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(10) A THF (100 mL) suspension of Co(pr-salen) (2.2 g, 4.95 mmol) was reacted with the stoicheiometric amount of potassium (0.2 g, 5.12 mmol). The mixture was heated at the boiling point of the THF and then was stirred vigorously for 24 h at room temperature. The deep green THF solution of [Co(pr-salen)K], upon exposure to a CO_2 atmosphere, gave on standing [Co(pr-salen)KCO_2THF] as deep red crystals (yield, ~75%). Calcd for [Co(pr-salen)KCO_2THF] ($C_{27}H_{34}N_2O_5CoK$): C, 57.44; H, 6.03; N, 4.96. Found: C, 56.48; H, 6.19; N, 4.71. The solid is stable under a CO_2 atmosphere only. It was found practically diamagnetic with a $\chi_g = 0.30 \times 10^{-6}$ cgs u at 293 K.
(11) With $^{13}CO_3^{2-}$ these bands are at 1610, 1250, 1192, and 732 cm^{-1}, respectively. IR data are from Nujol mulls.
(12) Standard deviations on intensity were computed as $\sigma(I) = [P + 0.25(T_p/T_B)^2(B_1 + B_2) + (0.04I)^2]^{1/2}$, where P is the total peak count in a scan of time T_p; B_1 and B_2 are the background counts each in a time T_B; I is the intensity equal to $P - 0.50(T_p/T_B)(B_1 + B_2)$.
(13) The usual Lorentz and polarization corrections were applied to the intensity data. Three reflections were measured every 180 min as a check on crystal and instrument stability. No significant change in the measured intensity of these reflections was observed during data collection.
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(15) The function minimized during least-squares refinement was $\Sigma_w(F_o - F_c)^2$, where the weighting factor w is $4F_o^2/\sigma(F_o^2)$.
(16) Owing to the large number of atoms to reflections ratio, anisotropic thermal parameters were refined only for noncarbon atoms, with the exception of the oxygen of the tetrahydrofuran group. Carbon atoms of the propylic chains of Co(pr-salen) are affected by relatively high apparent thermal motion, probably indicative of position disorder. All atoms of the tetrahydrofuran group have very high thermal parameters; this was ascribed to statistical site occupancy. Some least-squares cycles were carried out with reduced occupancy parameters. Results seem to indicate that thermal parameters assume acceptable values when the occupancy of the tetrahydrofuran group is ~50%. However, previous refinement was considered complete and adequate to reveal all structural features of chemical significance.
(17) The discrepancy index R is defined as $\Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. The scattering factors for Co, K, O, N, and C were taken from International Tables for X-ray Crystallography, Vol. III, Kynoch Press, Birmingham, 1962, p 202. To the form factors of Co a correction for anomalous dispersion ($\Delta F'$ and $\Delta F''$) was applied according to D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).
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(23) O(1), O(2), N(1), and N(2) are the donor atoms of the pr-salen ligand, whose organic part has been omitted for clarity. O(3) and O(4) are the oxygens of the CO_2; O(5) belongs to a THF molecule.

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Interaction of an Aliphatic Hydrogen Atom with a Transition Metal. The First Direct Observation of a Strong C—H···Metal Interaction Derived from a Single Crystal Neutron Diffraction Study[1] of $\{Fe[P(OCH_3)_3]_3(\eta^3\text{-}C_8H_{13})\}^+[BF_4]^-$

Sir:

It is generally agreed that metal-complex-induced C–H bond "activation", which is of extreme fundamental and commercial importance in homogeneously catalyzed chemical reactions,[2,3] often proceeds via a C—H···metal *intermediate* of heretofore unknown geometry.[3] Important structural questions associated with the process of C—H bond activation are (1) how much is a C—H bond stretched when the H atom interacts with a metal center, and (2) what angular deformations occur at the C atom upon formation of the C—H···M intermediate? Except for very strong B—H···Mo[4] and C—H···Mo[5,6] interactions discussed below, weak M···H interactions of ~2.6–2.9 Å derived mainly from X-ray diffraction investigations have been found in $PdI_2(PMe_2Ph)_2$,[7] $RuClH(PPh_3)_3$,[8] $Rh(SiCl_3)ClH(PPh_3)_2$,[9] $[Rh(PPh_3)_3]ClO_4\cdot CH_2Cl_2$,[10] $RuCl_2(PPh_3)_3$,[11] $Pd[PPh(t\text{-}Bu)_2]_2$,[12] and $Pt[PPh(t\text{-}Bu)_2]_2$.[12] In this regard, although numerous neutron diffraction studies of M—H and M—H—M systems have been reported,[13] *no* such studies of C—H···M systems have been reported.[31] We report the first *direct* structural observation of an unprecedentedly strong C—H···M interaction in the metal-hydrocarbon complex $\{Fe[P(OMe)_3]_3(\eta^3\text{-}C_8H_{13})\}^+[BF_4]^-$, **1**. The neutron diffraction study of **1** was undertaken in order to precisely define the structural geometry of a possible C—H···Fe intermediate which might be a possible precursor to aliphatic C—H bond scission.

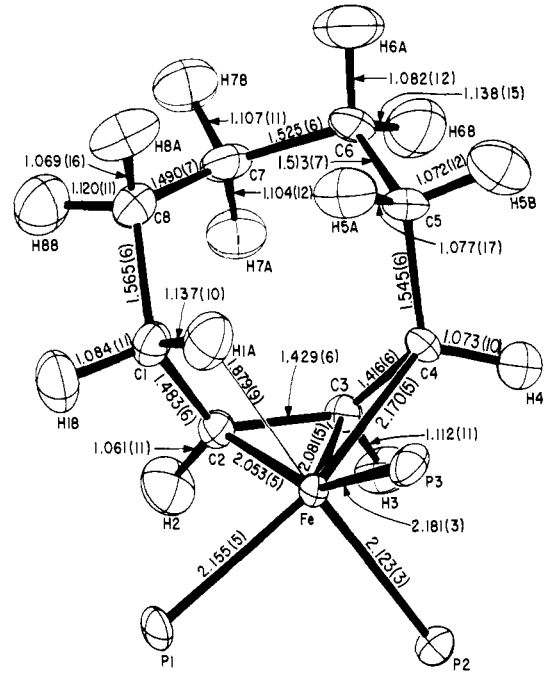

Figure 1. Atom labeling scheme for the $\{Fe[P(OCH_3)_3]_3(\eta^3\text{-}C_8H_{13})\}^+$ cation ($-OCH_3$ groups omitted for clarity) showing the distorted octahedral coordination around the Fe atom with the aliphatic H atom (H(1A)) occupying a coordination site. The very strong C(1)—H(1A)···Fe interaction, in which the Fe···H(1A) distance is ~0.1 Å greater than the sum of the covalent radii, is indicated with a faint line. The thermal ellipsoids of nuclear motion for all atoms are scaled to enclose 50% probability and important internuclear distances (uncorrected for thermal motion) are given with their estimated standard deviations. The C(1)–H(1A)–Fe angle is 100.6 (6)°. The C(2)–C(1)–C(8) angle is 116.6 (4)° while the other five tetrahedral angles subtended at C(1) are in the range of 104.2–110.8°. The range of C–C–C angles for the remaining aliphatic carbon atoms is from 114.5 to 117.4°.

