Diazomethane Insertion into Lanthanide− and Yttrium−C(allyl) Bonds To Form the η^2-Hydrazonato Complexes $(C_5Me_5)_2Ln[\eta^2(N,N')-RNN{=}CHSiMe_3]$ ($R = C_3H_5$)

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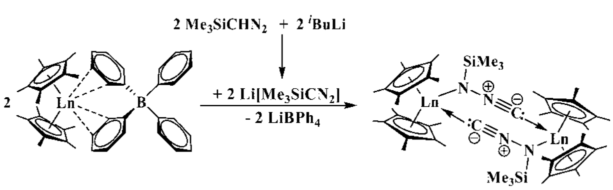
Received January 24, 2008

(Trimethylsilyl)diazomethane, Me_3SiCHN_2, is not metalated by the metallocene allyl complexes $(C_5Me_5)_2Ln(C_3H_5)$ but instead inserts to form the lanthanide hydrazonato complexes $(C_5Me_5)_2Ln[\eta^2(N,N')$-$RNN{=}CHSiMe_3]$ ($R = CH_2{=}CHCH_2$; Ln = Sm, La, Y). Although the La, Y, and Sm complexes are isomorphous, the double bond in the allyl substituent is oriented toward La and away from Y and Sm.

Introduction

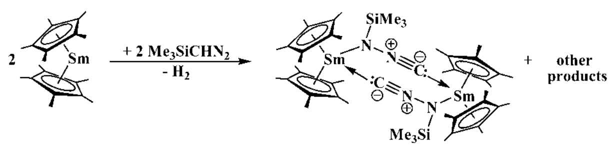
In efforts to expand diazomethane chemistry[1–3] to the f elements,[4] the reactivity of the complexes $[(C_5Me_5)_2Ln][(\mu\text{-}Ph)_2BPh_2]$ (Ln = Sm, La)[5,6] with $Li[Me_3SiCN_2]$, the salt obtained from isobutyllithium and (trimethylsilyl)diazomethane, was examined.[7] This led to an interesting series of complexes formulated as the isocyano amide species $\{(C_5Me_5)_2Ln[\mu\text{-}N(SiMe_3)NC]\}_2$ (Ln = Sm (**1**), La (**2**); eq 1).[7] The conversion of the Me_3SiCHN_2 starting material to the ligands in **1** and **2** apparently involved a migration of the trimethylsilyl group from carbon to nitrogen, but it was unknown if this occurred during the isobutyllithium metalation of Me_3SiCHN_2 or in the reaction of $Li[Me_3SiCN_2]$ with the lanthanide metallocene cation. Both experimental and theoretical studies of lithium salts of diazoalkanes have shown that several isomers are similar in energy.[8,9]



(1)

Ln = Sm, **1**; La, **2**

To avoid the use of the lithium reagent, the metalation of Me_3SiCHN_2 was examined. Although $(C_5Me_5)_2Sm$ and $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ react with Me_3SiCHN_2 to make **1** (eqs 2 and 3), the



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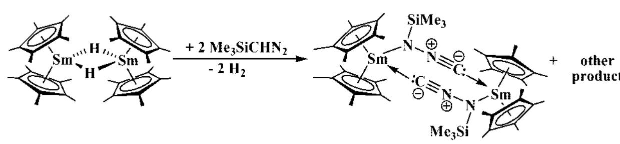

(3)

1

reactions generate multiple products and do not represent facile syntheses of this complex.[7] In an attempt to metalate Me_3SiCHN_2 with reagents containing Ln−C bonds, the reactions of Me_3SiCHN_2 with the allyl complexes $(C_5Me_5)_2Ln(\eta^3\text{-}CH_2CHCH_2)$[5,6] (Ln = Sm, La, Y) were examined. These allyl complexes were chosen since, in their η^1 forms, they can function as metallocene alkyls. For example, as precursors to the lanthanide hydride complexes $[(C_5Me_5)_2LnH]_x$,[5] via hydrogenolysis of Ln−C bonds, they are preferred over the more expensive $(C_5Me_5)_2Ln[CH(SiMe_3)_2]$ compounds[10,11] and the highly reactive, synthetically challenging $[(C_5Me_5)_2LnMe]_x$ complexes.[12,13] Lanthanide allyl complexes are also the preferred precursors to form the cationic metallocenes $[(C_5Me_5)_2Ln][(\mu\text{-}Ph)_2BPh_2]$, by reaction with $[Et_3NH][BPh_4]$[5,6] and have been used to metalate ϵ-caprolactam.[14] We report here that these allyl complexes do not metalate Me_3SiCHN_2 to make **1** and **2** but instead react via insertion to provide a facile route to the η^2-

