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Preliminary communication

THE SYNTHESIS AND REACTIONS OF CATIONIC RHODIUM AND IRIDIUM COMPLEXES; EVIDENCE FOR HYDROGEN-TRANSFER PROCESSES

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Summary

Reactions of rhodium(I) and iridium(I) chlorocomplexes of cyclohexa-1,3-diene, cyclohepta-1,3-diene, and cyclo-octa-1,3,5-triene with $AgBF_4/CH_2Cl_2$ afford respectively the cations $[M(C_6H_6)(1,3\text{-}C_6H_8)]^+$, $[M(\eta^5\text{-}C_7H_7)(\eta^5\text{-}C_7H_9)]^+$ and $[M(\eta^6\text{-}C_8H_{10})(\eta^4\text{-}C_8H_{10})]^+$; the latter complex is a hydrogenation catalyst for olefins.

In continuing a study [1,2] of the chemistry of cationic rhodium(I) and iridium(I) complexes we have obtained evidence for hydrogen-transfer reactions, and also interesting differences in bonding modes depending on the nature of the metal.

Treatment (room temp.) of a solution (CH_2Cl_2) of $[RhCl(1,3\text{-}C_6H_8)_2]$ or $[IrCl(1,3\text{-}C_6H_8)_2]$ with a molar equivalent of $AgBF_4$ in the presence of excess cyclohexa-1,3-diene leads to the precipitation of AgCl and the formation of the benzene complexes* I and II. The reaction involves a disproportionation of co-ordinated cyclohexa-1,3-diene [2] to benzene and cyclohexene, the benzene remaining coordinated, the cyclohexene being displaced by cyclohexa-1,3-diene. Although arene rhodium(I) cations have been previously obtained [2] by displacement of cod from $[Rh(cod)_2]^+BF_4^-$ by arenes, attempts to extend the reaction to iridium failed. Thus, the disproportionation reaction provides a route to these coordinatively saturated molecules. Reaction of either I or II with 1,3,5-trimethylbenzene led to the displacement of benzene and the formation of the corresponding substituted arene cation. In contrast, MeCN, pyridine PMe_3 or, PMe_2Ph, for example, displace benzene

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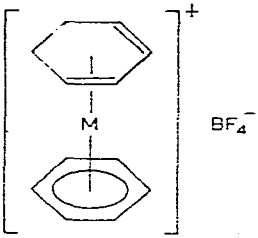
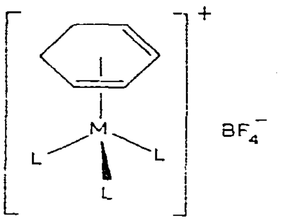
*Satisfactory elemental analyses and NMR spectra were obtained for all the new complexes described.

from I and II to form the respective five-coordinated cations III*, isostructural with tricarbonyl(cyclohexa-1,3-diene)iron.

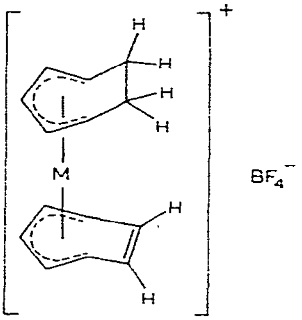
A similar reaction of the cyclohepta-1,3-diene complexes [$RhCl(1,3\text{-}C_7H_{10})_2$] and [$IrCl(1,3\text{-}C_7H_{10})_2$] led to an unusual hydrogen-transfer reaction, and the formation of the cations IV and V. It is likely that a disproportionation reaction occurs as in the cyclohexadiene system forming cycloheptene and cycloheptatriene, a further cycle of this reaction would then afford a bis(cycloheptatriene)rhodium(I) or iridium(I) cation, which then via a single hydrogen transfer reaction [Rh(I) → Rh(III) → Rh(I)] gives the C_7H_7 and C_7H_9 ligands present in IV and V. It is interesting that a co-condensation reaction of iron atoms and cycloheptatriene forms a complex [$Fe(\eta^5\text{-}C_7H_7)(\eta^5\text{-}C_7H_9)$] [4], which is presumably formed by an analogous H-transfer reaction within the molecule [$Fe(C_7H_8)_2$]. Variable temperature NMR experiments (^{13}C and ^1H) indicate that the rhodium and iridium cations are isostructural with the iron system, and undergo related dynamic processes.



