product of the reaction of diphenyldiazomethane with $H_2Os_3(CO)_{10}$.[8]

Finally, in this situation, the $(C_6H_5)C{=}N{-}N(CO)C(CH_3)C(OC_2H_5)$ fragment acts as a six-electron ligand, and considering the metal-metal bond, each iron atom is surrounded by 18-valence electrons.

A similar type of fragment $RNC(O)C(CF_3)C(CF_3)$ bridging two rhodium atoms in a similar way has been obtained by quite a different route.[9]

To conclude, the reaction of diphenyldiazomethane with 1 gives evidence of a further example of insertion reactions of diazoalkanes with transition-metal complexes. There has been previous report of insertion reactions with hydride ligand to give $NHNCR_2$ ligands[8,10] and with carbon monoxide to give either CH_2N-N-CO species[11] by coupling with nitrogen or the N-N-CH_2-CO[12] fragment by coupling with methylene carbon.

This reaction also provides a further example of coupling of the two alkylidyne ligands in 1. Coupling has soon been observed during the reaction of alkynes[1b] or carbon monoxide[1c] with 1, but in these reactions the trimetallic structure of 1 was preserved.

Supplementary Material Available: Tables of structure factors amplitudes, final atomic coordinates, final anisotropic thermal parameters, and bond lengths and angles for $Fe_2(CO)_6(C_6H_5)_2CNNC(O)C(CH_3)C(OC_2H_5)$ (21 pages). Ordering information is given on any current masthead page.

---

(5) Crystal data: $C_{25}H_{18}O_8N_2Fe_2$; M_r = 586.1; monoclinic; a = 8.602 (1) Å, b = 10.916 (1) Å, c = 27.656 (3) Å; β = 94.74 (1)°; V = 2588.0 (9) Å^3 (by least-squares refinement on a CAD4 diffractometer for 25 automatically centered reflections, λ = 0.71073 Å); space group $P2_1/n$ (C^5_{2h}, No. 14); Z = 4; D_{calcd} = 1.504 g·cm^{-3}; orange parallelepipedic crystal (0.25 × 0.15 × 0.55 mm) sealed on a glass fiber; μ(Mo Kα) = 11.7 cm^{-1} (T = 293 K).

Data Collection and Processing (Mosset, A.; Bonnet, J.-J.; Galy, J. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1977**, *B33*, 2639–2644). Intensity data were recorded by the ω–2θ scan technique (scan width = 0.80° + 0.35° tan θ; scan speed = 1.9–10.3 deg·min^{-1}). A set of 5963 independent reflections was collected ($1.5 < \theta\ 27°$; h,K,$\pm l$) and corrected for Lorentz and polarization effects (Frentz, B. A. SDP, Structure Determination Package; Enraf-Nonius: Delft, Holland, 1982). Standard intensity reflections, recorded periodically, showed only random statistical fluctuations. A total of 3229 reflections with $I > 4\sigma(I)$ were used in structure solution and refinement. No absorption corrections were made.

Structure Determination. Fe atoms were located from a Patterson map. Subsequent full-matrix least-squares refinement and interpretation of a difference Fourier map using SHELX (Sheldrick, G.M. SHELX-76, Program for Crystal Structure Determination; University of Cambridge: Cambridge, England, 1976) enabled the location of all non-hydrogen atoms which were refined anisotropically. Hydrogen atoms were located on a difference Fourier map at their expected positions and introduced in calculations in constrained geometry (C–H = 0.97 Å). Neutral scattering factors were used, those for the non-hydrogen atoms being corrected for anomalous dispersion (f', f'' (*International Tables for X-ray Crystallography*; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2.B, p 99; Table 2.3.1, p 149; Table 2.2.C, p 102). The final full-matrix least-squares refinement converged to R = 0.034 and R_w = 0.038 with unit weights. The error in an observation of the unit weight was S = 1.49 with 3229 observations and 334 variables. In the last cycle of refinement, mean parameters shifts were 0.08σ. A final difference Fourier map showed a residual electron density of 0.4 e/Å^3.

