The greater proportion of C–O over C–C bond formation also speaks[2e] in favor of the cationic mechanism.

In the absence of kinetic data it is not possible to rule out a concerted process (iii). If it obtains, however, N–O bond cleavage will have to have proceeded to a very large extent to account for the formation of compounds such as **3** and **4** (from rather poor nucleophiles).

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R. A. Abramovitch,* M. Inbasekaran, S. Kato
Department of Chemistry, University of Alabama
University, Alabama 35486

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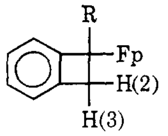
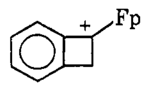
A Novel Cationic Carbene Complex Lacking Heteroatom Stabilization

Sir:

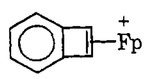
Although numerous carbene complexes[1] are known, the carbene ligand almost without exception must possess some special form of stabilization. Thus, the ligating carbon is most commonly (1) bonded to an adjacent heteroatom possessing nonbonding pairs of electrons, (2) incorporated into an aromatic nucleus, or (3) bonded to a cluster of metal atoms. In the absence of stabilizing groups or structures, carbene complexes are apparently too reactive to be isolated. Complexes containing unstabilized carbene ligands have been proposed as intermediates during the reactions of chloromethyl[2] and cyclopropyl complexes[3] and the transition metal catalyzed rearrangement of strained hydrocarbons.[4] We now report the serendipitous preparation and isolation of h^1-1-benzocyclobutenylidene-h^5-cyclopentadienyldicarbonyliron hexafluorophosphate (**2**)—a carbene complex lacking special stabilization.



1a, R = H(1)
b, R = D
c, R = OMe
d, R = OH
e, R = PPh_3^+



2



3

Fp = h^5-CpFe$(CO)_2$

We are interested in *dihapto*cyclobutadienoid transition metal complexes and set out to generate such a complex of benzocyclobutadiene (**3**) by β-hydride abstraction from h^1-**1**-benzocyclobutenyl-h^5-cyclopentadienyldicarbonyliron (**1a**), which was prepared in 50% yield by the addition of sodium h^5-cyclopentadienyldicarbonylferrate to 1-bromobenzocyclobutene:[5] **1a**; ir (neat) 2003, 1942 cm^{-1} (C≡O); nmr (CS_2) τ 5.95 (m, 1, ^{1}H), 7.31 (m, 1, $J_{^1H^2H}$ = 2.1 Hz, $J_{^2H^3H}$ = 13.5 Hz, ^{2}H), 6.56 (m, 1, $J_{^1H^3H}$ = 4.9 Hz, ^{3}H), 5.37 (s, 5, Cp), 3.18 (m, 4, Ar). Surprisingly, treatment of **1a** with trityl hexafluorophosphate in methylene chloride gave **2** in yields up to 90% as deep orange-red crystals.[6] The spectroscopic properties of **2** alone are not sufficient to distinguish between structures **2** and **3**. Thus, the nmr (CD_3NO_2) spectrum of **2** exhibited singlets at τ 5.35 and 4.10 and a multiplet centered at 2.17 with relative intensities of 2:5:4. The aromatic multiplet was, however, not of the AA′-BB′ type and therefore appeared to be inconsistent with **3** which normally would be expected to possess a plane of symmetry. The carbonyl stretching frequencies of **2** (2065 and 2020 cm^{-1}) are very similar to those observed for the cationic olefin complexes of h^5-cyclopentadienyldicarbonyliron. A clear distinction between structures **2** and **3** is possible on the basis of the chemistry of **2**. **2** is readily reduced by lithium aluminum hydride in diethyl ether to **1a**. The use of the analogous deuteride gave **1b**, the nmr spectrum of which exhibited two doublets at τ 6.53 and 7.28 with $J_{^2H^3H}$ = 14.7 Hz in addition to the resonances attributed to the aromatic and cyclopentadienyl protons. The large coupling constant clearly indicates that the protons on the four-membered ring are geminal[7] and that the deuterium is attached to the ligating carbon. Treatment of **1b** with trityl hexafluorophosphate results in the formation of **2** without incorporation of deuterium and thereby demonstrates that **2** is formed by direct α-hydride abstraction.

