JACS
ARTICLES
Published on Web 06/10/2008

Reductive Reactivity of the Organolanthanide Hydrides, $[(C_5Me_5)_2LnH]_x$, Leads to *ansa*-Allyl Cyclopentadienyl $(\eta^5\text{-}C_5Me_4CH_2{-}C_5Me_4CH_2\text{-}\eta^3)^{2-}$ and Trianionic Cyclooctatetraenyl $(C_8H_7)^{3-}$ Ligands

William J. Evans,*,† Benjamin M. Schmiege,† Sara E. Lorenz,† Kevin A. Miller,† Timothy M. Champagne,† Joseph W. Ziller,† Antonio G. DiPasquale,‡ and Arnold L. Rheingold‡

Department of Chemistry, University of California, Irvine, California 92697-2025, and Department of Chemistry and Biochemistry, University of California, San Diego, 9500 Gilman Drive, MC 0358 La Jolla, California 92093-0358

Received February 15, 2008; E-mail: wevans@uci.edu

Abstract: The reductive reactivity of lanthanide hydride ligands in the $[(C_5Me_5)_2LnH]_x$ complexes (Ln = Sm, La, Y) was examined to see if these hydride ligands would react like the actinide hydrides in $[(C_5Me_5)_2AnH_2]_2$ (An = U, Th) and $[(C_5Me_5)_2UH]_2$. Each lanthanide hydride complex reduces PhSSPh to make $[(C_5Me_5)_2Ln(\mu\text{-SPh})]_2$ in ~90% yield. $[(C_5Me_5)_2SmH]_2$ reduces phenazine and anthracene to make $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^3{:}\eta^3\text{-}C_{12}H_8N_2)$ and $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^3{:}\eta^3\text{-}C_{10}H_{14})$, respectively, but the analogous $[(C_5Me_5)_2LaH]_x$ and $[(C_5Me_5)_2YH]_2$ reactions are more complicated. All three lanthanide hydrides reduce C_8H_8 to make $(C_5Me_5)Ln(C_8H_8)$ and $(C_5Me_5)_3Ln$, a reaction that constitutes another synthetic route to $(C_5Me_5)_3Ln$ complexes. In the reaction of $[(C_5Me_5)_2YH]_2$ with C_8H_8, two unusual byproducts are obtained. In benzene, a $(C_5Me_5)Y[(\eta^5\text{-}C_5Me_4CH_2{-}C_5Me_4CH_2\text{-}\eta^3)]$ complex forms in which two $(C_5Me_5)^{1-}$ rings are linked to make a new type of *ansa*-allyl-cyclopentadienyl dianion that binds as a pentahapto−trihapto chelate. In cyclohexane, a $(C_5Me_5)_2Y(\mu\text{-}\eta^8{:}\eta^1\text{-}C_8H_7)Y(C_5Me_5)$ complex forms in which a $(C_8H_8)^{2-}$ ring is metalated to form a bridging $(C_8H_7)^{3-}$ trianion.

Introduction

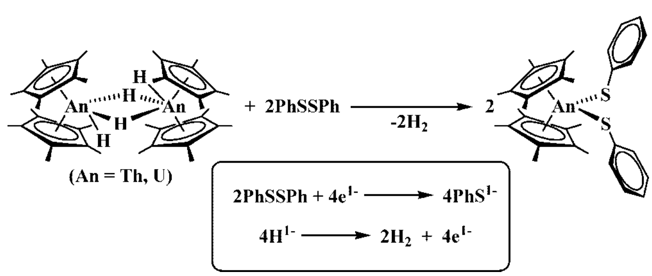
Recent efforts in organoactinide chemistry have shown that the hydride ligands in the uranium and thorium hydrides, $[(C_5Me_5)_2UH]_2$,[1,2] $[(C_5Me_5)_2UH_2]_2$,[1,2] and $[(C_5Me_5)_2ThH_2]_2$,[1] can act as effective reductants formally providing one electron per hydride ligand and generating H_2 as a byproduct, as formally shown in eq 1 and Scheme 1.[2] Although hydride ligands are well-known to be reducing agents,in f element complexes their

$$2H^{1-} \rightarrow 2e^{1-} + H_2 \tag{1}$$

reactivity[3] more commonly involves insertion[4–7] and σ bond metathesis[8–15] rather than reductive chemistry. The fact that the hydride ligands in these organoactinide complexes can act as single electron reductants adds to the variety of transformations available to this class of f element complexes.

To determine if this type of hydride reductive reactivity was also present in organolanthanide hydrides, the reductive chemistry of $[(C_5Me_5)_2SmH]_2$,[16] **1**, $[(C_5Me_5)_2LaH]_x$,[4] **2**, and $[(C_5Me_5)_2YH]_2$, **3**,[13] was examined. The samarium complex was

Scheme 1



chosen since a $Sm^{3+}\text{-}H^{1-}$ unit in which the hydride formally provides one electron according to eq 1 could have reactivity

† University of California, Irvine.
‡ University of California, San Diego.

(1) Marks, T. J.; Fagan, P. J.; Manriquez, J. M.; Maatta, E. A.; Seyam, A. M. *J. Am. Chem. Soc.* **1981**, *103*, 6650.
(2) Evans, W. J.; Miller, K. A.; Kozimor, S. A.; Ziller, J. W.; DiPasquale, A. G.; Rheingold, A. L. *Organometallics* **2007**, *26*, 3568.
(3) Ephritikhine, M. *Chem. Rev.* **1997**, *97*, 2193.
(4) Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8091.
(5) Marks, T. J.; Lin, Z. J. *J. Am. Chem. Soc.* **1990**, *112*, 5515.
(6) Evans, W. J.; Grate, J. W.; Doedens, R. J. *J. Am. Chem. Soc.* **1985**, *107*, 1671.
(7) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 2314.
(8) Thompson, M. E.; Bercaw, J. E. *Pure Appl. Chem.* **1984**, *56*, 1.
(9) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51.
(10) den Haan, K. H.; Teuben, J. H. *J. Chem. Soc., Chem. Commun.* **1986**, 682.
(11) Marks, T. J.; Lin, Z. J. *J. Am. Chem. Soc.* **1987**, *109*, 7979.
(12) Sadow, A. D.; Tilley, T. D. *J. Am. Chem. Soc.* **2003**, *125*, 7971.
(13) den Haan, K. H.; Wielstra, Y.; Teuben, J. H. *Organometallics* **1987**, *6*, 2053.
(14) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *Organometallics* **1991**, *10*, 134.

equivalent to that of Sm^{2+}. This would allow the potential reduction products to be immediately identified if they were identical to those previously synthesized via Sm^{2+}reduction[17] using either $(C_5Me_5)_2Sm(THF)_2$[18] or $(C_5Me_5)_2Sm$.[19] The lanthanum and yttrium complexes were chosen to see if this reduction chemistry could be extended to large and small diamagnetic lanthanides that do not have easily accessible divalent oxidation states.[20,21] The following substrates were examined in order to study the reactivity broadly: PhSSPh, phenazine, 1,3,5,7-cyclooctatetraene, and anthracene.

We report here that the hydride ligands in these lanthanide complexes can effect reductive chemistry as described above. However, these studies have also shown that these lanthanide hydrides can expand f element chemistry in unanticipated ways when examined as reductants with these substrates. This is demonstrated here by (1) the identification of a new route to the sterically crowded $(C_5Me_5)_3Ln$ complexes,[22] (2) the synthesis of an unprecedented example of an *ansa*-allyl-cyclopentadienyl complex, containing a $(\eta^5\text{-}C_5Me_4CH_2{-}C_5Me_4CH_2\text{-}\eta^3)^{2-}$ ligand derived from $(C_5Me_5)^{1-}$ ligands, and (3) the isolation of a complex containing a metalated cyclooctatetraenyl trianion, $(\eta^8\text{:}\eta^1\text{-}C_8H_7)^{3-}$.

Experimental Section

The manipulations described below were performed under argon with rigorous exclusion of air and water using Schlenk, vacuum line, and glovebox techniques. Solvents were dried over Q-5 molecular sieves, and saturated with UHP argon using GlassContour[23] columns. Toluene-d_8, benzene-d_6, and cyclohexane-d_{12} were dried over NaK alloy and vacuum transferred before use. $[(C_5Me_5)_2SmH]_2$, **1**, $[(C_5Me_5)_2LaH]_x$, **2**, and $[(C_5Me_5)_2YH]_2$, **3**, were prepared as previously reported for Nd.[24] $(C_5Me_5)_3Y$[28] was prepared as previously described. Tetramethylfulvene was synthesized by literature methods.[26] PhSSPh, $C_{12}H_8N_2$, and $C_{14}H_{10}$ were purchased from Aldrich and sublimed before use. 1,3,5,7-C_8H_8 was distilled onto molecular sieves and degassed by three freeze−pump−thaw cycles before use. ^1H and ^{13}C NMR spectra were recorded with a Bruker DRX 500 MHz and Varian Inova 800 MHz spectrometers. Infrared spectra were recorded as KBr pellets on a PerkinElmer Spectrum One FT-IR spectrometer. Elemental analyses were performed by Analytische Laboratorien, Lindlar, Germany or on a PerkinElmer series II 2400 C/H/N elemental analyzer. Complexometric analyses were carried out as previously described.[27] X-ray data collection parameters are given in Tables 1 and 2 and full crystallographic information is available in the Supporting Information. The following reactions were all conducted in an argon-filled glovebox free of coordinating solvents.