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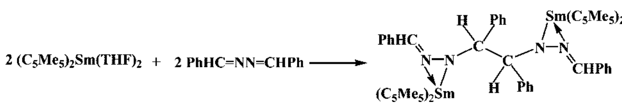
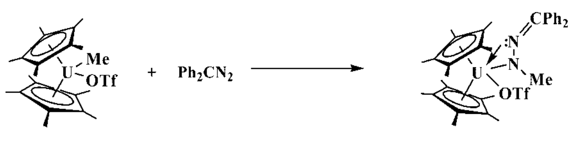
10.1021/om800065j CCC: $40.75
Publication on Web 06/25/2008

hydrazonato lanthanide complexes $(C_5Me_5)_2Ln[\eta^2(N,N')$-$RNN{=}CHSiMe_3]$ (R = $CH_2{=}CHCH_2$; Ln = Sm (**3**), La (**4**), Y (**5**)).

Formation of f element hydrazonato and bis(hydrazonato) complexes have previously been observed in the reductive coupling of benzaldehyde azine by decamethylsamarocene[15] (eq 4) and in the reactions of the actinide complexes $(C_5Me_5)_2U(Me)X$ (X = Cl, OSO_2CF_3)[16] and $(C_5Me_5)_2AnR_2$ (An = U, R = Me, CH_2Ph; An = Th, R = Ph, CH_2Ph)[17] with 1 and 2 equiv of Ph_2CN_2, respectively (e.g. eq 5). In the AnR/Ph_2CN_2 reactions, no C−H group was available to metalate. A chelated hydrazonato uranium complex, $(C_5Me_5)_2U(Ph_2C{=}NNCH_2CMe_2C_6H_2{}^tBu_2NH)$, was also reported from an oxidation/cyclometalation reaction of Ph_2CN_2 with $(C_5Me_5)_2U({=}NC_6H_2{}^tBu_3$-2,4,6).[18]



(4)



(5)

Experimental Section

The manipulations described below were conducted under argon or nitrogen with rigorous exclusion of air and water using Schlenk, vacuum line, and glovebox (Vacuum Atmospheres NEXUS model) techniques. Solvents were sparged with UHP argon and dried over columns containing Q-5 and molecular sieves. NMR solvents (Cambridge Isotope Laboratories) were dried over sodium−potassium alloy, degassed, and vacuum-transferred before use. $(C_5Me_5)_2Ln(\eta^3$-CH_2-$CHCH_2)$[5,6] complexes were prepared according to literature methods. Me_3SiCHN_2 (2.0 M in hexanes, Sigma-Aldrich) was dried over activated 4 Å molecular sieves and degassed by three freeze−pump−thaw cycles before use. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX500 spectrometer at 25 °C. ^1H and ^{13}C NMR resonances were located and confirmed by HMQC correlation experiments. Infrared spectra were recorded as KBr pellets on a Varian 1000 FTIR spectrophotometer at 25 °C. Elemental analyses were performed by Desert Analytics (Tucson, AZ) and on a Perkin-Elmer Series II CHNS/O Analyzer 2400. Lanthanide metal analyses were carried out by complexometric titration.[19]

