ORGANOMETALLICS

Reactivity of the Y³⁺ Tuck-Over Hydride Complex, $(C_5Me_5)_2Y(\mu-H)(\mu-CH_2C_5Me_4)Y(C_5Me_5)$

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Supporting Information

ABSTRACT: The trivalent yttrium tuck-over hydride complex, $(C_5Me_5)_2Y(\mu-H)(\mu-\eta^{1}:\eta^5-CH_2C_5Me_4)Y(C_5Me_5)$, **1**, acts as a reductant in reactions in which the $(\mu-H)^-$ hydride ligand and the bridging Y–C alkyl anion linkage in the $(\mu-\eta^{1}:\eta^5-CH_2C_5Me_4)^{2^-}$ ligand combine to form a C–H bond in $(C_5Me_5)^-$ and deliver two electrons to a substrate. Complex **1** reacts with PhSSPh, AgOTf



(OTf = OSO₂CF₃), and Et₃NHBPh₄ to form $[(C_5Me_5)_2Y(\mu$ -SPh)]_2, $[(C_5Me_5)_2Y(\mu$ -OTf)]_2, and $(C_5Me_5)_2Y(\mu$ -Ph)_2BPh₂, respectively. The reactivity of the Y–H and Y–CH₂C₅Me₄ linkages in 1 was probed via carbodiimide insertion reactions. ⁱPrN= C=NⁱPr inserts into both Y–H and Y–C bonds to yield $(C_5Me_5)[^{i}PrNC(H)N^{i}Pr]Y\{\mu$ - η^5 - $C_5Me_4CH_2[^{i}PrNCN^{i}Pr]\}Y(C_5Me_5)_2$. Carbodiimide insertion with $[(C_5Me_5)_2YH]_2$, **2**, was also examined for comparison, and $(C_5Me_5)_2Y[^{i}PrNC(H)N^{i}Pr$ - $\kappa^2N,N']$ was isolated and structurally characterized. To examine the possibility of selective reactivity of the bridging ligands, μ -H versus μ -CH₂C₅Me₄, trimethylsilylchloride was reacted with 1, and the tuck-over chloride complex, $(C_5Me_5)_2Y(\mu$ -Cl) $(\mu$ - η^1 : η^5 -CH₂C₅Me₄)Y(C₅Me₅), was isolated.

INTRODUCTION

Recent advances in f-element ligand-based redox processes have shown that the hydride complexes, $[(C_5Me_5)_2MH_x]_y$ (M = U,¹ Th,¹ La,² Sm,³ Y⁴), can act as reductants,⁵ in addition to their well-known insertion^{2,6} and σ -bond metathesis reactivity.^{4,7} An example is shown in Scheme 1 in which the trivalent yttrium

Scheme 1. Reduction of Cyclooctate traene by $[(C_5Me_5)_2YH]_2$ and Formal Half-Reactions



hydride, $[(C_5Me_5)_2YH]_{27}^4$ effects a formal two-electron reduction of 1,3,5,7-cyclooctatetraene to form $(C_5Me_5)Y-(C_8H_8).^{5a}$ Hydrogen is the observed byproduct of the formal $H^- \rightarrow e^- + {}^1/_2 H_2$ reactions that generate the reducing electrons. $(C_5Me_5)_3Y$ is the organometallic byproduct that forms with $(C_5Me_5)Y(C_8H_8)$ upon ligand redistribution. 5a

Examination of the reductive reactivity of hydride ligands in the unusual tuck-in⁸ tuck-over dihydride, $(C_5Me_5)U[\mu-\eta^5:\eta^1:\eta^1-C_5Me_3(CH_2)_2](\mu-H)_2U(C_5Me_5)_2$,⁹ revealed that *combinations* of M–H and M–C bonds in metalated pentamethylcyclopentadienyl rings could also deliver two electrons to a substrate and form C–H bonds (Scheme 2).¹⁰ This formally involves Scheme 2. Reduction of Cyclooctatetraene by $(C_5Me_5)U[\mu-\eta^5:\eta^1:\eta^1-C_5Me_3(CH_2)_2](\mu-H)_2U(C_5Me_5)_2$ and Formal Half-Reactions



reductive elimination of a U–H and U– $CH_2(ring)$ linkage to reform the CH_3 groups of the $(C_5Me_5)^-$ ligand. Although reductive elimination is common in transition-metal chemistry when the metal can undergo a M^n -to- M^{n-2} change in oxidation state, this is a rare type of reaction in f-element chemistry. Since the combination of an anionic hydride with an anionic alkyl anion is not electrostatically favored, it was not expected that these two anions could come together in a U⁴⁺ complex and form a C–H bond while delivering two electrons.

It was of interest to determine if metal hydride and metal alkyl groups would react similarly in lanthanide and yttrium complexes. Although no lanthanide or yttrium tuck-in complexes involving terminal $(\eta^{1}:\eta^{5}-\text{CH}_2\text{C}_5\text{Me}_4)^{2-}$ ligands have been isolated, the $(\text{CH}_2\text{C}_5\text{Me}_4)^{2-}$ ligand has been isolated

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in a bridging mode in tuck-over complexes, such as $(C_5Me_5)_2Y(\mu-H)(\mu-\eta^{1}:\eta^{5}-CH_2C_5Me_4)Y(C_5Me_5)$, 1 (eq 1).^{7g}



Complex 1 has the requisite M–H and M– $CH_2(ring)$ units to allow a test of this type of reductive chemistry in an yttrium complex. The single set of M–H and M– $CH_2(ring)$ bonds and the predominance of a single oxidation state for this metal, Y^{3+} , may simplify this system in comparison to the uranium example in Scheme 2. The reaction chemistry of 1 with reducible substrates is reported here as well as reactions designed to probe the relative reactivity of the Y–H and Y–C bonds in this complex.

