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Reactions of benzene complexes of ruthenium(II)

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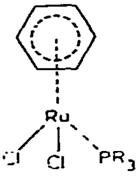
In 1967, Winkhaus and Singer[1] reported the preparation of insoluble, presumably polymeric π-$C_6H_6RuCl_2$ from the reaction of cyclo-1,3-hexadiene and ruthenium trichloride. This compound seemed interesting to us for three reasons: (1) reactions of arene rings coordinated to metals in oxidation states higher than 0 and +1 have been little studied[2]; (2) the tributylphosphine derivative, π-$C_6H_6RuCl_2PBu_3$. was formulated as a dimer with each benzene ring presumably donating only two pairs of electrons[1]; (3) the role of π-benzene complexes in the platinum(II)-catalyzed H–D exchange of benzene[3] has not been clearly defined. Coordination of a benzene ring to a strongly polarizing platinum metal ion might well activate the ring protons to base-catalyzed exchange because of inductive effects.

We find that cyclo-1,3-hexadiene reacts with $RuCl_3$ in aqueous ethanol to give a dark red soluble form of π-$C_6H_6RuCl_2$. Although the compound may be dimeric in the solid state (ν(RuCl) 294, 256 and 248 cm^{-1} (sh)), it is sufficiently soluble in the coordinating solvents water, acetonitrile and dimethylsulfoxide that reactions can be studied by NMR. The compound is monomeric in all three solvents, is a 2/1 electrolyte in water, but is essentially a non-electrolyte in acetonitrile. Metathetical reactions in water readily yield the blood-red π-$C_6H_6RuBr_2$ and the violet-red π-$C_6H_6RuI_2$.

We have also prepared the orange adducts, π-$C_6H_6RuCl_2L$ (L = PPh_3, $PMePh_2$, PMe_2Ph, PBu_3, PEt_3, $P(OPh)_3$, $P(OEt)_3$, $P(OMe)_3$, $AsPh_3$), all of which are monomeric in chloroform solution. The benzene chemical shifts ($CDCl_3$ solutions) vary from τ4.25 (L = $P(OMe)_3$) to 4.77 (L = $P(OPh)_3$), and coupling with ^{31}P is observed (0.5–1.0 Hz) when L = tertiary phosphine. The complexes are all non-electrolytes in acetonitrile, exhibit terminal ν(RuCl) at approximately 290 and 270 cm^{-1}, and should be formulated as monomeric six-coordinate ruthenium(II) complexes, the arene rings being symmetrically coordinated to the metal ions (I).

The compound π-$C_6H_6RuCl_2$ undergoes a variety of interesting reactions with both electrophilic and nucleophilic reagents. Reaction with $HgCl_2$ in acetonitrile yields the ionic [π-$C_6H_6RuCl(CH_3CN)_2$] [$HgCl_3$] while reaction in CD_3CN with $HgMe_2$ gives a violet

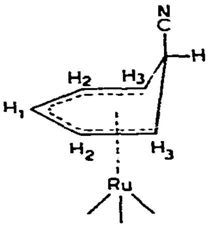


(I)

solution which, from its NMR spectrum, contains monomethylruthenium ($\tau(CH_3)$ 8.90) and dimethylruthenium ($\tau(CH_3)$ 8.82) complexes, as well as an equivalent amount of MeHgCl.

Since attempted Friedel–Crafts acylation of π-$C_6H_6RuCl_2PEt_3$ failed, and since no H–D exchange of π-$C_6H_6RuCl_2$ in concentrated D_2SO_4 was observed after three days, the coordinated benzene ring is apparently inert to electrophilic attack. H–D exchange of π-$C_6H_6RuCl_2$ is catalyzed, however, by sodium ethoxide in 1/1 EtOD–$(CD_3)_2SO$. Since benzene is unaffected under these conditions, coordination to ruthenium(II) does make benzene more susceptible to nucleophilic attack.