$(C_5Me_5)_2Sm[\eta^2(N,N')$-$CH_2{=}CHCH_2NN{=}CHSiMe_3]$ (3). In an argon-filled glovebox, a solution of Me_3SiCHN_2 (166 μL, 0.331 mmol) in hexane was added dropwise via syringe to a stirred solution of $(C_5Me_5)_2Sm(\eta^3$-$CH_2CHCH_2)$ (153 mg, 0.331 mmol) in hexane (10 mL). The red solution immediately turned yellow. After 30 min, the mixture was filtered and solvent was removed under vacuum, leaving **3** as a yellow solid (185 mg, 97%). Yellow crystals of **3** suitable for X-ray diffraction were grown from a hexane solution at −35 °C. Anal. Calcd for $C_{27}H_{45}N_2SiSm$: C, 56.28; H, 7.89; N, 4.86; Si, 4.87; Sm, 26.10. Found: C, 56.48; H, 8.02; N, 4.59; Si, 4.89; Sm, 26.50. ^1H NMR (C_6D_6): δ 6.50 (s, 1H, C*H*SiMe$_3$), 4.80 (d, 2H, C*H*$_2$CH=CH$_2$), 3.29 (d, 1H, CH$_2$CH=C*H*$_2$), 3.25 (m, 1H, CH$_2$C*H*=CH$_2$), 2.95 (d, 1H, CH$_2$CH=C*H*$_2$), 0.93 (s, 30H, C$_5$*Me*$_5$), −4.14 (s, 9H, Si*Me*$_3$). ^{13}C NMR (C_6D_6): δ 135.2 (s, CH$_2$*C*H=CH$_2$), 118.3 (*C*$_5$Me$_5$), 116.3 (s, *C*HSiMe$_3$), 116.2 (s, CH$_2$CH=*C*H$_2$), 50.9 (s, *C*H$_2$CH=CH$_2$), 19.7 (C$_5$*Me*$_5$), −3.4 (s, Si*Me*$_3$). IR: 3086 w, 2958 s, 2906 s, 2858 s, 2726 w, 1460 m, 1437 m, 1378 w, 1312 w, 1244 m, 1171 w, 1088 w, 1024 w, 988 w, 944 m, 865 m, 838 m, 741 w, 689 w, 637 w, 580 w cm^{-1}.

$(C_5Me_5)_2La[\eta^2(N,N')$-$CH_2{=}CHCH_2NN{=}CHSiMe_3]$ (4). As described for **3**, **4** was obtained as a pale yellow solid (179 mg, 95%) from Me_3SiCHN_2 (168 μL, 0.335 mmol) and $(C_5Me_5)_2La(\eta^3$-$CH_2CHCH_2)$ (151 mg, 0.335 mmol) in hexane (10 mL). Colorless crystals of **4** suitable for X-ray diffraction were grown from hexane at −35 °C. Anal. Calcd for $C_{27}H_{45}N_2SiLa$: C, 57.42; H, 8.03; N, 4.96; La, 24.6. Found: C, 56.75; H, 8.11; N, 5.20; La, 24.3. ^1H NMR (C_6D_6): δ 6.19 (m, 1H, CH$_2$C*H*=CH$_2$), 6.18 (s, 1H, C*H*SiMe$_3$), 5.21 (d, 1H, CH$_2$CH=C*H*$_2$), 5.18 (d, 1H, CH$_2$CH=C*H*$_2$), 3.62 (d, 2H, C*H*$_2$CH=CH$_2$), 1.93 (s, 30H, C$_5$*Me*$_5$), 0.25 (s, 9H, Si*Me*$_3$). ^{13}C NMR (C_6D_6): δ 136.7 (CH$_2$*C*H=CH$_2$), 121.0 (*C*HSiMe$_3$), 119.8 (*C*$_5$Me$_5$), 116.7 (CH$_2$CH=*C*H$_2$), 54.0 (*C*H$_2$CH=CH$_2$), 11.0 (C$_5$*Me*$_5$), −0.1 (Si*Me*$_3$). IR: 3086 w, 2958 s, 2910 s, 2857 s, 2726 w, 1497 m, 1439 s, 1378 m, 1319 w, 1252 m, 1088 w, 1062 w, 1019 w, 962 w, 902 w, 862 m, 843 m, 803 w, 742 w, 695 w, 628 w, 549 w cm^{-1}.