EXPERIMENTAL SECTION

The manipulations described below were performed under argon with rigorous exclusion of air, water, and coordinating solvents using Schlenk, vacuum line, and glovebox techniques. Solvents were dried over Q-5 and 4A molecular sieves and saturated with UHP argon using GlassContour¹¹ columns. Benzene- d_6 and cyclohexane- d_{12} were dried over NaK alloy, degassed using three freeze–pump–thaw cycles, and vacuum-transferred before use. $[(C_3Me_5)_2YH]_2$, 2,⁴ was prepared as previously reported for the Nd analogue.¹² Diphenyldisulfide was purchased from Aldrich and sublimed before use. Trimethylsilylchloride was purchased from Aldrich and used as received. Thiophenol and 1,3,5,7-C8H8 were purchased from Aldrich, distilled onto 4A molecular sieves, and degassed using three freeze-pump-thaw cycles before use. Silver triflate was purchased from Strem and used as received. Diisopropylcarbodiimide was purchased from Aldrich, dried over 4A molecular sieves, and degassed using three freeze-pumpthaw cycles before use. Et₃NHBPh₄¹³ and Et₃NDBPh₄^{13,14} were prepared according to the literature. ¹H and ¹³C NMR spectra were recorded with a Bruker DRX 500 MHz spectrometer. ¹⁹F NMR spectra were recorded with a Bruker DRX 400 MHz spectrometer. Infrared spectra were recorded as KBr pellets on a PerkinElmer Spectrum One FT-IR spectrometer. Elemental analyses were performed on a PerkinElmer Series II 2400 C/H/N/S elemental analyzer.

New Synthesis of $(C_5Me_5)_2Y(\mu-H)(\mu-\eta^1:\eta^5-CH_2C_5Me_4)Y-(C_5Me_5),^{79}$ 1. $[(C_5Me_5)_2YH]_2$, 2 (585 mg, 0.81 mmol), was placed in a glass tube fitted with a greaseless Teflon stopcock and heated to 90 °C at 10⁻⁴ Torr for 24 h. Complex 1 was obtained as an orange-red powder (572 mg, 98%). IR, ¹H NMR, and ¹³C NMR spectra were consistent with data reported in the literature for $(C_5Me_5)_2Y(\mu-H)(\mu-\eta^1:\eta^5-CH_2C_5Me_4)Y(C_5Me_5).^{7g}$

 $[(C_5Me_5)_2Y(\mu-SPh)]_2$, **4**. A solution of PhSSPh (9 mg, 0.04 mmol) in benzene (1 mL) was added to a stirred benzene (5 mL) solution of **1** (30 mg, 0.04 mmol). The color gradually changed from red-orange to pale yellow over 4 h. The pale yellow solution was evaporated to give a pale yellow powder (31 mg, 78%). The ¹H NMR spectrum matched that previously reported for $[(C_5Me_5)_2Y(\mu-SPh)]_2$, **4**.^{5a}

4 from 1 and PhSH. PhSH (41 μ L, 0.40 mmol) was added to a stirred solution of **1** (116 mg, 0.16 mmol) in methylcyclohexane (2 mL). After 30 min, the resulting clear yellow solution was evaporated to give **4** as a pale yellow powder (91 mg, 61%). The product was identified by ¹H NMR spectroscopy.^{Sa}

 $[(C_5Me_5)_2$ YOTf]₂, 5. Complex 2 (50 mg, 0.07 mmol) was added to a suspension of silver triflate (36 mg, 0.14 mmol) in methylcyclohex-

ane (3 mL). The reaction quickly turned black and was stirred 1 h. The reaction mixture was centrifuged and filtered to remove insoluble Ag metal, leaving a clear faint yellow solution. After removal of solvent under vacuum, a white solid was isolated (68 mg, 97%). X-ray quality crystals were grown from a saturated solution in pentane at -35 °C. ¹H NMR (C₆D₆): δ 2.05 (s, C₅Me₅, 60H). ¹³C NMR (C₆D₆): δ 11.8 (C₅Me₅), 120.9 (C₅Me₅). ¹⁹F NMR (C₆D₆): -76.3 (CF₃). IR: 2918 s, 2864 s, 2731 w, 1448 m, 1383 m, 1328 s, 1221 s, 1194 s, 1029 s, 628 s, 514 m cm⁻¹. Anal. Calcd for C₄₂H₆₀F₆O₆S₂Y₂: C, 49.61; H, 5.95. Found: C, 49.16; H, 6.01.

5 from 1 and AgOTf. A solution of 1 (40 mg, 0.06 mmol) in toluene (2 mL) was added to a stirred toluene (2 mL) slurry of silver triflate (29 mg, 0.11 mmol). The reaction mixture quickly turned black and was allowed to stir for 1 h. The reaction mixture was centrifuged and filtered to remove insoluble Ag metal, leaving a clear faint orange solution. After removal of solvent under vacuum, a tacky light orange solid was isolated. Recrystallization from pentane at -35 °C yielded **5** as a white solid (29 mg, 51%). ¹H, ¹³C, and ¹⁹F NMR spectroscopy confirmed the identity of **5**.