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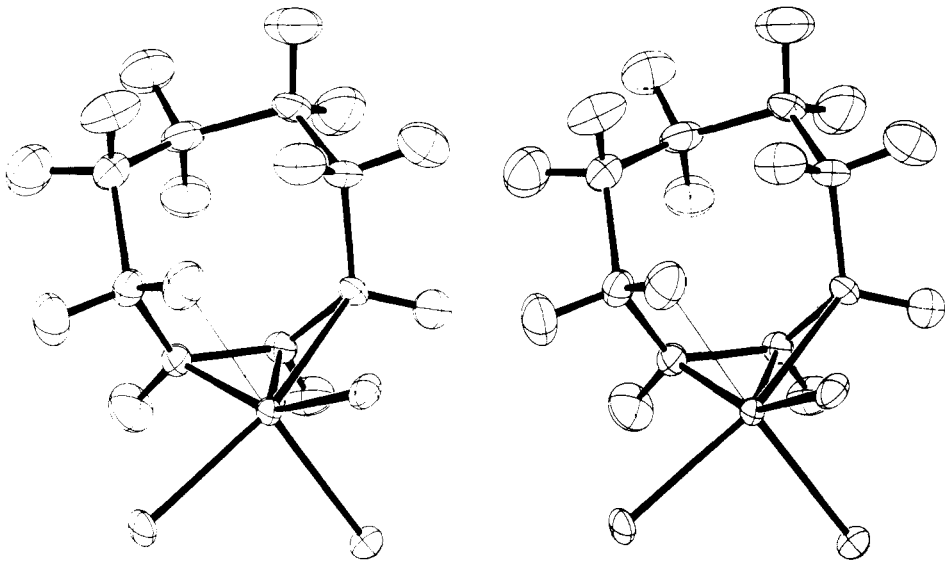
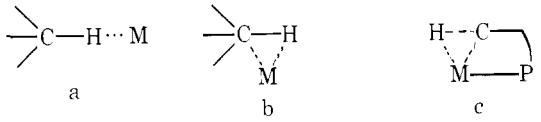


Figure 2. Stereoscopic drawing of the $\{Fe[P(OCH_3)_3]_3(\eta^3\text{-}C_8H_{13})\}^+$ cation ($-OCH_3$ groups omitted) which clearly shows the C_8H_{13} ring distortion which accompanies the formation of the strong C—H···Fe interaction (indicated by a faint line). The terminal C atoms of the allylic group appear to occupy (approximately) two Fe coordination sites.

Two models (a and b), meant to represent extremes of C—H···M type interactions were proposed by Cotton and co-workers in their pioneering X-ray diffraction[5,6] and NMR[7] studies of B—H···Mo and C—H···Mo interactions in molybdenum pyrazolylborate complexes. Parshall[3] has suggested a



transition state similar to b as denoted by c. In the case of the molybdenum pyrazolylborate complexes, convincing arguments were given that the 3-center "bond" was linear, that it was best represented by a above, and that for the C—H···Mo system the Mo···H distance was short at ~2.2 Å.[14] This distance is ~0.4-0.5 Å longer than terminal (Mo—H_t) or bridging (Mo—H_b) separations which have been determined recently.[15]

In a recent report[18] describing **1**, two independent fluxional processes were described. The first involved the phosphite ligands only and the second was ascribed to the C_8H_{13} ring whereby one proton on each α-carbon (C(1) and C(5)) atom was alternately involved in a C—H···Fe interaction. It was observed that **1** is not an Fe hydride as was reported for the protonated cyclohexadiene tricarbonyliron system,[19] **2**. Both **1** and **2** were similar in that the existence of strong Fe···H···C interactions[20] was suggested. We have confirmed the existence of a very strong Fe···H interaction in **1** and the geometry of the $[FeL_3(\pi\text{-enyl})]^+$ cation, derived from our single crystal neutron diffraction study, is presented in Figure 1.[21] A stereopair of the cation is displayed in Figure 2 for clarity. The most important finding involves the 3-center C(1)—H(1A)···Fe interaction which contains a very short H(1A)···Fe distance of 1.879 (9) Å. Using published covalent radii (Fe (1.40 Å)[24] and H (0.37 Å)[13]), we would expect a terminal *covalent* Fe—H_t (H = hydride) distance to be ~1.77 Å. This distance agrees very well, after allowing for the usual 0.1-0.2 Å shortening due to the X-ray experiment, with the value of Fe—H_t = 1.57 ± 0.12 Å observed[25] in $[(Ph_3P)_2N]^+[HFe(CO)_4]^-$. Therefore, we would expect an Fe—H_t separation to be ~1.8 Å, which is only ~0.1 Å less than that observed in **1**.[32] Considering that bridging X—H_b—X bonds (X = B, N, O, F, Cl, and many metals) are usually 0.1-0.2 Å longer[13] than X—H_t, then the value of 1.879 (9) Å observed in **1** indicates a "bonding" interaction with the metal. This is clearly visible in Figure 2 in which the H atom occupies a coordination site in the distorted octahedral array around the Fe atom. This is exemplified by the H(1A)-Fe-P(1), H(1A)-Fe-P(2), and H(1A)-Fe-P(3) angles of 93.5 (3), 176.8 (3), and 89.1 (3)°, respectively. While the Fe···H distance determined here indicates considerable M···H interaction, the experimentally derived C(1)—H(1A) distance of 1.137 (10) Å is not significantly longer than the other aliphatic C—H distances in the C_8H_{13} ring or that of 1.10 Å established by spectroscopic methods.[26,27] However, an upper limit of 1.17 Å for the C(1)—H(1A) bond, based on a 3σ criterion, cannot be ruled out. Because of a lack of significant C(1)—H(1A) bond lengthening, a condition which we would expect if electron density from the C—H bond were delocalized into the C—H···Fe system, we hesitate to describe the C—H···Fe interaction in terms of a fully delocalized[30] 2-electron 3-center bond, but rather as a *precursor* to a 2-electron 3-center bond. There may also be an analogy between the C—H···Fe interaction observed here and that of "semibridging" carbonyl groups[28] observed in transition metal complexes.

