Five-co-ordinate Rhodium(I) and Iridium(I) Organomercury Complexes

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A series of five-co-ordinate rhodium and iridium organomercury complexes has been prepared. N.m.r. spectra and other analytical data have been used to confirm the structure, which includes a metal–metal bond from the organomercury group to the transition metal.

COMPLEXES containing metal–metal bonds are of interest [1,2] because of their versatility in synthesis.[3] We have now prepared a series of organomercury complexes of rhodium(I) and iridium(I). Although complexes containing mercury–rhodium or mercury–iridium bonds are known,[4,5] analogous organomercury-containing complexes have not been reported before; * they may, however, be intermediates in several types of reaction.[6,7]

The complexes were obtained by the oxidative addition of organomercury salts to rhodium or iridium complexes in which the formal oxidation state of the transition metal was −1. The preparation of the starting material has been described by Collman *et al.*[8] Tetrahydrofuran (THF) solutions of $[Ir(CO)_3PPh_3]^-$ or $[Rh(CO)_2(PPh_3)_2]^-$ were obtained by sodium amalgam reduction, under an atmosphere of carbon monoxide,

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* It has been brought to the authors' attention by a referee that J. P. Collman, *J. Amer. Chem. Soc.*, 1967, **89**, 844, has previously reported the preparation of a mercury acetylide complex, $IrCl(HgC{\equiv}CR)(C{\equiv}CR)(CO)(PPh_3)_2$.

[1] J. Lewis and R. S. Nyholm, *Sci. Progr.*, 1964, **52**, 557.

[2] B. King, *Organometallic Chem. Rev.*, 1968, **4**, 158.

[3] H. Patel and W. Graham, *J. Amer. Chem. Soc.*, 1965, **87**, 673.

[4] R. S. Nyholm and K. Vrieze, *J. Chem. Soc.*, 1965, 5331; 1965, 5337.

[5] J. P. Collman and C. T. Sears, *Inorg. Chem.*, 1968, **7**, 27.

[6] R. F. Heck, *J. Amer. Chem. Soc.*, 1968, **90**, 5518.

[7] D. Seyforth and R. J. Spahn, *J. Amer. Chem. Soc.*, 1969, **91**, 3037.

[8] J. P. Collman, F. D. Vastine, and W. R. Roper, *J. Amer. Chem. Soc.*, 1968, **90**, 2282.

of chlorocarbonylbis(triphenylphosphine)iridium(I) [9] or its rhodium analogue. Upon addition of the desired organomercury complex to these solutions, initially only a bridged species was observed [reaction (1)].

$$2Na^+[Ir(CO)_3PPh_3]^- + 2RHgCl \xrightarrow[N_2]{THF} 2NaCl + [Ir(CO)_3PPh_3]_2Hg + Hg^0 + R{-}R \quad (1)$$

Bridged species of this type had already been described. Since phenylmercury chloride should be stable under these conditions, we felt that the presence of metallic mercury and the coupled organic product (in this case biphenyl) indicated formation of an organomercury adduct as an intermediate. Upon careful investigation it was found that the desired product is formed but is air, moisture, and light sensitive. When proper precautions were subsequently taken the following reaction could be carried out.

$$Na^+[Ir(CO)_3PPh_3]^- + RHgCl \xrightarrow[N_2\ dark]{THF} Ir(CO)_3PPh_3HgR$$

On exposure to light, air, or moisture, this complex disproportionates [reaction (2)].*

$$2Ir(CO)_3PPh_3HgR \xrightarrow{light} [Ir(CO)_3PPh_3]_2Hg + Hg^0 + R{-}R \quad (2)$$

The biphenyl which is formed was identified by comparison of gas chromatographic retention time with that of an authentic sample.