 $(C_5Me_5)_2Y(\mu-Ph)_2BPh_2$, 6. Et₃NHBPh₄ (62 mg, 0.14 mmol) was added to a benzene (10 mL) solution of 1 (50 mg, 0.07 mmol). After 10 min, the cloudy white mixture was centrifuged and filtered to remove the insoluble material. The solvent was removed from the colorless supernatant under vacuum to yield a white solid (83 mg, 87%). The ¹H NMR spectrum of the white solid matched that previously reported for $(C_5Me_5)_2Y(\mu-Ph)_2BPh_2$.¹⁵ When the same reaction was performed in a sealed NMR tube, Et₃N and H₂ were identified as byproducts by ¹H NMR spectroscopy.¹⁶ In a similar experiment, a C_6D_6 (0.7 mL) solution of 1 (12 mg, 0.017 mmol) was added to Et₃NDBPh₄ in an NMR tube and quickly capped. The ¹H NMR spectrum showed evidence for HD,¹⁷ in addition to resonances of 6 and Et₃N. In a related experiment, a C_6H_6 (0.7 mL) solution of 1 (12 mg, 0.017 mmol) was added to Et₃NDBPh₄ in an NMR tube and quickly capped. The ²H NMR spectrum showed resonances at 1.50 ppm consistent with incorporation of deuterium into a $(C_5Me_5)^-$ ring of 6.

 $(C_5Me_5)_2Y{\mu-\eta^5-C_5Me_4CH_2[i^{i}PrNCN^{i}Pr-\kappa^2N,N']}Y(C_5Me_5)[i^{i}PrNC-$ (H)N'Pr- $\kappa^2 N, N'$], 7. 'PrN=C=N'Pr (48 μ L, 0.31 mmol) was added to a stirred hexane (10 mL) solution of 1 (100 mg, 0.14 mmol). Upon addition, the solution turned pale yellow. After 12 h, the solution was colorless. The solvent was removed under vacuum to yield 7 as a white microcrystalline powder (135 mg, 99%). ¹H NMR (C_6D_6): δ 1.04 (d, $CH(Me_3)_2$, ${}^{3}J_{HH} = 6$ Hz, 12H), 1.14 (d, $CH(Me_3)_2$, ${}^{3}J_{HH} = 6$ Hz, 6H), 1.15 (d, $CH(Me_3)_2$, ${}^{3}J_{HH} = 6$ Hz, 6H), 1.99 (s, $C_5Me_4CH_2$, 6H), 2.01 (s, C₅Me₅, 15H), 2.11 (s, C₅Me₅, 30H), 2.16 (s, C₅Me₄CH₂, 6H), 3.39 (m, CHMe₂, 2H), 3.72 (s, C₅Me₄CH₂, 2H), 3.75 (m, CHMe₂, 2H), 8.00 (d, NC(H)N, ${}^{3}J_{YH}$ = 6.5 Hz, 1H). ${}^{13}C$ NMR (C₆D₆): δ 12.1 $(C_5Me_4CH_2)$, 12.2 (C_5Me_5) , 12.7 (C_5Me_5) , 13.6 $(C_5Me_4CH_2)$, 26.0 (CHMe₂), 26.2 (CHMe₂), 26.7 (CHMe₂), 28.8 (NC(CH₂)N), 46.2 (CHMe₂), 50.2 (CHMe₂), 117.1 (C₅Me₄CH₂), 117.2 (C₅Me₄CH₂), 117.6 (C_5Me_5), 117.7 (C_5Me_5), 117.9 ($C_5Me_4CH_2$), 162.1 [NC(H)-N], 168.8 [(NC(CH₂)N]. IR: 2965 s, 2905 s, 2858 s, 2723 m, 2599 w, 1539 s, 1452 s, 1377 s, 1318 s, 1280 s, 1193 s, 1116 m, 1026 m, 837 s, 708 s, 590 s, 461 s cm⁻¹. Anal. Calcd for $C_{54}H_{88}N_4Y_2$: C, 66.79; H, 9.13; N, 5.77. Found: C, 66.58; H, 9.54; N, 5.74.

 $(C_5Me_5)_2$ **Y**[^{*i*}**PrNC(H)N**^{*i*}**Pr**-*κ*²*N*,*N*'], **8**. A cloudy pink suspension of $[(C_5Me_5)_2$ YH]₂ (200 mg, 0.28 mmol) in methylcyclohexane (5 mL) turned clear and colorless upon ^{*i*}PrN=C=N^{*i*}Pr (86 μL, 0.56 mmol) addition. The solvent was removed under vacuum to yield **8** as a white microcrystalline powder (270 mg, 99%). X-ray quality crystals of **8** were grown from a saturated solution in pentane at −35 °C. ¹H NMR (C_6D_6): δ 1.09 (d, CHM e_2 , ³ J_{HH} = 6 Hz, 12H), 1.99 (s, C_5Me_5 , 30H), 3.29 (m, CHM e_2 , 2H), 7.88 (d, NC(H)N, ³ J_{YH} = 6 Hz, 1H). ¹³C NMR (C_6D_6): δ 12.1 (C_5Me_5), 26.1 (CHM e_2), 49.9 (CHM e_2), 117.2 (C_5Me_5), 161.7 (NC(H)N). IR: 2965 s, 2909 s, 2859 s, 2723 w, 2125 w, 1536 s, 1451 m, 1378 m, 1358 m, 1328 m, 1287 m, 1192 m, 1168 m, 1116 w, 1026 w cm⁻¹. Anal. Calcd for $C_{27}H_{45}N_2$ Y: C, 66.65; H, 9.32; N, 5.76. Found: C, 66.26; H, 9.41; N, 5.73.

