above experiments is that mild oxidation of **2** leads to the formation of **3**, which undergoes a retro-Diels–Alder reaction to form cyclobutadiene (**11**) and nitrogen with great ease. The unique antiaromatic properties of **11** do not significantly retard the reaction that is observed with 2,3-diazabicyclo[2.2.2]octa-2,5-diene[14] and many other related systems. The facile ring opening that a Dewar pyridine, 2-azabicyclo[2.2.0]hexa-2,5-diene,[15] undergoes does not compete in the case of **3**. Thus the utility of **2** as a metal-free precursor of **11** is obvious. The exclusive formation of dimer **9** from **11** is in agreement with several independent experiments, using metal-free precursors,[16] but is (presumably insignificantly) inconsistent with an earlier report[12] that oxidation of **4** provides a 1:5 mixture of the anti and syn dimers.[17] Because of the reactivity (short lifetime), the pot-to-pot transfer of either **3** or **11** by means of vacuum distillation appears to be impossible.[16b,18]

Finally, it is emphasized that reagent **1** promises well for the synthesis of diazane derivatives that have heat-, acid-, and even alkali-sensitive functional groups (e.g., esters) and systems, since conditions even milder than those used in the present work easily bring about the cleavage, as already demonstrated in the synthesis of peptides and other systems.[5,19]

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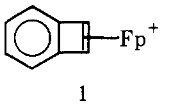
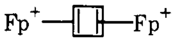
η^2 Cyclobutadienoid Transition Metal Complexes. The Generation and Trapping of a Cationic η^2-Cyclobutadiene Iron Complex

Sir:

Recently we reported the preparation of two reactive η^2 cyclobutadienoid transition metal complexes—a η^2-benzocyclobutadiene complex **1**[1] and a binuclear complex possessing a bridging cyclobutadiene ligand **2**.[2]



1



2

Fp = $Cp(CO)_2Fe^+$

We now report the trapping of the first cationic η^2 cyclobutadiene complex, η^2-cyclobutadiene-η^5-cyclopentadienyldicarbonyliron hexafluorophosphate (**3**), which is generated by chloride abstraction from η^1-4-(3-chlorocyclobutenyl)-η^5-cyclopentadienyldicarbonyliron (**4**). Complex **4**, is obtained by allowing an approximately equimolar tetrahydrofuran solution of *cis*-3,4-dichlorocyclobutene and NaCp$(CO)_2$Fe to stand at −78° for 16 hr followed by sequential warming to 0°, and rotary evaporation of the solvent. Extraction of the residue with petroleum ether and cooling (−78°) of the extract affords **4** as dark yellow crystals in 17% yield.[3] The NMR spectra and other physical data for all new compounds are presented in Table I. The structure of **4** was established by consideration of its spectroscopic properties and the quantitative thermal isomerization of **4** to the trans,trans chlorobutadiene complex **5**.

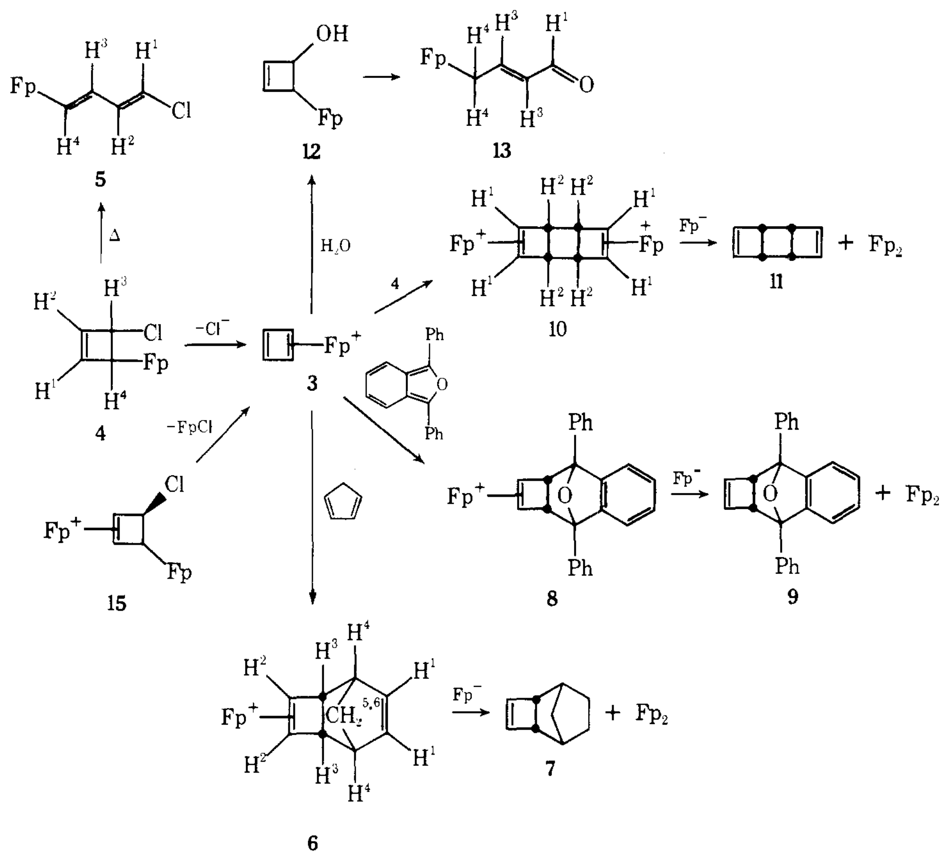
Although complex **4** fails to react with cyclopentadiene in methylene chloride at 25° over a 4-hr period, a rapid reaction ensues when a methylene chloride solution of **4** is added to a mixture of silver hexafluorophosphate and excess cyclo-