Table 1. X-ray Data Collection Parameters for $[(C_5Me_5)_2Ln(\mu\text{-SPh})]_2$, Ln = La, **9**; Y, **13**.

empirical formula	$C_{52}H_{70}S_2La_2 \cdot 2(C_7H_8)$, **9**	$C_{52}H_{70}S_2Y_2 \cdot 2(C_7H_8)$, **13**
formula weight	1221.29	1121.29
temperature (K)	163(2)	163(2)
crystal system	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a (Å)	10.3920(10)	10.3399(11)
b (Å)	10.6563(11)	10.4821(11)
c (Å)	14.8522(15)	14.6925(16)
α (deg)	110.9480(10)°	69.574(2)°
β (deg)	98.645(2)°	76.507(2)°
γ(deg)	95.866(2)°	83.370(2)°
volume Å^3	1496.7(3)	1450.1(3)
Z	1	1
ρ_{calcd} (Mg/m^3)	1.355	1.284
μ (mm^{-1})	1.515	2.102
R1 [$I < 2.0\sigma(I)$]^a	0.0245	0.0390
wR2 (all data)^a	0.0648	0.0982

^{a} Definitions: $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$, $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

Table 2. X-ray Data Collection Parameters for $(C_5Me_5)Y(C_8H_8)$, **14**, $(C_5Me_5)Y(\eta^5\text{-}C_5Me_4CH_2\text{-}C_5Me_4CH_2\text{-}\eta^3)$, **16**, and $(C_5Me_5)Y(\mu\text{-}\eta^8\text{:}\eta^1\text{-}C_8H_7)Y(C_5Me_5)_2$, **17**.

empirical formula	$C_{18}H_{23}Y$, **14**	$C_{30}H_{43}Y$, **16**	$C_{38}H_{52}Y_2$, **17**
formula weight	328.27	492.55	686.62
temperature (K)	163(2)	163(2)	208(2)
crystal system	orthorhombic	triclinic	monoclinic
space group	*Pnma*	$P\bar{1}$	$P2_1/n$
a (Å)	10.3396(13)	9.2799(10)	8.420(3)
b (Å)	12.9085(16)	11.1103(12)	16.807(5)
c (Å)	11.7145(14)	12.6823(14)	24.239(8)
α (deg)	90°	83.277(2)°	90°
β (deg)	90°	78.810(2)°	93.001(5)°
γ (deg)	90°	83.363(2)°	90°
volume Å^3	1563.5(3)	1268.1(2)	3425.6(2)
Z	4	2	4
ρ_{calcd} (Mg/m^3)	1.395	1.290	1.331
μ (mm^{-1})	3.715	2.314	3.394
R1 [$I > 2.0\sigma(I)$]^a	0.0298	0.0256	0.0524
wR2 (all data)^a	0.0730	0.0656	0.1285

$[(C_5Me_5)_2Sm(\mu\text{-SPh})]_2$, 4. PhSSPh (6 mg, 0.027 mmol) in 1 mL of benzene-d_6 was added to a J-Young tube containing a frozen solution of **1** (23 mg, 0.027 mmol) in 1 mL of benzene-d_6. The J-Young tube was immediately sealed. As the mixture slowly warmed from −35 °C to room temperature, the color changed from brown to red and bubbles were observed. ^1H NMR spectroscopy showed the quantitative conversion of **1** to previously characterized $[(C_5Me_5)_2Sm(\mu\text{-SPh})]_2$, **4**,[28] and a resonance at 4.46 ppm was indicative of the formation of H_2.

Reaction of 1 with Phenazine. As described above, $C_{12}H_8N_2$ (3 mg, 0.015 mmol) reacted with **1** (11 mg, 0.026 mmol) to form the previously characterized $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^3\text{:}\eta^3\text{-}C_{12}H_8N_2)$,[29] **5**, and H_2. In addition to the formation of **5**, two other $(C_5Me_5)^{1-}$ resonances at 1.16 and 1.03 ppm were observed in a 3:3:1 ratio with that of **5**.

Reaction of 1 with Cyclooctatetraene. As described for **4**, C_8H_8 (1.4 μL, 0.013 mmol) reacted with **1** (11 mg, 0.025 mmol) to form previously characterized $(C_5Me_5)_3Sm$, **6**,[30] and $(C_5Me_5)Sm(C_8H_8)$, **7**,[30] in a 1:1 ratio and H_2.

(15) Booij, M.; Deelman, B.-J.; Duchateau, R.; Postma, D. S.; Meetsma, A.; Teuben, J. H. *Organometallics* **1993**, *12*, 3531.
(16) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 1401.
(17) Evans, W. J. *J. Organomet. Chem.* **2002**, *652*, 61.
(18) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6507.
(19) Evans, W. J.; Hughes, L. A.; Hanusa, T. P. *J. Am. Chem. Soc.* **1984**, *106*, 4270.
(20) Cassani, M. C.; Duncalf, D. J.; Lappert, M. F. *J. Am. Chem. Soc.* **1998**, *120*, 12958.
(21) Hitchcock, P. B.; Lappert, M. F.; Maron, L.; Protchenko, A. V. *Angew. Chem., Int. Ed.* **2008**, *47*, 1.
(22) Evans, W. J.; Davis, B. L. *Chem. Rev.* **2002**, *102*, 2119.
(23) For more information on drying systems see, www.glasscontoursolventsystems.com.
(24) Evans, W. J.; Seibel, C. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1998**, *120*, 6745.
(25) Evans, W. J.; Davis, B. L.; Champagne, T. M.; Ziller, J. W. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 12678.
(26) Jutzi, P.; Heidemann, T.; Neumann, B.; Stammler, H. G. *Synthesis* **1992**, 1096.
(27) Evans, W. J.; Engerer, S. C.; Coleson, K. M. *J. Am. Chem. Soc.* **1981**, *103*, 6672.
(28) Evans, W. J.; Miller, K. A.; Lee, D. S.; Ziller, J. W. *Inorg. Chem.* **2005**, *44*, 4326.
(29) Evans, W. J.; Gonzales, S. L.; Ziller, J. W. *J. Am. Chem. Soc.* **1994**, *116*, 2600.
(30) Evans, W. J.; Gonzales, S. L.; Ziller, J. W. *J. Am. Chem. Soc.* **1991**, *113*, 7423.

Reaction of 1 with Anthracene. As described for **4**, $C_{14}H_{10}$ (8 mg, 0.020 mmol) was added to **1** (2 mg, 0.010 mmol). As the mixture slowly warmed from −35 °C to room temperature, the color changed from brown to dark brown-green and bubbles were observed. ^{1}H NMR spectroscopy showed the conversion of **1** to previously characterized $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^3{:}\eta^3\text{-}C_{14}H_{10})$,[29] **8**, and a resonance at 4.46 ppm was indicative of the formation of H_2, along with unreacted starting material, **1**. In addition to the 1.26 and 1.42 ppm resonances of **8**, three other resonances of similar intensity in the $(C_5Me_5)^{1-}$ region were observed at 1.50, 1.11, and 0.40 ppm.

$[(C_5Me_5)_2La(\mu\text{-SPh})]_2$, 9. PhSSPh (26 mg, 0.12 mmol) was added to a stirred solution of pale-yellow $[(C_5Me_5)_2LaH]_x$, **2**, (97 mg, 0.12 mmol) in benzene (5 mL). The color changed to a lighter yellow and bubbles were observed. After the mixture was stirred for 12 h, the pale-yellow solution was evaporated to yield **9** as a pale-yellow crystalline powder (112 mg, 91%). ^{1}H NMR (500 MHz, benzene-d_6) δ 2.17 (s, 30H, C_5Me_5), 6.97 (t, 1H, $^3J_{HH}$ = 7 Hz, *p*-H), 7.13 (t, 2H, $^3J_{HH}$ = 7 Hz, *m*-H), 7.23 (d, $^3J_{HH}$ = 8 Hz, *o*-H). ^{13}C NMR (125 MHz, benzene-d_6) δ 12.5 (C_5Me_5), 122.9 (C_5Me$_5$), 124.5 (*p*-phenyl), 129.4 (*m*-phenyl), 132.4 (*o*-phenyl). IR (KBr) 3059w, 2906s, 2856s, 2726w, 1579m, 1474s, 1436m, 1379w, 1083m, 1024m, 737vs, 692s cm^{-1}. Anal. Calcd for $C_{52}H_{70}S_2La_2$: C, 60.23; H, 6.80; S, 6.18; La, 26.79. Found: C, 58.93; H, 6.19; S, 6.08; La, 27.6. A similar reaction was carried out with PhSSPh (3 mg, 0.02 mmol) and **2** (10 mg, 0.02 mmol) in benzene-d_6 in a sealed J-Young tube. After 20 min, the ^{1}H NMR spectra showed complete conversion of starting materials to new products displaying resonances consistent with the formation of H_2 (4.46 ppm) and **9**.