		Found [a]				Calculated			
Compound		C	H	P	Ir	C	H	P	Ir
$Rh(CO)_2(PPh_3)_2Hg(p\text{-tolyl})$	Cream	55·25	3·8	6·15		55·45	3·8	6·35	
$Rh(CO)_2(PPh_3)_2Hg(\text{phenyl})$	Green-yellow	55·25	3·7	6·6		55·0	3·65	6·45	
$[Rh(CO)_2(PPh_3)_2]_2Hg$	Yellow	58·35	3·85	7·95		58·25	3·85	7·9	
$Ir(CO)_3PPh_3Hg(p\text{-tolyl})$	Cream	40·6	2·75	3·8		40·55	2·65	3·75	
$Ir(CO)_3PPh_3Hg(\text{phenyl})$	Pale yellow	39·85	2·65	3·8	29·0	29·75	2·45	3·8	28·85
$Ir(CO)_3PPh_3Hg(\text{benzyl})$	Cream	40·35	2·6	3·85		40·55	2·65	3·75	
$[Ir(CO)_3PPh_3]_2Hg$	Yellow	39·55	2·4	4·9	30·6	39·5	2·35	4·85	30·4

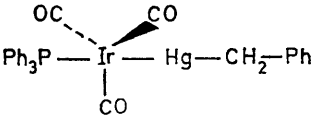
[a] All analytical results were obtained by Galbraith Laboratories, Knoxville, Tennessee.

In this manner either the intermediate organomercury complex or the bridged species could be isolated. By varying the organomercury chloride a series of analogous complexes was obtained. A list of the compounds prepared in this manner along with the analytical data are given in the Table.

Melting point determination in sealed capillaries indicated that all compounds decomposed without melting above 200 °C.

The i.r. spectra of these complexes are consistent with those of Collman's. The iridium complexes all have a very intense broad band centred at 1950 cm^{-1} and a medium band at 2000 cm^{-1}. The rhodium complexes have a strong group of bands † at 1975 cm^{-1} and a medium band at 1920 cm^{-1}. Both of the tolyl complexes also have an absorption at 790 cm^{-1} and a group of absorptions at *ca.* 2900 cm^{-1}. These correspond to, respectively, the characteristic aromatic hydrogen wag for *para*-substituted toluene and the CH stretch of the methyl group. The presence of the bands in the i.r. spectra, in addition to confirming the presence of the tolyl group in the complex, also confirms that no rearrangement of the *para*-substitution of the tolyl group has occurred.

The n.m.r. spectra offered further confirmation of the structure. In addition to the triphenylphosphine resonance at τ 2·3 and 2·6, the rhodium compounds have absorptions at τ 2·7 and 7·6 for the tolyl compound and τ 2·8 for the phenyl analogue. Relative areas are consistent with assignment of the low-field resonances to the aromatic protons and the high-field resonance to the CH_3 protons. The triphenylphosphine protons of the iridium complexes cover the regions between τ 2·5—3·0 thus obscuring the aromatic protons of the organomercury group. However, the $-CH_3$ resonance at τ 7·4 and the $-CH_2-$ resonance at τ 7·6 can clearly be seen for the tolyl and benzyl derivatives, respectively. The benzyl complex offers additional information about the structure. Since ^{199}Hg (17% natural abundance) has a nuclear spin of 1/2 it can couple with the benzyl protons. In dibenzylmercury the coupling constant, J(Hg–H) is 134 Hz. Iridium on the other hand has a nuclear spin of 3/2 and is therefore expected only to broaden the methylene resonance. The n.m.r. of the iridium–mercury–benzyl complex shows mercury coupling with coupling constant, J(Hg–H) 176 Hz. This then allows one to assign the following as the most probable structure.



While no positive evidence for this trigonal bipyramidal structure exists, there is ample precedence for suggesting it. Hieber [10] has suggested that the trigonal bipyramidal structure is favoured over a tetragonal

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* The disproportionation directly to Hg^0 and R–R may be somewhat surprising since related cobalt systems have been shown to disproportionate as follows: $2(CO)_4CoHgR \longrightarrow [(CO)_4Co]_2Hg + HgR_2$ (W. Hieber and R. Breu, *Chem. Ber.*, 1957, **90**, 1270). However, under our conditions HgR_2 is stable, discounting the possibility that the diorganomercury is first formed followed by subsequent elimination of mercury to yield the observed products. The possibility of an 'iridium-catalysed' decomposition of HgR_2 cannot, of course, be strictly ruled out but since this would imply some sort of iridium–organomercury intermediate anyway, it becomes a circular argument.

