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Reductive distortion of azobenzene by an organosamarium(II) reagent to form [(C5Me5)2Sm]2(C6H5)2N2: an x-ray crystallographic snapshot of an agostic hydrogen complex on an ortho-metalation reaction coordinate

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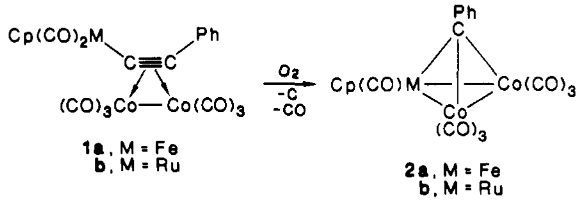
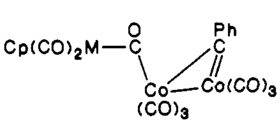
Scheme I



C≡C bonds[7], is not involved in the reaction.

The available evidence suggests that the inner carbon atom in 1, i.e., the one which is attached to three metal atoms, is the one which is attacked by oxygen, and the resulting CO unit is lost subsequently by decarbonylation. In view of the possibilities of alkyne ligand scissions with[7] and without[8] chemical attack at the alkyne C atoms two types of possible reaction intermediates come into mind. Adhering to the 18-electron rule 3 could result from C≡C scission followed by oxidation whereas 4 would represent initial oxidation and loss of one CO ligand. Although at the moment this mechanism is purely speculative, in both cases the emergence of the CPh ligand which has to become μ_3 bridging can be visualized.



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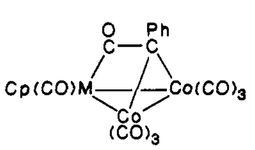

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Cluster model systems related to surface-catalyzed CO interconversions have focused on the deoxygenation of CO ligands forming carbide species[9] which then undergo C–C couplings[10]. The reactions presented herein represent the reversal of such sequences and underline our proposition that by variation of its metal constituents a polymetallic system can be tuned such that it supports organic reactions in its ligand sphere in both possible directions.[11] Further work will elucidate the course of the reaction by isotopic labeling studies and test the possible generalization of this approach.

Acknowledgment. This work was supported by the Fonds der Chemischen Industrie and by a NATO grant allowing for scientific interaction with Prof. Shapley's group at Urbana, IL.

Registry No. [1]a, 104575-70-4; **1b**, 104575-71-5; **2a**, 89253-31-6; **2b**, 104575-72-6; Co, 7440-48-4; Fe, 7439-89-6; Ru, 7440-18-8.

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(6) In a typical control experiment **1b** (42 mg, 0.07 mmol) was kept at 40 °C for $4^1/_2$ h in 15 mL of the original reaction solvent (hexane/dichloromethane, 2:1) under an argon atmosphere without any reaction. Addition of 1 mL of deoxygenated and Ar-saturated water and vigorous stirring for 12 h did not lead to any change. When a slow stream of O_2 was subsequently bubbled through the solution for 30 s and stirring was continued, TLC tests indicated the beginning formation of **2b** after 30 min and the complete disappearance of **1b** after 5 h. Chromatography over silica gel then yielded 15 mg (39%) of **2b.**

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Reductive Distortion of Azobenzene by an Organosamarium(II) Reagent To Form $[(C_5Me_5)_2Sm]_2(C_6H_5)_2N_2$: An X-ray Crystallographic Snapshot of an Agostic Hydrogen Complex on an Ortho-Metalation Reaction Coordinate[1]