(6) Krüger, C.; Barnett, B. L.; Brauer, D. In *The Organic Chemistry of Iron*; Koerner von Gurstorf, E. A.; Grevels, F. W., Fischler, I., Eds.; Academic Press: New York, 1978; pp 1–112.

(7) Colborn, R. E.; Dyke, A. F.; Knox, S. A. R.; Mead, K. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1983**, 2099–2108.

(8) Burgess, K.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1982**, 263–269.

(9) Dickson, R. S.; Nesbit, R. J.; Patteras, H.; Baimbridge, W. *Organometallics* **1985**, *4*, 2128–2134.

(10) Gambarotta, S.; Basso-Bert, M.; Floriani, C.; Guastini, G. *J. Chem. Soc., Chem. Soc., Chem. Commun.* **1982**, 374–375.

(11) Herrmann, W. A.; Ziegler, M. L.; Weidenhammer, K.; Biersack, H.; Mayer, K. K.; Minard, R. D. *Agnew. Chem., Int. Ed. Engl.* **1976**, *15*, 164–165.

(12) Ferguson, G.; Lawo, W. J.; Parvez, M.; Puddephatt, R. J. *Organometallics* **1983**, *2*, 276–280.

Electronic Charge Control of Stable Sites and Mobilities of Hydrogen Atoms on a Main-Group–Transition-Metal Cluster Surface. A Comparison of $[HFe_4(CO)_{12-n}(PPhMe_2)_nBH]PPN$ (n = 1, 2) and $HFe_4(CO)_{12}CH$

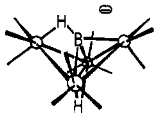
Catherine E. Housecroft and Thomas P. Fehlner*

Department of Chemistry, University of Notre Dame
Notre Dame, Indiana 46556

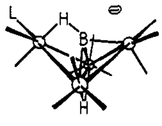
Received February 26, 1986

Summary: The phosphine-substituted ferraboranes $[HFe_4(CO)_{12-n}(PPhMe_2)_nBH]PPN$ (n = 1, 2) have been prepared by direct substitution on the parent "butterfly" cluster. Substitution is specific being "wing-tip" for monosubstitution and "wing-tip"–"wing-tip" for disubstitution. The former increases the barrier for the fluxional process whereby the endo hydrogens are exchanged and the latter results in the net conversion of a FeHFe into a FeHB interaction. Comparison of the fluxional properties of the ferraborane anion with those of $HFe_4(CO)_{12}CH$ demonstrates specific differences rationalized on the basis of the FeHB vs. the FeHC interactions. Calculations suggest that a model consisting of protons on a cluster surface seeking maximum available electron density is consistent with the experimental observations.

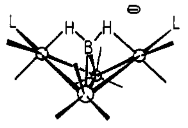
Besides possessing their own significant chemistry,[1] discrete transition-metal cluster hydrides are experimentally accessible models for hydrogen-metal interactions.[2] The site of coordination and intramolecular exchange processes of the hydrogen ligand on metal clusters have been revealed by structural[3] and dynamic[4] studies and some principles are beginning to be understood. A particularly interesting cluster hydride is one that contains both main-group and transition-metal atoms in the cluster network.[5] An understanding of stable location and mobility of hydrogen atoms on such heteronuclear clusters bears directly on the problem of modeling CH_x fragment hydrogenation/dehydrogenation on a multinuclear metal site.[6] Here we present a preliminary account of the effect of substitution of phosphines for CO's on $HFe_4(CO)_{12}BH^-$ (I) and "substitution" of C for B^- in I, i.e., comparison with



I



II



III

---

(1) *Transition Metal Hydrides*; Bau, R., Ed.; Advances in Chemistry 167; American Chemical Society: Washington, DC, 1978.

(2) Band, E.; Muetterties, E. L. *Chem. Rev.* **1978**, *78*, 639.

(3) Teller, R. G.; Bau, R. *Struct. Bonding (Berlin)* **1981**, *44*, 1.

(4) See, for example: Stuntz, G. F.; Shapley, J. R. *J. Am. Chem. Soc.* **1977**, *99*, 607.

(5) Housecroft, C. E.; Fehlner, T. P. *Adv. Organomet. Chem.* **1982**, *21*, 57.