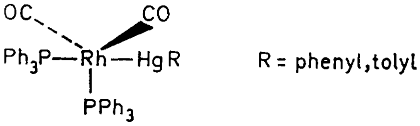
† Unfortunately, solution spectra of these complexes could not be obtained due to the sensitivity of the solutions to light. The mull and KBr spectra of the solids are undoubtedly complicated by solid-state effects, especially in the CO stretching region.

[9] L. Vaska and J. W. Diluzo, *J. Amer. Chem. Soc.*, 1961, **83**, 2784.

[10] W. Hieber and E. Lindener, *Chem. Ber.*, 1965, **98**, 3921.

pyramid while Manning[11] has shown that the analogous complex $[Co(CO)_4]_2Hg$ reacts with PPh_3 to form $[Co(CO)_3PPh_3]_2Hg$ in which the mercury is *trans* to the phosphine.

Similarly the most likely structure for the rhodium complexes is:



The oxidative addition of organomercury salts to rhodium(−1) or iridium(−1) complexes therefore appears to yield an organomercury adduct in which the mercury–carbon bond remains intact. This result becomes even more intriguing in view of recent work in this laboratory[12] indicating that oxidative-addition of organomercury salts to rhodium(+1) and iridium(+1) complexes results in the cleavage of the mercury–carbon bond, not the mercury–halogen bond.

EXPERIMENTAL

I.r. spectra were obtained from Nujol or Kel-F mulls or from CsI or KBr pellets using a Beckman Model IR 12 grating spectrometer with a range of 200—4000 cm^{-1}. M.p.s were determined using a Mel-temp capillary melting-point apparatus. N.m.r. spectra were obtained on a Varian Associates Model T 60 spectrometer using deuteriochloroform or $[^2H_2]$methylene chloride as solvent and tetramethylsilane as internal standard.

Rhodium trichloride trihydrate and iridium trichloride trihydrate were obtained from Matthey–Bishop, Inc. Triphenylphosphine, dibenzylmercury, and diphenylmercury were obtained from Strem Chemicals, Inc., and used without further purification. Di-*p*-tolylmercury was obtained from Eastman Chemicals. Metallic sodium, mercury, and reagent grade solvents were all obtained from Fisher Chemical. All solvents were dried, distilled, and deaerated prior to use.

Preparation of Triscarbonyl(triphenylphosphine)iridium-(−1) *Solution and Biscarbonylbis(triphenylphosphine)rhodium*(−1) *Solution*.—Stock solutions of these anions were prepared by Collman's method.[8] It was found that filtration of this solution through diatomaceous earth to remove colloidal particles greatly aided the isolation of pure compounds in later steps.

Preparation of Organomercuric Chlorides.—Equimolar amounts of the diorganomercury compound and mercuric chloride were heated under reflux overnight in ethanol. On cooling the desired compound was obtained and was recrystallized from ethanol.

Preparation of Complexes.—Aliquots from the stock solutions of the rhodium or iridium anions were added to equimolar amounts of the organomercuric chloride in a dark bottle. After 30 min these solutions were filtered in the dark to remove the NaCl which formed. The clear solution which remained was evaporated *in vacuo* at room temperature to a small volume. A small amount of methanol or ethanol was then added to induce crystallization. In some cases it was found necessary to cool the solution in a solid CO_2–acetone bath before precipitating the product to prevent the deposition of mercury which occurred at room temperature. All steps in the preparation were done under nitrogen. Attempts to recrystallize these compounds proved unsuccessful due to further reaction to form the bridge complex $[Ir(CO)_3PPh_3]_2Hg$.

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[11] A. R. Manning, *J. Chem. Soc.* (*A*), 1968, 1018.
[12] G. M. Intille, to be published.