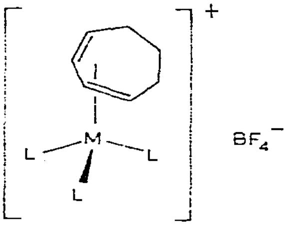
(I, M = Rh)
(II, M = Ir)



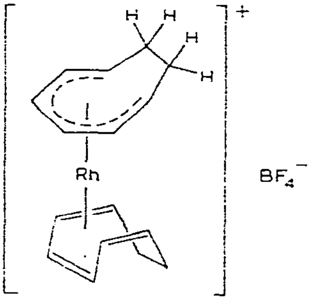
(III, M = Rh, Ir, L = MeCN, Py, PMe_2Ph, PMe_3)



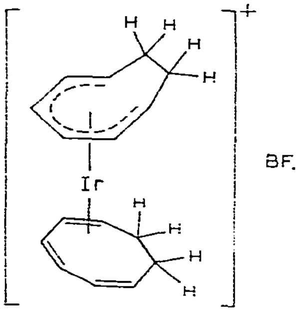
(IV, M = Rh)
(V, M = Ir)



(VI, M = Rh, Ir, L = Me_2SO, Py, PEt_3)



(VII)



(VIII)

If the reaction of $AgBF_4$ with the cyclohepta-1,3-diene chloro-complexes is conducted in the presence of dimethylsulphoxide**, pyridine or triethyl-

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*The ^{31}P NMR spectrum of, for example, [$Ir(1,3\text{-}C_6H_8)(PMe_3)_3$]$^+BF_4^-$ showed a single resonance at room temperature, collapsing (ΔG 8.7 ± 0.6 kcal/mol^{-1}) to two resonances (intensity 2:1 respectively at −87.1 ppm (d, $^2J(PP)$ 17.5 Hz.) and −101.5 ppm (t, $^2J(PP)$ 17.5 Hz.). The value of ΔG for [$Fe(1,3\text{-}C_6H_8)(CO)_3$] has been reported [3] as 7.4 ± 0.2 kcal mol^{-1}.

**The IR spectrum of the $Me_2S{=}O$ complex suggested that S-bonding is involved.

phosphine then a straightforward reaction occurs with formation of the five-coordinate cations VI, which showed similar dynamic behaviour to that observed with the cyclohexa-1,3-diene cations.

In contrast, a halide abstraction reaction with $AgBF_4/CH_2Cl_2$ on the cycloocta-1,3,5-triene complexes $[RhCl(C_8H_{10})_2]$ [5] and $[IrCl(C_8H_{10})_2]$ [5]* leads to the formation respectively of the cations VII and VIII, there being no evidence for H-transfer reactions. Interestingly, examination of the ^{13}C and ^1H NMR spectra of these species showed that different bonding modes were adopted for these 18-electron cations. The rhodium cation is bonded as a η^5- and 1,2,5,6-η^4-system, whereas, in the case of the iridium cation a η^6- and 1,2,3,4-η^4-bonding arrangement is preferred. In this connection it is interesting that Lewis and coworkers [5] observed that the low-temperature protonation of $[Ir(\eta^5\text{-}C_5H_5)(1,3,5\text{-}C_8H_{10})]$ gave the isomeric cations $[IrH(\eta^5\text{-}C_5H_5)(1,2,5,6\text{-}\eta^4\text{-}C_8H_{10})]^+$ and $[IrH(\eta^5\text{-}C_5H_5)(1,2,3,4\text{-}\eta^4\text{-}C_8H_{10})]^+$ in the ratio of 1:4.

Bicyclo[2,2,1]heptadiene, 2,3-dimethylbuta-1,3-diene and 1,3,5-$C_6H_3Me_3$ react (room temp., CH_2Cl_2) with VII or VIII forming the cations $[M(1,2,5,6\text{-}\eta^4\text{-}C_8H_{10})(C_7H_8)]^+$ (M = Rh, Ir), $[Ir(1,2,5,6\text{-}\eta^4\text{-}C_8H_{10})(2,3\text{-dimethylbuta-1,3-diene})]^+$ and $[Rh(1,2,5,6\text{-}\eta^4\text{-}C_8H_{10})(1,3,5\text{-}C_6H_3Me_3)]^+$, which can also be obtained directly by reaction of the corresponding chloro-complex with $AgBF_4/CH_2Cl_2$ and the respective diene or arene. A similar reaction with cyclohexa-1,3-diene led to a catalytic disproportionation reaction and the formation of $[M(C_6H_6)(1,2,5,6\text{-}\eta^4\text{-}C_8H_{10})]^+$ (M = Rh, Ir). The cations VII and VIII are also active catalysts for the hydrogenation (1 atm, room temp.) of olefins, the rhodium system being more reactive. Initial studies with hex-1-ene have shown that olefin isomerisation also occurs, there being a non-linear relationship between hydrogen uptake and reaction time.

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References

1 M. Green, T.A. Kuc and S.H. Taylor, J. Chem. Soc. A, (1971) 2334.
2 M. Green and T.A. Kuc, J. Chem. Soc. Dalton, (1972) 832.
3 L. Kruczynski and J. Takats, J. Amer. Chem. Soc., 96 (1974) 932.
4 J.R. Blackborow, K. Hildenbrand, E. Koerner von Gustorf, A. Scrivanti, C.R. Eady, D. Ehntolt and C. Krüger, J.C.S. Chem. Comm., (1976) 16.
5 J. Evans, B.F.G. Johnson and J. Lewis, J. Chem. Soc. Dalton, (1972), 2668.

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*The complex $[IrCl(C_8H_{10})_2]$ can be prepared more satisfactorily by reaction of cyclo-octa-1,3,5-triene with bis(cyclc-octene)iridium chloride dimer.