In accord with this conclusion, addition of KCN to a DMSO solution of π-$C_6H_6RuCl_2$ ($[CN^-]/[Ru^{2+}] = 1$) causes a rapid color change from deep red to pale yellow. The benzene resonance in the NMR spectrum disappears completely, and is replaced by four resonances at τ4.00 (broad multiplet), τ4.95 (triplet), τ6.17 (triplet) and τ7.12 (triplet), with relative intensities 1/2/1/2, respectively. The spectrum can readily be interpreted in terms of a cyclohexadienyl structure (II).

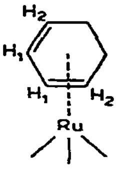


(II)

The resonance at τ4.00 can be assigned to H_1, that at τ4.95 to H_2 ($J(H_1H_2)$ and $J(H_2H_3)$ 5 Hz), that at τ6.17 to H_{endo} ($J(H_3H_{endo})$ 6 Hz) and that at τ7.12 to H_3. Decoupling experiments confirm these assignments, and the chemical shifts and coupling constants are very similar to those of $C_6H_6CNMn(CO)_3$ [4].

A similar cyclohexadienyl complex is also obtained with hydroxide ion. Both cyclohexadienyl complexes are too unstable to be isolated, and thus the identity of the other ligands on the ruthenium remains uncertain.

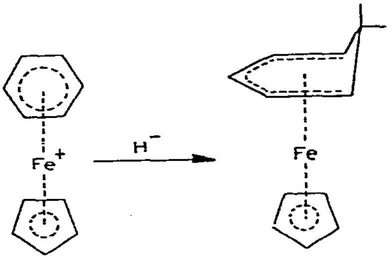
Reaction of π-$C_6H_6RuCl_2$ with hydride ion (added as $NaBH_4$) in DMSO-d_6 was more complex, although weak lines in the NMR spectrum at low BH_4^-/Ru^{2+} ratios suggested the presence of a cyclohexadienylruthenium complex. The main product of the reaction, however, appeared to be a cyclo-1,3-hexadiene complex of ruthenium (III).



(III)

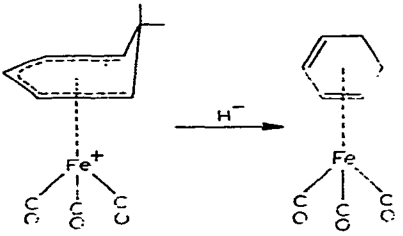
The resonance of protons H_1 appeared at $\tau 5.18$ as a 1/1/1/1 quartet, while the resonances of H_2 and the aliphatic protons were complex multiplets at $\tau 7.95$ and $\tau 8.52$, respectively. Decoupling experiments reinforced the assignments, and the spectrum is very similar to that of cyclo-1,3-hexadienetricarbonyliron[5]. Extraction of a reaction mixture with cyclohexane after excess $NaBH_4$ had been added showed (NMR) the presence of free benzene and both cyclo-1,3-hexa- and cyclo-1,4-hexadiene.

Interconversion between benzene, cyclohexadienyl and cyclo-1,3-hexadiene complexes appears to be very facile, and it is interesting to note that complex IV is



(IV) (V)

reduced only to the dienyl stage (V)[6], although the dienyl tricarbonyl complex, VI, is reduced to the diene complex, VII[7]. The greater π-acid properties of the three carbonyl groups of VI than of the cyclopentadienyl group of V thus makes the former more susceptible to nucleophilic attack by hydride ion.



(VI) (VII)

It appears that ruthenium(II) is a sufficiently strong Lewis acid that a coordinated benzene molecule can accept two hydride ions, in effect reducing the metal to the zerovalent state. A similar result has been reported by Wilkinson *et al.*[6], who found that $(\pi\text{-}C_6H_6)_2Ru^{II}$ salts are reduced by hydride donors to either benzenecyclo-1,3-hexadieneruthenium or dicyclohexadienylruthenium complexes, depending on reaction conditions.

ACKNOWLEDGEMENTS

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