrasts with typical reactions of transition metal hydrides with chloroform, which yield metal chlorides.

Insertion Reactions. Upon reaction of **3** with organic substrates such as isocyanates (^{t}BuNCO, PhNCO), carbodiimides (^{i}PrNCN^{i}Pr, *p*-tolNCN-*p*-tol), aldehydes (PhCHO), esters (PhCOOPh), or isocyanides (xylNC), a mixture of products was formed. These mixtures proved to be inseparable upon workup and were not pursued further. On the other hand, reactions with acetonitrile, carbon monoxide, and carbon disulfide cleanly gave a single product in each case, as detailed below.

When **3** was exposed to 1 equiv of CH_3CN in toluene, no reaction was observed at room temperature. Upon warming to 90 °C, however, a clean insertion reaction proceeded smoothly over a period of 36 h to form a new compound (**7**), in which the alkylidene proton is shifted to higher field (from 4.205 ppm in **3** to 3.854 ppm in **7**). The remaining proton signals, though altered slightly, showed little change, with the molecule retaining the low symmetry of the starting alkylidene. The ^{7}Li signal also changed slightly, from 2.986 ppm in **3** to 2.699 ppm in **7**. These data are consistent with clean insertion of the acetonitrile into the alkylidene metal bond followed by a rearrangement to form a bridging eneimido species (Scheme 2) and are related to reactivity observed in terminal alkylidenes, which form terminal eneimido ligands.[32]

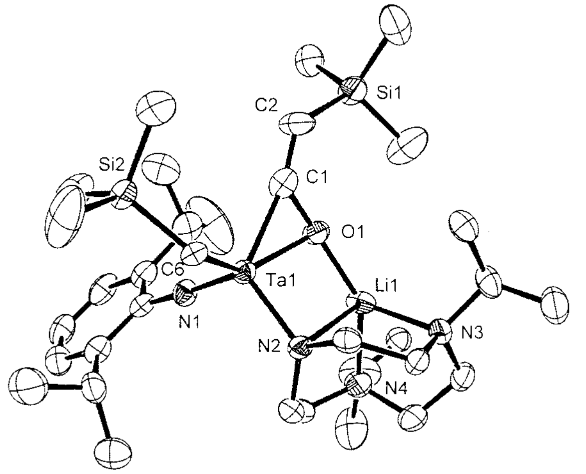


Figure 4. ORTEP view of **8** with 50% thermal ellipsoids. Selected bond lengths (Å): Ta1−C1 = 2.134(7), Tal−C6 = 2.166(7), Ta1−O1 = 2.067(4), Ta1−N1 = 1.793(5), Ta1−N2 = 2.025(5), Li1−O1 = 1.82(1), Li1−N2 = 2.22(1), Li1−N3 = 2.07(1), Li1−N4 = 2.08(1), C1−O1 = 1.398(8), C1−C2 = 1.345(9).

In general, carbon monoxide inserts into $M{=}CR_2$ double bonds to form the corresponding η_2-ketene species $[M(\eta_2\text{-}OCCR_2)]$, in which both carbon and oxygen are bound to the metal center.[72−74] To further investigate its alkylidene-like reactivity, **3** was exposed to carbon monoxide (1 atm) at ambient temperature in toluene,[53] and quantitative conversion to a new compound (**8**) was observed (Scheme 2). The NMR spectra of this product were qualitatively very similar to that of **3**, except that the alkylidene CH resonance shifted significantly (from 4.205 ppm (^{1}H) and 57.4 ppm (^{13}C) in **3** to 5.517 ppm (^{1}H) and 93.5 ppm (^{13}C) in **8**). Additionally, the ^{7}Li NMR resonance shifted considerably, from 2.986 ppm (**3**) to 1.874 ppm (**8**). On the basis of these data, an insertion of CO at the alkylidene functionality to form a ketene complex (**8**) was postulated, which was subsequently confirmed by X-ray crystallography (Figure 4).[53]

The bridging structure of the ^{i}Pr$_2$-tacn$^-$ is retained in **8**, bound to Ta through the anionic nitrogen and coordinated to Li through three N−Li dative bonds. The ketene moiety bridges the Ta and Li atoms, with bond lengths [Ta1−C1 = 2.134(7) Å, Ta1−O1 = 2.067(4) Å] similar to those in a related η_2-Zr ketene complex.[75] These lengths also parallel those found in a related η_2-Ta acyl complex,[76] while the Li−O distance [1.82(1) Å] is similar to that observed for related carboxylate species.[77,78] Virtually no changes in the remaining metal−ligand bond lengths from that of the precursor **3** were observed.