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Summary: $(C_5Me_2)_2Sm(THF)_2$ reacts with $C_6H_5N{=}NC_6H_5$ in toluene to form $[(C_5Me_5)_2Sm](C_6H_5)NN(C_6H_5)[Sm(C_5Me_5)_2]$ characterized by X-ray crystallography and spectroscopic techniques. The complex crystallizes from toluene at −30 °C in space group $P2_1/n$ with a = 10.855 (7) Å, b = 20.435 (5) Å, c = 21.686 (9) Å, β = 106.68 (4)°, and D_{calcd} = 1.48 g cm^{-3} for Z = 4 dimers. The $(C_5Me_5)_2Sm$ groups are coordinated to the NN unit (NN distance = 1.25 (1) Å) in a trans manner with Sm–N distances of 2.40 (1) and 2.41 (1) Å. The C_6H_5 groups are attached to the NN unit in a trans geometry with C–N distances of 1.56 (2) and 1.61 (1) Å. The above four groups are arranged asymmetrically around the NN unit such that the two samarium atoms are closer to one of the phenyl rings than to the other. Short (phenyl ortho hydrogen)–samarium distances of 2.29 and 2.34 Å are observed.

The soluble divalent organosamarium(II) complex $(C_5Me_5)_2Sm(THF)_2$[3] previously has been found to display unusual reductive chemistry with CO[4] and with CO/alkyne combinations.[5] We report here that this reducing agent also can react with nitrogen-containing substrates in a unique way. With azobenzene, it is possible to trap an unusual complex displaying agostic metal hydrogen interactions[6] which may be related to ortho-metalation reaction pathways.[7,8]

Addition of $C_6H_5N{=}NC_6H_5$ (0.032 g, 0.177 mmol) to purple $(C_5Me_5)_2Sm(THF)_2$ (0.200 g, 0.354 mmol) in 10 mL of toluene in a nitrogen-filled glovebox resulted in an immediate color change to dark blue. After the solution was stirred 6 h, the solvent and THF were removed by rotary evaporation to give a dark blue complex identified as $[(C_5Me_5)_2Sm]_2N_2(C_6H_5)_2$ (0.179 g, 90%) by analytical[9] and X-ray methods[10] (eq 1).

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(1) Reported in part at the 190th National Meeting of the American Chemical Society, Chicago, IL, Sept 1985.

(2) (a) Alfred P. Sloan Research Fellow. (b) University of California, Irvine. (c) University of Alabama.

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(9) Complexometric metal analysis. Calcd for $SmNC_{26}H_{35}$: Sm, 29.37. Found: Sm, 28.6. A complete elemental analysis (Analytische Laboratorien) was incomplete (Sm, 27.95; C, 57.28; H, 6.13; N, 2.39) but gave a reasonable elemental ratio of Sm:N:C:H = 1:0.92:26:33. UV–vis (15.5 mg in 100 mL of toluene): 600 (br, ϵ 1300), 372 (shoulder, ϵ 5300) nm. UV–vis (4.65 mg in 100 mL of toluene): 272 (ϵ 22 000), 210 (ϵ 16 000) nm.

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$$2(C_5Me_5)_2Sm(THF)_2 + C_6H_5N{=}NC_6H_5 \rightarrow [(C_5Me_5)_2Sm](C_6H_5)NN(C_6H_5)[Sm(C_5Me_5)_2] + 4THF \qquad (1)$$

The ORTEP diagram in Figure 1 shows that the connectivity of the atoms is consistent with a reaction in which the solvating THF molecules were displaced by the lone pairs of the azobenzene nitrogen atoms to form a formally Sm^{2+} adduct of azobenzene. However, spectroscopic data and the structural details of the X-ray study suggest a different mode of bonding. The ^1H NMR spectrum showed line widths and positions consistent with a Sm(III) complex,[11] and the room-temperature magnetic susceptibility was close to the normal Sm(III) range.[12] The infrared spectrum[16] also suggested that this was not a simple symmetrical Sm(II) azobenzene complex. In the crystal structure, the average Sm–C(ring) distance, 2.74 Å, is in the range found for Sm(III) C_5Me_5 complexes,[4,5,14,15,17] rather than for Sm(II) species.[3,18] The Sm–N bond distances, 2.40 (1) and 2.41 (1) Å, are considerably shorter than those expected for Sm(III)←:N or Sm(II)←:N bonds[19] and are closer to the range expected for a Sm(III)–N single bond.