Reaction of 2 with Phenazine. As described for **4**, $C_{12}H_8N_2$ (3 mg, 0.016 mmol) was added to **2** (13 mg, 0.032 mmol). As the mixture slowly warmed from −35 °C to room temperature, the color changed from pale yellow to bright red and bubbles were observed. ^{1}H NMR spectroscopy showed the conversion of **2** to previously characterized $[(C_5Me_5)_2La]_2(\mu\text{-}\eta^3{:}\eta^3\text{-}C_{12}H_8N_2)$, **10**,[31] and a resonance at 4.46 ppm was indicative of the formation of H_2. In addition to the 2.06 ppm $(C_5Me_5)^{1-}$ resonance of **10**, two other $(C_5Me_5)^{1-}$ resonances at 1.96 and 1.82 ppm were observed each with 1.5 times the intensity of that of the 2.06 resonance.

Reaction of 2 with Cyclooctatetraene. As described for **4**, C_8H_8 (2 μL, 0.020 mmol) was added via syringe to **2** (16 mg, 0.039 mmol). As the mixture warmed to room temperature, a transient purple solution formed. Subsequently (∼10 min), the color changed from pale yellow to orange, and bubbles were observed. The ^{1}H NMR spectrum contained several resonances in the $(C_5Me_5)^{1-}$ region, but the resonance at 2.00 ppm that matched that reported for $(C_5Me_5)_3La$, **12**[32] was predominant. A resonance at 4.46 ppm matched that for H_2. Addition of THF to the sample generated the 1.80 and 6.36 ppm resonances of previously characterized $(C_5Me_5)La(C_8H_8)(THF)$.[33,34]

$[(C_5Me_5)_2Y(\mu\text{-SPh})]_2$, 13. PhSSPh (30 mg, 0.14 mmol) was added to a stirred suspension of pale-pink $[(C_5Me_5)_2YH]_2$, **3**, (100 mg, 0.14 mmol) in hexane (5 mL). The color changed to a light yellow and bubbles were observed. After the mixture was stirred for 30 min, the pale-yellow solution was evaporated to yield **13** as a pale-yellow powder (117 mg, 90%). Crystals of **13** suitable for X-ray diffraction were grown at −35 °C from a concentrated toluene solution. ^{1}H NMR (500 MHz, cyclohexane-d_{12}) δ 2.00 (s, C_5Me_5, 60H), 6.88 (d, 4H, $^3J_{HH}$ = 8 Hz, *m*-H), 6.92 (t, 2H, $^3J_{HH}$ = 7 Hz, *p*-H), 7.01 (m, 4H,$^3J_{HH}$ = 7 Hz, *o*-H) ^{13}C NMR (125 MHz, cyclohexane-d_{12}) δ 12.3 (C_5Me_5), 121.0 (C_5Me$_5$), 124.5 (*m*-phenyl), 130.0 (*o*-phenyl), 131.7 (*p*-phenyl). IR (KBr) 2910s, 2859s, 1578s, 1473s, 1435s, 1380m, 1089s, 1023s, 732s, 689s cm^{-1}. Anal. Calcd. for $C_{52}H_{70}S_2Y_2$: Y, 19.5. Found: 19.0. A similar reaction was carried out with PhSSPh (2 mg, 0.01 mmol) and **3** (7 mg, 0.01 mmol) in cyclohexane-d_{12} in a sealed J-young tube. After 20 min, the ^{1}H NMR spectra showed complete conversion of the starting material to new products displaying resonances consistent with H_2 and **13**.

$(C_5Me_5)Y(\eta^5\text{-}C_5Me_4CH_2\text{−}C_5Me_4CH_2\text{-}\eta^3)$, 16. C_8H_8 (2.4 μL, 0.021 mmol) was added via syringe to a stirred slurry of **3** (15 mg, 0.021 mmol) in 0.5 mL of benzene-d_6. The white slurry immediately changed to a deep red. The formation of previously characterized $(C_5Me_5)Y(C_8H_8)$, **14**,[33,34] and tetramethylfulvene was observed along with a new resonance in the ^{1}H NMR spectrum at 2.01 ppm. Red crystals of **16** suitable for X-ray diffraction were grown via slow evaporation of the solution at 25 °C in an NMR tube. Yellow crystals of **14** suitable for X-ray diffraction were also isolated and structurally characterized. ^{13}C NMR spectroscopy revealed the presence of $(C_5Me_5)_3Y$, **15**,[25] whose ^{1}H NMR resonance overlapped with the 2.01 ppm resonance. On the basis of these overlapping resonances the maximum yield of **16** appears to be less than 50% of that obtained for **14**.

$(C_5Me_5)_2Y(\mu\text{-}\eta^8{:}\eta^1\text{-}C_8H_7)Y(C_5Me_5)$, 17. C_8H_8 (7 μL, 0.065 mmol) was added via syringe to a suspension of **3** (46 mg, 0.065 mmol) stirred in cyclohexane. Upon addition, a transient dark-purple color immediately formed that quickly turned red. The solution was stirred for 1.5 h, and the solvent was removed under vacuum leaving a bright red-orange powder. Pale-orange crystals of **17** (7 mg, 15%) suitable for X-ray diffraction were selectively grown from a saturated solution of hexanes at −35 °C over 24 h. After isolation of **17**, solvent was removed under vacuum leaving a red-orange powder. ^{1}H NMR spectroscopy showed a 1:1 ratio of $(C_5Me_5)Y(C_8H_8)$, **14**: $(C_5Me_5)_3Y$, **15**.[25] ^{1}H NMR (500 MHz, cyclohexane-d_{12}) δ 6.24 (m, 2H, C_8H_7), 6.15 (m, 3H, C_8H_7), 5.53 (d, 2H, $^3J_{HH}$ = 9 Hz, C_8H_7), 2.07 (s, 15H, C_5Me_5), 1.77 (s, 15H, C_5Me_5), 1.18 (s, 15H, C_5Me_5). ^{13}C NMR (cyclohexane-d_{12}) δ 157.0 (C_8H_7, d, $^1J_{YC}$ = 34 Hz), 118.7 (C_5Me$_5$), 118.2 (C_5Me$_5$), 116.0 (C_5Me$_5$), 97.9 (C_8H_7, d, $^1J_{YC}$ = 3 Hz, β-*C*), 97.5 (C_8H_7, d, $^1J_{YC}$ = 3 Hz, γ-*C*), 96.8 (C_8H_7, dd, $^1J_{YC}$ = 4 Hz, α-*C*), 95.2 (C_8H_7, d, $^1J_{YC}$ = 4 Hz, δ-*C*), 11.8 (C_5Me_5), 10.6 (C_5Me_5), 10.1 (C_5Me_5). IR (KBr) 2947s, 2905s, 2857s, 2725m, 2591m, 1429s, 1377s, 1021m, 872s, 742s, 711s cm^{-1}. Anal. Calcd for $C_{38}H_{52}Y_2$: C, 66.47; H, 7.63. Found: C, 67.06; H, 8.25.

Reaction of $(C_5Me_5)Y(C_8H_8)$, 14, with $(C_5Me_5)_3Y$, 15. 15 (9 mg, 0.018 mmol) was added to a solution of **14** (4 mg, 0.012 mmol) in cyclohexane-d_{12} (0.6 mL). The solution immediately turned red. After 2 days, resonances consistent with **17** and C_5Me_5H as well as both unreacted starting materials, $(C_5Me_5)Y(C_8H_8)$ and $(C_5Me_5)_3Y$, were observed by ^{1}H NMR spectroscopy.

Reaction of 17 with H_2. A J-Young tube containing a suspension of **17** (10 mg, 0.01 mmol) in cyclohexane-d_{12} was attached to a high vacuum line. The suspension was degassed by three freeze−pump−thaw cycles, and 1 atm of H_2 was introduced. The solution gradually became a darker pink color and all solids dissolved. After 2 h ^{1}H NMR spectroscopy showed resonances consistent with the formation of $(C_5Me_5)Y(C_8H_8)$, **14**, and $[(C_5Me_5)_2YH]_2$, **3** in a 2:1 ratio.

X-ray Data Collection, Structure Solution and Refinement. **$[(C_5Me_5)_2La(\mu\text{-SPh})]_2$, 9.** A colorless crystal of approximate dimensions 0.25 mm × 0.30 mm × 0.50 mm was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The SMART[35] program package was used to determine the unit cell parameters and for data collection (20 s/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT[36] and SADABS[37] to yield the reflection data file. Subse-

(31) Scholz, J.; Scholz, A.; Weinmann, R.; Janiak, C.; Schumann, H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1171.
(32) Evans, W. J.; Davis, B. L.; Ziller, J. W. *Inorg. Chem.* **2001**, *40*, 6341.
(33) Bruin, P.; Booij, M.; Teuben, J. H.; Oskam, A. *J. Organomet. Chem.* **1988**, *350*, 17.
(34) Schumann, H.; Kohn, R. D.; Reier, F.-W.; Dietrich, A.; Pickardt, J. *Organometallics* **1989**, *8*, 1388.
(35) SMART Software Users Guide,Version 5.1; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1999.
(36) SMART Software Users Guide,Version 6.0; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1999.
(37) Sheldrick G. M., SADABS, Version 2.10; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 2002.

quent calculations were carried out using the SHELXTL[38] program. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[39] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. The molecule was a dimer and was located about an inversion center. There were two molecules of toluene solvent present per dimeric formula unit. The solvent molecules were disordered and included using multiple components, partial site-occupancy-factors and isotropic thermal parameters. At convergence, wR2 = 0.0648 and Goof = 1.055 for 280 variables refined against 7281 data (0.75 Å), R1 = 0.0245 for those 6812 data with $I > 2.0\sigma(I)$. Details are in Table 1.