As was the case for the insertion of acetonitrile, reaction between **3** and CS_2 required elevated temper-

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atures. After stirring the two compounds in toluene at 85 °C for 14 h, the clean conversion to a new product (**9**) was observed. The ^{1}H NMR spectrum again showed an asymmetric species, with the only equilibration of protons due to rapid rotation of the phenyl imido unit. Notably, the CH alkylidene resonance was strongly downfield shifted, to 5.754 ppm. The six isopropyl methyl doublets and two $SiMe_3$ resonances were typical for these low-symmetry compounds, located at chemical shifts well within the expected ranges. Another important spectroscopic change upon reaction was the large downfield shift in the ^{7}Li NMR resonance to a new value of 4.224 ppm in **9** (as compared to 2.986 ppm in **3**). Compound **9** was therefore formulated as a bridging enedithiolato complex, resulting from formal insertion of each of the double bonds of CS_2 into the alkylidene metal bonds (Scheme 2). A number of enedithiolato ligands, generated by oxidative cleavage of tetrathiane moieties,[79] deprotonation of enedithiols,[80] or deprotonation of β-hydroxydithiocarboxylate ligands,[81−84] are known.

Reaction with Acid Chlorides. In the case of a monometallic alkylidene complex, acid chlorides are known to react at the nucleophilic carbon of the alkylidene; keto−enol tautomerization then occurs, resulting in conversion of the metal alkylidene to the corresponding enolate metal chloride. For example, the reaction of $(Me_3CCH_2)_3Ta-(=CHCMe_3)$ with RCOCl results in the formation of $(Me_3CCH_2)_3ClTa-(OCR=CHCMe_3)$.[32]

The tantalum−lithium bridging alkylidene **3** was found to react readily with 1 equiv of *p*-tolCOCl at room temperature in toluene. After filtration to remove LiCl, the product (**10**) was crystallized from pentane. The most noteworthy aspect of the ^{1}H NMR spectrum of **10** is a singlet at 5.079 ppm. The remainder of the spectrum showed the usual lack of symmetry seen throughout the compounds presented here. On the basis of the loss of lithium chloride and the presence of the low-field NMR resonance at 5.079 ppm, **10** was formulated as the enolate, $(Me_3SiCH_2)(ArN=)(\eta_3\text{-}^iPr_2\text{-tacn})Ta[OC(p\text{-tol})=CHSiMe_3]$ (Scheme 2).

Even though the compound could be recrystallized from pentane, the crystals of **10** that were obtained did not diffract well, preventing the acquisition of a high quality X-ray structure of this species. A low-resolution structure was obtained which at least confirmed connectivity.[85] The structure shows an anionic tacn bonded to tantalum in a tridentate fashion. The tantalum coordination sphere is completed by one alkyl ligand, one imido group, and the newly formed enolate ligand. Though the reaction of **3** with the acid chloride follows a reaction pathway very similar to that of a standard alkylidene, it is noteworthy that upon departure of the lithium chloride from this species, the anionic tacn ligand returns to a tridentate coordination mode. This indicates that the tacn moiety responds to the electronic needs of the complexes formed by coordination of an appropriate number of nitrogen atoms, to stabilize these compounds.

Conclusions

The tantalum complexes reported here demonstrate conclusively that the anionic tacn ligand has the ability to function as a hemilabile ligand which, depending on the steric and electronic demands of the metal to which it is bound, can act as a mono- or tridentate donor to a single metal center. Furthermore, this work has provided unusual examples of the tacn moiety's ability to act as a ligand to two different metals that are also bridged by an additional ligand, in a μ-η_1:η_3-fashion. The presence of lithium in the absence of a good leaving group (such as chloride, for example), invariably leads to such a structural arrangement, a finding that presumably reflects the relative tenacity with which lithium is bound by tacn. The structural effects of this unusual type of coordination behavior are apparent from NMR spectroscopy and X-ray crystallography; our understanding of the electronic contributions to this unusual mode of bonding is the focus of continuing synthetic and theoretical work.

Acknowledgment. The authors gratefully acknowledge the NSF for funding, the Department of Defense Science and Engineering Graduate (NDSEG) Fellowship Program for fellowship support (J.A.R.S.), and Drs. Fred Hollander and Allen Oliver for insightful discussions.

Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

OM020175C

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