From Figure 2 it is also readily apparent that the Fe···H(1A) interaction is of sufficient strength to cause a distortion of the C_8H_{13} ring such that C(1) is displaced toward Fe, and C(4) is displaced away from Fe, as H(1A) moves to occupy the available Fe octahedral coordination site. From the solution NMR[18] studies it is the dynamic interaction, alternately involving C(1) and C(5) and one proton from each, which results in the Fe···H 2-site interaction.[29] Thus, the solid-state molecular structure as determined by this neutron diffraction study most likely represents one of two possible extremes observed during the fluxional process of the C_8H_{13} ring. The fact that this configuration is observed, rather than one with the H atoms of C(1) and C(5) equidistant from the Fe atom, indicates that positioning a hydrogen atom in an octahedral coordination site of Fe is an energetically stabilizing effect. Finally, it is tempting to speculate that, in certain homogeneously catalyzed reactions, an otherwise inert C—H bond is activated (lengthened and weakened) as a result of the formation of a delocalized 3-center 2-electron C—H→M bond.

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(1) This work was performed under the auspices of the Division of Basic Energy Sciences of the U.S. Department of Energy. We also wish to acknowledge the partial support of this collaborative research by the National Science Foundation (Grant No. CHE-77-22650) through a grant to J.M.W. and G.D.S. G.D.S. also acknowledges support by NSF Grant NSF-CHE-77-24964.
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(14) We now realize that, although the C—H···Mo[5] and B—H···Mo[4] systems were both described as 2-electron 3-center bonds, there is a very important difference between them in *the crystalline state*. Based on the X-ray crystallographic results for the B—H···Mo[4] system, which appear to be very internally consistent, the derived distances for B—H_t = 0.92 (6) and 0.98 (6) Å, while the bridging bonds were much longer, B—H_b (to Mo) = 1.23 (4) and 1.29 (5) Å. However, the C—H···Mo system gave C—H_b = 0.97 (8) Å; i.e., there was no observed C—H bond lengthening which suggests that the bridge bonds in the B—H···Mo and C—H···Mo systems are different. Therefore, the B—H···Mo interaction might be best described as a delocalized 2-electron 3-center bond, while that for the C—H···Mo case would be an *incipient* 2-electron 3-center bond. While there is considerable crystallographic evidence for B—H bond lengthening upon formation of a B—H···X bond, none exists for C—H.
(15) The H···Mo distance of ~2.2 Å may be compared with the terminal (Mo—H_t) distance of 1.685 (3) Å that we derived[16] in $H_2Mo(C_5H_5)_2$ and the *bridging* (Mo—H_b—Mo) distances of 1.851 (4) and 1.869 (4) Å that we obtained[17] for $HMo_2(C_5H_5)_2(CO)_4(PCH_3)_2$.