$[(C_5Me_5)_2Y(\mu\text{-SPh})]_2$, 13. A pale-yellow crystal of approximate dimensions 0.23 mm × 0.26 mm × 0.32 mm was handled as described for **9**, but with 30 s/frame scan time for a sphere of diffraction data. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct. The molecule was a dimer and was located about an inversion center. There were two molecules of toluene solvent present per dimeric formula unit. At convergence, wR2 = 0.0982 and Goof = 1.057 for 327 variables refined against 7023 data (0.75 Å), R1 = 0.0390 for those 6248 data with $I > 2.0\sigma(I)$.

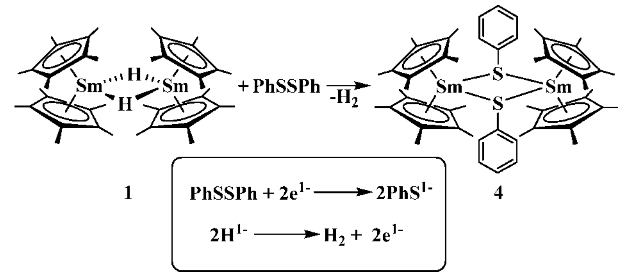
$(C_5Me_5)Y(C_8H_8)$, 14. A yellow crystal of approximate dimensions 0.22 mm × 0.29 mm × 0.30 mm was handled as described for **9**, but with 45 s/frame scan time for a sphere of diffraction data.. The diffraction symmetry was *mmm* and the systematic absences were consistent with the orthorhombic space group *Pnma* that was later determined to be correct. The structure was solved using the coordinates of the samarium analogue[28] and refined on F^2 by full-matrix least-squares techniques. Hydrogen atoms were located from a difference-Fourier map and refined (x,y,z and U_{iso}). The molecule was located on a mirror plane. At convergence, wR2 = 0.0730 and Goof = 1.085 for 138 variables refined against 2000 data (0.75 Å), R1 = 0.0298 for those 1705 data with $I > 2.0\sigma(I)$. Details are in Table 2.

$(C_5Me_5)Y(\eta^5\text{-}C_5Me_4CH_2{-}C_5Me_4CH_2\text{-}\eta^3)$, 16. A red crystal of approximate dimensions 0.10 mm × 0.33 mm × 0.37 mm was handled as described for **9**. Hydrogen atoms were located from a difference-Fourier map and refined (x,y,z and U_{iso}). At convergence, wR2 = 0.0656 and Goof = 1.058 for 452 variables refined against 6114 data (0.75 Å). As a comparison for refinement on F, R1 = 0.0256 for those 5575 data with $I > 2.0\sigma(I)$.

$(C_5Me_5)_2Y(\mu\text{-}\eta^8\text{:}\eta^1\text{-}C_8H_7)Y(C_5Me_5)$, 17. A light-yellow plate 0.15 mm × 0.10 mm × 0.02 mm in size was mounted on a cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 208(2) K using ϕ and ω scans. Crystal-to-detector distance was 60 mm, and exposure time was 20 s per frame using a scan width of 0.5°. Data collection was 99.9% complete to 25.00° in Θ. A total of 19053 reflections were collected covering the indices, $-9 \leq h \leq 10$, $-9 \leq k \leq 20$, $-28 \leq l \leq 28$; 6034 reflections were found to be symmetry independent, with an R_{int} of 0.0747. Indexing and unit cell refinement indicated a primitive, monoclinic lattice. The space group was found to be $P2_1/n$ (No. 14). The data were integrated using the Bruker SAINT[36] software program and scaled using the SADABS[37] software program. Solution by direct methods (SIR-97) produced a complete heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-97). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-97.

(38) Sheldrick, G. M. SHETLXTL Version 6.12,; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 2001.
(39) *International Tables for X-Ray Crystallography*; Kluwer Academic Publishers: Dordrecht, 1992; *Vol. C*.

Scheme 2

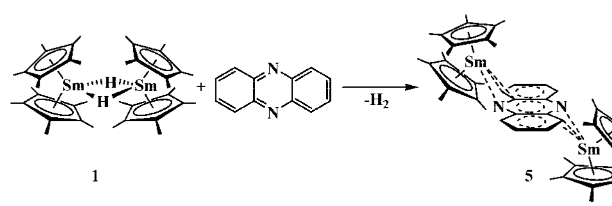


Results

$[(C_5Me_5)_2SmH]_2$ Reactivity. The initial studies of Ln^{3+}-H^{1-} reductive reactivity were done with $[(C_5Me_5)_2SmH]_2$ since examples of possible products were already known from Sm^{2+} reduction chemistry.[17,28–30] Diphenyldisulfide was initially examined as a substrate since (a) it has a substantial reduction potential, −1.7 V vs SCE,[40] (b) it is unlikely to engage in insertion reactivity with lanthanide hydride bonds, and (c) it was successfully reduced by the actinide hydrides, Scheme 1.

$[(C_5Me_5)_2SmH]_2$, **1**, reacts with 1 equiv of PhSSPh to produce crystalline $[(C_5Me_5)_2Sm(\mu\text{-SPh})]_2$, **4**, quantitatively. The ^{1}H NMR spectrum of the reaction mixture also contained a resonance at 4.46 ppm consistent with H_2 as a byproduct, Scheme 2. In this reaction, an overall two-electron reduction of PhSSPh occurred with the electrons formally provided by the two H^{1-} ligands. This synthesis generates **4** in comparable purity and yield to the synthesis from $(C_5Me_5)_2Sm$ and PhSSPh.[28]

Phenazine was examined next since it has been successfully reduced by several lanthanide reduction systems including divalent complexes,[29] $(C_5Me_5)_3Ln$,[41] and the lanthanum dinitrogen complex, $[(C_5Me_5)_2(THF)La]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$.[42] Since phenazine has a reduction potential of −0.364 V vs SCE,[43] the reduction should be successful based in Scheme 2 if no side reactions occur. Indeed **1** reacts with phenazine to form a dark-red product that has a ^{1}H NMR spectrum consistent with the previously characterized $[(C_5Me_5)_2Sm)]_2(\mu\text{-}\eta^3\text{:}\eta^3\text{-}C_{12}H_8N_2)$, **5**, and H_2, eq 2. However, **5** is not the major product and two

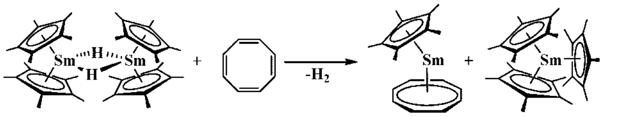


(2)

other resonances were also observed in the $(C_5Me_5)^{1-}$ region. Hence, this route to **5** is complicated by side reactions and the synthesis from $(C_5Me_5)_2Sm$ is preferred.

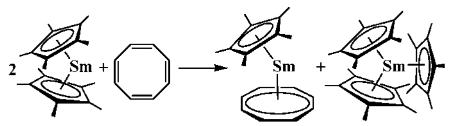
(40) Bradbury, J. R.; Masters, A. F.; McDonell, A. C.; Brunette, A. A.; Bond, A. M.; Wedd, A. G *J. Am. Chem. Soc.* **1981**, *103*, 1959.
(41) Evans, W. J.; Perotti, J. M.; Kozimor, S. A.; Champagne, T. M.; Davis, B. L.; Nyce, G. W.; Fujimoto, C. H.; Clark, R. D.; Johnston, M. A.; Ziller, J. W. *Organometallics* **2005**, *24*, 3916.
(42) Evans, W. J.; Lee, D. S.; Ziller, J. W.; Kaltsoyannis, N. *J. Am. Chem. Soc.* **2006**, *128*, 14176.
(43) Nechaeva, O. N.; Pushkareva, Z. V. *Zh. Obshch. Khim.* **1958**, *28*, 2693.

Complex **1** also reacts with 1,3,5,7-cyclooctatetraene (reduction potentials −1.62 and −1.86 V vs SCE[44]) to form a red-brown solution that has a ^{1}H NMR spectrum consistent with the previously characterized $(C_5Me_5)Sm(C_8H_8)$,[30] **6**, and $(C_5Me_5)_3Sm$,[30] **7**, in a 1:1 ratio, eq 3. It is interesting to note that the analogous reaction between divalent $(C_5Me_5)_2Sm$ and



1 6 7 (3)

C_8H_8, eq 4,[30] was the reaction that generated the first example of a tris(pentamethylcyclopentadienyl) complex, $(C_5Me_5)_3Sm$, a compound that has revealed new $(C_5Me_5)^{1-}$ reactivity due to



6 7 (4)

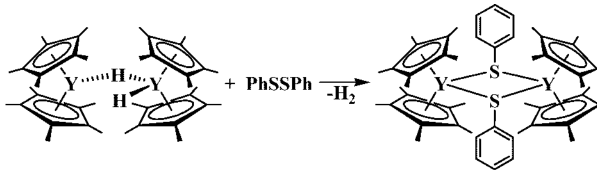
the steric crowding.[22,45] Evidently $(C_5Me_5)_3Sm$ could have been discovered through samarium hydride chemistry according to eq 3 and separated from **6** as described earlier.[30] Equations 3 and 4 demonstrate the equivalence of reduction chemistry between Sm^{3+}-H^{1-} and Sm^{2+}.

Complex **1** also reduces anthracene which has reduction potentials of −1.83 to −1.99 V vs SCE.[46] The previously known $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^3\text{:}\eta^3\text{-}C_{14}H_{10})$, **8**,[29] is formed, but at least three other $(C_5Me_5)^{1-}$ resonances are observed in the ^{1}H NMR spectrum.