(6) In some work on a carbon capped-trinuclear iron cluster, we have demonstrated the existence of several isomers differing in hydrogen location as well as facile mobility of the hydrogens over a cluster surface that includes the main-group atom. Vites, J. C.; Jacobsen, G.; Dutta, T. K.; Fehlner, T. P. *J. Am. Chem. Soc.* **1985**, *107*, 5563.

0276-7333/86/2305-1279$01.50/0

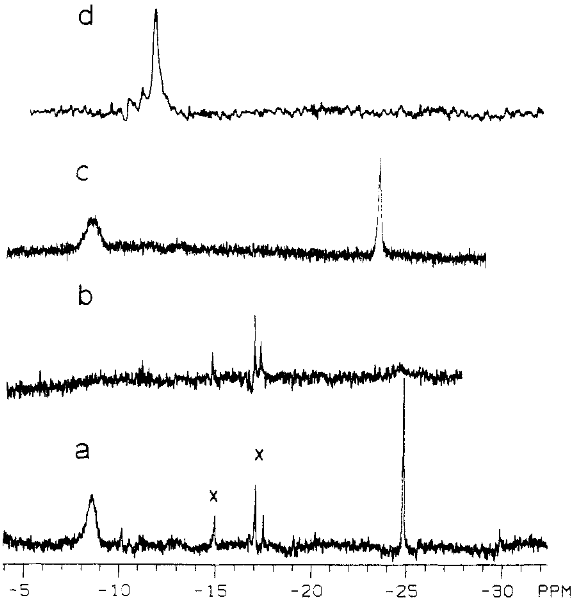


Figure 1. Proton spectra of (a) I at -60 °C (x's refer to known impurities), (b) I (same sample) at 20 °C, (c) II at 20 °C, and (d) III at -80 °C; except for thermal decoupling at the lower temperatures, spectrum d is independent of temperature.

the isoelectronic and isoprotonic $HFe_4(CO)_{12}CH$,[7] on hydrogen atom location and mobility.[8] In doing so we demonstrate some factors important in controlling hydrogen location, barrier heights for hydrogen migration, and relative strengths of the metal- and main-group atom-hydrogen interactions.

The preparation and characterization of I has been described previously.[9] On treatment of I with 1 molar equiv of $PPhMe_2$ it is smoothly (via an intermediate) converted to II.[10] The ^{11}B and ^1H NMR shifts along with the infrared spectrum show that the "butterfly" structure is retained with FeHB and FeHFe protons. The ^{31}P NMR spectrum, the chemical shift, and the observed phosphorus coupling with the FeHB proton suggest that a single isomer is produced in which a "wing-tip" CO has been replaced by the phosphine.[11] Addition of a second mole of phosphine results in conversion of II to III[12] via a slower process accompanied by significant (20%) cluster degradation to known mononuclear compounds and $Fe_3(CO)_9(PPhMe_2)BH_2^-$. The ^{31}P NMR data allow us to characterize the product as III; i.e., at 20 °C only a single ligand resonance is observed and the chemical shift is similar to that observed for II.[13]

The most striking effect of adding phosphine ligands to I is shown in Figure 1. Substitution of one CO by $PPhMe_2$ leads to II with the endo-hydrogen locations unchanged with respect to I but with an increased barrier to proton scrambling. Substitution of a second CO on the other wing-tip leads to the conversion of an FeHFe interaction into a FeHB interaction.[14] This is confirmed by the ^1H (Figure 1) and ^{11}B NMR chemical shifts for III which are similar to those of $HFe_4(CO)_{12}BH_2$.[15] Extended Hückel calculations[16] suggest that the phosphine substituent attacks the most positive ("wing-tip") iron of I and the hydrogens move to positions whereby they gain maximum negative charge while at the same time "neutralizing" the excess charge introduced by phosphine replacement of CO.