$(C_5Me_5)_2Y[\eta^2(N,N')$-$CH_2{=}CHCH_2NN{=}CHSiMe_3]$ (5). As described for **3**, **5** was obtained as a white solid (178 mg, 93%) from Me_3SiCHN_2 (186 μL, 0.372 mmol) and $(C_5Me_5)_2Y(\eta^3$-$CH_2CHCH_2)$ (149 mg, 0.372 mmol) in hexane (10 mL). Colorless crystals of **5** suitable for X-ray diffraction were grown from hexane at −35 °C. Anal. Calcd for $YC_{27}H_{45}N_2Si$: C, 63.00; H, 8.81; N, 5.44; Y, 17.3. Found: C, 63.05; H, 9.14; N, 5.49; Y, 16.9. ^1H NMR (C_6D_6): δ 6.11 (m, 1H, CH$_2$C*H*=CH$_2$), 5.99 (s, 1H, C*H*SiMe$_3$), 5.19 (d, 1H, CH$_2$CH=C*H*$_2$), 5.15 (d, 1H, CH$_2$CH=C*H*$_2$), 3.63 (d, 2H, C*H*$_2$CH=CH$_2$), 1.92 (s, 30H, C$_5$*Me*$_5$), 0.24 (s, 9H, Si*Me*$_3$). ^{13}C NMR (C_6D_6): δ 136.6 (CH$_2$*C*H=CH$_2$), 121.9 (*C*HSiMe$_3$), 118.2 (*C*$_5$Me$_5$), 116.8 (CH$_2$CH=*C*H$_2$), 53.6 (*C*H$_2$CH=CH$_2$), 11.4 (C$_5$*Me*$_5$), −0.2 (Si*Me*$_3$). IR: 3089 w, 2960 s, 2902 s, 2858 s, 2725 w, 1647 w, 1461 s, 1435 s, 1378 m, 1344 m, 1312 m, 1245 s, 1179 m, 1090 w, 1031 m, 987 w, 956 w, 915 m, 903 w, 868 s, 838 s, 800 w, 688 w, 638 m, 564 w cm^{-1}.

X-ray Data Collection, Structure Determination, and Refinement for $(C_5Me_5)_2Sm[\eta^2(N,N')$-$CH_2{=}CHCH_2NN{=}CHSiMe_3]$ (3). A yellow crystal of approximate dimensions 0.12 × 0.23 × 0.42 mm was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The SMART[20] program package was used to determine the unit-cell parameters and for data collection (25 s/frame scan time for a sphere of diffraction data). The raw frame data were processed using SAINT[21] and SADABS[22] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[23] program. The diffraction symmetry was *mmm*, and the systematic absences were consistent with the orthorhombic space group *Pbca*, which was later determined to be correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. Analytical scattering factors[24] for neutral atoms were used throughout the analysis. There were two molecules of the formula unit present (Z = 16). Hydrogen atoms were included using a riding model. The pentamethylcyclopentadienyl ligands defined by atoms C(28)−C(37B) and C(38)−C(47B) were disordered and included using multiple components, partial site occupancy factors, and fixed isotropic displacement parameters.

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Table 1. X-ray Data Collection Parameters for $(C_5Me_5)_2Sm[\eta^2(N,N')\text{-}CH_2{=}CHCH_2NN{=}CHSiMe_3]$ (3), $(C_5Me_5)_2La[\eta^2(N,N')\text{-}CH_2{=}CHCH_2NN{=}CHSiMe_3]$ (4), and $(C_5Me_5)_2Y[\eta^2(N,N')\text{-}CH_2{=}CHCH_2NN{=}CHSiMe_3]$ (5)

	3	4	5
empirical formula	$C_{27}H_{45}N_2SiSm$	$C_{27}H_{45}N_2SiLa$	$C_{27}H_{45}N_2SiY$
formula wt	576.09	564.65	514.65
temp (K)	163(2)	100(2)	100(2)
cryst syst	orthorhombic	monoclinic	monoclinic
space group	*Pbca*	$P2_1/c$	$P2_1/c$
a (Å)	16.093(3)	11.5050(18)	11.5090(15)
b (Å)	21.424(4)	14.053(2)	13.9781(19)
c (Å)	33.139(5)	17.978(3)	18.573(3)
α (deg)	90	90	90
β (deg)	90	102.539(2)	106.132(2)
γ (deg)	90	90	90
V (Å^3)	11 425(3)	2837.3(8)	2870.2(7)
Z	16	4	4
ρ_{calcd} (Mg/m^3)	1.340	1.322	1.191
μ (mm^{-1})	2.113	1.563	2.089
R1^a ($I > 2.0\sigma(I)$)	0.0569	0.0339	0.0443
wR2^b (all data)	0.1340	0.0677	0.1168

^{a} $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $wR2 = [\sum [w(F_o^2 - F_c^2)^2/\sum[w(F_o^2)^2]]^{1/2}$.