$[(C_5Me_5)_2LaH]_x$ Reactivity. The reactions examined with **1** were also repeated with $[(C_5Me_5)_2LaH]_x$, **2**,[4] to determine the effect of the larger metal on reactivity. Complex **2** reacts with PhSSPh to form $[(C_5Me_5)_2La(\mu\text{-SPh})]_2$, **9**, in a reaction analogous to that of **1**, shown in Scheme 2. The X-ray crystal structure of **9** will be discussed later with that of its isomorphous yttrium analogue.

Complex **2** also reacts with phenazine and C_8H_8 in a manner similar to that of **1**. Hence, the previously characterized $[(C_5Me_5)_2La]_2(\mu\text{-}\eta^3\text{:}\eta^3\text{-}C_{12}H_8N_2)$,[31] **10**, was formed from phenazine analogous to eq 2, but two other resonances were also observed by ^{1}H NMR spectroscopy in the $(C_5Me_5)^{1-}$ region. Complex **2** reacts with C_8H_8 as in eq 3 to form $(C_5Me_5)La(C_8H_8)$, **11**,[33,34] $(C_5Me_5)_3La$, **12**,[32] and H_2, but other products also are formed. The reaction of **2** with anthracene gave a mixture of products none of which corresponded to the anthracenide product, $[(C_5Me_5)_2La]_2(\mu\text{-}\eta^3\text{:}\eta^3\text{-}C_{10}H_{14})$,[47] reported previously.

$[(C_5Me_5)_2YH]_2$ Reactivity. When the reactions described above were examined with the hydride of the smaller metal yttrium, $[(C_5Me_5)_2YH]_2$, **3**,[13] the reaction chemistry was more complicated. As shown in eq 5, **3** reacts cleanly with PhSSPh to effect a two-electron reduction of PhSSPh to make two $(SPh)^{1-}$ ligands and H_2 analogous to Scheme 2, but the reactions

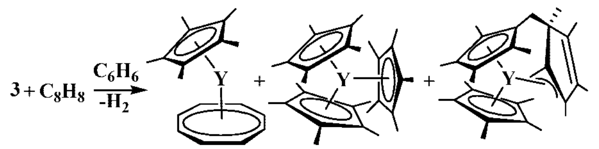


3 13 (5)

with phenazine and anthracene gave mixtures of products that were not easy to separate.

On the other hand, the reactivity of **3** with C_8H_8 showed some new directions in the metallocene chemistry of these metals. In both benzene and cyclohexane $[(C_5Me_5)_2YH]_2$, **3**, reacts with C_8H_8 to form the three products analogous to those in eq 3, i.e. $(C_5Me_5)Y(C_8H_8)$, **14**,[33,34] $(C_5Me_5)_3Y$, **15**,[25] and H_2, but in each solvent an unusual byproduct was isolated.

In benzene a red solution forms from which the unusual *ansa*-allyl-cyclopentadienyl product, $(C_5Me_5)Y(\eta^5\text{-}C_5Me_4CH_2\text{—}C_5Me_4CH_2\text{-}\eta^3)$, **16**, shown in Figure 1 and eq 6, was isolated. The byproducts **14**, **15**, and H_2, were identified by ^{1}H and ^{13}C NMR



14 15 16 (6)

spectroscopy and **16** was identified by X-ray crystallography. It was difficult to identify the ^{1}H NMR resonances of $(C_5Me_5)_3Y$, **15**, due to overlap with complex **16**, but ^{13}C NMR spectroscopy confirmed the presence of $(C_5Me_5)_3Y$.

The $C_{30}H_{43}Y$ composition of **16** is just two hydrogens less than that of $(C_5Me_5)_3Y$, but the structure of **16** is the first of its type. Complex **16** contains one conventional $(C_5Me_5)^{1-}$ ligand, one pentahapto ligand with a CH_2 group [C(6)] in place of a methyl, i.e. a $(\eta^5\text{-}C_5Me_4CH_2)^{1-}$ ligand, and a third five-carbon ring that is substituted with four methyl groups and one CH_2 group that binds as a trihapto allyl ligand, i.e. a $(\eta^3\text{-}C_5Me_4CH_2)^{1-}$ ligand. The latter two ligands are connected via a 1.554(2) Å C(6) to C(21) single bond, where C(21) is a saturated tetrahedral carbon. This bridge forms an unusual *ansa*-type ligand, formally the dianion $(\eta^5\text{-}C_5Me_4CH_2\text{—}C_5Me_4CH_2\text{-}\eta^3)^{1-}$.

The Y−C(η^5-pentamethylcyclopentadienyl) linkages in **16** are very similar to those in the previously characterized allyl complex, $(C_5Me_5)_2Y(\eta^3\text{-}C_3H_5)$.[48] The 2.410 Å Y−($C_5Me_5$ ring centroid) and 2.365 Å Y−($C_5Me_4CH_2$ ring centroid) distances are close to the 2.362−2.381 Å range for $(C_5Me_5)_2Y(\eta^3\text{-}C_3H_5)$.[48] Likewise, the 137.3° (ring centroid)−Y−(ring centroid) angle in **16** is similar to the 138.8° value in the latter compound. The C(21)−C(25) ring is planar to within 0.013 Å, and the 1.341(2) Å C(24)−C(25) distance is consistent with a localized double bond, as shown in eq 6. The C(21)−C(22), C(21)−C(25), and C(23)−C(24) distances are in the 1.476(2)−1.533(2) Å range, Table 3.

The Y−C(η^3-allyl) linkage in **16** is not as symmetrical as it is in $(C_5Me)_2Y(\eta^3\text{-}C_3H_5)$ and has a stronger η^1-component through C(27). The 1.380(2) Å C(22)−C(23) and 1.434(2) Å C(22)−C(27) distances that form part of the allyl component bound to yttrium are not as similar as the analogous distances, 1.391(3) and 1.392(3) Å, in $(C_5Me_5)_2Y(\eta^3\text{-}C_3H_5)$. The 2.450(2)

(44) Mann, C. K.; Barnes, K. K. *Electrochemical Reactions in Nonaqueous Systems*; Bard, A. J., Ed.; Marcel Dekker, Inc.: New York, NY, 1970.
(45) Evans, W. J. *Inorg. Chem.* **2007**, *46*, 3435.
(46) de Boer, E. *Adv. Organomet. Chem.* **1964**, *2*, 115.
(47) Thiele, K.-H.; Bambirra, S.; Schumann, H.; Hemling, H. *J. Organomet. Chem.* **1996**, *517*, 161.
(48) Evans, W. J.; Kozimor, S. A.; Brady, J. C.; Davis, B. L.; Nyce, G. W.; Seibel, C. A.; Ziller, J. W.; Doedens, R. J. *Organometallics* **2005**, *24*, 2269.

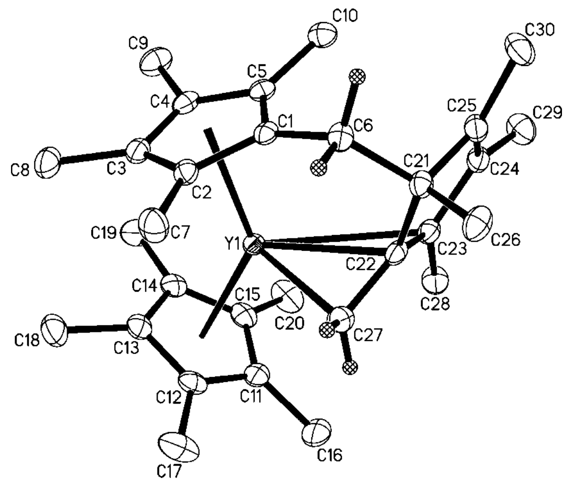


Figure 1. Molecular structure of $(C_5Me_5)Y(\eta^5\text{-}C_5Me_4CH_2{-}C_5Me_4CH_2\text{-}\eta^3)$, **16**, with thermal ellipsoids drawn at the 50% level. Hydrogen atoms have been omitted for clarity.

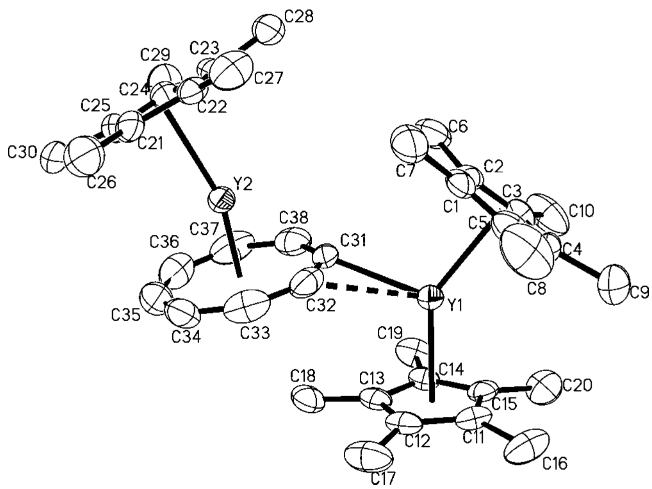
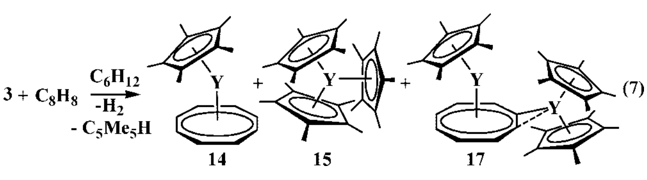


Figure 2. Molecular structure of $(C_5Me_5)Y(\mu\text{-}\eta^8{:}\eta^1\text{-}C_8H_7)Y(C_5Me_5)_2$, **17**, with thermal ellipsoids drawn at the 50% level. Hydrogen atoms have been omitted for clarity.

