The Synthesis and Some Reactions of Bis(acetonitrile)(diene)-rhodium and -iridium Tetrafluoroborate

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Summary The synthetic and catalytic properties of the complexes $[M(diene)_2]^+BF_4^-$, $[M(diene)(CH_3CN)_2]^+BF_4^-$, and $[M(diene)L_2]^+BF_4^-$ (M = Rh or Ir, L = phosphines or bipyridyl) are discussed.

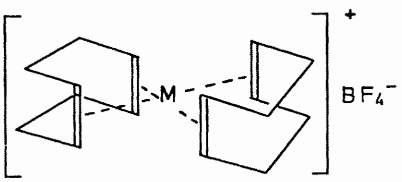
RECENTLY[1] it has been shown that if the dinuclear complexes $[M(diene)Cl]_2$ (M = Rh or Ir), react with triphenylphosphine in a polar solvent then the cationic species $[M(diene)(PPh_3)_2]^+$ can be isolated as tetraphenylborate or perchlorate salts. In an important and alternative approach to compounds of this type it was shown[2] that reaction of $[Rh(1,5\text{-}C_8H_{12})acac]$ with trityl tetrafluoroborate in the presence of a phosphine (L) led to the formation of $[Rh(1,5\text{-}C_8H_{12})L_2]^+BF_4^-$. Previously,[3] the related cationic d^8 species $[M(1,5\text{-}C_8H_{12})_2]^+BPh_4^-$ (M = Rh or Ir) have been isolated by the addition of $NaBPh_4$ to an aqueous dimethylformamide solution of $[M(1,5\text{-}C_8H_{12})_2SnCl_3]$; however, nothing has been previously reported on the chemistry of these potentially interesting cationic systems. Herein, we report a more versatile synthesis and some reactions of this type of cationic complex.

Treatment of [M(diene)acac] (M = Rh or Ir) with $Ph_3C^+BF_4^-$ in the presence of an excess of the diene (diene $= 1,5\text{-}C_8H_{12}$, or norbornadiene) affords the corresponding cationic complex $[M(diene)_2]^+BF_4^-$ in high yield. For example, (I) $[Rh(1,5\text{-}C_8H_{12})_2]^+BF_4^-$ (m.p. 200—201°) and (II) $[Ir(1,5\text{-}C_8H_{12})_2]^+BF_4^-$ (m.p. 141—145°) are obtained, respectively, as moderately air-stable methylene chloride- and acetone-soluble crystalline orange-red and purple-red complexes.

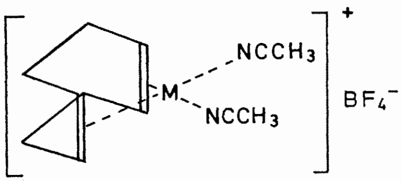
As co-ordinatively unsaturated d^8 systems, the cations $[M(diene)_2]^+BF_4^-$ react with a variety of donor ligands, but of particular interest is the reaction with an excess of acetonitrile, which affords, for example, the yellow crystalline complexes (III) $[Rh(1,5\text{-}C_8H_{12})(CH_3CN)_2]^+BF_4^-$ (m.p. 188—190°, ν_{CN} 2320s and 2300s cm^{-1}) and (IV) $[Ir(1,5\text{-}C_8H_{12})(CH_3CN)_2]^+BF_4^-$ (m.p. 107—108°, ν_{CN} 2317s and 2292s cm^{-1}) as air-stable complexes, in which the co-ordinated acetonitrile acts only as a σ-donor; there being no back-bonding as indicated by the increase in ν_{CN} on co-ordination (ν_{MeCN} unco-ordinated 2295s and 2254s cm^{-1}).[4] These novel complexes clearly provide a new entry to rhodium(I) and iridium(I) chemistry.

The co-ordinated acetonitrile is readily displaced. For example, complexes with the structure (V) are formed on reaction of (III) with PPh_3 or $(Ph_2PCH_2)_2$ or of (IV) with PPh_3, PPh_2Me, PPh_2OMe, $(Ph_2PCH_2)_2$, or bipyridyl. In contrast, cyclo-octa-1,5-diene is also displaced on reaction of (III) with $PPhMe_2$ or on reaction of (IV) with PPh_2OMe to give the complexes (VI) $[ML_4]^+BF_4^-$ (M = Rh or Ir).

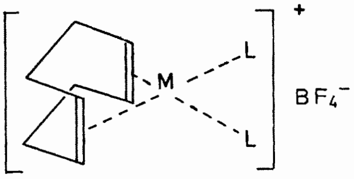
Whereas treatment of (III) or (IV) with cyclo-octa-1,5-diene regenerates the parent compounds (I) and (II), reaction of the rhodium complex (III) with cyclohexa-1,3-diene results in the catalytic disproportionation of the diene to benzene and cyclohexene; the corresponding iridium system (IV) showing no ability to disproportionate. In contrast, both (III) and (IV) are catalysts for the *concurrent* isomerisation of cyclohexa-1,4-diene to -1,3-diene and disproportionation of -1,4-diene to benzene and cyclohexene. Preliminary experiments have shown that $[Rh(1,5\text{-}C_8H_{12})(PPh_3)_2]^+BF_4^-$ can disproportionate cyclohexa-1,3-diene.



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



(III) M = Rh
(IV) M = Ir



[(V), M = Rh, L = PPh_3, L_2 = $(Ph_2PCH_2)_2$;
M = Ir, L = PPh_3, PPh_2Me, PPh_2OMe,
L_2 = $(Ph_2PCH_2)_2$ or bipy].

It is interesting to compare these observations with previous reports of disproportionation reactions. The complex $(1,3\text{-}C_6H_8)(\pi\text{-}C_5Me_5)Rh$ disproportionates cyclohexa-1,3-diene, but must first isomerise the 1,4-diene before disproportionation can occur.[5] However, Vaska-type complexes are reported[6] to be able to only effect the disproportionation of the 1,4-diene. Clearly the cationic systems described here represent more versatile catalysts.

In line with the above observations hex-1-ene is catalytically isomerised to the 2- and 3-enes by the iridium complex (IV) and not by (III).

Both (III) and (IV) are hydrogenation catalysts, the complexes catalysing the hydrogenation of hex-1-ene to hexane and cyclo-octa-1,5-diene to cyclo-octene; there being no evidence for further hydrogenation to cyclo-octane. In contrast, cyclo-octa-1,3-diene is not hydrogenated. In the case of hex-1-ene the iridium system (IV) also causes concurrent isomerisation to occur, but this is not observed with the more active rhodium hydrogenation catalyst. The rate of hydrogenation was found to be solvent dependent, *i.e.* acetone > tetrahydrofuran ~ acetic acid.

It is important to compare these new non-phosphine-containing hydrogenation catalysts with the system $[M(1,5\text{-}C_8H_{12})(PPh_3)_2]^+ClO_4^-$ (M = Rh or Ir) studied by Osborn and his co-workers.[1] We have found that $[Ir(1,5\text{-}C_8H_{12})(PPh_3)_2]^+BF_4^-$ is a less effective catalyst than (IV) for the hydrogenation of cyclo-octa-1,5-diene; moreover, the complex $[Ir(1,5\text{-}C_8H_{12})(PPh_2Me)_2]^+BF_4^-$ does not catalyse the hydrogenation of either hex-1-ene or $1,5\text{-}C_8H_{12}$, but causes rapid isomerisation of the linear olefin and 1,5 to 1,3 isomerisation of the cyclic olefin.

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