Least-squares analysis yielded wR2 = 0.1340 and GOF = 1.191 for 533 variables refined against 9731 data (0.85 Å). As a comparison for refinement on *F*, R1 = 0.0569 for those 6016 data with $I > 2.0\sigma(I)$. Details are given in Table 1.

X-ray Data Collection, Structure Determination, and Refinement for $(C_5Me_5)_2La[\eta^2(N,N')\text{-}CH_2{=}CHCH_2NN{=}CHSiMe_3]$ (4). A yellow plate 0.10 × 0.10 × 0.04 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using ψ and ω scans. The crystal-to-detector distance was 60 mm, and the exposure time was 10 s per frame using a scan width of 0.3°. Data collection was 99.9% complete to 25.00° in θ. A total of 23 844 reflections were collected covering the indices $-15 \le h \le 15$, $-17 \le k \le 18$, and $-23 \le l \le 23$. A total of 6573 reflections were found to be symmetry-independent, with an R_{int} value of 0.0367. Indexing and unit cell refinement indicated a primitive, monoclinic lattice. The space group was found to be $P2_1/c$ (No. 14). The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by direct methods (SIR-2004) 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.

X-ray Data Collection, Structure Determination, and Refinement for $(C_5Me_5)_2Y[\eta^2(N,N')\text{-}CH_2{=}CHCH_2NN{=}CHSiMe_3]$ (5). A colorless plate 0.09 × 0.23 × 0.23 mm in size was handled as described for **4**. The exposure time was 5 s per frame using a scan width of 0.3°. A total of 14 976 reflections were collected covering the indices $-14 \le h \le 7$, $-17 \le k \le 14$, and $-22 \le l \le 22$. A total of 5577 reflections were found to be symmetry-independent, with an R_{int} value of 0.0393. Solution by direct methods (SHELXS-97) produced a complete heavy-atom phasing model consistent with the proposed structure.

Results and Discussion

Synthesis. Although $\{(C_5Me_5)_2Sm[\mu\text{-}N(SiMe_3)NC]\}_2$ is a product of the metalation of Me_3SiCHN_2 by $(C_5Me_5)_2Sm$ and $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ (eqs 2 and 3),[7] a different product is obtained from the reaction of the allyl complex $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCH_2)$ with Me_3SiCHN_2. As shown in eq 6, insertion of Me_3SiCHN_2 into the Sm−C(allyl) bond occurs to form the η^2-hydrazonato complex $(C_5Me_5)_2Sm[\eta^2(N,N')\text{-}RNN{=}CHSiMe_3]$ (**3**; R = $CH_2{=}CHCH_2$) in high yield (97%). Reactions of analogous allyl complexes of both a larger ion, lanthanum, and a smaller ion, yttrium,[25] gave the analogous complexes **4** and **5**, respectively, in high yield (>90%). These complexes were readily isolated by crystallization from hexane and characterized by X-ray crystallography (Figures 1 and 2).

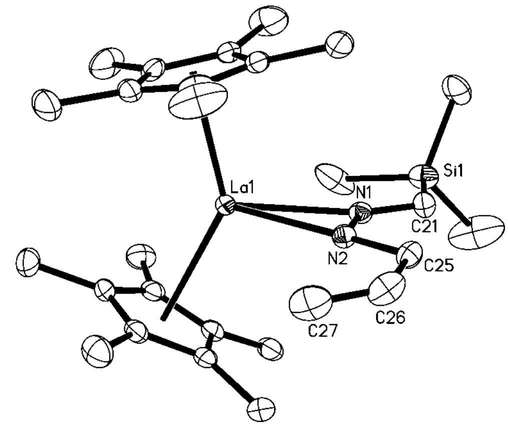


Figure 1. Thermal ellipsoid plot of $(C_5Me_5)_2La[\eta^2(N,N')\text{-}RNN{=}CHSiMe_3]$ (**4**; R = $CH_2{=}CHCH_2$) drawn at the 50% probability level. Hydrogen atoms have been excluded for clarity.

