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.

(27) Bruce, M. I.; Goodall, B. L. in *The Chemistry of the Hydrazo, Azo and Azoxy Groups*; Patai, S., Ed.; Wiley: New York, 1975; Chapter 9.

(28) Hoare, R. J.; Mills, O. S. *J. Chem. Soc., Dalton Trans.* **1972**, 2138–2141, 2141–2145.

(29) Fochi, G.; Floriani, C.; Bart, J. C. J.; Giunchi, G. *J. Chem. Soc., Dalton Trans.* **1983**, 1515–1521.

(30) Gambarotta, S.; Floriani, C.; Chiesa-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1983**, *105*, 7295–7301.

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

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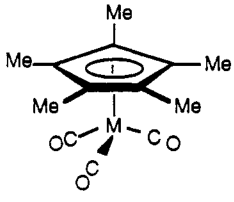
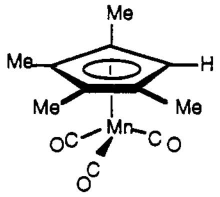
Summary: In contrast to previous reports, the thermal reaction of $Mn_2(CO)_{10}$ with neat pentamethylcyclopentadiene affords an approximately 77:23 mixture of $Mn(\eta^5\text{-}C_5Me_5)(CO)_3$ (**1a**) and $Mn(\eta^5\text{-}C_5Me_4H)(CO)_3$ (**2**), via competitive activation of the doubly allylic 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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(1) Bernal, I.; Korp, J. D.; Herrmann, W. A.; Serrano, R. *Chem. Ber.* **1984**, *117*, 434–444.

(2) Merrifield, J. H.; Lin, G.-Y.; Kiel, W. A.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5811–5819.

(3) Manriquez, J.; Fagan, P. J.; Schertz, L. D.; Marks, T. J. *Inorg. Synth.* **1982**, *21*, 181.

(4) GC/MS were run on a Finnigan 4000 spectrometer with an INCOS data system, using a 25-m Hewlett-Packard column of 0.20 mm i.d. containing a 0.33 μm film of cross-linked 5% phenylmethylsilicate. GC conditions: initial 1-μL injection of a 1 mg/mL solution of crude reaction product in CH_2Cl_2 using He carrier gas; separator at 200 °C; column at 50 °C for 1 min and then heated at 10 °C/min to 230 °C and held at this temperature for 10 min. MS conditions: ionizer mode EI/direct; emission current, 0.30 mA, electron multiplier, 1870 V; electron energy, 70 eV; calibration standard, perfluorotributylamine; scans of 45–450 amu were made every 1.05 s.

Table I. Relative Yields of 1a and 2

conditions	% ratio of 1a/2 (by GC/MS)[4]
(a) see text for conditions	77:23
(b) sample a recrystallized from hexane (−20 °C)	80:20
(c) sample b recrystallized from hexane (−20 °C)	94:6
(d) sample c recrystallized from hexane (−20 °C)	97:3
(e) conditions reported in ref 1	82:18

parison of its spectral properties with those of the minor product.[6]

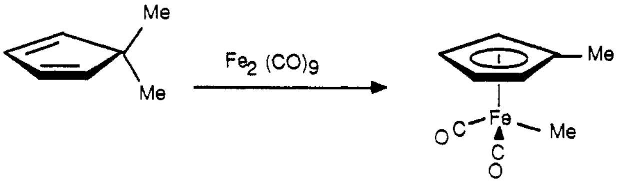
Varying the reaction temperature has little effect on the relative yields of **1a** and **2**. Carrying out the reaction under the conditions originally used by Herrmann[1] (180 °C, 13 h) resulted in an 82:18 (±3) mixture of **1a**/**2** (Table I, entry e). This reaction was repeated twice in our laboratories, and analogous GC/MS results were obtained on material prepared by using this methodology by the research group of Professor J. L. Hubbard (University of Vermont).

GC/MS analysis of a pure sample of **1a** under identical conditions[4] confirmed that **2** was not formed by degradation of **1a** during the analysis. Compound **1a** was also shown to be stable under the synthetic reaction conditions. When the reaction with $Mn_2(CO)_{10}$ was carried out in a sealed system and the product gases were subjected to FT-IR analysis, the presence of substantial quantities of methane was confirmed by comparison with an authentic sample. No IR evidence was obtained for significant quantities of other organic materials including ethane.[7] Finally heating Cp*H in the absence of metal carbonyl (180 °C, 13 h) showed no evidence for formation of degradation products. It seems clear that the mixture of **1a** and **2** is the result of competitive activation of the doubly allylic C–H and $C–CH_3$ bonds of Cp*H during the reaction with $Mn_2(CO)_{10}$.