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

4	Nmr (CS_2) τ 3.72 (m,[b] 1, H^1), 4.37 (m,[b] 1, H^2), 5.18 (s, 5, Cp, 5.59 (m,[b] 1, H^3), 6.17 (m,[b] 1, H^4); ir (Nujol) 2000, 1950 cm^{-1} (C═O); mp 65–67°
5	Nmr (CS_2) τ 2.98 (d, 1, H^1, $J_{1,2}$ = 14.25 Hz), 3.81 (m, 2, H^2 and H^3), 4.35 (d, 1, H^4, $J_{3,4}$ = 12.75 Hz), 5.27 (s, 5, Cp); ir (neat) 2003, 1947 cm^{-1} (C═O)
6	Nmr (CD_3COCD_3) τ 3.60 (m, 2, H^1), 4.20 (s, 5, Cp), 4.38 (s, 5, Cp 2, H^2), 7.01 (m, 2, H^3, $J_{3,4}$ = 3.8 Hz), 7.25 (m, 2, H^4), 8.09 (m, 1, H^5), 8.35 (m, 1, H^6); ir (Nujol) 2065, 2015 cm^{-1} (C═O)
10	Nmr (CD_2NO_2) τ 4.21 (s, 4, H^1), 4.30 (s, 10, Cp), 7.05 (s, 4, H^2); ir (Nujol) 2080, 2035 cm^{-1} (C═O)
13	Nmr (CS_2) τ 0.71 (d, 1, H^1, $J_{1,3}$ = 7.5 Hz), 3.06 (m, 1, H^2, $J_{2,3}$ = 15 Hz, $J_{2,4}$ = 9 Hz), 4.18 (m, 1, H^3), 5.25 (s, 5, Cp), 7.85 (d, 2, H^4); ir (neat) 2000, 1940 cm^{-1} (C═O), 1648 cm^{-1} (–CH═O)

[a] All neutral complexes gave satisfactory analyses for carbon and hydrogen. Cationic olefin complexes were characterized by ir and NMR spectroscopy and by liberation and identification of the olefin ligand. [b] Narrow multiplet.

Scheme I

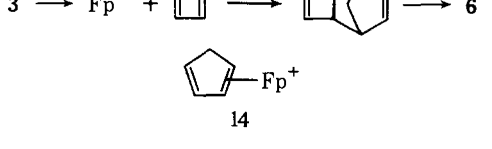


Fp = η^5-Cp(CO)$_2$Fe

pentadiene in methylene chloride at −78° to afford a 58% yield of the cationic complex (**6**) of *syn*-tricyclo[4.2.1.0^{2,5}]-3,7-nonadiene.[4] Reductive demetalation[5] of **6** with NaCp(CO)$_2$Fe affords the known tricyclic hydrocarbon **7**.[7] When 1,3-diphenylisobenzofuran is used as the trapping agent, complex **8** is formed which upon treatment with NaCp(CO)$_2$Fe affords the known Diels-Alder adduct **9** of 1,3-diphenylisobenzofuran and cyclobutadiene.[8] When a methylene chloride solution of silver hexafluorophosphate is slowly added to a methylene chloride solution of **4** at −78°, the binuclear *syn*-tricyclooctadiene complex **10** is obtained in 29% yield. Treatment of **10** with NaCp(CO)$_2$Fe affords the *syn*-tricyclooctadiene **11**.[9] If **4** is added to a solution of silver hexafluorophosphate, a single uncharacterized product is obtained. Complex **4** is readily hydrolyzed on neutral activity I alumina to the known butenal complex **13**,[10] whereas *cis*-3,4-dichlorocyclobutene is stable under similar conditions. (See Scheme I.)