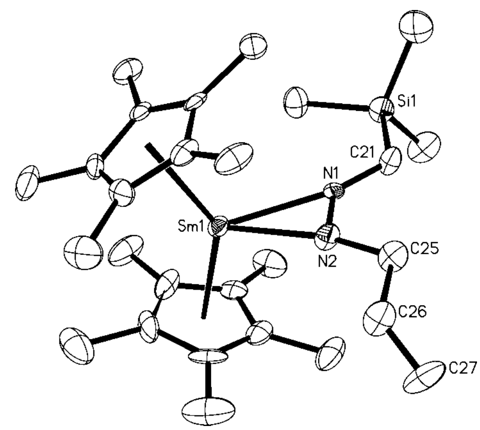
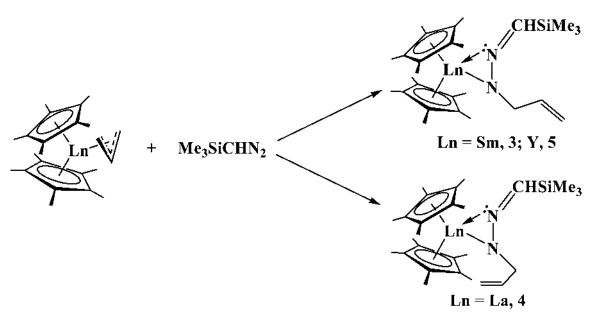


Figure 2. Thermal ellipsoid plot of $(C_5Me_5)_2Sm[\eta^2(N,N')\text{-}RNN{=}CHSiMe_3]$ (**3**; R = $CH_2{=}CHCH_2$) drawn at the 50% probability level. Hydrogen atoms have been excluded for clarity. The yttrium complex **5** has an analogous structure.



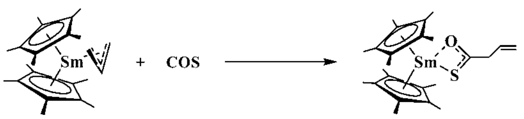
(6)

The ^1H NMR spectra of complexes **3**−**5** in C_6D_6 contain resonances for the C_5Me_5, $CH_2CH{=}CH_2$, and $CHSiMe_3$ components in the ratios expected. The infrared spectra of **3**−**5** do not show any absorptions in the 1950−2300 cm^{-1} region

(25) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751–767.

characteristic of diazo compounds,[26] and each complex contains an absorption at 3086−3089 cm^{-1} assignable to an NC−H stretch. These data and elemental analyses of **3**−**5** were in agreement with the products identified by X-ray crystallography.

Evidently, insertion of Me_3SiCHN_2 into the Ln−C(allyl) bonds of the $(C_5Me_5)_2Ln(C_3H_5)$[5,6] complexes to form **3**−**5** is preferred to metalation of the diazoalkane to produce $\{(C_5Me_5)_2Ln[\mu\text{-}N(SiMe_3)NC]\}_2$ and propene. The insertion reactivity observed for the $(C_5Me_5)_2Ln(C_3H_5)$ complexes has precedence with substrates such as CO_2, CS_2, and COS (e.g. eq 7).[27]



(7)

Insertion is also typically observed in transition-metal reactions, since the diazoalkanes used in those studies did not have hydrogen as a substituent. For example, insertion of the diazoalkanes R_2CN_2 (R = Ph, C_6H_4Me, CO_2Et) into Zr−C[28−30] and Ti−C[31,32] bonds to produce hydrazonato ligands has been previously reported.

The variability in metalation reactivity often observed between f-element hydrides and alkyls[33] is highlighted by the fact that $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ reacts with Me_3SiCHN_2 by metalation (eq 3) rather than by insertion when the $(C_5Me_5)_2Ln(C_3H_5)$ complexes have the opposite reactivity pattern. It should be noted that the samarium hydride reaction gives a mixture of products.

