from eq 4 but not from eq 3. Thus application of the method described above for discriminating between pathways 1 and 2 clearly shows that the latter is the route for the hydrolysis of 5-nitrocoumaranone.

The generality of eq 2 as the pathway for the hydrolysis of readily ionizable esters such as 5-nitrocoumaranone is difficult to assess. Since aryl N-monoalkylcarbamate esters hydrolyze 10^6 times faster than aryl N,N-dialkylcarbamate esters[9] eq 1 is the most likely pathway for the hydrolysis of the former compounds. Consideration of the resonance involved in the carbanion described here, carbamate esters, and the structures of isocyanates and ketenes leads to the conclusion that there are enough structural differences between aryl N-monoalkylcarbamate esters and readily ionizable lactones so that they could easily hydrolyze *via* different pathways.

The excellent agreement of the predicted and observed kinetic solvent isotope effects makes this method very attractive for the investigation of carbanion-catalyzed hydrolyses.

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(10) Public Health Service Predoctoral Trainee.

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Carbon- and Oxygen-Coordinated Carbon Monoxide. $Fe_2(\pi\text{-}C_5H_5)_2(CO)_2(COAl(C_2H_5)_3)_2$ and $Fe_4(\pi\text{-}C_5H_5)_4(COAl(C_2H_5)_3)_4$

Sir:

While many compounds are known in which cyanide is coordinated through carbon and nitrogen,[1] the isoelectronic CO ligand has been known to bond only through carbon. We report here the first examples of carbon monoxide coordinated through both carbon and oxygen.

Addition of a slight excess of $Al_2(C_2H_5)_6$ to a benzene solution of $Fe_2(\pi\text{-}C_5H_5)_2(CO)_4$[2] produces immediate lightening of the red solution. Bright red crystals of $Fe_2(\pi\text{-}C_5H_5)_2(CO)_4 \cdot 2Al(C_2H_5)_3$ are obtained by addition of heptane followed by partial removal of solvent.[3] *Anal.* Calcd for $C_{26}H_{40}Al_2Fe_2O_4$: C_2H_5, 28.22; Fe, 19.2. Found: C_2H_5 (by hydrolysis), 28.64; Fe, 20.5. The parent compound, $Fe_2(\pi\text{-}C_5H_5)_2(CO)_4$, is nearly quantitatively regenerated upon hydrolysis or reaction with trimethylamine. Experiments conducted on the vacuum line demonstrate that no gases, such as CO, are evolved upon reaction of aluminum trialkyl with the iron dimer. Nmr chemical shifts are τ 5.62 (singlet), 8.43 (triplet), and 9.51 (quartet) with relative intensities 9.6:18:13.1. The expected ratios are 10:18:12 for C_5H_5, CH_3, and CH_2, respectively.

Molecular weight and infrared data indicate significant dissociation of the adduct in solution. For the most concentrated solution studied (nominal 9.2×10^{-3} M) the molecular weight is 505 as determined cryoscopically in benzene (calcd 582). In the presence of excess triethylaluminum infrared absorptions are found at 2044 s, 2004, 2009 (doublet) vs, and 1682 vs cm^{-1} in heptane solution. These represent an increase of *ca.* 40 cm^{-1} for terminal CO stretching frequencies and a decrease of 112 cm^{-1} from the bridging CO stretching frequency of the parent iron complex.[4] The latter decrease suggests coordination to the oxygen of the bridging carbonyl since similar frequency shifts are found upon the coordination of ketones to Lewis acids.[5]

Coordination of $Al(C_2H_5)_3$ to the bridging carbonyls is clearly demonstrated by single-crystal X-ray diffraction. Preliminary Weissenberg and precession photographs show monoclinic symmetry and cell constants $a = 14.45\ (2)$, $b = 14.19\ (2)$, $c = 14.70\ (3)$ Å, and $\beta = 100°\ 50\ (15)'$. Systematic absences of hkl, $h + k \neq 2n$, and $h0l$, $l \neq 2n$, are consistent with space group C2/c or Cc; the observed density of 1.31 g cm^{-3} (by helium displacement) indicates four molecules per unit cell ($\rho_{calcd} = 1.31$ g cm^{-3}). As described below, the correct space group is C2/c for which the molecule must contain a twofold axis, whereas for Cc no symmetry needs to be imposed on the molecule.

A crystal of approximately cubic dimensions was mounted along its $[\bar{1}\bar{1}0]$ axis and six layers of integrated equiinclination Weissenberg photographs were taken at room temperature using Mo Kα radiation. Intensities of the reflections were estimated visually and were corrected for Lorentz and polarization effects but not absorption (linear absorption coefficient for Mo Kα is 11 cm^{-1}). The data were interscaled by comparison of common reflections to yield structural amplitudes for 815 reflections.

The Patterson function clearly indicates the centrosymmetric space group, and therefore the molecule has twofold symmetry. After two least-squares cycles using the trial coordinates, a difference Fourier map gave the positions of the remaining nonhydrogen atoms. At the present state of refinement with all atoms having isotropic temperature factors and without including hydrogen atoms $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o| = 0.12$, and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF^2)^{1/2} = 0.13$. ($|F_o|$ and $|F_c|$ are observed and calculated structure amplitudes, respectively, and $w = 256/F_o{}^2$ for $I > 16$ and $w = I^2/F_o{}^2$ for $I \leq 16$ where I is the raw intensity.)

