(2) The reaction of $TaCp(CHCMe_3)Cl_2$ with $C_6H_5CH{=}CD_2$ gives $C_6H_5CH{=}CDCHDCMe_3$, consistent with this proposal.
(3) (a) The Ti^{4+} metallocycle, $TiCp_2(C_4H_8)$, decomposes to give ethylene and 1-butene; metallocyclopentane complexes are more stable than their acyclic analogues since β-hydride elimination is suppressed, probably for steric reasons: J. X. McDermott, M. E. Wilson, and G. M. Whitesides, *J. Am. Chem. Soc.*, **98**, 6529 (1976). (b) R. H. Grubbs, A. Miyashita, M. M. Liu, and P. L. Burk, ibid., **99**, 3863 (1977).
(4) See, for example (a) R. F. Heck, "Organotransition Metal Chemistry", Academic Press, New York, N.Y., 1974; (b) O. Novaro, S. Chow, and P. Magnouat, *J. Catal.*, **41**, 91 (1976); (c) G. Lefebvre and Y. Chauvin in "Aspects of Homogeneous Catalysis", Vol. 1, R. Ugo, Ed., Carlo-Manfredi Editore—Milano.
(5) Complexes of the type $Mo(\eta^5\text{-}C_5H_5)L_4$ are known to be tetragonal pyramids in the solid state and often stereochemically nonrigid; see, for example, J. W. Faller and A. S. Anderson, *J. Am. Chem. Soc.*, **92**, 5852 (1970). We assume for the present that the structure and the "pseudorotation" process in complexes such as **2** are each analogous to those for the Mo complexes.
(6) At −35 °C the 67.89-MHz $^{13}C\{^1H\}$ NMR spectrum of **2** shows equal area peaks for C_β (51.5), $C_{\beta'}$ (48.7), C_γ (27.2), and $C_{\gamma'}$ (23.5); the peaks for C_α and $C_{\alpha'}$ are apparently coincident, or nearly so. For C_γ and $C_{\gamma'}$, $\delta\nu_\infty$ = 258 Hz and k_c = 573 s^{-1} at $T_c \approx$ 258 K or $\Delta G^\ddagger$ = 11.8 kcal mol^{-1}.
(7) The conditions are 10 mL of decane, 0.20 mmol of Ta, 45 °C, and 40 psig of propylene. The initial rate (two turnovers per hour) steadily decreases as an orange, paramagnetic complex precipitates; total turnovers = 20 under these conditions. We cannot yet exclude the possibility that the catalyst is deactivated primarily by water and/or oxygen, in the propylene or solvent, or introduced when removing a sample for GC analysis.
(8) One means by which tetramethylethylene could form is by selective decomposition of an α,α,β-trimethyltantallocyclobutane formed by addition of the hydride ligand to the terminal methylene group in the butenyl–hydride intermediate, overall a ring contraction from five to four. The ratio of tetramethylethylene to 2,3-dimethyl-1-butene remains constant throughout, thus eliminating the possibility that it forms by isomerization of 2,3-dimethyl-1-butene.
(9) Conditions are 10 mL of mesitylene and 0.20 mmol of Ta. Turnovers to 1-butene = 9.5 in 2 h, 15 in 5 h. At t = 2 h, the composition is 89% 1-butene, 3% 2-butenes, and 8% codimers. At t = 5 h, the composition is 78% 1-butene, 3% 2-butenes, and 19% codimers.
(10) In the gated decoupled spectrum the peaks are (left to right for one isomer) a doublet for Cp, and a triplet, doublet, triplet, and triplet (with characteristic aliphatic carbon–hydrogen coupling constants) for the carbon atoms in the bicyclic ring (cf. the ^{13}C spectrum of **2**). The trans assignment is based on the fact that the C_α peak at 82.7 ppm collapses (T_c = 273 K at 67.89 MHz) to two peaks of approximately equal area at 96.0 and 69.1 ppm at 237 K; the cyclopentadienyl peak for neither isomer has changed at this temperature.