Structure. Although the respective Sm and Y complexes **3** and **5** have analogous molecular structures, complex **3** crystallizes in space group *Pbca*, whereas **5** crystallizes in $P2_1/c$. The La complex **4** also crystallizes in $P2_1/c$, but its structure differs from those of **3** and **5** in the orientation of the unsaturated C(26)−C(27) bond (Figures 1 and 2). Each complex has an eight-coordinate Ln^{3+} center ligated by two $(C_5Me_5)^-$ ligands and the two nitrogen atoms of a η^2-hydrazonato ligand.

The metallocene units in **3**−**5** have crystallographic parameters that are normal for metallocenes containing $[(C_5Me_5)_2M]^+$ moieties with two additional ligands.[34] For example, the 139.2−139.6° (C_5Me_5 ring centroid)−Ln−(C_5Me_5 ring centroid) angles fall in a narrow range and the Ln−C(C_5Me_5) average distances decrease in the order 2.814(9), 2.71(2), and 2.65(1) Å, consistent with the decreasing order of eight-coordinate ionic radii for La^{3+}, Sm^{3+}, and Y^{3+}: 1.160, 1.079, and 1.019 Å, respectively.[25] Selected bond lengths and angles for **3**−**5** are provided in Table 2.

In the hydrazonato ligands in **3**−**5**, the range of N(1)−N(2) distances, 1.333(10)−1.343(3) Å, is longer than the 1.12−1.13 Å N−N distance for uncomplexed diazoalkanes[35] and these distances are intermediate between single and double N−N bonds.[36] This suggests some delocalization compared to the resonance structure in eq 6. The 1.301(3)−1.338(12) Å N(1)−C(21) distances are similar to those in diazoalkanes, 1.28−1.32 Å,[35] but again are between the single- and double-bond ranges such that a delocalized view is appropriate. The 1.434(3)−1.449(14) Å N(2)−C(25) distances are closer to N−C single-bond (1.46−1.49 Å) than N−C double-bond distances (1.28−1.31 Å).[36] In **3** and **4**, the 1.311(15) and 1.298(5) Å C(26)−C(27) bond distances are in the double-bond range[36] such that this linkage in the allyl portion of the ligand is a localized double bond. In **5**, the analogous distance refines to be inexplicably shorter, 1.223(5) Å.

Table 2. Bond Distances (Å) and Angles (deg) in $(C_5Me_5)_2Sm[\eta^2(N,N')\text{-}CH_2{=}CHCH_2NN{=}CHSiMe_3]$ (3), $(C_5Me_5)_2La[\eta^2(N,N''\text{-}CH_2{=}CHCH_2NN{=}CHSiMe_3]$ (4), and $(C_5Me_5)_2Y[\eta^2(N,N')\text{-}CH_2{=}CHCH_2NN{=}CHSiMe_3]$ (5)

bond distance/angle	4	3	5
Ln(1)−Cnt	2.543/2.545	2.427/2.438	2.361/2.362
Ln(1)−C(C_5Me_5) avg	2.814(9)	2.71(2)	2.65(1)
Ln(1)−N(2)	2.397(2)	2.287(9)	2.235(2)
Ln(1)−N(1)	2.476(2)	2.367(7)	2.346(2)
Ln(1)···C(26)	4.418	4.280/4.307	4.204
Ln(1)···C(27)	4.182	5.389/5.423	5.207
N(1)−N(2)	1.343(3)	1.333(10)	1.343(3)
N(2)−C(25)	1.434(3)	1.449(14)	1.441(3)
N(1)−C(21)	1.310(3)	1.338(12)	1.301(3)
C(25)−C(26)	1.493(4)	1.494(14)	1.487(4)
C(26)−C(27)	1.298(5)	1.311(15)	1.223(5)
C(21)−Si(1)	1.854(3)	1.851(10)	1.856(3)
Cnt1−Ln(1)−Cnt2	139.6	139.6	139.2
Cnt−Ln(1)−N(2)	106.5/108.8	108.1/108.2	108.8/109.6
Cnt−Ln(1)−N(1)	107.4/113.0	109.5/110.5	108.7/110.8
N(1)−Ln(1)−N(2)	31.94(7)	33.2(3)	33.99(7)
N(1)−N(2)−C(25)	116.8(2)	116.3(8)	117.6(2)
N(1)−N(2)−Ln(1)	77.27(14)	76.7(5)	77.54(13)
C(25)−N(2)−Ln(1)	165.13(18)	166.9(7)	164.56(18)
N(2)−N(1)−C(21)	128.1(2)	128.0(8)	126.4(2)
N(2)−N(1)−Ln(1)	70.79(13)	70.1(5)	68.46(12)
C(21)−N(1)−Ln(1)	160.7(2)	161.9(6)	164.99(19)
N(2)−C(25)−C(26)	113.2(2)	109.9(9)	110.9(2)
C(27)−C(26)−C(25)	127.3(3)	125.4(11)	128.8(4)
N(1)−C(21)−Si(1)	117.5(2)	118.0(7)	123.4(2)