Although **2** is stable when cold and under nitrogen, it slowly decomposes in moist air at room temperature. **2** rapidly decomposes in the presence of nucleophilic solvents such as tetrahydrofuran, acetone, alcohols, or water but is indefinitely stable in degassed anhydrous nitromethane, sulfur dioxide, or methylene chloride. As might be expected **2** behaves in a manner similar to the trityl salts and forms a number of 1:1 adducts with a variety of nucleophiles. The methoxy adduct (**1c**) is readily prepared by dissolving **2** in methanol in the presence of sodium bicarbonate: **1c** ir (Nujol) 1989, 1916 cm^{-1} (C≡O); nmr (CS_2) τ 6.76 (s, 3, CH_3), 6.78 (d, 1, *J* = 13.5 Hz, ^{2}H) 6.43 (d, 1, ^{3}H), 5.25 (s, 5, Cp), 3.01 (m, 4, Ar). The hydroxy adduct (**1d**) prepared by treatment of a methylene chloride solution of **2** with aqueous sodium bicarbonate is unstable and readily decomposes to benzocyclobutenone and h^5-cyclopentadienyldicarbonyliron dimer. Triphenylphosphine also adds to **2** to form the adduct **1e**. Treatment of **2** with lithium iodide in anhydrous nitromethane resulted in the formation of 1-iodobenzocyclobutene, h^5-cyclopentadienyldicarbonyliron iodide, and **1a**. **2** is also a potent hydride abstractor, capable of converting cycloheptatriene to the tropylium ion and ethyl-h^5-cyclopentadienyldicarbonyliron to the cationic ethylene complex. Attempts to alkylate or deprotonate **2** with organomagnesium or -lithium reagents or tertiary amines

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(1) D. J. Cardin, B. Cetinkaya, and M. F. Lappert, *Chem. Rev.*, 72, 547 (1972).

(2) P. W. Jolly and R. Pettit, *J. Amer. Chem. Soc.*, 88, 5044 (1966); M. L. H. Green, M. Ishaq, and R. N. Whitely, *J. Chem. Soc. A*, 1508 (1967).

(3) A. Cutler, R. W. Fish, W. P. Giering, and M. Rosenblum, *J. Amer. Chem. Soc.*, 94, 4354 (1972).

(4) M. Sakai, H. H. Westburg, H. Yamaguchi, and S. Masamune, *ibid.*, 93, 4611 (1971); P. G. Gassman and T. Nakai, *ibid.*, 93, 5897 (1971); L. A. Paquette, R. P. Henzel, and S. E. Wilson, *ibid.*, 93, 2335 (1971).

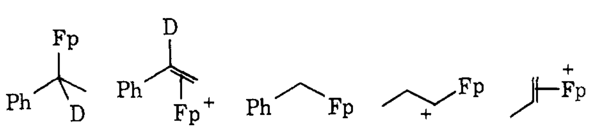
(5) M. P. Cava and D. R. Napier, *ibid.*, 80, 2255 (1958).

(6) All new compounds gave satisfactory elemental analyses for carbon and hydrogen.

(7) I. L. Klundt, *Chem. Rev.*, 70, 471 (1970).

yield sparingly soluble, brightly colored, uncharacterized metal-containing solids and **1a**.

α-Hydride abstraction from a hydrocarbon ligand to our knowledge is without precedent. Generally β-hydride abstraction occurs if possible. Thus **4** is



4 5 6 7 8

converted to the styrene complex **5** by β-hydride abstraction with complete retention of deuterium. In the absence of β-hydrogens such as in the benzyl complex **6**, trityl adds directly to the ligating carbon to form 1,1,1,2-tetraphenylethane. It is interesting that **1a** undergoes neither of these processes. The reluctance of **1a** to undergo β-hydride abstraction to form **3** suggests that the *dihapto*benzocyclobutadiene ligand in **3** may retain some of the antiaromaticity of the parent hydrocarbon and thus destabilize **3** relative to **2**. A further indication that **3** may be unusually energetic is the failure of **2** to rearrange to **3** in a manner similar to the reported rearrangement of the propylidene complex[3] (**7**) to the corresponding propene complex (**8**). The addition of trityl to the ligating carbon in **1a** seems to be precluded on steric grounds.

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(8) EPDA Part E Fellow 1971–1973.

A. Sanders,[8] L. Cohen,[8] W. P. Giering*
D. Kenedy,[8] C. V. Magatti
Department of Chemistry, Boston University
Boston, Massachusetts 02215

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Reversible Addition of Nitric Oxide to a Solid Ferric Porphinato Complex. Thermodynamics of Formation and Characterization of a Peculiar NO Adduct

Sir:

We wish to report an unusual interaction involving chlorotetraphenylporphinatoiron(III) ([FeCl(TPP)]) and nitric oxide (eq 1) and producing a weakly bonded NO

$$\underset{\mathbf{1}}{[\mathrm{FeCl(TPP)}](s)} + \mathrm{NO}(g) \underset{k_{-1}}{\overset{k_2}{\rightleftharpoons}} \underset{\mathbf{2}}{[\mathrm{(NO)FeCl(TPP)}](s)} \qquad (1)$$

addition compound (**2**) which rapidly reverts to the square-pyramidal starting material (**1**)[1] on removal of nitric oxide from the environment. NO gas (purified, $-78°$, KOH) uptake by crystalline **1** is slow under mild conditions: at $P_{\mathrm{NO}} = 760$ mm and 25°, the equilibrium is attained after *ca.* 7 days, and about 92% conversion to **2** is observed (98% at 0°). In solution (CH_2Cl_2 or $CHCl_3$), the formation of the same NO adduct is complete within seconds, and purple crystals of **2** are obtained when solutions of **1** ($CHCl_3$) and NO (EtOH) are mixed. *Anal.* Calcd for $FeClON_5C_{44}H_{28}$: Fe, 7.61; N, 9.54; C, 71.99; H, 3.85. Found: Fe, 7.96; N, 9.71; C, 71.28; H, 4.01; N:Fe = 4.9.