 $(C_5Me_5)_2Y(\mu-Cl)(\mu-\eta^1:\eta^5-CH_2C_5Me_4)Y(C_5Me_5)$, 9. Trimethylsilylchloride (19 μ L, 0.15 mmol) was added by syringe to a stirred pentane (10 mL) solution of **1** (100 mg, 0.14 mmol). After 1.5 h, the orange mixture was centrifuged and the solvent was removed from the supernatant under vacuum, leaving **9** as an orange microcrystalline solid (101 mg, 96%). X-ray quality crystals were grown from a saturated benzene solution of **9**. ¹H NMR (C₆D₆): δ 1.13 (d, C₅Me₄CH₂, ²J_{YH} = 4.5 Hz, 2H), 1.89 (s, C₅Me₅, 15H), 1.98 (s, C₅Me₄CH₂, 6H), 2.02 (s, C₅Me₄CH₂, 6H), 2.09 (s, C₅Me₅, 30H). ¹³C NMR (C₆D₆): δ 11.6 (C₅Me₄CH₂), 11.9 (C₅Me₅), 14.4 (C₅Me₄CH₂), 14.7 (C₅Me₄CH₂), 32.2 (d, C₅Me₄CH₂), 120.5 (C₅Me₅), 149.7 (YCH₂C). IR: 2967 s, 2907 s, 2859 s, 2726 w, 1495 w, 1439 s, 1379 s, 1246 w, 1151 m, 1059 w, 1022 m, 927 m, 857 w, 804 w, 645 m, 603 w, 559 w, 451 w cm⁻¹. Anal. Calcd for C₄₀H₅₉ClY₂: C, 63.79; H, 7.90. Found: C, 63.34; H, 7.97.

(C₅Me₅)₂Y(*μ*-Cl)(C≡CPh)Y(C₅Me₅)₂], 10. Phenylacetylene (8.3 *μ*L, 0.08 mmol) was added by syringe to a stirred methylcyclohexane (10 mL) solution of 9 (56 mg, 0.07 mmol). After 30 min, the solvent was removed under vacuum. The off-white solid was washed with pentane and dried under vacuum to yield 10 as an off-white powder (59 mg, 93%). ¹H NMR (C₆D₆): δ 1.87 (s, C₅Me₅, 30H), 2.27 (s, C₅Me₅, 30H), 7.02 (m, *p*-C₆H₅, 1H), 7.15 (m, *m*-C₆H₅, 2H), 7.74 (d, *o*-C₆H₅, ³J_{HH} = 7.5 Hz, 2H). ¹³C NMR (C₆D₆): δ 11.4 (C₅Me₅), 12.7 (C₅Me₅), 110.2 (d, C≡CPh, ²J_{YC} = 12 Hz), 117.8 (C₅Me₅), 122.6 (C₅Me₅), 128.7 (*m*-C₆H₅), 129.7 (*i*-C₆H₅), 132.1 (*o*-C₆H₅), 149.5 (d, C≡CPh, ¹J_{YC} = 69 Hz). IR: 2958 s, 2906 s, 2858 s, 2724 w, 2361 w, 2339 w, 1594 m, 1483 s, 1439 s, 1381 m, 1259 w, 1198 m, 1066 w, 1024 m, 776 m, 757 s, 694 s, 519 m cm⁻¹.

 $(C_5Me_5)_2Y(C \equiv CPh)(THF)$ and $(C_5Me_5)_2YCI(THF)$ from 10. Tetrahydrofuran (2 mL) was added to 10 (40 mg, 0.040 mmol), and the resulting solution was stirred for 5 min. The solvent was removed under vacuum to give a white solid. This was extracted with hexane to give a clear solution and a white solid. Solvent was removed from this solution under vacuum, and the resulting solid was recrystallized from hexane to give microcrystalline $(C_5Me_5)_2Y(C \equiv$ CPh)(THF)¹⁸ identified by ¹H NMR spectroscopy. The ¹H NMR spectrum of the hexane insoluble white solid in C_6D_6 matched that reported for $(C_5Me_5)_2YCI(THF).$ ¹⁹

X-ray Data Collection, Structure Determination, and Refinement. Crystallographic information on complexes 5, 8, and 9 is presented in Tables 1–3 and in the Supporting Information.

Table 1. X-ray Data Collection Parameters for $[(C_5Me_5)_2Y(\mu$ -OTf)]_2, 5; $(C_5Me_5)_2Y[^iPrNC(H)N^iPr-\kappa^2N,N']$, 8; and $(C_5Me_5)_2Y(\mu$ -Cl) $(\mu$ - η^1 : η^5 -CH₂C₅Me₄)Y(C₅Me₅), 9

| | 5 | 8 | 9 |
|---------------------------------|------------------------------|--------------------|----------------------------------|
| empirical formula | $C_{48}H_{66}F_6O_6S_2Y_2\\$ | $C_{27}H_{45}N_2Y$ | $C_{40}H_{59}ClY_2 \cdot C_6H_6$ |
| fw | 1094.95 | 486.56 | 831.25 |
| temp (K) | 148(2) | 98(2) | 98(2) |
| cryst syst | monoclinic | monoclinic | monoclinic |
| space group | $P2_1/n$ | $P2_1/n$ | C2 |
| a (Å) | 11.4771(7) | 18.3638(9) | 19.2433(6) |
| b (Å) | 14.4940(9) | 16.0124(8) | 16.9361(6) |
| c (Å) | 30.0175(18) | 20.0770(10) | 14.1667(5) |
| $\alpha = \gamma \text{ (deg)}$ | 90 | 90 | 90 |
| β (deg) | 93.5590(10) | 117.1547(6) | 116.0716(4) |
| volume (Å ³) | 4983.8(5) | 5252.9(5) | 4147.2(2) |
| Ζ | 4 | 8 | 4 |
| $ ho_{ m calcd}~({ m Mg/m^3})$ | 1.459 | 1.230 | 1.331 |
| $\mu (\text{mm}^{-1})$ | 2.469 | 2.235 | 2.879 |
| $R1^{a} [I > 2.0\sigma(I)]$ | 0.0342 | 0.0413 | 0.0253 |
| wR2 ^b (all data) | 0.0883 | 0.0988 | 0.0620 |

