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Preliminary communication

3—5-η-CYCLOOCTATRIENYL COMPLEXES OF IRON AND RUTHENIUM

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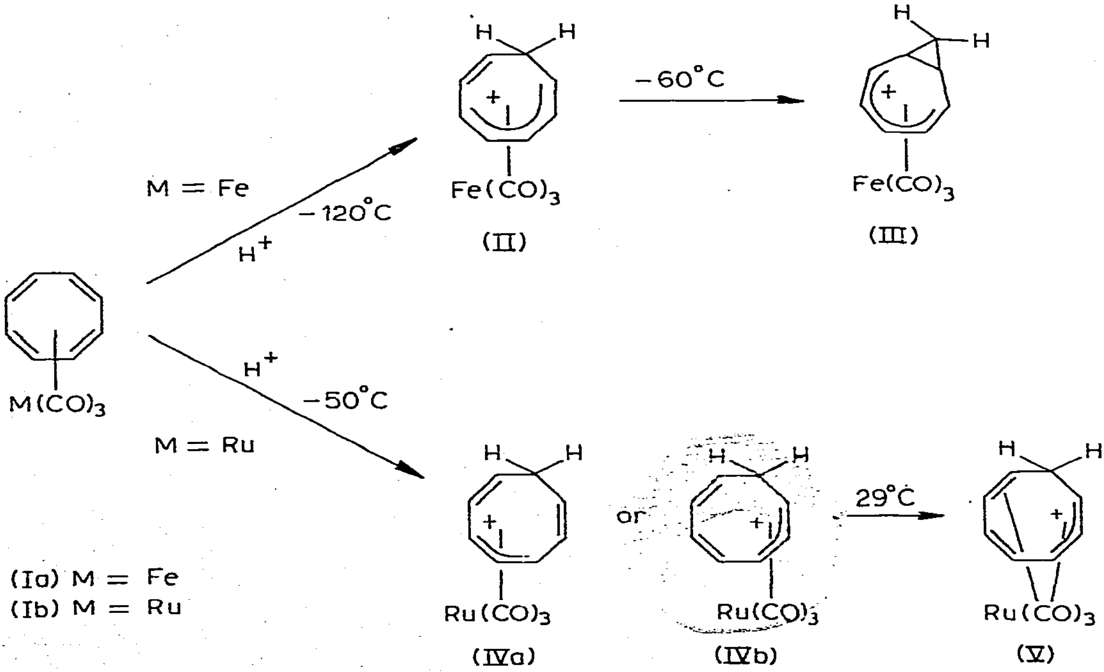
Summary

Reaction of HCl with COTFe$(CO)_3$ and COTRu$(CO)_3$ gives monocyclic complexes containing an allyl M$(CO)_3$Cl unit.

The protonation of cyclooctatetraene complexes of tricarbonyl-iron and -ruthenium by non-coordinating acids has been extensively studied [1—4]. Protonation of Ia at −120°C has been shown [1] to yield the planar monocyclic



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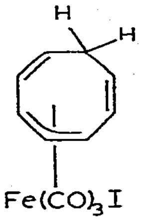
cation II, which subsequently rearranged to give the previously known [2] bicyclo [5.1.0] structure III. The protonation of the ruthenium complex Ib is not so straightforward, the nature of the products being dependent on the acid media used [3]. However, in CF_3CO_2H at −50°C a planar monocyclic cation has been observed, which has a ^1H NMR consistent with structures IVa or IVb. On warming to room temperature, the planar cation V was produced [4].

In contrast, there exist relatively few examples of the protonation of olefin complexes by coordinating acids. The reactions of some acyclic systems with HCl have been studied, where the products were coordinatively saturated η^3 complexes [5]. We have examined the reactions of Ia and Ib with HCl and have prepared complexes containing a C_8 ring bound to the metal in a η^3 fashion.

Several workers [6—9] have studied the reaction of III with nucleophiles. In particular, Aumann [8] has shown that reaction of III with LiI produces the neutral product VI, via a postulated planar intermediate.

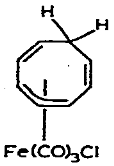
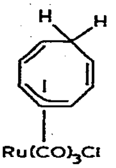


(VI)

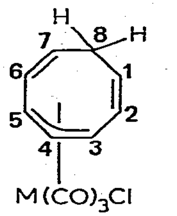
We have prepared an analogous complex by treating a solution of Ia in diethyl ether with dry HCl under an inert atmosphere at 0°C. Complex VIIa separated as yellow needles (57%) on pouring into pentane and was characterised by IR and mass spectrometry (see Table 1). The IR shows three high-energy carbonyl

TABLE 1

IR AND MASS SPECTRAL DATA FOR COMPOUNDS VIIa AND VIIb

	IR (hexane) (cm^{-1})	Mass spectrum *m/e*
 (VIIa)	2088 2036 2017	280, 252, 245, 224, 217, 196, 160
 (VIIb)	2102 2044 2024	326, 298, 270, 242, 206

stretching frequencies, and the mass spectrum shows a molecular parent peak at *m/e* 280, with subsequent loss of three carbonyls and one chlorine. Attempts to obtain a satisfactory ^{1}H NMR were unsuccessful, even at low temperature, due to decomposition with consequent paramagnetic broadening. However, in CCl_4 at 0°C, broad peaks were observed at τ 4.0 (6H), 5.5 (t,1H), and 7.1 ppm (2H). This is not inconsistent with Aumann's [8] reported spectrum of VI.



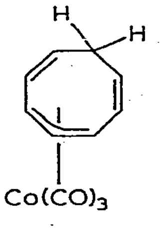
(VIIa) M = Fe
(VIIb) M = Ru

Subsequent reaction of VIIa with LiI yielded an unstable complex with an IR (hexane) 2070, 2020, 2015 cm^{-1}. These values are almost identical with those reported [8] for VI.

On the basis of this information, we propose a similar structure for VIIa, containing a η^3 Fe(CO)$_3$Cl unit. The formation of this complex does not necessarily involve III as an intermediate [8]. Initial protonation may occur to give the monocyclic cation II, which is immediately trapped by nucleophilic attack of Cl$^-$ at the metal.

We have also prepared the corresponding ruthenium complex. COTRu(CO)$_3$ (Ib) in dry diethyl ether was treated with dry HCl at 20°C. The solvent was removed to give pale-yellow crystals. The IR and mass spectra are shown in Table 1. This complex proved to be more stable than its iron counterpart. The ^{1}H NMR in $CDCl_3$ showed signals at τ 3.80 (dd) (J(2,1) 10, J(2,3) 4 Hz) H(2,6), 4.40 (m) H(1,3,5,7), 5.55 (t) (J(4,3) 9 Hz) H(4), 6.83 and 7.22 (m) H(8). Assignments were made on the basis of spin decoupling experiments. Comparison with the ^{1}H NMR of VI [8] shows many similarities, and we propose that this compound has the structure VIIb.

The ^{1}H NMR of IV is very similar to that of VIIb, and also to that of the neutral cobalt complex VIII [10]. This provides further confirmation for the idea that the metal centre in IV is a 16 electron species coordinated to an allyl π-bond on the ring [4]. Reaction might occur with a coordinating anion such as Cl$^-$ to give VIIb, and it may be that IV is an intermediate in the reaction of Ib with HCl.



(VIII)

Acknowledgments

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