so the extent to which configuration is lost during dimerization of 1 to 2, will depend on the relative activation energies of the two "forbidden" processes 6 → 7 and 6 → 8. Since both have very low activation energies, the difference between them must be correspondingly small. The conversion of 1 to 2, or of 2 to 1, should therefore take place with partial retention, but much loss, of configuration. This is the case.[15]

The loss of configuration in these reactions is due to the formation first of the "wrong" intermediate (6 in the case of 1 → 2) which has to undergo a "forbidden" conversion to the "right" one (7). If the latter were formed directly, it should collapse to cyclobutane with little or no loss of configuration. Bartlett and Porter[16] have indeed found that photolysis of 10 gives 12 with little of the trans isomer; in this case loss of N_2 from 10 gives the biradicaloid 11 analogous to 7.

10   11   12
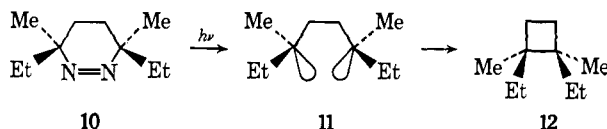
Benson[7] estimated the heat of formation (ΔH_f) of the biradical 5 assuming it to have a classical localized structure, the difference between it and 1-n-butyl radical being the same as that between 1-n-butyl and n-butane. Apart from general objections to the use of the localized bond model for biradicals, this argument specifically neglects the effects of spin correlation. The biradical can exist as a singlet state or a threefold degenerate triplet. Benson's method gives an average of the four. His value is therefore less than that of the singlet by three-quarters of the singlet–triplet separation or $1.5K_{\mu\nu}$ where $K_{\mu\nu}$ is the exchange integral between the two singly occupied orbitals. Since the latter are not localized AO's but delocalized MO's, and consequently overlap with one another, $K_{\mu\nu}$ would not be expected to vanish. MINDO/3 indeed predicts a value of 5 kcal/mol for $K_{\mu\nu}$ for the cis structure 5. It is therefore not surprising that Benson's value of ΔH_f for the biradical was less (by 6 kcal/mol) than that observed for the transition state for conversion of 1 to 2 and his conclusion that the biradical must consequently be a stable intermediate is therefore not valid.

(15) C. T. Genaux and W. D. Walters, J. Amer. Chem. Soc., 73, 4497 (1951).
(16) P. D. Bartlett and N. A. Porter, J. Amer. Chem. Soc., 90, 5317 (1968).

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η^2-Cyclobutadienoid Transition Metal Complexes. The Preparation and Characterization of a Binuclear Complex Possessing a Bridging Cyclobutadiene Ligand

Sir:

We wish to report the first example of a complex in which a cyclobutadiene ligand is simultaneously η^2 bonded to two metals. Although binuclear η^2-cyclobutadienoid complexes have been proposed as intermediates in ligand transfer reactions,[1,2] no previous

(1) D. F. Polluck and P. M. Maitlis, Can. J. Chem. 44, 2673 (1966).

experimental evidence has been presented supporting the existence of such species.

Our recent preparation of η^2-benzocyclobutadiene-η^5-cyclopentadienyldicarbonyliron hexafluorophosphate (2)[3] suggested that the analogous binuclear cyclobutene

1   2
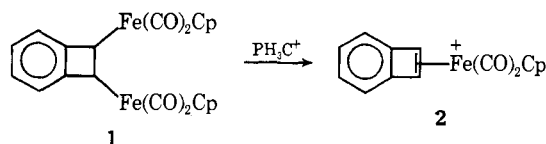
complex (3) might serve as a precursor for the preparation of a cationic η^2-cyclobutadiene complex (9) via oxidative demetallation. The reaction between 3,4-dichlorocyclobutene and sodium η^5-cyclopentadienyldicarbonylferrate is known to yield the binuclear butadiene complex 5,[4–9] the structure of which has been determined both in the crystal[5,6] and in solution.[7–9] We have reinvestigated this reaction and found that the progenitor of 5, the binuclear cyclobutene complex 3, is readily prepared in 47% yield. The preparation of 3 was effected by the sequential mixing of tetrahydrofuran solutions of sodium η^5-cyclopentadienyldicarbonylferrate and the dichlorocyclobutene at $-78°$, allowing the reaction mixture to warm to $0°$, filtering, rotary evaporating the filtrate (without external heating), washing the residue with cold ($0°$) petroleum ether, and finally recrystallizing from carbon disulfide at $-78°$ to afford 3 as dark yellow-brown crystals. The spectroscopic properties (^{1}H nmr and ir) of 3 and of all other new compounds are presented in Table I. The

Table I. ^{1}H Nmr and Ir for New Complexes[a]