 ${}^{a}R1 = \sum_{v} ||F_{o}| - |F_{c}|| / \sum |F_{o}|. \quad {}^{b}wR2 = \left[\sum_{v} [w(F_{o}^{2} - F_{c}^{2})^{2}] / \sum_{v} [w(F_{o}^{2})^{2}]^{1/2}.\right]$

Table 2. Selected Bond Distances (Å) and Angles (deg) for $[(C_5Me_5)_2Y(\mu$ -OTf)]₂, 5, and $(C_5Me_5)_2Y[^iPrNC(H)N^iPr-\kappa^2N,N']$, 8

| 5 | | 8 | |
|-------------|----------|----------------|----------|
| Y(1)-Cnt1 | 2.357 | Y(1)-Cnt1 | 2.392 |
| Y(1)-Cnt2 | 2.356 | Y(1)-Cnt2 | 2.382 |
| Y(1) - O(1) | 2.343(2) | Y(1) - N(1) | 2.350(2) |
| Y(1) - O(2) | 2.367(2) | Y(1) - N(2) | 2.351(2) |
| S(1) - O(1) | 1.454(2) | Y(1) - C(21) | 2.695(3) |
| S(1) - O(2) | 1.455(2) | | |
| | | Cnt1-Y(1)-Cnt2 | 136.2 |
| | | N(1)-Y(1)-N(2) | 58.69(8) |

Table 3. Selected Bond Distances (Å) and Angles (deg) for $(C_5Me_5)_2Y(\mu-Cl)(\mu-\eta^{1}:\eta^5-CH_2C_5Me_4)Y(C_5Me_5)$, 9

| Y(1)-Cnt1 Y(1)-Cnt2 Y(2)-Cnt3 | 2.383 2.349 2.367 | Cnt1-Y(1)-Cnt2 Cnt3-Y(1)-Cnt4 Y(2)-Cl(1)-Y(1) | 136.1 135.3 106.7 |
|--|------------------------------------|---|-------------------------|
| Y(2)-Cnt4 Y(1)-C(36) Y(2)-C(16) | 2.346 2.724(3) | | |
| Y(2)-Cl(1) Y(1)-Cl(1) Y(2)-Cl(1) | 2.786(3) 2.6827(6) 2.7005(6) | | |

RESULTS

Precursor Synthesis. The original synthesis of $(C_5Me_5)_2Y$ - $(\mu-H)(\mu-\eta^{1:}\eta^{5}-CH_2C_5Me_4)Y(C_5Me_5)$, 1, from $[(C_5Me_5)_2YH]_2$, 2, as reported in the literature, required 4 days of stirring and two recrystallizations to obtain an 85% yield (eq 1).^{7g} During the course of these studies, a more efficient synthesis was developed that takes less time and does not require recrystallization. Specifically, complex 1 can be obtained directly from 2 in the solid state by heating under high vacuum (10^{-4} Torr) for 1 day (eq 2). This generates analytically pure 1 in 98% yield.



1 with 1,3,5,7-Cyclooctatetraene. The reaction of 1 with 1,3,5,7-cyclooctatetraene was examined for direct comparison with the reaction of 2 shown in Scheme 1.^{5a} No reaction was observed between 1 and C_8H_8 in both arene and alkane solvents, even upon heating. Since the reduction potentials of C_8H_8 are -1.62 and -1.86 vs SCE,²⁰ this indicated a limit of the reductive capacity of 1 and demonstrated that it is not as reducing as 2.

1 with PhSSPh and PhSH. In contrast to the cyclooctatetraene reaction, complex 1 reacts readily with PhSSPh in benzene over 4 h to generate in 78% yield the arylsulfide complex, $[(C_5Me_5)_2Y(\mu$ -SPh)]_2, 4,^{5a} previously made from $[(C_5Me_5)_2YH]_2$, 2, and PhSSPh. As shown in Scheme 3, this formally involves a two-electron reduction of PhSSPh and the combination of the hydride with the tuck-over methylene carbon to make a C–H bond in a $(C_5Me_5)^-$ ring. The formal half-reactions are shown in Scheme 3. The H⁻ + $(C_5Me_4CH_2)^{2-}$ half-reaction is consistent with the reductive reactivity observed for $(C_5Me_5)U[\mu$ - η ⁵: η ¹: η ¹- $C_5Me_3(CH_2)_2](\mu$ - Scheme 3. Reduction of Diphenyldisulfide by 1 and Possible Half-Reactions



H)₂U(C_5Me_5)₂, 3 (Scheme 2),²¹ with PhSSPh, PhN=NPh, and C_8H_8 substrates.

An alternative route for the formation of $[(C_5Me_5)_2Y(\mu SPh)]_2$, 4, involving σ -bond metathesis is shown in Scheme 4. Specifically, if PhSSPh reacts first with the Y–H bond, it could generate one Y–SPh linkage and PhSH. If PhSH subsequently reacts with the Y–CH₂ bond, it would make the second Y–SPh linkage and regenerate a $(C_5Me_5)^-$ anion as observed. To probe this possibility, further studies of the reactivity of 1 were conducted with PhSH.