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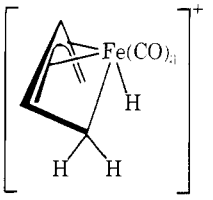
A Novel 16-Electron Cyclooctenyliron(II) Cation

Sir:

We wish to report the first isolated and well-characterized example of the often-cited class of compounds $[FeL_3(\pi\text{-enyl})]^+$. Early work on the protonation of diene iron tricarbonyl complexes with coordinating acids was shown to give the 18-electron π-enyliron tricarbonyl halides.[1] Protonation with noncoordinating acids was originally thought to yield coordinatively unsaturated 16-electron enyliron tricarbonyl cations.[2] It was later shown that the isolated products were actually tetracarbonyl species with the extra carbonyl arising from partial decomposition of the starting material.[3] More recently, it has been shown that the interaction of butadiene[4,5] and cyclohexadiene[6] iron tricarbonyl systems with strong acids gives



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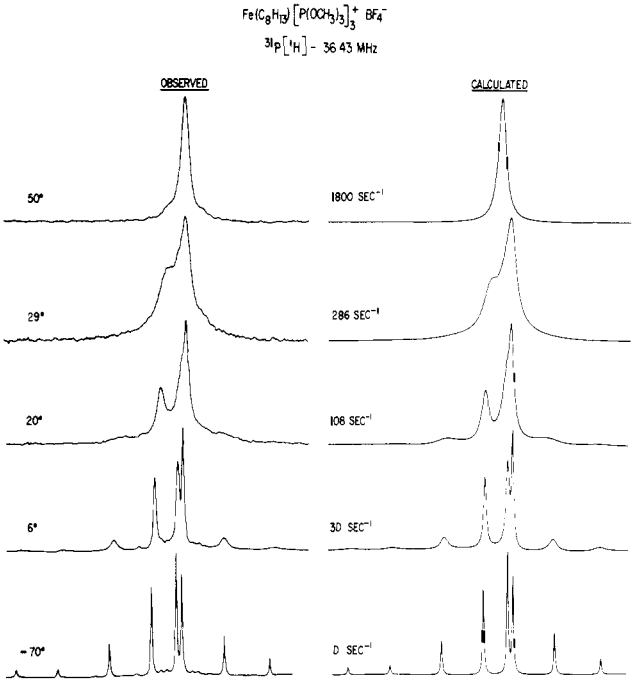
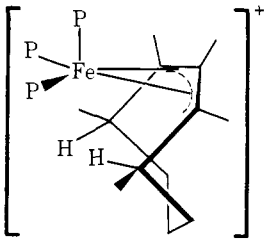


Figure 1. Observed and calculated $^{31}P\{^1H\}$ spectra for **2** as a function of temperature using an AB_2 model.

species formulated as σ-π allyl hydride complexes A. In the case of cyclohexadiene species the formulation was modified to include a three-center interaction involving the iron, hydrogen, and σ-carbon of the allyl.[6]

Protonation of $Fe(P(OMe)_3)_3(\eta_4\text{-}C_8H_{12})$[7] (**1**, C_8H_{12} = 1,3-cyclooctadiene) with methanolic acids (such as HBF_4, HCl, CF_3CO_2H, and CH_3CO_2H) gives $[Fe(P(OMe)_3)_3(\eta_3\text{-}C_8H_{13})]^+$ (**2**, C_8H_{13} = cyclooctenyl), conveniently iso-



2

lated as the BF_4^- or BPh_4^- salts. This ease of protonation is in contrast to the strong acid systems[1-6] necessary to effect the protonation in the tricarbonyl systems. The greatly enhanced basicity of phosphite analogues of carbonyl compounds has been pointed out elsewhere.[8,9] The field desorption mass spectrum[10] gives the parent cation at mass 537. The $^{31}P\{^1H\}$ NMR spectra shown in Figure 1 indicate the fluxional nature of the complex; at room temperature the three phosphorus nuclei are equivalent; at −70 °C the exchange process is frozen out, resulting in a non-first-order AB_2 spin system (δ_A −173.7, δ_B −168.6 ppm, J_{AB} = 154 Hz). Lowering the temperature further (to −140 °C) results in no additional changes. The activation parameters for the fluxional process are $\Delta G^\ddagger_{288}$ = 14.4 kcal mol^{-1}, $\Delta H^\ddagger$ = 16.5 kcal mol^{-1}, and $\Delta S^\ddagger$ = 7.4 cal mol^{-1} deg^{-1}.