Å Y−C(27) connection is much shorter than the 2.699(2) Å Y(1)−C(22) and 2.990(2) Å Y(1)−C(23) distances.[48] In $(C_5Me_5)_2Y(\eta^3\text{-}C_3H_5)$,[48] the Y−C(allyl) distances are 2.582(2), 2.582(2), and 2.601(2) Å.

When the reaction of $[(C_5Me_5)_2YH]_2$ with C_8H_8 is conducted in cyclohexane instead of benzene, $(C_5Me_5)Y(C_8H_8)$, **14**, $(C_5Me_5)_3Y$, **15**, and H_2 are again formed, but a different byproduct results. Pale-orange crystals of **17**, the least soluble product in the reaction mixture, could be isolated by crystallization from hexanes at −35 °C. This compound was identified by X-ray crystallography, ^1H and ^{13}C NMR spectroscopy, and reaction chemistry as $(C_5Me_5)Y(\mu\text{-}\eta^8{:}\eta^1\text{-}C_8H_7)Y(C_5Me_5)_2$, **17**, Figure 2. Hence, the overall reaction is shown in eq 7.



The X-ray crystal structure of **17** contained three $(C_5Me_5)^{1-}$ ligands and one C_8 ring. A difference-Fourier map did not locate the hydrogen atoms on the C_8 ring, and initially it was not certain how this $(C_8H_x)^{n-}$ moiety was bound to Y(1). If the C_8 ring is present in the conventional form as $(C_8H_8)^{2-}$, charge balance would suggest the presence of a hydride ligand on one of the yttrium metal centers. Alternatively, metalation of the C_8 ring could result in the formation of a previously unknown $(\eta^8{:}\eta^1\text{-}C_8H_7)^{3-}$ ligand. As discussed below, the structural details and NMR spectroscopy support the latter assignment.

As shown in Table 4, the metrical parameters for Y(2) in **17** are very similar to those in $(C_5Me_5)Y(C_8H_8)$, **14**,[33,34] which was crystallographically characterized in this study for comparison. Hence, the Y−(C_5Me_5 ring centroid) and Y−(C_8H_8 ring centroid) distances in the two complexes are equivalent within the error limits. The 161.7° (C_5Me_5 ring centroid)−Y−(C_8H_7 centroid) angle is smaller than the 171.1° in $(C_5Me_5)Y(C_8H_8)$,

Table 3. Selected Bond Distances (Å) and Angles (deg) for $(C_5Me_5)Y(\eta^5\text{-}C_5Me_4CH_2{-}C_5Me_4CH_2\text{-}\eta^3)$, **16**.[a]

Bond distances	
Y(1)−Cnt(1)	2.365
Y(1)−Cnt(2)	2.410
Y(1)−C(22)	2.6985(15)
Y(1)−C(23)	2.9897(16)
Y(1)−C(27)	2.4502(16)
C(6)−C(21)	1.554(2)
C(1)−C(6)	1.506(2)
C(21)−C(22)	1.533(2)
C(22)−C(23)	1.380(2)
C(22)−C(27)	1.434(2)
C(23)−C(24)	1.476(2)
C(24)−C(25)	1.341(2)
C(25)−C(21)	1.516(2)

Bond Angles	
Cnt(1)−Y(1)−Cnt(2)	137.3
Y(1)−C(1)−C(5)	31.11(4)
Y(1)−C(11)−C(15)	73.63(9)
C(1)−C(6)−C(21)	116.98(12)
C(25)−C(21)−C(22)	103.25(12)
C(25)−C(21)−C(26)	109.34(13
C(22)−C(21)−C(26)	110.08(13)
C(25)−C(21)−C(6)	113.44(13)
C(22)−C(21)−C(6)	112.22(12)
C(26)−C(21)−C(6)	108.43(12)

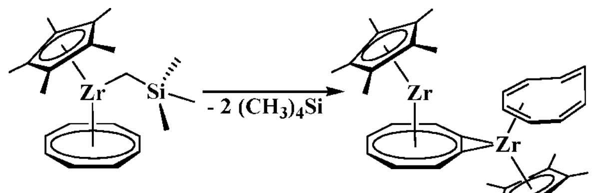
[a] **16** Cnt 1, C(1)−C(5); Cnt 2, C(11)−C(15).

Table 4. Selected Bond Distances (Å) and Angles (deg) for $(C_5Me_5)Y(C_8H_8)$, **14**, and $(C_5Me_5)_2Y(\mu\text{-}\eta^8{:}\eta^1\text{-}C_8H_7)Y(C_5Me_5)$, **17**.

14[a]		**17**[b]	
Y(1)−Cnt1	2.295	Y(2)−Cnt(1)	2.324
Y(1)-Cnt2	1.734	Y(2)−Cnt(2)	1.717
		Y(1)−Cnt(3)	2.347
		Y(1)−Cnt(4)	2.341
Cnt1−Ln(1)−Cnt2	171.1	Cnt1−Ln(2)−Cnt2	161.7
		Cnt3−Ln(1)−Cnt4	141.1
		Y(1)−C(31)	2.374
		Y(1)−C(32)	2.686
C(7)−C(7′)	1.437(11)	C(31)−C(32)	1.394(9)
C(7)−C(8)	1.403(6)	C(32)−C(33)	1.404(9)
C(8)−C(9)	1.362(6)	C(33)−C(34)	1.391(10)
C(9)−C(10)	1.371(6)	C(34)−C(35)	1.365(10)
C(10)−C(10′)	1.383(10)	C(35)−C(36)	1.391(11)
		C(36)−C(37)	1.409(10)
		C(37)−C(38)	1.420(9)
		C(38)−C(31)	1.400(9)

[a] **14** Cnt 1, C(1), C(1′), C(2), C(2′), C(3); Cnt 2, C(7)−C(10′). [b] **17** Cnt 1, C(21)−C(25); Cnt 2, C(31)−C(38); Cnt 3, C(1)−C(5); Cnt 4, C(11)−C(15).

but this could be due to the presence of the C(1)−C(5) $(C_5Me_5)^{1-}$ ring bound to Y(1). This angular difference is similar to that between two zirconium complexes that differ in the degree of C_8 ring metalation: $(C_5Me_5)Zr(C_8H_8)$[49] and $(C_5Me_5)Zr(\mu\text{-}\eta^8\text{:}\eta^2\text{-}C_8H_6)Zr(\eta^4\text{-}C_8H_8)$,[49] **18**, in eq 8. Complex **18** has a doubly metalated $(C_8H_6)^{4-}$ ring and differs from **17** in that it contains

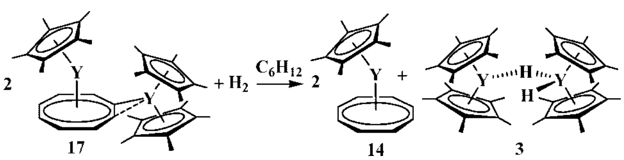


18

a neutral C_8H_8 ligand in place of one of the $(C_5Me_5)^{1-}$ ligands on Y(1). The (C_5Me_5 ring centroid)−Zr−(C_8H_6 centroid angle) in **18** is approximately 10° smaller that that of $(C_5Me_5)Zr(C_8H_8)$,[49] a difference similar to that between **14** and **17**.

In support of a metalated $(C_8H_7)^{3-}$ ligand, the 2.374(7) Å Y(1)−C(31) distance is more consistent with a Y−C single bond than a bond to carbon in a polyhapto ring. For example, in **14** and **17** the Y−C(C_5Me_5) distances are 2.593(2)−2.625(6) Å and the Y−C(C_8 ring) distances are 2.490(6)−2.522(7) Å. In fact, Y(1)−C(31) is on the short side of Y−C single bonds: the Y−C(alkyl) distances in $(C_5Me_5)_2YMe(THF)$[50] and $(C_5Me_5)_2Y[CH(SiMe_3)_2]$[51] are 2.44(2) Å and 2.468(7) Å, respectively. The 2.686(7) Å Y(1)−C(32) distance is reasonable for an agostic interaction. For example, the agostic Y−C(Me) distances in $(C_5Me_5)_2Y[CH(SiMe_3)_2]$ and $(C_5Me_5)_2Y[N(SiMe_3)_2]$[51] are 2.878(7) Å and 2.970(6) Å, respectively.

Since Ln−C(alkyl) bonds will typically undergo σ bond metathesis with H_2 to form Ln−H and the hydrogenated organic fragment, the reaction of **17** with H_2 was examined. ^1H NMR spectroscopy showed the consumption of **17** under H_2 and the formation of **3** and **14** in a 1:2 ratio, eq 9. In the analogous D_2



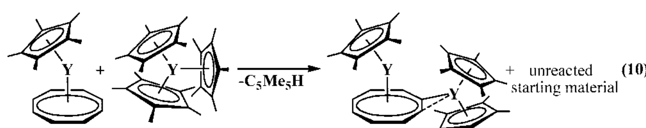
17 **14** **3**

reaction, ^2D NMR spectroscopy showed a single peak consistent with the formation of $(C_5Me_5)Y(C_8H_7D)$.