The crystal structure is composed of discrete monomeric molecular units (Figure 1). The iron–iron distance of 2.49 (1) Å is identical with that of the parent compound.[6] However, in contrast to the solid parent the terminal groups are in a *cis* configuration. Of greatest interest is the coordination of Al to oxygen of the bridging carbonyl. The Al–O distance is 2.00 (2) Å and the C–O–Al angle is 155 (2)°.

A similar adduct $Fe_4(\pi\text{-}C_5H_5)_4(CO)_4 \cdot 4Al(C_2H_5)_3$ may be synthesized from $Fe_4(\pi\text{-}C_5H_5)_4(CO)_4$[7] and $Al(C_2H_5)_3$.

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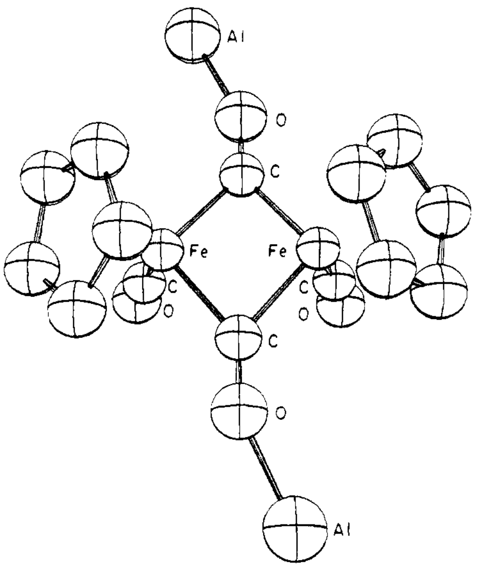

Figure 1. The structure of $Fe_2(\pi\text{-}C_5H_5)_2(CO)_2(COAl(C_2H_5)_3)_2$ viewed along a line which is 20° from the twofold axis. Ethyl groups and hydrogen atoms are not included.

Anal. Calcd for $C_{48}H_{80}Al_4Fe_4O_4$: C_2H_5, 31.14; Al, 10.25; Fe, 21.22; $Fe_4(\pi\text{-}C_5H_5)_4(CO)_4$, 56.61; mol wt, 1052. Found: C_2H_5, 32.30; Al, 10.68; Fe, 20.64; $Fe_4(\pi\text{-}C_5H_5)_4(CO)_4$ (after hydrolysis), 57.26; mol wt (cryoscopy in benzene), 1056.

This adduct displays a single CO stretching frequency at 1527 cm^{-1} (heptane solution) which represents a 125-cm^{-1} decrease from that of the parent carbonyl compound. This large decrease indicates that the 4 moles of aluminum triethyl are coordinated to the oxygens of the bridging carbon monoxide. Both molecular weight and solution infrared data indicate little dissociation. Thus the bridging carbonyl groups of the iron tetramer are significantly more basic than those of the iron dimer. In summary, the present results introduce a new structural feature in carbonyl chemistry and indicate that Lewis basicity may be a general property of the bridging carbonyl ligand.

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of a tetrahedral array of iron atoms with a π-cyclopentadiene at each vertex and bridging carbon monoxide projecting from each face.

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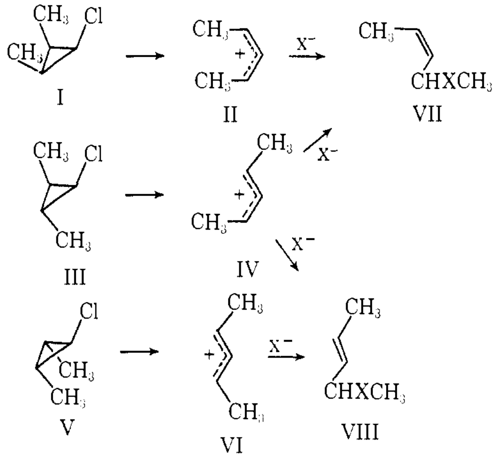
The Stereochemistry of Allyl Cations from the Isomeric 2,3-Dimethylcyclopropyl Chlorides. The Stereomutation of Allyl Cations

Sir:

In 1965 Woodward and Hoffmann predicted that the ring opening of cyclopropyl cations to allyl cations should follow either of two possible disrotatory paths.[1] Following a suggestion by DePuy,[2] the relationship of the mode of opening—outward or inward—to the orientation of the leaving group in a cyclopropyl derivative was examined.[2] Extended Hückel MO calculations indicated that concerted ionization–ring opening should be stereospecific: the groups at C_2 and C_3 *trans* to the leaving group should move outward, and the *cis* groups inward.[2] Specifically, the isomeric 2,3-dimethyl-1-cyclopropyl chlorides[3] should react as shown in Scheme I.

Scheme I



Experimental tests of these predictions have demonstrated their validity.[2,4,5] However, the evidence has been indirect, being based on the interpretation of kinetic data. For example, the tosylates corresponding to I, III, and V acetolyze at 150° with relative rates 1, 65, and 4500, respectively, an order corresponding to the expected steric strain changes in going from reactants to transition states.

Direct, complete stereochemical verification of the Woodward–Hoffmann prediction has been lacking. Under the usual solvolytic conditions, one of the two asymmetric centers present in the intermediate allyl cations (II, IV, and VI) inevitably is lost in going to covalent products (VII and VIII). It is therefore difficult to exclude the possibility that I may react to give IV, which could give VII by preferential reaction at the *trans* center. For this reason we have examined the stereochemistry of the ring-opening ionization of the cyclopropyl chlorides (I, III, and V) in strong acid media, in which the carbonium ion products (II, IV, and VI) are stable and the stereochemical fate of both

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