In addition to this Sm–N single bond, each nitrogen is attached to the other nitrogen atom by a short apparently double bond *and* to a phenyl carbon atom. The NN distance in this molecule is 1.25 (1) Å, which is equivalent to the 1.247 Å N=N distance in *trans*-azobenzene.[20] A perfectly sp^2-hybridized nitrogen atom would be coplanar with the three connected atoms: phenyl carbon, samarium, and the other nitrogen. Within each of the two such four atom sets in this complex, the atoms are roughly coplanar, but deviations as large as 0.18 Å from the planes are found.[21] The N–C(phenyl) distances of 1.56 (2) and 1.61 (1) Å are considerably longer than the normal average of 1.42 Å in azobenzene systems.[20]

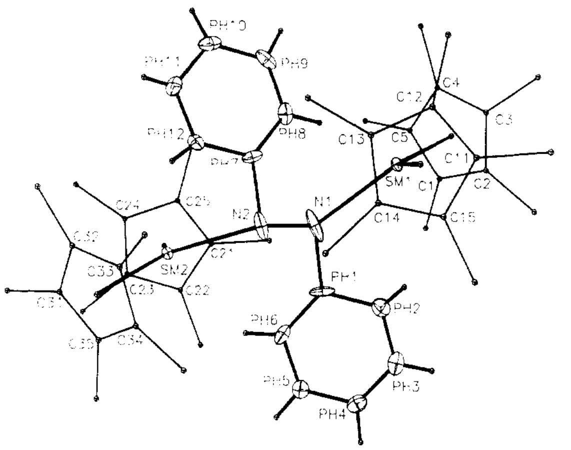

Figure 1. ORTEP plot of the molecular structure of $[(C_5Me_5)_2Sm]_2N_2(C_6H_5)_2$.

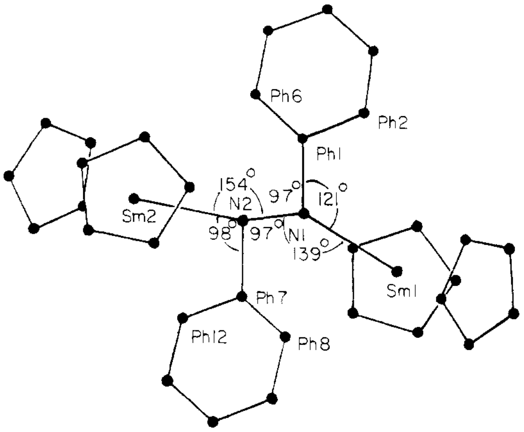

Figure 2. Top view of the molecular structure of $[(C_5Me_5)_2Sm]_2N_2(C_6H_5)_2$ showing asymmetry.

Figure 2 shows another distorted feature in this complex, namely, the asymmetry of the placement of the $(C_5Me_5)_2Sm$ units closer to phenyl ring 7–12 than to ring 1–6. For example, the Sm(1)–N(1)–Ph(1) angle is 120.8 (7)° compared to 98.4 (5)° for the analogous Sm(2)–N(2)–Ph(7) angle. This arrangement brings Sm(1) to within 2.29 Å of the ortho hydrogen atom attached to Ph(8); Sm(2) is within 2.34 Å of the hydrogen on Ph(12).[22] The angular relationship of the rings to the Sm centers also brings these hydrogen positions close to the metal.[24]

These samarium ortho hydrogen distances are within a few percent of the distance expected for a bridging Sm–H bond and within 15% of an expected terminal Sm–H bond distance.[25] Both of the short Sm–H distances are within

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(10) The space group is $P2_1/n$ with a = 10.855 (7) Å, b = 20.435 (5) Å, c = 21.686 (9) Å, β = 106.68 (4)°, V = 4608 Å^3, and D_{calcd} = 1.48 g cm^{-3} for Z = 4 (bimetallic units). Least-squares refinement on the basis of 4130 observed reflections led to a final $R = \sum|F_o| - |F_c|/\sum|F_o|$ = 0.033. All non-hydrogen atoms were refined with anisotropic temperature factors. Full crystallographic data are given in the supplementary material.