The formation of cycloadducts **6**, **8**, and **10** is strong evidence in support of the intermediacy of a reactive η^2-cyclobutadiene complex **3**. An alternative mechanism for the formation of **6**, **8**, and **10** involving the generation of free cyclobutadiene would require dissociation of **3**, followed by the formation of the Diels-Alder adducts **7**, **9**, and **11**, and subsequent recomplexation by Cp(CO)$_2$Fe$^+$ as shown in Scheme II. This mechanism is untenable for the following reasons. Displacement of the olefin ligand from Cp(CO)$_2$Fe(olefin)$^+$ involves a rate determining dissociative step with an activation energy of 16-25 kcal.[11] Cyclobutene ligands are relatively nonlabile and complex **10**, although dicationic, fails to react with iodide over a period of several hours at 24°. Cyclobutadiene should be a better donor ligand than cyclobutene derivatives and form a less labile iron-olefin bond. Thus it is unlikely that **3** would dissociate at −78°. The generation of Cp(CO)$_2$Fe$^+$ in the presence of cyclopentadiene would be expected to yield, in addition to **6**, the cyclopentadiene complex **14**, which is not observed. When **4** is allowed to react with silver hexafluorophosphate in the presence of the electrophilic dienophile, dimethyl fumarate, no consumption of the dienophile is observed. In contrast, cyclobutadiene is known to react with electrophilic dienophiles to give Diels-Alder adducts.[12-14] Finally, the facile hydrolysis (as compared to *cis*-3,4-dichlorocyclobutene) of **4** on alumina is best interpreted in terms of a metal assisted hydrolysis involving **3**. Thus it is reasonable to assume that free cyclobutadiene is not involved in the reactions of **4** with silver hexafluorophosphate.

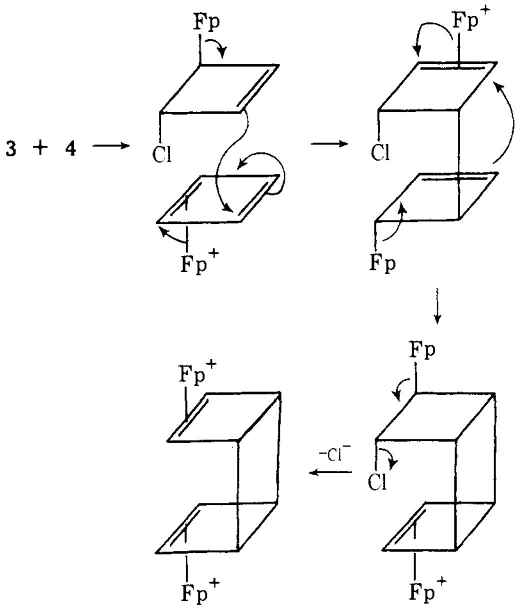
Scheme II



The thermal decomposition (25°) of the binuclear complex **15** also generates **3** which may be trapped by 1,3-diphenylisobenzofuran as the Diels-Alder adduct **8**. Subsequent reduction demetalation of **8** affords **9** in 48% yield. The failure of both **2** and **4** to react with 1,3-diphenylisobenzofuran under similar conditions militates against the intermediacy of these complexes in the formation of **8**. Also, the possibility that **15** directly reacts with 1,3-diphenylisobenzofuran may be excluded by the observation that other π-complexes such as Cp(CO)$_2$Fe(ethylene)$^+$ fail to react with 1,3-diphenylisobenzofuran.

The formation of **10** may be best accounted for by a sequence of metal assisted cycloaddition reactions[15] involving

Scheme III



10

3 and **4** as outlined in Scheme III. It is interesting that the syn tricyclooctadiene is formed rather than the anti isomer which would have been predicted on steric considerations. This result suggests an attractive interaction between the chloro group of **4** and the electrophilic cyclobutadiene ring of **3**.

