Four-, Five-, and Six-co-ordinate Cationic Isonitrile Complexes of Rhodium and Iridium

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Summary The isonitrile complexes, $[M(CNR)_4]^+$, $[M(PPh_3)_2(CNR)_2]^+$, and $[M(PPh_3)_2(CNR)_3]^+$ (M = Rh or Ir R = alkyl or aryl) have been prepared, and undergo oxidative-addition reactions giving $[M(CNR)_4XY]^+$ $[M(PPh_3)_2(CNR)_2XY]^+$, $[M(PPh_3)_2(CNR)_3X]^{2+}$, and $[M(PPh_3)_2(CNR)_2Y_2]^+$, (X = halogen, methyl acyl, allyl, HgCl, $SnCl_3$, Y = halogen)

ALTHOUGH the four-co-ordinate aryl isonitrile and mixed phosphine/isonitrile complexes of rhodium(I), $[Rh(CNAr)_4]X$,[1] ($X = Cl$ or ClO_4, Ar = Ph, p-ClC_6H_4, p-MeC_6H_4 or p-$MeOC_6H_4$) and $[Rh(PPh_3)_2(CNAr)_2]X$,[2] and iridium(I), $[IrCN(p\text{-}MeC_6H_4)_4]X$[3] ($X = Br$, I, or ClO_4), have been known for some time, surprisingly little is known of their chemistry. Furthermore, there have been no reports of the related alkyl isonitrile complexes. We might expect that these four-co-ordinate complexes should undergo oxidative-addition reactions, and herein report some of our preliminary studies of this type of chemistry.

The tetrakis-alkyl-, and -aryl-, isonitrile complexes of rhodium(I), $[Rh(CNR)_4]^+$ ($R = Bu^t$, Pr^i, cyclohexyl, p-ClC_6H_4, p-MeC_6H_4, or p-$MeOC_6H_4$), were most conveniently obtained by addition of CNR to $[Rh(CO)_2Cl]_2$, and were isolated as the Cl^- or PF_6^- salts.† The iridium complex, $[Ir(CNBu^t)_4]Cl$, was obtained from $[Ir(cyclooctene)_2(CO)Cl]$. Addition of CNR to *trans*-$[M(PPh_3)_2(CO)Cl]$ ($M = Rh$ or Ir) afforded either $[M(PPh_3)_2(CNR)_2]Cl$ ($R = Pr^i$ or p-ClC_6H_4) or $[M(PPh_3)_2(CNR)_3]Cl$ ($R = Bu^t$, Pr^i, p-ClC_6H_4, or p-MeC_6H_4). The four-co-ordinate phosphine/isonitrile compounds were converted into their five-co-ordinate analogues on prolonged contact with an excess of isonitrile, but we were unable to prepare $[M(PPh_3)_2(CNBu^t)_2]Cl$.

The tetrakis-isonitrile complexes, $[M(CNR)_4][PF_6]$, readily underwent oxidative-addition reactions giving a variety of six-co-ordinate monocations, *trans*-$[M(CNR)_4XY][PF_6]$, *e.g.* $X = Me$, C_3F_7, or I and $Y = I$, $X = MeCO$, $CH_2CH{=}CH_2$, HgCl, $SnCl_3$, $SnPh_3$, and $Y = Cl$, $X = Y = Br$, $X = CN$, $Y = Br$. However, when the counter-cation was Cl^-, oxidative-addition of halogen (X_2) to $[Rh(CNR)_4]^+$ occurred with loss of isonitrile and formation of $[Rh(CNR)_2X_2Cl]_2$, which is probably analogous to $[Rh(CO)_2X_3]_2$, obtained by halogenation of $Rh_6(CO)_{16}$.[4] The rhodium complexes also reacted with $NOPF_6$ giving the five-co-ordinate dications $[Rh(CNR)_4(NO)][PF_6]_2$ (ν_{NO} *ca.* 1770 cm^{-1}), SO_2 adducts were also formed.

The four co-ordinate mixed phosphine/isonitrile complexes underwent oxidative-addition reactions giving, for example, $[M(PPh_3)_2(CNR)_2MeI]^+$ when treated with methyl iodide.