The change in the strength of the BH interaction by sequential phosphine substitution is revealed by the magnitude of the BH coupling constants in I (86 Hz), II (67 Hz), and III (53 Hz).[17] The decrease in coupling constant with sequential "wing-tip" substitution is attributed to a net decrease in the strength of the BH interaction as the hydrogen is drawn toward the more electron-rich $Fe(CO)_2PR_3$ fragment. This decrease in the BH interaction might suggest that II should have a lower barrier for FeHFe/FeHB hydrogen exchange than I, but, as stated above, the opposite is true. Extended Hückel calculations[16] show, however, that the FeHB hydrogen in a position adjacent to the site of phosphine substitution is 4 kcal/mol more stable than a hydrogen in the nonadjacent position. This suggests that the stabilization of the proton adjacent to the substituted iron increases the reaction barrier more than the change in the BH interaction reduces it.

A comparison of I with $HFe_4(CO)_{12}CH$ permits a test of these conclusions. The ^1H NMR shows that the FeHB and FeHFe protons of I exchange more readily than do the FeHC and FeHFe protons of $HFe_4(CO)_{12}CH$,[7] i.e., the mobility of the endo hydrogens is much greater in the boron anion than in the carbon compound. Both compounds have the same relative proton locations, but the geometry of the FeHX interaction is skewed toward carbon; i.e., the FeB and FeC distances are nearly equal but the CH distance is less than the BH distance.[18] Clearly, the stronger CH interaction reduces the mobility of the hydrogens on the cluster surface.

---

(7) Tachikawa, M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1980**, *102*, 4541. Beno, M. A.; Williams, J. M.; Tachikawa, M.; Muetterties, E. L. *Ibid.* **1980**, *102*, 4542. Beno, M. A.; Williams, J. M.; Tachikawa, M.; Muetterties, E. L. *ibid* **1981**, *103*, 1485.

(8) The consequences of phosphine substitution on the exchange processes of $HFe_4(CO)_{12}CH$ has been explored. Muetterties, E. L.; Geerts, R. L., Tachikawa, M.; Burch, R. R.; Sennett, M. S.; Williams, J.; Beno, M. *Abstr. Pap.–Am. Chem. Soc.* **1982**, *182nd*, INORG 89. Wadepohl, H.; Muetterties, E. L.; Day, V. W. *GdCh. 20th Hauptversammlung*, Heidelberg, 1985.

(9) Housecroft, C. E.; Fehlner, T. P. *Organometallics* **1986**, *5*, 379.

(10) ^{11}B NMR ($CD_3C(O)CD_3$, 20 °C) δ 141.7 (br s, fwhm = 180 Hz); $\{^1H\}$ (fwhm = 140 Hz, J_{BH} = 65 Hz by line-width analysis); ^{31}P ($CD_3C(O)CD_3$, -80 °C) δ 30.0 (m, 1 P, $\{^1H\}$ selective, $J_{PH(FeHB)}$ = 12 Hz, $PhMe_2P$), 21.7 (m, 2 P, PPN^+); ^1H NMR ($CD_3C(O)CD_3$, 0 °C) δ 7.7–7.5 (m, 35 H, PPN^+ and $PhMe_2P$), 1.89 (d, 6 H, J_{PH} = 9 Hz, $PhMe_2P$), −8.4 (br, 1 H, FeHB), −23.8 (s, 1 H, FeHFe); ^{13}C NMR (CH_2Cl_2, −80 °C) δ 222.5 (2 CO), 218.1 (3 CO), 214 (br, 6 CO); IR ν_{CO} (CH_2Cl_2, cm^{-1}) 2048 w, 2034 w, 2004 sh, 1985 vs, 1977 vs, 1950 s.

(11) The magnitude of the ^{31}P coupling to the FeHB proton suggests equatorial substitution. (In the unsubstituted compound each iron has a pair of equivalent "equatorial" CO's and one "axial" CO.) The ligand methyl proton signal is a doublet, suggesting axial substitution or equatorial substitution combined with a fluxional process that takes the phosphine through the plane of symmetry defined by the boron and "wing-tip" irons. The ^{13}C NMR signal of the ligand methyl carbons shows that the phosphine is involved in an exchange process and, hence, equatorial (see structure II) substitution is suggested.