The aforementioned experiments demonstrate that there exists a class of cyclobutadiene transition metal complexes in which the cyclobutadiene ligand exhibits a degree of reactivity reminiscent of that attributed to free cyclobutadiene, and that the mode of reactivity of the η^2-cyclobutadiene ligand of **3** is somewhat altered as compared to cyclobutadiene in that the ligand is electrophilic and, in the Diels-Alder reaction, only functions as a dienophile. It is particularly important to note that the formation of *syn*-tricyclooctadiene can no longer be considered prima facie evidence for the intermediacy of free cyclobutadiene in reactions involving transition metals. Our results support the contention that transient cyclobutadiene complexes generated by the oxidative degradation of cyclobutadienetricarbonyliron are not involved in the formation of cyclobutadiene-dienophile adducts.[12-14] However, our results do suggest that η^2-cyclobutadiene complexes may indeed be involved in the formation of cyclobutadiene-diene adducts.

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(5) Reductive demetalation by $\mathrm{NaCp(CO)_2Fe}$ of the olefin ligand in $\mathrm{Cp(CO)_2Fe(olefin)^+}$ is virtually instantaneous and quantitative. In contrast we have found the iodide displacement[6] of olefin ligands to be extremely slow in certain instances.

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Chemical Reaction Paths. V. The SN1 Reaction of Tetrahedral Molecules

Sir:

In previous papers we have applied what we might call the principle of structural correlation[1] to map minimum energy pathways for a ligand exchange reaction (SN2 at tetrahedral $\mathrm{Cd^{II}}$)[2] and for nucleophilic addition to carbonyl groups.[3,4] We now report some new results concerning the chemical reaction path for the SN1 type of reaction.

Tetrahedral molecules that are known or expected to show T_d symmetry as isolated particles usually deviate from this symmetry in a crystal environment. A preliminary survey of the crystal structure data indicated that the more severe distortions are mainly of two types,[5] one maintaining approximate C_{2v} symmetry, the other approximate C_{3v} symmetry. We limit ourselves here to the latter type of deformation since fewer independent parameters are involved, and it is more directly relevant to the SN1 type of reaction.

The parameters describing $\mathrm{MX_4}$ and $\mathrm{YMX_3}$ groups with C_{3v} symmetry are shown in Figure 1a. The experimental sample points[6] for $\mathrm{SO_4{}^{2-}}$, $\mathrm{PO_4{}^{3-}}$, and $\mathrm{AlCl_4{}^-}$ tetrahedra from a wide variety of crystal structures show a common trend (b, c, d); as the axial bond distance r_2 increases, the central atom comes closer to the plane of the other three bonds, which become shorter. Results from $\mathrm{YSO_3}$, $\mathrm{YPO_3}$, and $\mathrm{YSnCl_3}$ species are shown in Figure 1e, f, and g. The correlation of r_1 or r_2 with θ is in all cases very similar to that in the corresponding $\mathrm{MX_4}$ species.[7] Indeed, if all sample points (about 200) for the species $\mathrm{YAlCl_3}$, $\mathrm{YSO_3}$, $\mathrm{YPO_3}$, $\mathrm{OPX_3}$, $\mathrm{YSnCl_3}$, $\mathrm{YGeCl_3}$, $\mathrm{YSiCl_3}$, $\mathrm{YSnBr_3}$, $\mathrm{YSnPh_3}$, $\mathrm{YPF_3}$, $\mathrm{YPCl_3}$, and $\mathrm{YPPh_3}$ are referred to a common origin (h) by replacing r_1 by $\Delta r_1 = r(\mathrm{MY}) - r_t(\mathrm{MY_4})$ and r_2 by $\Delta r_2 = r(\mathrm{MX}) - r_t(\mathrm{MX_4})$ where r_t refers to the corresponding T_d species,[9] all the Δr_1, θ points lie close to one curve and all the Δr_2, θ points close to another;[10] i.e., all these tetrahedral molecules deform along the same path in the subspace maintaining C_{3v} symmetry!

A simple model, based on three arbitrary assumptions, leads to the observed Δr_1, θ *and* Δr_2, θ relationships: (1) $\Delta r_i = -c \log n_i$, where n_i is Paulings "bond number";[11] (2) $n_2 + 3n_1 = 4$ is assumed to hold for all the tetrahedral molecules in question; (3) the displacement Δ of the central atom from the plane of the three basal ligands is a measure of n; when $\Delta = \Delta_t$ (regular tetrahedron), $n_2 = 1$, when $\Delta = 0$ (trigonal planar molecules) $n_2 = 0$. We find that $n_2 = (\Delta/\Delta_t)^2 = 9\cos^2\theta$, $n_1 = \frac{4}{3} - 3\cos^2\theta$, reproduce the ob-