The five-co-ordinate species, however, while undergoing oxidative-addition reactions, followed less predictable reaction pathways. Thus, halogenation provided a series of compounds which indicate that progressive elimination of phosphine can take place, *i.e.* $[Ir(PPh_3)_2(CNR)_3X]^{2+}$, $[Ir(PPh_3)(CNR)_3X_2]^+$, and $\{[Ir(CNR)_3X_2]_2\}^{2+}$ are formed, the latter probably containing both bridging and terminal X. The t-butyl and isopropyl isonitrile complexes reacted with methyl iodide giving exclusively $[Ir(PPh_3)(CNBu^t)_3MeI]^+$ and $[Ir(PPh_3)_2(CNPr^i)_2MeI]^+$, respectively. With allyl chloride, however, both $[Ir(PPh_3)_2(CNBu^t)_3(\sigma\text{-}C_3H_5)]^{2+}$ and $[Ir(PPh_3)(CNBu^t)_3(\sigma\text{-}C_3H_5)Cl]^+$ could be isolated. These five-co-ordinate complexes could also be protonated in glacial acetic acid, forming $[M(PPh_3)_2(CNR)_3H]^{2+}$, in which the PPh_3 groups were mutually *trans*, and were *cis* with respect to the hydrido-ligand;‡ reaction with HCl gave $[M(PPh_3)_2(CNR)_2Cl_2]^+$. However, when the iridium complexes were dissolved in methanol, they were rapidly oxidised with the formation of $[Ir(PPh_3)_2(CNR)_3(OMe)]^{2+}$. We suggest that these apparently contradictory results may be rationalised, in part, by considering that the five-co-ordinate species undergo prior *electrophilic* attack, for example by (halogen)$^+$, carbonium ions, or H^+ giving dicationic species. These compounds, by virtue of their high positive charge, would be particularly susceptible to *nucleophilic* attack by, for example, (halogen)$^-$ or OMe^-, forming monocationic species with incorporation of the incoming nucleophile and elimination of PPh_3, CNR or H^+.

The attack on iridium by methoxide ion is surprising, especially because the analogous carbonyl, $[Ir(PPh_3)_2(CO)_3]^+$, reacts very readily with methanol giving $[Ir(PPh_3)_2(CO)_2\{C\cdot O(OMe)\}]$,[5] and in the not unrelated platinum(II) complexes, $[Pt(PR_3)(CNR')Cl_2]$, attack by methanol on the isonitrile ligand affords a metal-co-ordinated carbene complex, $[Pt(PR_3)\{C(OMe)(NHR')\}Cl_2]$.[6]

The related mixed phosphine/isonitrile cobalt(I) complexes, obtained by addition of CNR to $[Co(PR_3)_2Cl_2]$ under mild reducing conditions, are exclusively five-co-ordinate, $[Co(PR_3)_2(CNR')_3]^+$, although with $Ph_2PCH_2CH_2PPh_2$ (diphos), under identical reaction conditions, only the cobalt(III) complex, $[Co(diphos)(CNR')_4]^{3+}$, could be obtained. These complexes undergo oxidative-addition reactions of a different type to those of their rhodium and iridium analogues, and are being further investigated.

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† All compounds were satisfactorily characterised by elemental analyses, conductivity measurements, and by i.r. and n.m.r. spectroscopy.

‡ The high-field ^1H n.m.r. spectra exhibited a triplet (J_{PH} 5.5 Hz) at τ 20—27.

[1] L. Malatesta and L. Vallarino, *J. Chem. Soc.*, 1956, 1867.
[2] L. Vallarino, *Gazzetta*, 1959, **89**, 1632.
[3] L. Malatesta and F. Bonati, "Isocyanide Complexes of Metals", Wiley, London, 1969, p. 146.
[4] B. F. G. Johnson, J. Lewis and P. W. Robinson, *J. Chem. Soc.* (*A*), 1970, 1100.
[5] L. Malatesta, G. Caglio and M. Angoletta, *J. Chem. Soc.*, 1965, 6974.
[6] E. M. Bradley, J. Chatt, and R. L. Richards, *J. Chem. Soc.* (*A*), 1971, 23.