(12) ^{11}B NMR ($CD_3C(O)CD_3$, 20 °C) δ 117.9 (br t, fwhm = 210 Hz); $\{^1H\}$ (fwhm = 175 Hz, J_{BH} = 53 Hz); ^{31}P NMR ($CD_3C(O)CD_3$, 20 °C) δ 31.0 (m, 2 P, $PhMe_2P$), 21.7 (m, 2 P, PPN^+); ^1H NMR ($CD_3C(O)CD_3$, −60 °C) δ 7.7–7.5 (m, PPN^+ and $PhMe_2P$), 1.9 (m, $PhMe_2P$), −11.6 (br, 2 H, FeHB).

(13) At −90 °C the ^{31}P NMR shows two resonances at 32.3 and 31.9 ppm which are attributed to structure III and the "trans" isomer.

(14) Changes in stable bridging hydrogen locations have been observed previously in all metal tetrahedral clusters. See, for example: Shapley, J. R.; Richter, S. I.; Churchill, M. R.; Lashewycz, R. A. *J. Am. Chem. Soc.* **1977**, *99*, 7384.

(15) Fehlner, T. P.; Housecroft, C. E.; Scheidt, W. R.; Wong, K. S. *Organomemtallics* **1983**, *2*, 825.

(16) The PH_3 ligand was used as a model for $PhMe_2P$ with d(PH) = 1.42 Å, *d*(FeP) = 2.24 Å, <HPH = 90°, and <FePH = 125.3°. Extended Hückel parameters were generated as previously described. Andersen, E. L.; DeKock, R. L.; Fehlner, T. P. *Inorg. Chem.* **1981**, *20*, 3291.

(17) Onak, T.; Leach, J. B.; Anderson, S.; Frisch, M. J.; Marynick, D. *J. Magn. Reson.* **1976**, *23*, 237.

(18) This comparison is between the structural parameters of $HFe_4(CO)_{12}BH_2$ and $HFe_4(CO)_{12}CH$.[15]

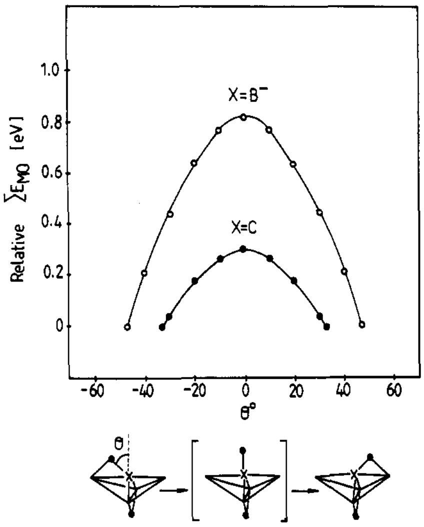


Figure 2. A possible mechanism for Fe–H–X exchange between the two FeX "wing-tip" sites and calculated barriers for X = C and B using the extended Hückel method. Zero energies are taken for the experimental geometries in each case.

The ^{13}C NMR of $HFe_4(CO)_{12}CH$ in the carbonyl region shows only four types of CO even at −80 °C, thereby showing that a low barrier path for FeHC proton exchange between the two carbon "wing-tip" sites (Figure 2) exists.[7] On the other hand, the ^{13}C NMR of I in the carbonyl region at −80 °C exhibits six types of CO (seven expected for the static structure), thereby demonstrating that no such low barrier path for the exchange of the FeHB proton between the two boron "wing-tip" sites exists. The process occurring in the former may be envisioned as a simple proton flip between the two carbon "wing-tip" sites as shown in Figure 2.[19] Modeling this process with extended Hückel calculations shows that the barrier associated with this mechanism in I is significantly larger than that in $HFe_4(CO)_{12}CH$ (Figure 2). This is attributed to a stronger FeH interaction in the FeHX unit when X is boron. Thus, as one goes from $HFe_4(CO)_{12}CH$ to I, processes in which the XH bond is retained and FeH broken are inhibited by stronger FeH interactions while processes whereby the hydrogen wanders over the cluster framework are enhanced by both stronger FeH and weaker XH interactions.

