Iridium Carbonyl Compounds from the Reaction of $Ir_4(CO)_{12}$ with Sodium

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Summary The hexanuclear $[Ir_6(CO)_{15}]^{2-}$ anion, the mononuclear $[Ir(CO)_4]^-$ anion and the cluster complex $Ir_6(CO)_{16}$ have been obtained for the first time.

IN the gradual reduction of a suspension of $Ir_4(CO)_{12}$ in tetrahydrofuran with sodium, a yellow solution was first obtained, containing the anion $[Ir_4(CO)_{11}H]^-$, which could be isolated as the Et_4N^+ salt, and was identical to the species obtained with K_2CO_3.[1] The solution on further reaction became dark brown and, after filtering and evaporating it *in vacuo* almost to dryness, the addition of a solution of Et_4NCl–90%-EtOH, produced brown diamagnetic crystals. These we consider to be the salt of the pentadecacarbonyliridate(2–) anion $[NEt_4]_2[Ir_6(CO)_{15}]$. This salt was stable indefinitely in the solid state in an inert atmosphere, but only moderately stable in solution. The stoicheiometry, in accordance with the analytical data and the electrical conductivity, was supported by the i.r. spectrum of $[Ir_6(CO)_{15}]^{2-}$, which was very similar to those of the corresponding $[Rh_6(CO)_{15}]^{2-}$ [2] and $[Co_6(CO)_{15}]^{2-}$. [3]

When the salt was suspended in acetic acid in a CO atmosphere for some days it gave, almost quantitatively, a red neutral crystalline substance very slightly soluble in all solvents studied, which we consider to be the polynuclear carbonyl $Ir_6(CO)_{16}$. The probable reactions are:

$$[Ir_6(CO)_{15}]^{2-} + 2\,H^+ = Ir_6(CO)_{15}H_2;$$
$$Ir_6(CO)_{15}H_2 + CO = Ir_6(CO)_{16} + H_2.$$

The identity of this highly stable compound, which could be isolated in a very pure state, was obtained from the analytical data, the close similarity of its i.r. spectrum to those of the well known $Co_6(CO)_{16}$ and $Rh_6(CO)_{16}$[4] and, above all, from its isomorphism with $Rh_6(CO)_{16}$, proved through *X*-ray diffraction.[5]

When the reaction of $Ir_4(CO)_{12}$ with sodium was carried on still further, beyond the point where the anion $[Ir_6(CO)_{15}]^{2-}$ was present, the solution became colourless, while a fraction of the iridium was precipitated as a brown insoluble substance. The latter, after being washed with some ethanol, appeared to be the sodium salt of a condensed carbonyliridate, whose spectrum (Nujol) indicated the presence of both terminal (ν_{CO} 1950 cm^{-1}) and bridging CO (ν_{CO} 1720 cm^{-1}). This salt was pyrophoric; it could be dissolved in water and precipitated from it with bulky cations still giving, however, pyrophoric substances which could not be purified further. From the position of the i.r. stretching bands of the terminal CO (*ca.* 1950 cm^{-1}) we can presume a high ratio between the charge of the anion and the number of metal atoms of the cluster.[6] The colourless tetrahydrofuran solution contained another sodium carbonyliridate, which we consider to be the simple anion $[Ir(CO)_4]^-$ suggested in 1940 by Hieber,[7] but now obtained for the first time and isolated as the trisphenanthrolinenickel salt. Once again, the nature of this compound was better proved by the comparison of its i.r. spectrum with the well known spectra of $[Rh(CO)_4]^-$ and $[Co(CO)_4]^-$,[8] rather than from the analytical data which, however, in this case, for the simpler formula, are more probative than usual.

Carbonyl stretching frequencies

$[Co(CO)_4]^-$	2010w	1890s	1840sh[a]					
$[Rh(CO)_4]^-$	2000w	1900s	1875sh					
$[Ir(CO)_4]^-$	2000w	1898s	1867sh					
$Co_6(CO)_{16}$	2103w	2061s	2057sh	2026w	2020mw	2018mw	1806w	1772s[b]
$Rh_6(CO)_{16}$	2105w	2070s	2047sh	2040w	2022mw	2020mw	1833w	1798s
$Ir_6(CO)_{16}$	2115w	2070s	2057sh	2047w	2034mw	2009mw	1800w	1765s
$[Co_6(CO)_{15}]^{2-}$	2042m	1982s	1959sh	1778s	1737s	1685m	[a]	
$[Rh_6(CO)_{15}]^{2-}$	2045sh	1980s	1960sh	1778s				
$[Ir_6(CO)_{15}]^{2-}$	2020sh	1970s	1910sh	1770s	1745s			

[a] Tetrahydrofuran solution. [b] Nujol.

The reaction of this compound with phosphoric acid gave the previously known tetranuclear hydride $H_2Ir_4(CO)_{11}$;[1] no $Ir_2(CO)_8$, which might arise by hydrogen loss from the hypothetical $HIr(CO)_4$, could be detected demonstrating the instability under these conditions of the dimeric carbonyl $Ir_2(CO)_8$, in contrast to Hieber's results.[7]

Recently, Whyman[9] obtained some i.r. evidence concerning the existence of $HIr(CO)_4$, by treating $Ir_4(CO)_{12}$ under 400 atm. of hydrogen and carbon monoxide. At ordinary pressures, however, the supposed mononuclear hydride decomposes, apparently yielding $Ir_4(CO)_{12}$, while we find $H_2Ir_4(CO)_{11}$.

This work indicates a variety of carbonyl iridate anions, and the trend of iridium compounds to give stable polynuclear carbonyls and carbonyliridates, but only very unstable mononuclear derivatives.

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