The ^1H and ^{13}C NMR spectra of **17** were also consistent with the $(C_8H_7)^{3-}$assignment. The ^1H NMR spectrum in cyclohexane-d_{12} displayed three resonances in the $(C_5Me_5)^{1-}$ region at 2.07, 1.77, and 1.18 ppm as well as a sharp doublet at 5.54 ppm corresponding to two protons, a triplet at 6.26 ppm corresponding to two protons, and a multiplet centered at 6.15 ppm that integrated to three protons. The integration corresponds to three $(C_5Me_5)^{1-}$ units as well as a $(C_8H_7)^{3-}$ ring that is not freely rotating.

In the ^{13}C NMR spectrum of **17**, the signal assignable to C(31) in the $(C_8H_7)^{3-}$ ring is split into a doublet by yttrium with a 34 Hz coupling constant. This is within the range observed for J_{Y-C} for other complexes containing Y−C(alkyl) single bonds.[51,52] Except for C(32) adjacent to C(31), the other carbon signals of the $(C_8H_7)^{3-}$ ring are doublets with splitting of 3−4 Hz. This Y−C coupling agrees with that reported for $(C_5Me_5)Y(C_8H_8)$[33,34] for a ring bound η^8 to yttrium. The carbon signal for the C(32) is a doublet of doublets each with 4 Hz coupling. This is consistent with the X-ray data that shows that this carbon is close enough to Y(1) to have an agostic interaction. Thus, the apparent triplet corresponds to the signal being split by both yttrium atoms each with a splitting of 4 Hz. To confirm that the doublets observed were indeed due to yttrium coupling and not due to multiple resonances, the ^{13}C NMR spectrum was examined at 201 MHz. The signals did not split further at this higher field.

When the reaction shown in eq 7 is done in a sealed NMR tube, resonances attributable to C_5Me_5H gradually are observed. This suggested that **17** could be formed by a reaction between the two major products, **14** and **15**. To test this, the reaction of independently isolated $(C_5Me_5)_3Y$[25] and $(C_5Me_5)Y(C_8H_8)$,[33,34] was examined and resonances attributable to **17** were observed by ^1H NMR spectroscopy as shown in eq 10. As in eq 7, only low yields of **17** have been obtained. $[(C_5Me_5)_2YH]_2$ will



14 **15** **17**

metalate both benzene and toluene to form $(C_5Me_5)_2Y(C_6H_5)$ and $(C_5Me_5)_2Y(CH_2C_6H_5)$ respectively,[25] but reaction of $[(C_5Me_5)_2YH]_2$ with $(C_5Me_5)Y(C_8H_8)$ does not form **17**. This reaction yields only unreacted **14** and the "tuckover" product $(C_5Me_5)_2Y(\mu\text{-H})(\mu\text{-}\eta^1\text{:}\eta^5\text{-}CH_2C_5Me_4)Y(C_5Me_5)_2$, that forms over time from solutions of $[(C_5Me_5)_2YH]_2$.[15]

$[(C_5Me_5)_2Ln(\mu\text{-SPh})]_2$ Structures. Both the Ln = La, **9**, and Ln = Y, **13**, examples of $[(C_5Me_5)_2Ln(\mu\text{-SPh})]_2$ were crystallographically characterized for comparison with the known Ln = Sm example.[28] Complex **13** was of particular interest because pentamethylcyclopentadienyl metallocene complexes of the smaller lanthanides generally are so sterically crowded that they form asymmetric bridged bimetallic structures. The four $(C_5Me_5)^{1-}$ rings in a dimer cannot easily fit around a central $Y_2(\mu\text{-X})_2$ core. For example, $[(C_5Me_5)_2YCl]_x$ and $[(C_5Me_5)_2LuMe]_x$ exist as $(C_5Me_5)_2Y(\mu\text{-Cl})YCl(C_5Me_5)_2$[53] and $(C_5Me_5)_2Lu(\mu\text{-Me})LuMe(C_5Me_5)_2$[54,55] in the solid state. Similarly, $[(C_5Me_5)_2YH]_x$ is reported to be an asymmetric dimer at room temperature by NMR spectroscopy.[13] Therefore, an asymmetric structure was expected for **13**.

As shown in Figure 3, **13** unexpectedly crystallizes as a *symmetrical* dimer that is isomorphous with $[(C_5Me_5)_2Sm(\mu\text{-SPh})]_2$[28] and $[(C_5Me_5)_2La(\mu\text{-SPh})]_2$, **9**. Table 5 shows a comparison of distances in the three structures. As expected for isomorphous structures, the bond angles are all similar. The two crystallographically independent Ln−(C_5Me_5 ring centroid) distances in each structure differ according to their eight

(49) Sinnema, P.-J.; Meetsma, A.; Teuben, J. H. *Organometallics* **1993**, *12*, 184.
(50) den Haan, K. H.; de Boer, J. L.; Teuben, J. H.; Smeets, W. J. J.; Spek, A. L. *J. Organomet. Chem.* **1987**, *327*, 31.
(51) den Haan, K. H.; de Boer, J. L.; Teuben, J. H.; Spek, A. L.; Kojic-Prodic, B.; Hays, G. R.; Huis, R. *Organometallics* **1986**, *5*, 1726.
(52) Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 54.
(53) Evans, W. J.; Peterson, T. T.; Rausch, M. D.; Hunter, W. E.; Zhang, H.; Atwood, J. L. *Organometallics* **1985**, *4*, 554.
(54) Evans, W. J.; Perotti, J. M.; Ziller, J. W. *J. Am. Chem. Soc.* **2005**, *127*, 3894.
(55) Watson, P. L.; Roe, D. C. *J. Am. Chem. Soc.* **1982**, *104*, 6741.

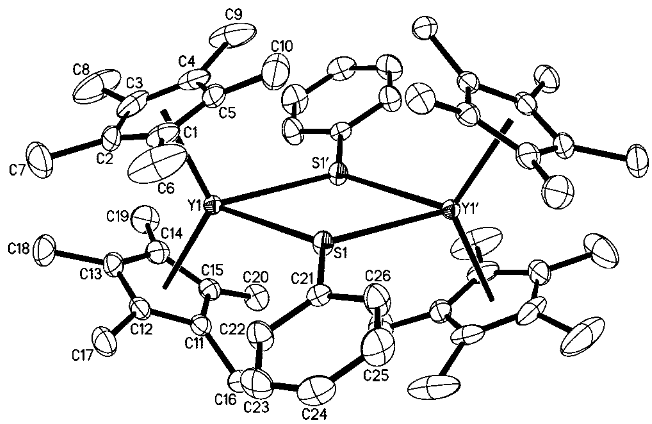


Figure 3. Molecular structure of $[(C_5Me_5)_2Y(\mu\text{-SPh})]_2$, **13**, with thermal ellipsoids drawn at the 50% probability level. $[(C_5Me_5)_2La(\mu\text{-SPh})]_2$, **9**, is isomorphous. Hydrogen atoms are omitted for clarity.

Table 5. Selected Bond Distances (Å) and Angles (deg) for $[(C_5Me_5)_2Ln(\mu\text{-SPh})]_2$ Complexes (Ln = La, **9**; Sm[28] ; Y, **13**)

Ln	La, **9**	Sm[28]	Y, **13**
eight-coordinate ionic radius[56]	1.160	1.079	1.019
Ln(1)−S(1)′	3.0076(6)	2.9341(6)	2.8931(6)
Ln(1)−S(1)	3.0102(6)	2.9388(6)	2.9031(6)
S(1)−C(21)	1.766(2)	1.765(2)	1.766(2)
Ln(1)−Cnt1	2.525	2.429	2.370
Ln(1)−Cnt2	2.560	2.464	2.402
S(1)′−Ln(1)−S(1)	62.841	61.99(2)	61.59(2)
Cnt1−Ln(1)−S(1)	108.6	106.7	107.4
Cnt2−Ln(1)−S(1)	115.2	116.4	116.0
Cnt1−Ln(1)−S(1)′	105.4	108.5	108.9
Cnt2-Ln(1)-S(1)′	116.8	115.5	115.3
Cnt1−Ln(1)−Cnt2	129.1	128.6	128.5
C(21)−S(1)−Ln(1)	116.96(7)	124.82(8)	117.02(8)
Ln(1)′−S(1)−Ln(1)	117.159(17)	118.01(2)	118.41(2)

coordinate ionic radii, 1.160, 1.079, and 1.019 Å for La, Sm, and Y, respectively.[56] The differences in the Ln−S bonds between the La and Sm complexes also follow the trend in ionic radii.