These observations constitute a basis for understanding some thermodynamic and kinetic factors responsible for moving a hydrogen atom to and away from a main-group atom bound to a multinuclear transition-metal cluster site. If the hydrogen is viewed as a proton, one factor revealed by the calculations and corroborated by the experiments seems rather elementary—the proton seeks maximum charge[20,21] and the greater the difference in availability of charge at potential sites, the greater the barrier to mobility. Phosphine substitution on iron increases the available electron density at adjacent sites, thereby attracting protons from elsewhere in the cluster into deeper potential wells. Carbon "substitution" for boron pulls in electron density and the proton with it. A more subtle point made by this work is the importance of viewing the C (or B) atom as a participant in the cluster framework bonding. Thus, because C(B)–Fe bonding exists, the endo hydrogens can be considered as protons chasing available charge and hydrogenation/dehydrogenation of the C(B)–H moiety can be rapid and easily reversed by relatively small perturbations. This exactly fulfils the requirements for an effective catalytic site.

Acknowledgment. The support of the National Science Foundation under Grant CHE 8408251 is gratefully acknowledged.

Registry No. I, 99582-34-0; II, 102132-76-3; III, 102132-77-4.

---

[19] There are obviously other mechanisms possible but this is a simple one that makes the point.

[20] This correlation has been suggested to account for the hydrogen locations in simpler systems. DeKock, R. L.; Jasperse, C. P. *Inorg. Chem.* **1983**, *22*, 3839.

[21] Not all possible edge-bridging sites have been calculationally explored. Because energy differences between different hydrogen arrangements are intrinsically small, other factors, e.g., steric, may be important also.

Synthetic, X-ray Structural, and Photoluminescence Studies on Pentamethylcyclopentadienyl Derivatives of Lanthanum, Cerium, and Praseodymium

Marvin D. Rausch* and Kevin J. Moriarty

Department of Chemistry, University of Massachusetts
Amherst, Massachusetts 01003

Jerry L. Atwood,* James A. Weeks, and
William E. Hunter

Department of Chemistry, University of Alabama
University, Alabama 35486

Harry G. Brittain*

Department of Chemistry, Seton Hall University
South Orange, New Jersey 07079

Received February 21, 1986

Summary: Reactions of anhydrous lanthanum, cerium, or praseodymium chlorides with 2 equiv of (pentamethylcyclopentadienyl)lithium in THF solution followed by solvent removal and crystallization from diethyl ether afford the crystalline complexes $(\eta^5\text{-}C_5Me_5)_2LnCl_2Li(OEt_2)_2$ (**1**, Ln = La; **2**, Ln = Ce; **3**, Ln = Pr) in good yields. Crystals of **2** belong to the tetragonal space group $P\bar{4}2_1m$ with a = 11.313 (4) Å, c = 12.959 (3) Å, and D_{calcd} = 1.27 g cm^{-3} for Z = 2. Least-squares refinement based on 760 observed reflections led to a final R value of 0.074. The Ce–Cl distance is 2.812 (1) Å. The photoluminescence spectrum of **2** is discussed and interpreted.

Although research concerning the organometallic chemistry of the lanthanides is currently expanding at a rapid rate, comparatively little is known about organic derivatives of the earliest lanthanides La (f^0), Ce (f^1) and Pr (f^2).[1] In particular, lanthanocene chloride complexes of the type $(Cp_2LnCl)_x$ are not available for these metals,[2,3] a feature

---

[1] (a) Evans, W. J. *Adv. Organomet. Chem.* **1985**, *24*, 131. (b) Schumann, H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 474. (c) Marks, T. J.; Ernst, R. D. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1982; Vol. 3, p 173. (d) Marks, T. J. *Prog. Inorg. Chem.* **1978**, *24*, 51.

[2] Maginn, R. E.; Manastyrskyj, S.; Dubeck, M. *J. Am. Chem. Soc.* **1963**, *85*, 672.

[3] The synthesis and molecular structure of the related neodymium analogue $[Cp_2NdCl(THF)]_2$ has been recently described: (a) Chen, W. *Yingyang Huaxue* **1983**, *1*, 55 [*Chem. Abstr.* **1984**, *101*, 192119u]; (b) Chen, W.; Jin, W.; Jin, Z.; Liu, Y., Poster at the NATO-ASI "Fundamental and Technological Aspects of Organo-f-Element Chemistry", Acquafredda di Maratea, Sept 1984.