When the reaction of 1 with 1 equiv of PhSH was conducted in a sealed NMR tube, the characteristic doublet of doublets resonance^{7c} in the ¹H NMR spectrum for the asymmetric bridging hydride ligand disappeared. Shifted tuck-over ligand resonances and new $(C_5Me_5)^-$ resonances at 2.11, 2.09, 1.88, and 1.80 ppm in a 6:30:6:15 ratio, consistent with the formation of **A**, Scheme 4, are present, and there is no evidence for **4** in the spectrum. This suggests that PhSH first reacts with the hydride ligand, but attempts to isolate this intermediate were unsuccessful. When a second equivalent of PhSH is added, **4** is formed.

1 with Silver Triflate. The reaction of **1** with silver triflate generates $[(C_5Me_5)_2Y(\mu\text{-OTf})]_2$, **5**, in 50% yield (eq 3). A black byproduct consistent with silver metal was also formed. The triflate complex, **5**, was identified by an X-ray crystallographic study of a sample made independently from $[(C_5Me_5)_2YH]_2$, **2**, with AgOTf (eq 4). This reaction also forms silver metal as a byproduct, but **5** could be isolated in a significantly higher yield, 97%.

Complex 5 exists in the solid state as a symmetrically bridged dimer (Figure 1). The bridging triflate unit provides enough



Figure 1. Thermal ellipsoid plot of $[(C_3Me_5)_2Y(\mu$ -OTf)]_2, 5, drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

separation between the two metal centers that the four ring centroids describe a square plane, rather than the tetrahedral arrangement more common with dimeric yttrium and lanthanide metallocenes with smaller bridging ligands, such as $[(C_5Me_5)_2Y]_2(\mu-\eta^2:\eta^2-N_2)^{.22}$ The structure of **5** is similar to that of other organometallic bis(ring) f-element bridging triflate complexes, such as $[(C_5H_5)_2Yb(\mu-OTf)]_2^{.23}$ and $[(C_5Me_5)-(C_8H_8)U(\mu-OTf)]_2^{.24}$ Bond lengths and angles (Table 2) are within the normal range and are given in the Supporting Information.

1 with Et₃NHBPh₄. The reaction of **1** with 2 equiv of Et_3NHBPh_4 cleanly produces the previously characterized $(C_5Me_5)_2Y(\mu$ -Ph)_2BPh_2, **6**,¹⁵ in good yield. H₂ and Et_3N were identified as byproducts by ¹H NMR spectroscopy¹⁶ (eq 5).

Scheme 4. Possible σ -Bond Metathesis Reaction Pathway to $[(C_5Me_5)_2Y(\mu$ -SPh)]_2, 4, from $(C_5Me_5)_2Y(\mu-H)(\mu-\eta^1:\eta^5-CH_2C_5Me_4)Y(C_5Me_5), 1$



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To probe the origin of the hydrogen atom that reacts with $(CH_2C_5Me_4)^{2-}$ to make $(C_5Me_5)^-$, the reaction of 1 with 2 equiv of Et₃NDBPh₄ was examined. The ²H NMR spectrum of the products of the reaction of 1 with 2 equiv of Et₃NDBPh₄ shows incorporation of deuterium into the $(C_5Me_5)^-$ ring as well as formation of HD.¹⁷ Et₃NDBPh₄ apparently deuterates both the M–H and the M–CH₂(ring) positions. Hence, eq 5 does not require a pathway in which the bridging $(H)^-$ ligand combines with $(CH_2C_5Me_4)^{2-}$ to form a $(C_5Me_5)^-$ ring.

Carbodiimide Insertion Chemistry. To determine if the reactivity of the $(C_5Me_4CH_2)^{2-}$ and $(H)^-$ ligands in 1 could be differentiated by insertion as well as by the PhSH reaction described above, reactivity with a carbodiimide was investigated. Carbodiimides are known to insert into both M–H and M–C bonds.²⁵ However, the reaction of 1 with diisopropyl-carbodiimide gives a product, 7, that has analytical and spectroscopic characteristics consistent with insertion into both Y–H and Y–C bonds, namely, $(C_5Me_5)_2Y{\mu-\eta^5-C_5Me_4CH_2[^iPrNCN^iPr-\kappa^2N,N']}Y(C_5Me_5)[^iPrNC(H)N^iPr-\kappa^2N,N'] (eq 6). Complex 7 was characterized by ¹H and ¹³C$



NMR and IR spectroscopy and by elemental analysis. The ¹H NMR spectrum shows resonances for two $(C_5Me_5)^-$ ligand environments in a 30:15 ratio and resonances in a 6:6:2 ratio for a former tuck-over ligand that is now tethered to an amidinate. The ¹³C NMR spectrum contains resonances at 162.1 and 168.8 ppm that are indicative of two unique amidinate environments. When 1 equiv of carbodiimide was used, only resonances consistent with 7 and 1 were observed.

For comparison with eq 6, the reaction of hydride 2 with diisopropylcarbodiimide was examined. This produced the insertion product $(C_5Me_5)_2Y[^{i}PrNC(H)N^{i}Pr-\kappa^2N,N']$, 8, in quantitative yield (eq 7). Complex 8 was characterized by X-ray



diffraction (Figure 2) and has a conventional 8-coordinate yttrium metallocene structure with the κ^2 -amidinate in the



Figure 2. Thermal ellipsoid plot of $(C_5 Me_5)_2 Y[^i PrNC(H)N^i Pr-\kappa^2 N, N']$, **8**, drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

metallocene wedge. The bond distances and angles match well with those of $(C_5Me_5)_2U[^iPrNC(Me)N^iPr-\kappa^2N_iN']^{26}$ when the 0.125 Å difference in ionic radii²⁷ of the metal centers are accounted for. Details on these normal distances and angles are given in Table 2 and the Supporting Information.