(11) ^1H NMR (17 mg in 0.5 mL of toluene-d_8): δ 1.57 (60 H, C_5Me_5, $\Delta\nu_{1/2}$ = 7 Hz), 2.49 (dd, 2 H), −1.00 (d, J = 6 Hz, 2 H), −6.32 (d, J = 7 Hz, 2 H). Ortho hydrogen atoms were not located presumably due to interaction with the Sm(III) center. The chemical shifts of the aryl protons vary with temperature, but the coupling pattern remains the same down to −60 °C.

(12) χ_M^{298K} = 1560 × 10^{-6} (cgs); μ_{eff} = 1.9 μ_B. Normal range for Sm(III): 1.3–1.9 μ_B. Normal range for Sm(II): 3.4–3.8 μ_B.[3,13-15]

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(16) IR (KBr): 2900 m br, 1580 s, 1460 m, 1385 m, 1330 m, 1305 m, 1180 w, 1020 w, 840 w br, 730 m cm^{-1}. The 1580 cm^{-1} absorption is in the range in which azobenzene NN stretching absorptions are found. However, in symmetrical azobenzenes, this absorption is Raman not IR active: Bellamy, L. J. *The Infrared Spectra of Complex Molecules*; Wiley: New York, 1964.

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(21) Deviations (Å) from planarity within each set: set 1, Sm(1), −0.035; N(1), 0.13; Ph(1) −0.035; N(2), −0.059; set 2, Sm(2), 0.052; N(2), −0.178; Ph(7), 0.025; N(1), 0.102.

(22) A difference map weighted in low-angle reflections showed sufficient H atoms to be able to assign all of them. All were put in with fixed positions and thermal parameters. Sm–H distances were calculated by using a C–H fixed distance of 1.05 Å.[23] Sm(1) is 2.70 Å away from the ortho hydrogen on Ph(2) in the distant phenyl ring. Sm(2) is 2.42 Å away from the ortho hydrogen on Ph(6).

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(24) Let M(1) be the midpoint of the vector between the centroids of the C_5Me_5 rings bonded to Sm(1) and let M(2) relate similarly to Sm(2). A torsional angle of ±180° (or 0°) would ideally be expected for a Sm–H bond. M(1)–Sm(1)–N(1)–H(48; on Ph 8) = −164°. M(1)–Sm(1)–N(1)–H(42; on Ph 2) = −22°. M(2)–Sm(2)–N(2)–H(52; on Ph 12) = −177°. M(2)–Sm(2)–N(2)–H(46; on Ph 6) = −22°.

the range cited as typical for agostic hydrogen interactions by Brookhart and Green.[6] These samarium–hydrogen distances are the shortest "nonbonding" lanthanide hydride distances reported and are the most definitive examples of agostic hydrogen interactions in lanthanide complexes.[26]

This samarium azobenzene complex is significantly different from any other azobenzene complex in the literature[8,27-30] including early transition-metal metallocene complexes such as $(C_5H_5)_2TiN_2(C_6H_5)_2$[29] and $[(C_5H_5)ClTi][\mu\text{-}N_2(C_6H_5)_2][\mu\text{-}NC_6H_5]$.[30] The samarium structure demonstrates that the azobenzene framework can be distorted simultaneously in several different ways by metal coordination. The observed interaction of the ortho phenyl hydrogen atoms with samarium in this complex is consistent with the ortho-metalation reactivity observed in several azobenzene metal systems.[8,27] However, this samarium system is unique in that it allows us to stop the ortho hydrogen metal interaction at the intermediate agostic stage because the samarium center cannot readily undergo oxidative addition to complete the metalation. The head-on, as opposed to sideways, approach of the samarium to the ortho hydrogen and the fact that both metals interact simultaneously with a single phenyl ring raise interesting possibilities for ortho-metalation pathways. The consequences in reactivity of the unusual structure of $[(C_5Me_5)_2Sm](C_6H_5)NN(C_6H_5)[Sm(C_5Me_5)_2]$ are under investigation.