3	Nmr (CS$_2$) τ 6.33 (m,[b] 2, H^1), 5.38 (s, 5, Cp), 4.29 (m,[b] 2, H^2); ir[c] 1981, 1922 cm^{-1} (C≡O)
4	Nmr (CS$_2$) τ 6.17 (m,[b] 1, H^1), 5.59 (m,[b] 1, H^2), 5.18 (s, 5, Cp), 4.37 (m,[b] 1, H^3), 3.72 (m,[b] 1, H^4); ir 2000, 1950 cm^{-1} (C≡O)
6	Nmr (CD$_3$NO$_2$) τ 4.53 (s, 4, H), 4.26 (s, 10, Cp); ir 2080, 2040 cm^{-1} (C≡O)
7	Nmr (CS$_2$) τ 6.45 (s, 3, OCH$_3$), 5.17 (s, 5, Cp), 4.79 (d, 1, H^1, $J_{1,2}$ = 15 Hz), 3.27 (m, 2, H^2 and H^3, $J_{2,3}$ = 10.5 Hz), 2.21 (d, 1, H^4, $J_{3,4}$ = 15 Hz); ir 2000, 1938 cm^{-1} (C≡O)
8	Nmr (CD$_3$)$_2$CO τ 6.57 (m,[b] 1, H^4), 5.46 (m,[b] 1, H^3), 4.98 (m,[b] 1, H^2), 4.69 (s, 5, Cp), 4.23 (s, 5, Cp^1), 3.20 (m,[b] 1, H^1); ir 2060, 2025, 2000, 1944 cm^{-1} (C≡O)

[a] All new compounds gave satisfactory analyses for carbon and hydrogen. [b] Narrow multiplet. [c] Ir spectra were taken as Nujol mulls.

assignment of the trans orientation of the metals in 3 is based on the quantitative electrocyclic isomerization of 3 to 5, which in the absence of any special electronic effects requires a trans disubstituted cyclobutene. We have also isolated, by fractional recrystallization of the

(2) P. M. Maitlis and A. Efraty, J. Organometal. Chem., 4, 175 (1965). Reviews: A. Efraty, J. Organometal. Chem., 57, 1 (1973); P. M. Maitlis, Advan. Organometal. Chem., 4, 95 (1966); A. Z. Rubezhov and S. P. Gubin, Advan. Organometal. Chem. 10, 347 (1972).
(3) A. Sanders, C. V. Magatti, and W. P. Giering, J. Amer. Chem. Soc., 96, 1610 (1974).
(4) M. R. Churchill, J. Wormald, W. P. Giering, and G. F. Emerson, Chem. Commun., 1217 (1968).
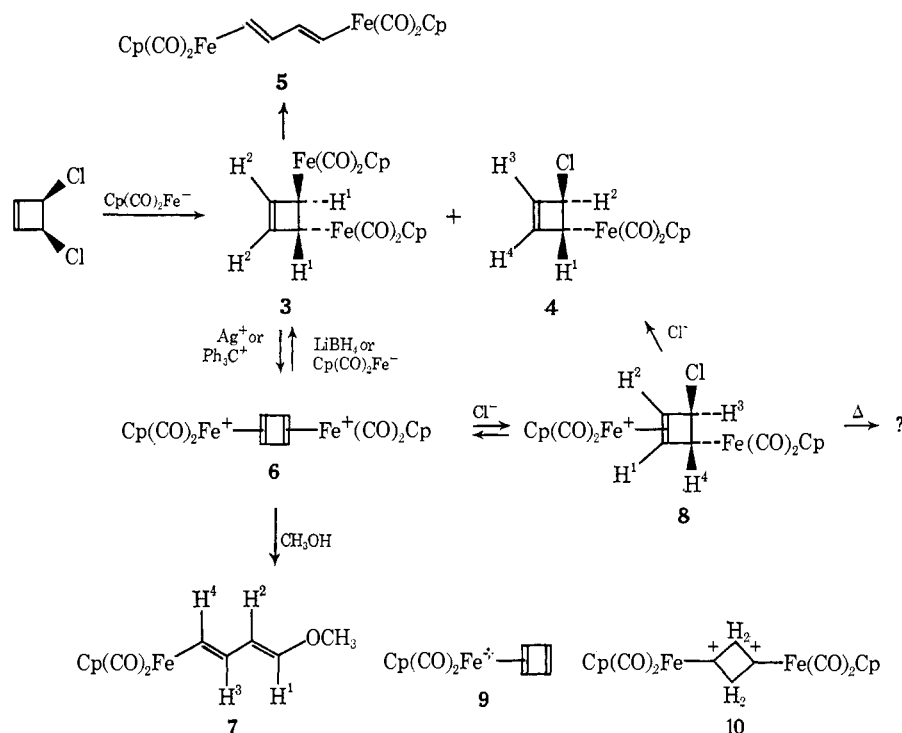(5) M. R. Churchill and J. Wormald, Inorg. Chem., 8, 1936 (1969).
(6) R. E. Davis, Chem. Commun., 1218 (1968).
(7) C. H. Campbell and M. L. H. Green, Chem. Commun., 1009 (1970).
(8) W. P. Giering Chem. Commun., 4 (1971).
(9) F. A. L. Anet and O. J. Abrams, Chem. Commun., 1611 (1970).