In contrast the reaction of $Re_2(CO)_{10}$ with Cp*H afforded **1b** as the only organometallic product by GC/MS and NMR analysis of the crude reaction mixture, in agreement with the literature report.[2] Curiously, while no tetramethylcyclopentadienyl ligand was detected in this reaction, small traces of methane were formed as identified by FT-IR.

It is not surprising that the formation of mixtures of **1a** and **2** under these conditions was not previously noted. We have been unable to separate mixtures of **1a** and **2** efficiently by conventional column or thin-layer chromatographic methods. While successive crystallizations from hexane afforded samples increasingly enriched in **1a**, even after three such crystallizations traces of **2** were still present as revealed by GC/MS (Table I, entries b-d). Moreover, the IR spectrum (hexane solution) of the crude and recrystallized material in the CO stretching region exhibited only a single set of peaks characteristic of a tricarbonylmetal fragment of effective C_{3v} symmetry and is therefore not a good criterion of purity. Thus, the presence of **2** as a reaction product can only be detected in the ^1H or $^{13}C\{^1H\}$ NMR spectra of the crude reaction product or by GC/MS analysis.

While carbon–carbon bond activation in 5,5-disubstituted cyclopentadienes has been observed previously, affording compounds such as **3**,[8,9] our results clearly indicate



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that competition between C–H and C–C activation can occur under suitable circumstances. Although the mechanisms of the reactions reported here and the reasons for the differing reactivity of the Mn and Re carbonyls are not yet clearly defined, the significance of these results seems clear; it should not always be assumed that the η-C_5Me_5 ligand is the only product possible from reactions of pentamethylcyclopentadiene with metal carbonyl derivatives. Further studies of the mechanism(s) of these reactions are in progress.

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Registry No. **1a**, 34807-89-1; **2**, 104215-32-9; $Mn_2(CO)_{10}$, 10170-69-1; $MnBr(CO)_5$, 14516-54-2; Cp*H, 41539-64-4; lithium tetramethylcyclopentadienide, 82061-21-0.

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[5] The use of tetramethylcyclopentadiene and its anion have been reported (Scholtz, H. J.; Werner, H. *J. Organomet. Chem.* **1986**, *303*, C8–C12. Jutzi, P.; Dickbreder, R. *Chem. Ber.* **1986**, *119*, 1750–1754), but no synthetic details were given. We prepared the diene by a modification of the Cp*H synthesis[3] using ethyl formate rather than ethyl acetate. The Li salt was prepared by reaction of the diene with BuLi. To a solution of this salt in THF was added $MnBr(CO)_5$, and the mixture was refluxed overnight, cooled and evaporated to dryness. Chromatography on silica (hexane) afforded **2** in 20% yield.[6]

[6] **2**: mp 88–90 °C; ^1H NMR ($CDCl_3$) δ 1.88 (br s, 12 H, Me), 4.33 (s, 1 H, CH); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 10.23 (Me), 12.03 (Me), 79.96 (*C*H), 97.15 (*C*Me), 97.25 (*C*Me), 226.43 (CO); IR (hexane) ν_{CO} 2010, 1930 cm^{-1}; MS, *m/e* 260 (M^+), 204 (M^+ − 2CO), 176 (M^+ − 3CO), 121 (M^+ − $Mn(CO)_3$), 55 (Mn). Anal. Calcd for $C_{12}H_{13}MnO_3$: C, 55.40; H, 5.04. Found: C, 55.34; H, 4.98.

[7] Herzberg, G. In *Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules*; Litton Educational Publishing: New York, 1945; Chapter 3.

[8] Eilbracht, P.; Dahler, P. *Chem. Ber.* **1980**, *113*, 542–554.

[9] A number of variations of this reaction have been reported, including the reactions of spirocyclic analogues of 5,5-dimethylcyclopentadiene (see ref 8 and Eilbracht, P.; Mayser, U. *Chem. Ber.* **1980**, *113*, 2211–2220) and reactions of acetylpentamethylcyclopentadiene (King, R. B.; Efraty, A. *J. Am. Chem. Soc.* **1972**, *94*, 3773–3779). In the latter case apparently selective activation of the acetyl-ring bond was observed.

Stable, Four-Coordinate, σ-Vinyl Platinum(II) Complexes†

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Summary: The single site oxidative addition reactions of $Pt(PPh_3)_4$ and a series of vinyl triflates are described. The products obtained are stable, crystalline *16*-electron Pt(II) complexes containing a σ-vinyl ligand and the noncoordinating triflate anion.

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† Dedicated to Professor Cheves Walling on the occasion of his 70th Birthday.