Protonation of Tricarbonyl(cyclo-octatetraene)-ruthenium(0) and -osmium(0)

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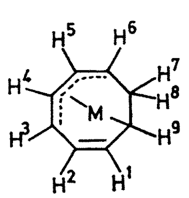
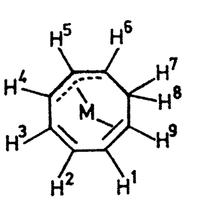
Summary Protonation of tricarbonyl(cyclo-octatetraene)-ruthenium gives a tricarbonyl(bicyclo[5,1,0]octadienium)-ruthenium cation, which isomerises to [h^5-1,2,5,6,7-$C_8H_9Ru(CO)_3]^+$; similar reaction occurs with α-C_8H_8-$Os(CO)_3$; the reaction of [h^5-1,2,5,6,7-$C_8H_9Ru(CO)_3]^+$ with CN^- and $CH_2NO_2^-$ is described

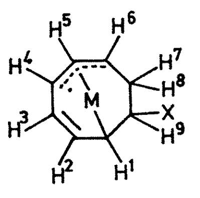
PROTONATION of tricarbonyl(cyclo-octatetraene)iron in strongly acidic media has been shown[1] to lead to the formation of the tricarbonyl(bicyclo[5,1,0]octadienium)iron cation which, it has been suggested, is formed by ring closure of an initially formed tricarbonyl(cyclo-octatrienylium)iron cation. The analogous ruthenium and osmium systems behave differently; an initially formed bicyclic cation undergoes a ring-opening reaction to give cations containing the C_8H_9 moiety bonded to the metal in a novel way.



(IIa), M = $Ru(CO)_3^+ PF_6^-$



(IIb), M = $Ru(CO)_3^+ BF_4^-$



(III), M = $Ru(CO)_3$
X = CN
(IV) M = $Ru(CO)_3$
X = CH_2NO_2

The ${}^1H$ n.m.r. spectrum of tricarbonyl(cyclo-octatetraene)ruthenium (conc. H_2SO_4) suggests the initial formation of a tricarbonyl(bicyclo[5,1,0]octadienium)ruthenium cation, but on leaving the sample at room temperature the spectrum changes to give finally resonances at τ 4·46 (dd, 1H), 4·89 (asymmetric d, 1H), 5·18 (asymmetric dd, 1H), 5·75 br (s, 3H), 6·49 (q, 1H), and 6·98 br (m, 2H).

A similar protonation in diethyl ether with aqueous HPF_6 afforded in quantitative yield a white crystalline material characterised by elemental analysis as $[C_8H_9Ru(CO)_3]^+PF_6^-$ (IIa), and examination of the ${}^1H$ n.m.r. spectrum (SO_2) revealed a 1 : 1 : 1 : 3 : 1 : 2 spectrum similar to that finally observed in sulphuric acid suggesting that in this solvent (Et_2O–H_2O) system an initially formed bicyclic cation rapidly isomerises. This was confirmed when it was observed that tricarbonyl(bicyclo[5,1,0]-octadienium)ruthenium tetrafluoroborate (I) can be prepared by addition of HBF_4–Ac_2O to $C_8H_8Ru(CO)_3$ followed by rapid precipitation of the resultant protonated species with diethyl ether. The ${}^1H$ n.m.r. spectrum (CD_3CN) of (I) showed resonances at τ 2·3 (m, 1H), 4·7 (m, 4H), 7·0 (m, 2H), and 8·0 (m, 2H), a pattern similar to that reported[1] for the related iron system, thus confirming the structural identity of (I).

The cation (I) isomerises† in HBF_4–Ac_2O to give (IIb), characterised as a $[C_8H_9Ru(CO)_3]^+BF_4^-$ isomer by elemental analysis, and i.r. spectroscopy [ν_{max} 2125vs (CO), 2060vs,br (CO), 1660m (C=C), and 796m (C=C) cm^{-1}]; except for the difference in anion (IIb) is identical to (IIa). The ${}^1H$ n.m.r. spectrum [100 MHz $(CD_3)_2CO$] (see Figure) of (IIa) and (IIb) showed resonances at τ 3·52 (dd, H^1, $J_{1,2}$ 2·3 Hz, $J_{1,9}$ 8·0 Hz), 4·32 (dd, A part of an AB system, H^3, $J_{2,3}$ 8·0 Hz, $J_{3,4}$ 3·9 Hz), 4·66 (dd, B part of an AB system, H^2, $J_{2,3}$ 8·0 Hz, $J_{1,2}$ 2·3 Hz), 4·94 (complex m, H^4, H^5, and H^6), 5·59 (q, H^9, $J_{1,9}$ 8·0 Hz, $J_{7,9} = J_{8,9} =$ 8·0 Hz), and 6·30 (overlapping m, H^7 and H^8); at 220 MHz the complex multiplet‡ ascribed to H^4, H^5, and H^6 appeared as two multiplets centred at τ 4·82 and 4·95, and the methylene hydrogens H^7 and H^8 appeared as two multiplets of equal intensity centred at τ 6·18 and 6·43.