However, the difference between the Y−S distances, 2.9031(6) Å Y(1)−S(1) and 2.8931(6) Å Y(1)−S(1A), and Sm−S analogues, 2.9341(6) and 2.9388(6) Å does not match exactly the 0.06 Å difference in ionic radii of Sm and Y. The Y−S distances are not very much longer than expected, but this may allow the symmetrical dimer to form. The Y−S distances in **13** are much longer than the Y(μ-Cl)Y distances in $(C_5Me_5)_2Y(\mu\text{-Cl})YCl(C_5Me_5)_2$, 2.640(5) and 2.776(5) Å, whereas the 2.370 and 2.402 Å Y−(C_5Me_5 ring centroid) distances in **13** are very similar to the 2.38 and 2.40 Å analogues. To further support that there is little steric crowding in this complex, the four $(C_5Me_5)^{1-}$ ring centroids are arranged in a square planar rather than the more space-efficient tetrahedral arrangement found in many $[(C_5Me_5)_2LnX]_2$ dimers such as $[(C_5Me_5)_2Y]_2(\mu\text{-O})$,[57] $[(C_5Me_5)_2Sm]_2(\mu\text{-O})$,[58] $[(C_5Me_5)_2Sm(\mu\text{-H})]_2$,[16] and $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-N}_2)$.[59]

Discussion

The reactivity of $[(C_5Me_5)_2SmH]_2$ with PhSSPh, phenazine, 1,3,5,7-cyclooctatetraene, and anthracene shows that the hydride ligands in this complex can act as reductants according to eq 1. The $Sm{-}H^{1-}$ unit reacts with these substrates like the Sm^{2+} ion in the divalent samarium metallocenes, $(C_5Me_5)_2Sm(THF)_2$ and $(C_5Me_5)_2Sm$. Although analogous reaction pathways were observed, only with PhSSPh and C_8H_8 were byproduct-free reactions observed.

With $[(C_5Me_5)_2LaH]_x$ and $[(C_5Me_5)_2YH]_2$, clean reductions according to eq 1 were only observed with PhSSPh. Hence, it appears, on the basis of this preliminary data, that hydride ligands in lanthanide complexes have a wider range of reactivity beyond eq 1 compared to hydride ligands in actinide complexes.[2] Since metals both larger and smaller than Sm appear to have a more diverse reaction chemistry, this additional reactivity may be heavily dependent on metal size. This is consistent with a strong metal size dependence on reactivity in the f element series.

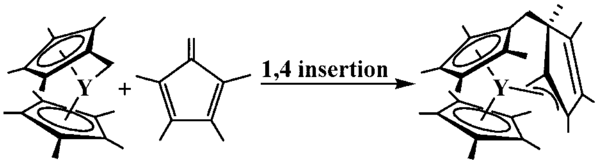
Although these studies revealed that $Ln^{3+}{-}H^{1-}$ complexes are not ideal Ln^{2+} replacements, they do show that $Ln^{3+}{-}H^{1-}$ complexes can participate in reduction chemistry according to eq 1. This is a reaction pathway not traditionally considered for these hydride complexes. Hence, the $(C_5Me_5)_3Ln$ complexes were discovered via Ln^{2+} (eq 4) rather than $Ln^{3+}{-}H^{1-}$ reductive chemistry (eq 3). This reduction reactivity pathway via eq 1 may complicate other types of lanthanide hydride-based reactions. Indeed, obtaining clean reaction chemistry from complexes such as $[(C_5Me_5)_2LaH]_x$ and $[(C_5Me_5)_2YH]_2$ is notoriously difficult. This may be due in part to reductive side reactions according to eq 1.

Although the reactions of $[(C_5Me_5)_2YH]_2$ did not lead to clean reduction as shown in eq 1, they did reveal some new horizons in f element pentamethylcyclopentadienyl and cyclooctatetraenyl chemistry. To our knowledge, $(C_5Me_5)Y(\mu\text{-}\eta^8\text{:}\eta^1\text{-}C_8H_7)Y(C_5Me_5)_2$, **17**, is the first example of a structurally characterized $(\mu\text{-}\eta^8\text{:}\eta^1\text{-}C_8H_7)^{3-}$ ligand in not only f element chemistry but also organometallic chemistry in general.[60] Unusual bridging cyclooctatetraenyl ligands are known in f element complexes, e.g. in $(C_8H_8)Nd(\mu\text{-}\eta^2\text{:}\eta^8\text{-}C_8H_8)Nd(C_8H_8)$,[61] the porphyrinogen complexes, $(C_{38}N_4H_{54})Sm(\mu\text{-}\eta^2\text{:}\eta^2\text{-}C_8H_8)Sm(C_{38}N_4H_{54})$[62] and $[(C_8H_8)(C_5Me_5)An]_2(\mu\text{-}\eta^3\text{:}\eta^3\text{-}C_8H_8)$ (An = U,[63] Th[2]), but they involve $(C_8H_8)^{2-}$ ligands. As described above, a doubly metalated cyclooctatetraenyl group has been identified in a zirconium complex, $(C_5Me_5)Zr(\mu\text{-}\eta^8\text{:}\eta^2\text{-}C_8H_6)Zr(\eta^4\text{-}C_8H_8)$.[49,60] Since $(C_5Me_5)_3Y$ is known to metalate toluene and benzene,[25] the metalation of $(C_5Me_5)Y(C_8H_8)$ by $(C_5Me_5)_3Y$ to form **17** is reasonable. This reaction is an example of C−H activation reactions between complexes, a type of reaction much less investigated than those between complexes and metal-free substrates.

The formation of $(C_5Me_5)Y(\eta^5\text{-}C_5Me_4CH_2{-}C_5Me_4CH_2\text{-}\eta^3)$, **16**, is not as easy to rationalize as that of **17**. However, the isolation of **16** suggests that much remains to be learned about pentamethylcyclopentadienyl chemistry. One conceivable route to **16** involves the reaction of the “tuck-in” complex,

(56) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.
(57) Ringelberg, S. N.; Meetsma, A.; Troyanov, S. I.; Hessen, B.; Teuben, J. H. *Organometallics* **2002**, *21*, 1759.
(58) Evans, W. J.; Grate, J. W.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 405.
(59) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1988**, *110*, 6877.
(60) (a) See the following papers for the closest related species in the literature: Veige, A. S.; Wolczanski, P. T.; Lobkovsky, E. B. *Angew. Chem., Int. Ed.* **2001**, *40*, 3629. (b) Cloke, F. G. N.; Hitchcock, P. B.; Joseph, S. C. P. *J. Chem. Soc., Chem. Commun.* **1994**, 1207. (c) Yin, J.; Klosin, J.; Abboud, K. A.; Jones, W. M. *Tetrahedron Lett.* **1995**, *36*, 3107.
(61) DeKock, C. W.; Ely, S. R.; Hopkins, T. E.; Brault, M. A. *Inorg. Chem.* **1978**, *17*, 625.
(62) Frey, A. S. P.; Gardiner, M. G.; Stringer, D. N.; Yates, B. F.; George, A. V.; Jensen, P.; Turner, P. *Organometallics* **2007**, *26*, 1299.
(63) Evans, W. J.; Nyce, G. W.; Ziller, J. W. *Angew. Chem., Int. Ed.* **2000**, *39*, 240.

$[(C_5Me_5)Y(C_5Me_4CH_2)]_x$, or its equivalent with tetramethylfulvene as shown hypothetically in eq 11. Tetramethylfulvene has



(11)

16

been observed to form in reactions designed to make "$(C_5Me_5)_3Lu$" and could arise from β-hydrogen elimination from a $(C_5Me_5)_2Y(\eta^1\text{-}C_5Me_5)$ form of $(C_5Me_5)_3Y$.[22] $[(C_5Me_5)_2YH]_2$ is known to have C−H activation reactivity with $(C_5Me_5)^{1-}$ ligands and forms the "tuck-over" complex, $(C_5Me_5)_2Y(\mu\text{-H})(\mu\text{-}\eta^1{:}\eta^5\text{-}CH_2C_5Me_4)Y(C_5Me_5)$.[15] Insertion of a tetramethylfulvene double bond into the yttrium alkyl linkage of the $Y-CH_2$ "tuck-over"or its monometallic "tuck-in" variant could lead to **16** by reactions with precedent with this type of small metal metallocene.

Conclusion

Although the hydride ligands in lanthanide complexes $[(C_5Me_5)_2SmH]_2$, $[(C_5Me_5)_2LaH]_x$, and $[(C_5Me_5)_2YH]_2$ can act as reductants according to eq 1 with some substrates, their reaction chemistry is more complicated than that observed for the actinide hydrides, $[(C_5Me_5)_2UH]_2$, $[(C_5Me_5)_2UH_2]_2$, and $[(C_5Me_5)_2ThH_2]_2$.[2] The latter complexes cleanly reduce C_8H_8, PhSSPh, and PhNNPh, whereas the $[(C_5Me_5)_2LnH]_x$ complexes react cleanly only with PhSSPh. The reactions of $[(C_5Me_5)_2YH]_2$ with C_8H_8 are particularly unusual and show new opportunities in lanthanide metallocene C−H activation and insertion chemistry. The isolation of the $(\eta^8{:}\eta^1\text{-}C_8H_7)^{3-}$ and $(\eta^5\text{-}C_5Me_4CH_2-C_5Me_4CH_2\text{-}\eta^3)^{2-}$ ligands from this reaction manifold indicates that new aspects of $(C_5Me_5)^{1-}$ reaction and coordination chemistry remain to be discovered with these metals.

Acknowledgment. We thank the Chemical Sciences, Geosciences, and Biosciences Division of the Office of Basic Energy Sciences of the Department of Energy for support and Dr. Evgeny Fadeev for help with the 800 MHz NMR experiments.

Supporting Information Available: X-ray diffraction data, atomic coordinates, thermal parameters, and complete bond distances and angles for compounds **9**, **13**−**14**, and **16**−**17**. This material is available free of charge via the Internet at http://pubs.acs.org.

JA8011726