Complex **2** instantly loses nitric oxide when dissolved in (NO-free) organic solvents. In the solid state (in air), gradual dissociation of NO from **2** occurs, and a quantitative recovery of [FeCl(TPP)] has been observed within 3 days; on pumping (25°), the conversion (k_{-1}, eq 1) is complete in minutes. The thermodynamics of the solid–gas reaction (eq 1) have been determined by measuring the equilibrium NO pressure (220–685 nm) as a function of temperature (25–70°).[2] At 25°, the calculated parameters are: K_p, 3.45 atm^{-1}, $\Delta G = -0.74$ (0.03) kcal/mol, $\Delta H = -5.26$ (0.14) kcal/mol, $\Delta S = -15$ (0.5) eu. These data conform with the qualitative observations on the facile reversibility of the reaction, and it is seen that the small enthalpy change (ΔH)[3,4] barely compensates for the unfavorable negative entropy (expected for simple addition reactions of this type[4]).

The spectral properties of the NO adduct are also somewhat unexpected. (a) No change in the Fe–Cl stretching frequency accompanies the reaction; in both **1** and **2**, $\nu_{\mathrm{FeCl}} = 378$ cm^{-1}.[5] (b) There is no significant change in the electronic spectrum in the 400–1000-nm region when nitric oxide is added to a degassed CH_2Cl_2 solution of [FeCl(TPP)];[6] however, a new weak band at 380 nm and a stronger one near 250 nm are observed. (c) The ir spectrum of **2** shows a strong absorption band at 1881 cm^{-1}, assignable to coordinated ν_{NO}, but which only slightly differs from the corresponding value of gaseous nitric oxide, 1876 cm^{-1}.[7a] There is another new band at 680 cm^{-1} which may derive from $\nu_{\mathrm{Fe-NO}}$.[7b]

Some of these spectral data, together with the facile removal of NO even from crystalline [(NO)FeCl(TPP)], and the low heat of its formation, may seem to suggest that the nitric oxide in **2** is associated with a peripheral part of the complex (ligands), rather than the central metal atom, and/or involve some kind of "physical adsorption."[3] The latter possibility, however, is excluded by the observed *stoichiometry* of the reaction (eq 1) substantiated above.

Evidence for a Fe–NO linkage in **2** (supported by the rapidity of the reaction in solution) and a possible explanation for the relative weakness of this bond derive from magnetic data. Addition of NO to the high-spin

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(1) J. L. Hoard, G. H. Cohen, and M. D. Click, *J. Amer. Chem. Soc.*, **89**, 1992 (1967).

(2) We thank Professor H. H. G. Jellinek for loan of the apparatus; H. H. G. Jellinek and J. E. Clark, *Can. J. Chem.*, **41**, 355 (1963).

(3) (a) It is generally considered that heats ($-\Delta H$) of gas–solid interactions in the range of 2–5 kcal reflect physical adsorption; (b) G. C. Bond, "Catalysis by Metals," Academic Press, New York, N. Y., 1962, p 52.

(4) (a) For simple addition reactions related to the type reported here, the negative enthalpies are usually larger than the one found here. (b) L. Vaska, *Accounts Chem. Res.*, **1**, 335 (1968); (c) L. Vaska and M. F. Werneke, *Trans. N. Y. Acad. Sci.*, **33**, 70 (1971); (d) L. Vaska, L. S. Chen, and C. V. Senoff, *Science*, **174**, 587 (1971).

(5) (a) There are, however, precedents for similar insensitivities when axial ligands are added[5b] or the oxidation state of the metal is changed.[5c] (b) M. Tsutsui, D. Ostfeld, and L. M. Hoffman, *J. Amer. Chem. Soc.*, **93**, 1820 (1971); (c) J. Takemoto, B. Hutchinson, and K. Nakamoto, *Chem. Commun.*, 1007 (1971).

(6) (a) This observation is compatible with a report that no visible spectral changes are detected when iron porphyrinato complexes are treated with NO in *neutral* aqueous solution; changes do occur, however, when the solution is alkaline or acidic.[6c] See also (b) J. C. W. Chien, *J. Amer. Chem. Soc.*, **91**, 2166 (1969); (c) J. Keilin, *Biochem. J.*, **59**, 571 (1955).

(7) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," 2nd ed, Wiley-Interscience, New York, N. Y., 1970, (a) p 78; (b) p 201.