Scheme I

Cp(CO)₂Fe〜〜Fe(CO)₂Cp

5

↑

Cp(CO)₂Fe⁻

H² Fe(CO)₂Cp
--H¹
--Fe(CO)₂Cp
H² H¹

3

+

H³ Cl
--H²
--Fe(CO)₂Cp
H⁴ H¹

4

Ag⁺ or Ph₃C⁺ ⇅ LiBH₄ or Cp(CO)₂Fe⁻

Cp(CO)₂Fe⁺—☐—Fe⁺(CO)₂Cp

6

Cl⁻ ⇌ Cp(CO)₂Fe⁺—

H² Cl
--H³
--Fe(CO)₂Cp
H¹ H⁴

8

Δ → ?

Cl⁻

↓ CH₃OH

H⁴ H²
Cp(CO)₂Fe〜〜OCH₃
H³ H¹

7

Cp(CO)₂Fe⁺—☐   Cp(CO)₂Fe—◇—Fe(CO)₂Cp

9   **10**

petroleum ether soluble complexes, the novel trans η¹-4-(3-chlorocyclobutenyl) complex **4**.[10]

When methylene chloride solutions of **3** and trityl or silver hexafluorophosphate are mixed at −78° and warmed to room temperature, the binuclear cyclobutadiene complex (**6**) is formed in 56% yield as a bright yellow, methylene chloride insoluble, air stable solid (Scheme I). **6** may be further purified by recrystallization from nitromethane.

The structure of **6** is clearly established by consideration of its spectroscopic and chemical properties. Thus the equivalence of the two iron groups is indicated by the observation of a ten proton singlet resonance at τ 4.26, which occurs in a region characteristic of cationic complexes of the type Cp(CO)₂Fe(olefin)⁺, and by the observation of two metal carbonyl bands (2080 and 2040 cm⁻¹) in the infrared spectrum of **6**. The only additional resonance in the nmr spectrum of **6** is a four-proton singlet at τ 4.53, which is assigned to the equivalent protons of the four-membered ring. The proton decoupled ¹³C nmr spectrum of **6** exhibits three singlets at 206.0, 92.8, and 74.8 ppm downfield from tetramethylsilane which are assigned to the carbonyl, cyclopentadienyl, and cyclobutadiene carbons, respectively. The ¹³C chemical shifts compare well with the values reported for other Cp(CO)₂Fe(olefin)⁺ complexes.[11,12] The proton coupled ¹³C nmr spectrum of **6** exhibits a singlet for the carbonyl groups; however, the resonances attributed to the cyclopentadienyl and cyclobutadiene ligands are both split into doublets (J = 178 and 182 Hz, respectively). The observation of a doublet for the cyclobutadiene ligand demonstrates that only one hydrogen is attached to each carbon of the four-membered ring and thereby militates against the dicarbenium structure **10**.[13]

(10) The chemistry of **4** will be reported in the near future.
(11) P. Lennon, A. Rosan, and M. Rosenblum, unpublished results.
(12) K. R. Arvis, V. Arvis, and J. M. Brown, *J. Organometal. Chem.*, **42**, C67 (1972).

In contrast to the reduction of the benzocyclobutadiene complex[3] (**2**) and other Cp(CO)₂Fe(olefin)⁺ complexes, LiBH₄ does not add hydride to **6** but rather effects a two-electron reduction of **6** to **3**. Similarly, Cp(CO)₂Fe⁻, which is known to liberate the olefin from Cp(CO)₂Fe(olefin)⁺,[14] also reduces **6** to **3**. Although **6** is a dicationic complex, neither iron appears to be labile. Thus treatment of **6** with benzyltriethylammonium chloride affords the chloride addition product **8**. Although **8** is stable in solution when kept below 20°, at higher temperatures the complex decomposes to Cp(CO)₂FeCl and unidentified products. If the decomposition is carried out in the presence of excess chloride, small amounts of **4** are formed. Treatment of **8** with silver hexafluorophosphate regenerates **6** in 58% yield. Finally, the treatment of **6** with a mixture of methanol and sodium bicarbonate affords the methoxybutadiene complex (**7**). The chemistry of **6** demonstrates that the integrity of the four-membered ring is maintained in **6** and thereby, in conjunction with the spectroscopic data, strongly supports the bridging cyclobutadiene structure.

(13) The first examples of stable metallocarbenium ions have recently been reported. A. Sanders, L. Cohen, W. P. Giering, D. Kenedy, and C. Magatti, *J. Amer. Chem. Soc.*, **95**, 5430 (1973). W. P. Giering, A. Sanders, C. V. Magatti, presented at the Sixth International Conference on Organometallic Chemistry, Aug 1973, Amherst, Mass. L. Cohen, W. P. Giering, D. Kenedy, C. V. Magatti, and A. Sanders, *J. Organometal. Chem.*, **65**, C57 (1974).
(14) D. J. Ehnholt, unpublished results.

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