Acknowledgment. We thank the National Science Foundation for support of the research. We also thank the Alfred P. Sloan Foundation for a Research Fellowship (to W.J.E.).

Supplementary Material Available: Tables of crystal data, bond distances and angles, final fractional coordinates, and thermal parameters (11 pages); a listing of observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.

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(25) Based on the X-ray diffraction structure of $[(CH_3C_5H_4)_2Y(\mu\text{-}H)(THF)]_2$ (Evans, W. J.; Meadows, J. H.; Wayda, A. L.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 2008–2014) and the neutron diffraction structure of $[(C_5Me_5)[_2ThH(\mu\text{-}H)]_2$ (Broach, R. W.; Schultz, A. J.; Williams, J. M.; Brown, G. M.; Manriquez, J. M.; Fagan, P. J.; Marks, T. J. *Science (Washington, D.C.)* **1979**, *203*, 172–174) after correcting for the different radial sizes of the metals (Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, 1980).

(26) Cf. Jeske, G.; Schock, L. E.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8103–8110.

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Competitive C–H and C–C Activation in the Reaction of Pentamethylcyclopentadiene with Decacarbonyldimanganese

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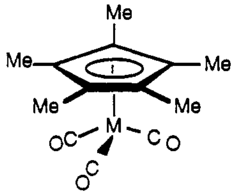
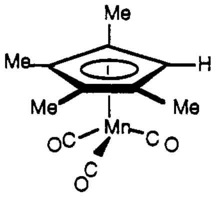
Summary: In contrast to previous reports, the thermal reaction of $Mn_2(CO)_{10}$ with neat pentamethylcyclopentadiene affords an approximately 77:23 mixture of $Mn(\eta^5\text{-}C_5Me_5)(CO)_3$ (**1a**) and $Mn(\eta^5\text{-}C_5Me_4H)(CO)_3$ (**2**), via competitive activation of the doubly allylic C–H and C–CH_3 bonds of the diene.

The direct thermal reaction of pentamethylcyclopentadiene (Cp*H) with $Mn_2(CO)_{10}$, using the diene as solvent, has been employed for the preparation of large quantities of $Mn(\eta\text{-}C_5Me_5)(CO)_3$ (**1a**).[1] Purification was carried out by column chromatography or filtration through silica, and further recrystallization was deemed unnecessary.[1] Similar conditions have been used for the synthesis of the Re analogue **1b**.[2] These compounds are precursors for a variety of important organometallic compounds of manganese and rhenium.[1,2] In this cautionary communication we report that while this methodology appears to be a good selective route to **1b**, reaction of Cp*H with $Mn_2(CO)_{10}$ under these reaction and workup conditions affords a product mixture containing, in addition to **1a**, appreciable amounts of the *tetramethyl*cyclopentadienyl complex **2**.



1 a. M = Mn
b. M = Re



2

The reaction of $Mn_2(CO)_{10}$ with neat Cp*H (97% pure by GC)[3] was initially carried out at 155 °C (0.5 h) followed by raising the temperature to 205 °C over 3 h and continued heating at this temperature (0.5 h), at which time gas evolution had ceased. Removal of excess Cp*H under reduced pressure yielded an oily red-yellow solid which was extracted with hexane, filtered through Celite, and evaporated to give a yellow crystalline solid, in >70% yield. Gas chromatographic/mass spectral (GC/MS) analysis[4] of this crude material revealed the presence of two components (Table I, entry a). The reaction was repeated four times under these conditions, and a small (±3%) variation in relative product yields was observed by GC/MS analysis.

The major component (77 ± 3%) exhibited a molecular ion peak at m/e 274 as expected for **1a**, while the minor fraction (23 ± 3%) was characterized by a molecular ion peak at m/e 260, suggestive of the tetramethylcyclopentadienyl complex **2**. Additional resonances in the ^1H and ^{13}C NMR spectra of the mixture also suggested the presence of **2**. Confirmation was obtained by the unambiguous synthesis of pure **2** from the reaction of lithium tetramethylcyclopentadienide[5] and $MnBr(CO)_5$ and com-

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