1 with Trimethylsilyl Chloride. The reactivity of 1 with Me₃SiCl was examined since this reagent previously differentiated reactivity with uranium hydrides and alkyls and produced an unusual tethered metallocene, $(C_5Me_5)(Cl)U$ - $(\eta^5-C_5Me_4CH_2SiMe_2CH_2-\kappa C)$,²¹ in the reaction with the tuck-in tuck-over dihydride uranium bimetallic complex, (C_5Me_5) - $U[\mu-\eta^5:\eta^1:\eta^1-C_5Me_3(CH_2)_2](\mu-H)_2U(C_5Me_5)_2$, 3⁹ (eq 8).



Since the presence of multiple reactive sites and the variable oxidation states of uranium in 3 gave many potential reaction pathways for eq 8, it was of interest to examine the less complicated yttrium reaction. Trimethylsilyl chloride has previously been found to react with bridging alkyl groups in lanthanide metallocenes, as shown in eq $9.^{28}$



As shown in eq 10, 1 equiv of Me_3SiCl reacts exclusively with the bridging hydride in 1 to form the tuck-over halide complex



 $(C_5Me_5)_2Y(\mu$ -Cl) $(\mu$ - η^1 : η^5 -CH₂ $C_5Me_4)Y(C_5Me_5)$, 9, in 96% yield. Complex 9 was definitively identified by X-ray crystallography (Figure 3).



Figure 3. Thermal ellipsoid plot of $(C_5Me_5)_2Y(\mu-Cl)(\mu-\eta^1:\eta^5-CH_2C_5Me_4)Y(C_5Me_5)$, **9**, drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

The ¹³C NMR spectrum of **9** contains a doublet at 32.4 ppm assigned to the tuck-over carbon. The ${}^{1}J_{\rm YC}$ coupling constant of 40 Hz is similar to the 35 Hz coupling constant seen in **1** and in the range (25–56 Hz) of other Y–C bonds.²⁹ To our knowledge, tuck-over chloride **9** is the first example of a tuck-over metallocene containing a halide ligand.

Structure of $(C_5 Me_5)_2 Y(\mu - CI)(\overline{\mu} - \eta^1 : \eta^5 - CH_2 C_5 Me_4) Y$ - (C_5Me_5) , 9. The analysis of the structure of 9 is not as straightforward as that of the hydride analogue, $(C_sMe_s)_2Y(\mu$ -H) $(\mu - \eta^{1}: \eta^{5}-CH_{2}C_{5}Me_{4})Y(C_{5}Me_{5})$, 1, since, in 9, the crystallographic data (Table 3) display two Y-C distances that could be tuck-over connections. The 2.766(3) Å Y(2)-C(16) distance is similar to the 2.724(3) Å Y(1)-C(36) distance, and either of these could be the Y-CH₂C₅Me₄ tuck-over linkage. In contrast, in 1, the $Y-CH_2C_5Me_4$ tuck-over distance is 2.631 Å and the shortest Y…CH₃ nonbonding distance is 2.846 Å. The NMR data on 9 as well as its reactivity clearly indicate that it contains a single Y-CH₂ bond. It was not possible to uniquely assign carbon atoms C(16) and C(36) as either CH_2 or CH_3 units. The most reasonable model results by assuming that the CH₂ and CH₃ units are disordered over these two positions. For the scrambled atoms, six hydrogen atoms, each with 5/6 site occupancy, were included using a riding model to account for five hydrogen atoms equally distributed over the two sites.

The Y–Cl bond distances also do not indicate a specific C(16) versus C(36) assignment since they are similar. The Shannon ionic radii²⁷ for seven- and eight-coordinate Y³⁺differ by 0.059 Å, but the 2.6827(6) and 2.7005(6) Å Y(2)–Cl(1) and Y(1)–Cl(1) bond distances are much closer. In contrast, the Y–(μ -Cl) bond distances in (C₅Me₅)₂Y(μ -Cl)YCl-(C₅Me₅)₂³⁰ are 2.776(5) and 2.640(5) Å.

The substitution of the larger $(Cl)^-$ ligand for $(H)^-$ in 9 versus 1 showed the following differences in structure. The Y…Y nonbonding distance expanded from 3.911 Å in 1 to

4.319 Å in 9. As a result of the increased distance between the metal centers, the Cnt1-Y(1)-Cnt2/Cnt3-Y(2)-Cnt4 dihedral angle decreased from 81.1° in 1 to 60.8° in 9, which is reasonable due to the larger Y…Y distance (cf. 5 above).

Reactivity of a Tuck-Over Chloride with Phenylacetylene. Tuck-over chloride 9 offers the chance to examine the reactivity of the tuck-over bond without the presence of the hydride ligand. Complex 9 reacts with HC \equiv CPh to form a new complex formulated as $(C_5Me_5)_2Y(\mu$ -Cl) $Y(C_5Me_5)_2(C\equiv$ CPh), 10 (eq 11). Protonation of the tuck-over linkage



evidently reformed a $(C_5Me_5)^-$ ligand in this reaction. Since single crystals were not obtainable, its structure is proposed based on spectroscopic data and the fact that addition of THF forms the previously identified THF adducts, $(C_5Me_5)_2Y(C \equiv CPh)(THF)^{18}$ and $(C_5Me_5)_2YCI(THF)^{19}$ (eq 11). The ¹³C NMR spectrum of **10** is indicative of a terminal alkynide bound to yttrium, showing a doublet for both the α and the β carbons of the alkynide. The ¹ $J_{YC} = 69$ Hz and ² $J_{YC} = 12$ Hz values for **10** are similar to those reported for terminal alkynides bound to yttrium (53–74 and 5–13 Hz, respectively).^{4,18,31} If the alkynide bridged both yttrium centers, the ¹³C NMR resonance for the α carbon would be expected as a triplet (typically, ¹ $J_{YC} =$ 20 Hz) due to coupling to both yttrium atoms.