The two Ln−N linkages that connect the hydrazonato ligands to the metals in **3**−**5** are not equivalent, but they are closer in value than is typical for hydrazonato ligands.[16,28,29,31,37] This too is suggestive of delocalization in these complexes. For example, the 2.287(9) Å Sm(1)−N(2) and 2.367(7) Å Sm(1)−N(1) distances in **3** can be compared to the pairs of U−N distances in $(C_5Me_5)_2U[\eta^2(N,N')\text{-}MeNN{=}CPh_2](OSO_2CF_3)$ (2.25(2) and 2.46(2) Å), $(C_5Me_5)_2U[\eta^2(N,N')\text{-}MeNN{=}CPh_2](Cl)$ (2.212(7) and 2.473(7) Å),[16] and $(C_5Me_5)_2U(Ph_2C{=}NNCH_2CMe_2C_6H_2{}^tBu_2NH)$ (2.228(10) and 2.496(12) Å).[18] The two Sm−N distances in **3** can also be compared to the 2.301(3) Å Sm−N bond length in the formally seven-coordinate $(C_5Me_5)_2Sm[N(SiMe_3)_2]$.[38] The Sm−N distances are also in the range of distances found in other samarium cyclopentadienyl complexes with two adja-

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cent nitrogens coordinated to the metal: $[(C_5Me_5)_2Sm]_2(\mu,\eta^4$-(PhHC=NNCNPh−)$_2]$[15] (2.315(13)−2.431(14) Å), $(C_5Me_5)_2Sm(\eta^2$-$N_2Ph_2)$(THF)[39] (2.39(1)−2.45 Å), and $(C_5Me_5)Sm[(\mu$-η^6:η^1-Ph)$BPh_3](\eta^2$-$N_2Ph_2)$[40] (2.249(4)−2.530(4) Å). Metrical comparisons with the hydrazonato complex in eq 4 would normally be made, but they are not possible, since the crystallographic data on that complex were sufficient only to establish connectivity. The distances involving lanthanum in **4** and yttrium in **5** parallel those in **3** but are larger and smaller, respectively, consistent with the larger and smaller metal ion.[25]

In the complex of the largest metal **4**, the C(26)−C(27) double bond of the allyl substituent is oriented toward the metal center, whereas in **3** and **5** this bond points away from the metals (Figures 1 and 2). However, the 4.418 Å La···C(26) and 4.182 Å La···C(27) distances are too long for a significant interaction.

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Conclusion

The reaction of allyl metallocenes, $(C_5Me_5)_2Ln(C_3H_5)$, with Me_3SiCHN_2 provides a facile route to the crystallographically characterized hydrazonato complexes of yttrium and lanthanide metals. These hydrazonato ligands contain a tethered olefin derived from the allyl group and can be obtained from diazoalkanes that have a hydrogen substituent.

Acknowledgment. We thank the Chemical Sciences, Geosciences, and Biosciences Division of the Office of Basic Energy Sciences of the Department of Energy for support. This research was facilitated in part by a National Physical Science Consortium Fellowship and by stipend support from Los Alamos National Laboratory (to E.M.).

Supporting Information Available: CIF files giving X-ray diffraction data, atomic coordinates, thermal parameters, and complete bond distances and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

OM800065J