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(21) A single crystal of $\{Fe[P(OMe)_3]_3(\eta^3\text{-}C_8H_{13})\}^+[BF_4]^-$, weighing 30 mg, was sealed under dry N_2 in a Pb glass capillary for protection. A total of 3784 three-dimensional data, of which 2748 had $F_o^2 > \sigma F_o^2$, were collected on the Chemistry Division neutron diffractometer at the Argonne CP-5 reactor. All data were collected at 110 K, using a device based on the Strouse[22] design, out to sin θ/λ = 0.563 (λ = 1.142 (1) Å). A least-square fit of 23 automatically centered reflections (40° < 2θ < 60°) confirmed the monocinic unit cell ($P2_1/c$) with a = 8.947 (6) Å, b = 18.508 (13) Å, c = 16.594 (11) Å, β = 101.71 (7)°, V = 2690.7 Å^3, and d_{calcd} = 1.541 g cm^{-3} for Z = 4. All integrated intensities were corrected for absorption (μ_c = 3.01 cm^{-1}) and the range of transmission coefficients was 0.353–0.485. Using initial nonhydrogen atom coordinates from an X-ray investigation[23] all atoms were located using Fourier techniques. Final anisotropic full-matrix least-squares refinement of all 75 atoms (677 parameters) on the Argonne IBM 370/195 computer gave $R(F_o^2)$ = 0.142 and $R(F_o)$ = 0.156 with a "goodness of fit" of 1.53 for all data and $R(F_o^2)$ = 0.122 and $R(F_o)$ = 0.098 for 2748 data with $F_o^2 > \sigma F_o^2$.
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(29) Thus, there is considerable similarity between the process described here and that discussed by Cotton and Stanislowski[6] in which two hydrogen atoms of an α-carbon atom of an ethyl group change places while involved in a C—H···Mo interaction.
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(32) Considering that the Mn—H_t distance in $HMn(CO)_5$ is 1.60 (2) Å,[33] and that Mn and Fe have very similar covalent radii, then a better value for the Fe—H_t distance may be ~1.60 Å. If this is the case then the observed Fe—H_t distance in **1** is ~0.3 Å longer than a Fe—H_t separation.
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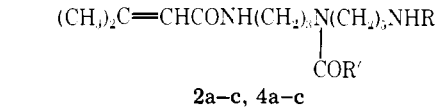
Polyandrocarpidines: Antimicrobial and Cytotoxic Agents from a Marine Tunicate (*Polyandrocarpa* sp.) from the Gulf of California[1]

Sir:

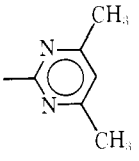
During the Illini-Trojan Baja expedition of 1976,[2] a red encrusting colonial tunicate was identified in our mobile laboratory as possessing potent activity against *Bacillus subtilis*. Subsequently, the tunicate was identified as a *Polyandrocarpa* sp.,[3] and its extracts were demonstrated to have cytotoxic (L1210[4a] and KB[4b] cells) as well as antibacterial activity. We assign here the structure of the major bioactive component of this species (polyandrocarpidine I) as **1a** (Chart I) and the minor component (polyandrocarpidine II) as **1b**. The polyandrocarpidines are remarkable, both for the occurrence of the highly strained cyclopropene ring (heretofore found in nature only in sterculic and related acids[5a,b] and in calysterol[5c]) and for their relationship to the recently discovered acarnidines (**2a–c**),[6] which occur in a sponge (*Acarnus erithacus*), in a



2a–c, 4a–c

2a–c, R = C(=NH)NH_2
2a, R′ = $(CH_2)_{10}CH_3$
b, R′ = $(CH_2)_3CH{=}CH(CH_2)_5CH_3$ (*Z*)
c, R′ = $(CH_2)_3(CH{=}CHCH_2)_3CH_3$ (all-*Z*)

4a–c, R =



4a, R′ = $(CH_2)_{10}CH_3$
b, R′ = $(CH_2)_3CH{=}CH(CH_2)_5CH_3$ (*Z*)
c, R′ = $(CH_2)_3(CH{=}CHCH_2)_3CH_3$ (all-*Z*)

phylum (Porifera) very distant from that of the tunicates (Chordata).

A sample of the *Polyandrocarpa* species was homogenized in the ethanol in which it had been stored and the chloroform-soluble fraction of the concentrated ethanol extract was chromatographed over a silica gel column. Elution with chloroform–methanol (3:2) gave a mixture consisting of 90%

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