DISCUSSION

The reaction of $(C_5Me_5)_2Y(\mu-H)(\mu-\eta^{1}:\eta^5-CH_2C_5Me_4)Y-(C_5Me_5)$, 1, with silver triflate (eq 3) is the most straightforward example of the reduction chemistry shown in Scheme 3, in which a hydride ligand and an alkyl anion combine to make a methyl C–H bond in a $(C_5Me_5)^-$ ligand and deliver two electrons to a substrate. In this system, other than the toluene solvent, there is no other source of hydrogen, except the hydride attached to yttrium, to convert the $(CH_2C_5Me_4)^{2-}$ ligand to $(C_5Me_5)^-$. Hence, in the absence of other reaction pathways, 1 can function as a two-electron reductant according to the formal half-reaction in eq 12. This is



similar to the reactivity of 3^9 (Scheme 2). The details of how the hydrides and alkyl anions combine in these complexes, including the viability of radical intermediates, are unknown.

In all the other reduction reactions in this study, the net reaction is a two-electron reduction with formation of a C–H bond, but pathways other than combining the hydride and alkyl anion are possible. In the case of the Et_3NDBPh_4 reaction (eq 5), the incorporation of deuterium into the (C_5Me_5)⁻ product and formation of HD clearly indicate that protonolysis reactions with the Y–H and Y–C (tuck-over) bonds are

occurring. This is the first definitive evidence that a conventional mechanistic alternative, protonolysis, can be functioning in hydride alkyl anion reactions of electropositive elements.

The reaction of Me₃SiCl with **1** to form $(C_5Me_5)_2Y(\mu$ -Cl) $(\mu$ - $\eta^1:\eta^5$ -CH₂C₅Me₄)Y(C₅Me₅), **9** (eq 10), similarly demonstrates that σ -bond metathesis occurs, in this case, between an Y–H bond and a Si–Cl bond. It also shows that, at least with Me₃SiCl, the hydride moiety in **1** is the more reactive.

The Me₃SiCl reaction, eq 10, is significantly different from the reaction with 3,^{9,21} eq 8, but this may be due to the complication of the U⁴⁺/U³⁺ redox couple available in 3. Reactions of 1 with carbodiimide to form $(C_5Me_5)_2Y{\mu-\eta^5}$ - $C_5Me_4CH_2[^{i}PrNCN^{i}Pr-\kappa^2N,N']$ }Y $(C_5Me_5)[^{i}PrNC(H)N^{i}Pr-\kappa^2N,N']$, 7, did not differentiate the reactivity of these two functionalities. A variety of amidinate complexes of f-elements have been synthesized,³² but they usually are prepared either by salt metathesis or by insertion^{25b-d,33} into an M–C or M–N bond. Only recently has the first example of an insertion of a carbodiimide into a Ln–H bond (Ln = rare earth element) been reported.^{25e} Complexes 7 and 8 show that this reaction has some generality.

The PhSSPh reaction (Scheme 3) can also occur via σ -bond metathesis if the Y–H bond reacts first with PhSSPh to form PhSH as an intermediate. This requires a specific sequence that depends on the hydride being more reactive, which is the case with Me₃SiCl. The PhSH reaction (Scheme 4) supports this idea as the distinctive hydride resonance of 1 disappears with addition of 1 equiv of PhSH.

The reaction of $(C_5Me_5)_2Y(\mu-Cl)(\mu-\eta^{1}:\eta^5-CH_2C_5Me_4)Y-(C_5Me_5)$, 9, with $HC\equiv CPh$ to form $(C_5Me_5)_2Y(\mu-Cl)Y-(C_5Me_5)_2(C\equiv CPh)$, 10 (eq 11), demonstrates that the tuckover alkyl linkage can be readily protonated by external reagents if there are no more reactive moieties (like the hydride) present. The reaction of 9 with $HC\equiv CPh$ is consistent with the second reaction in Scheme 4, in which a protic reagent reacts with the tuck-over M-C bond.

CONCLUSION

The yttrium tuck-over complex, $(C_5Me_5)_2Y(\mu-H)(\mu-\eta^1:\eta^5 CH_2C_5Me_4$)Y(C₅Me₅), 1, like the uranium tuck-in tuck-over complex, $(C_5Me_5)U[\mu-\eta^5:\eta^1:\eta^1-C_5Me_3(CH_2)_2](\mu-H)_2U$ - $(C_5Me_5)_{2i}$, 3, is capable of accomplishing net reductive chemistry, in which an alkyl and a hydride combine to form a C-H bond and release two electrons to a substrate. With silver triflate, this appears to occur via combination of an alkyl anion and a hydride. However, with all the other substrates examined in this study, protonolysis/ σ -bond metathesis appear to be viable alternative mechanisms. Strong evidence for σ bond metathesis is found in Et₃NHBPh₄ and Me₃SiCl reactions. The PhSSPh and PhSH reactions also suggest that this more conventional route is viable. As found in studies on 3, the reaction mechanism may be substrate-dependent. Regardless of the mechanism(s), two-electron reduction must be added to the list of reactions possible with tuck-over hydrides of Y³⁺.

ASSOCIATED CONTENT

Supporting Information

X-ray diffraction data, atomic coordinates, thermal parameters, and complete bond distances and angles for compounds 5, 8, and 9 (CCDC numbers 820378–820380, respectively). This

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

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Notes

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