The ^1H NMR spectrum of **2** has several unusual features. The cyclooctenyl group displays the expected allylic resonances at 5.54 (1, t)[11] and 5.00 ppm (2, q) and resonances attributable to eight of the aliphatic protons between 1.64 and 1.25 ppm. There is an additional resonance at −6.54 ppm (2, br q) which is assigned to protons endo to the metal (as indicated in **2**) on the carbon atom one bond removed from the allylic group. Heteronuclear decoupling experiments show no observable

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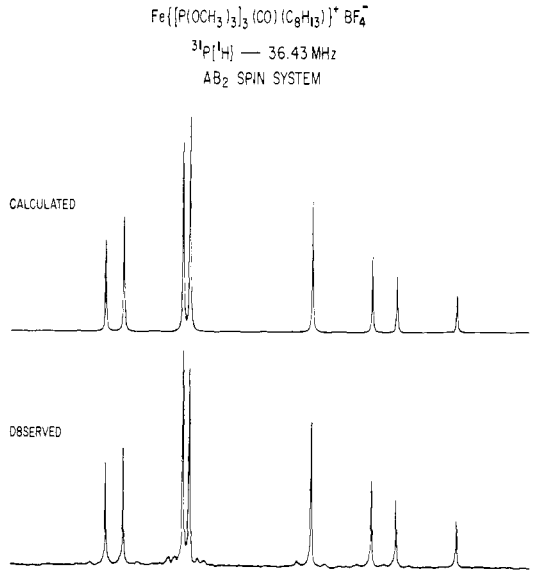

Figure 2. Observed and calculated $^{31}P\{^1H\}$ spectra[10] for the stereochemically rigid species, **3**.

coupling to phosphorus, ruling out a metal hydride. The fluxional process involving the phosphorus ligands has almost no effect on the ring proton resonances; there is little change going from +30 to −140 °C. In addition, $^1H\{^{31}P\}$ NMR experiments indicate ^{31}P coupling only to the two allylic hydrogens at 5.00 ppm (~1 Hz) and homonuclear ^1H decoupling experiments indicate coupling of the high-field resonance to three of the ring protons. The $^{13}C\{^1H\}$ NMR spectrum was normal with allylic resonances at 95.73 (1) and 67.20 (2) ppm and the remaining ring carbon atoms at 27.17 (2), 21.25 (1), and 22.49 (2) ppm.

The extreme high-field shift of the two ring protons coupled with the observation of normal chemical shifts for the two carbon atoms to which they are attached can be explained on the basis of a nonbonded interaction of the ring protons with the metal center. Though we were not able to freeze out any dynamic process involving the cyclooctenyl group, we believe that the metal-hydrogen interactions involve one hydrogen at a time. Since it would take only a small conformational change to exchange hydrogen atoms, this failure to freeze out the exchange is not unexpected.[12] The coordinative unsaturation of the complex, unusual, if not unprecedented, for systems of this type, is apparently slightly relieved by the metal-hydrogen interaction. When **1** is reacted with DCl in methanol-d_1, one deuterium is incorporated into the complex (as indicated by FDMS[10] peak at 538) in one of the two positions indicated in **2** (as indicated by ^1H NMR). There is no further deuterium incorporation even on stirring in DCl/MeOD for 4 h. Thus, the protonation, which takes place through a hydrido intermediate resulting in exclusive endo attack, is an irreversible process. This is in contrast to the cyclohexadiene iron tricarbonyl system where mutliple deuterium incorporation is observed.[5]

Steric effects may account for the lack of further reaction of **2** after protonation by coordinating acids. The starting cyclooctadiene complex can be protonated with methanolic HCl and isolated as the chloride salt (though the material does not crystallize well). The cyclooctenyl complex, **2**, does not react with additional trimethyl phosphite, even in large excess; thus, a tetrakis phosphite species similar to that observed in the π-allyl system[8] is not observed. It does, however, react with sterically less demanding[13] molecules such as CO and t-BuNC, to give the 18-electron systems, *fac*-$[Fe(P(OMe)_3)_3L(C_8H_{13})][BF_4]$[14] (**3**, L = CO; **4**, L = t-BuNC). The complexes are yellow, as expected for saturated species. The NMR spectra of these complexes have no unusual features; the proton resonance which is shifted to high field in **2** is now in the normal aliphatic range for both complexes. The $^{31}P\{^1H\}$ NMR spectra are AB_2[15] spin systems (Figure 2) as expected for stereochemically rigid octahedral complexes. The infrared spectra show absorptions for ν_{CO} at 1982 and ν_{NC} at 2140 cm^{-1} for **3** and **4** respectively.