Double irradiation experiments support this analysis; in particular, the arrangement $CH^3{\cdot}CH^2{\cdot}CH^1{\cdot}CH^9{\cdot}CH^7H^8$ was firmly established. Thus, as illustrated, either a h^5-1,4,5,6,7- or a h^5-1,2,5,6,7-cyclic structure for (II) is consistent with

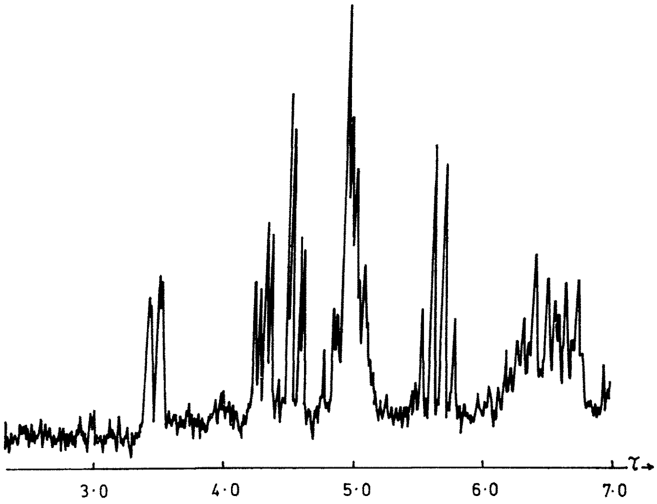


FIGURE. ${}^1H$ *N.m.r. spectrum* (100 *MHz*) *of compounds* (IIa) *and* (IIb)

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† Over a long period of time in CD_3CN the isomerisation is reversed *i.e.* (II) → (I).

‡ In the related triphenylphosphine derivative $[C_8H_9Ru(CO)_2PPh_3]^+PF_6^-$ H^4, H^5, and H^6 appear as separate resonances.

these observations; an alternative h^5-1,2,3,4,5-bonding arrangement is not compatible with the chemical shift and coupling constant data.

Treatment of (II) with cyanide ions or nitromethane–Na_2CO_3 afforded respectively the neutral complexes (III) and (IV), which were shown to be isostructural by comparison of their spectral data. The ^1H n.m.r. spectrum of (IV) showed resonances at τ 4·34 (dd, H^3, $J_{2,3}$ 7·0 Hz, $J_{3,4}$ 4·0 Hz), 4·52 (dd, H^2, $J_{2,3}$ 7·0 Hz, $J_{1,2}$ 4·0 Hz), 4·96 (complex m, H^6), 4·98 (dd, H^4, $J_{3,4}$ 4·0 Hz, $J_{4,5}$ 9·0 Hz), 5·51 (apparent t, H^5, $J_{5,6} = J_{4,5}$ 9·0 Hz), 5·99 (d, CH_2NO_2, $J_{HH'}$ 8·0 Hz), 6·86 (complex m, H^9), 7·48 (apparent t, H^1, $J_{1,2}$ 4·0 Hz, $J_{1,9}$ 4·0 Hz), and 7·93 (overlapping d, H^7 and H^8). These observations, which are supported by double and triple resonance experiments, suggest the illustrated σ–π h^4-1,4,5,6-bonded structure for (III) and (IV).

A h^4-1,4,5,6-bonded system has been previously[2] proposed for β-$C_8H_8Os(CO)_3$ and comparison of their n.m.r. data supports this analogy. Moreover, comparison of the chemical shift and coupling constant data for the structurally common hydrogens in (II), (III), and (IV), *i.e.* H^2, H^3, H^4, H^5, and H^6, strongly suggests that the cation (II) has the C_8H_9 group bonded as a h^5-1,2,5,6,7-system. If this is true then it is interesting that in contrast to the π-allylic-olefin complexes of other d^8 metal ions, *e.g.* Co^I, Rh^I, or Ir^I,[3] addition of nucleophiles to (II) occurs at the co-ordinated double bond rather than at the π-allylic system.

The action of protonic acids on α-$C_8H_8Os(CO)_3$ generates two isomeric forms of the protonated species $[C_8H_9Os(CO)_3]^+$. One is isostructural with the ruthenium complex (II); and the other which isomerises to the first in solution, is identical to the bicyclic iron and ruthenium cations.

It is apparent that even within a given transition metal triad the rôle of the metal is critically important in deciding the isomeric form adopted by an organo-group on co-ordination. If it is assumed that in the bicyclic system the methylene bridge is *exo* to the metal then the isomerisation (I) $\rightarrow$ (II) can be seen as an intramolecular attack on the internal cyclopropane C–C bond, a reaction which is facilitated by a disrotatory ring opening. It is interesting that the iron system does not undergo an analogous isomerisation.

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