Since the submission of this report, we have been able to prepare and characterize the cyclohexenyl and cycloheptenyl analogues of **2**. Preliminary $^{31}P\{^1H\}$ NMR studies indicate a progressive change in spin system type ($ABC \rightarrow AB_2 \rightarrow A_3$) with increasing temperature for these new systems. Examination of the $^{31}P\{^1H\}$ spectrum of **2** at −150 °C reveals features (relative to the −140 °C spectrum) which we now know to be characteristic of rapid exchange ($k \approx 10^4$) of the two hydrogen atoms at the metal coordination site. We estimate that at −150 °C $\Delta G^{\ddagger}$ is <5 kcal/mol for this process. These results confirm our interpretation of the dynamics of the metal-hydrogen interaction. Protonation of acyclic diene complexes gives species which display related behavior.

References and Notes

(1) F. J. Impastato and K. G. Ihrman, *J. Am. Chem. Soc.*, **83**, 3726 (1961).
(2) G. F. Emerson and R. Pettit, *J. Am. Chem. Soc.*, **84**, 451 (1962).
(3) D. H. Gibson and P. L. Vonnahme, *J. Am. Chem. Soc.*, **94**, 5090 (1972); *J. Chem. Soc., Chem. Commun.*, 1021 (1972).
(4) M. Brookhart and D. L. Harris, *Inorg. Chem.*, **13**, 1540 (1974).
(5) T. H. Whitesides and R. W. Arhart, *Inorg. Chem.*, **14**, 209 (1975); *J. Am. Chem. Soc.*, **93**, 5296 (1971).
(6) M. Brookhart, T. H. Whitesides, and J. M. Crockett, *Inorg. Chem.*, **15**, 1550 (1976).
(7) A. D. English, J. P. Jesson, and C. A. Tolman, *Inorg. Chem.*, **15**, 1730 (1976).
(8) E. L. Muetterties and J. N. Rathke, *J. Chem. Soc., Chem.* Commun., 851 (1974).
(9) S. D. Ittel, A. D. English, F. A. Van-Catledge, C. A. Tolman, and J. P. Jesson, unpublished work.
(10) The field desorption mass spectrum (FDMS) technique used for these compounds has been discussed elsewhere: C. N. McEwen and S. D. Ittel, presented at Mass Spectroscopy Meeting of the American Chemical Society, Washington, D. C., May 1977.
(11) Shifts in parts per million Me_4Si (integration; t = triplet, q = quartet, and br = broad).
(12) This is in contrast to the protonated cyclohexadienyl iron tricarbonyl complex[6] where the exchange process is frozen out at −80 °C. In that system a stronger interaction involving C–H cleavage was postulated, but we feel this is not the case. Substitution of one carbonyl by a phosphorus ligand was shown to lower the barrier for the exchange process: M. Brookhart, private communication.
(13) C. A. Tolman, *Chem. Rev.*, **77**, 313 (1977). cone angles: $P(OMe)_3$, 107°; Cl, 102°; CO, t-BuNC, 95°.
(14) FDMS gives a peak at 565 for **3** and at 620 for **4**.
(15) $^{31}P\{^1H\}$ NMR: **3**, AB_2, δ_A −150.0, δ_B −163.6 ppm (J_{AB} = 171 Hz); **4**, AB_2, δ_A −159.9, δ_B −169.7 ppm (J_{AB} = 161 Hz).
(16) Contribution No. 2519.

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Binding and Activation of Enzymic Substrates by Metal Complexes. 4. Structural Evidence for Acetylene as a Four-Electron Donor in $W(CO)(C_2H_2)(S_2CNEt_2)_2$

Sir:

Recently, the reactions of $Mo(CO)_2L_2$ (L = S_2CNEt_2, $S_2P(i-Pr)_2$) with C_2H_2 and its substituted analogues to give products of two forms, $Mo(CO)(RC_2R')L_2$ and $Mo(RC_2R')_2L_2$, were described.[1,2] Their spectral data were interpreted in terms of the complexes being 18-electron systems with RC_2R' acting as a four-electron donor in the former type and a three-electron donor in the latter. X-ray structural

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