

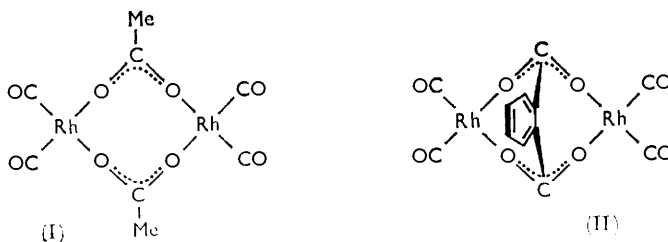
346. Bridge-splitting and Replacement Reactions of Rhodium Carbonyl Chloride

By D. N. LAWSON and G. WILKINSON

A series of bridged compounds $[\text{Rh}(\text{CO})_2\text{X}]_2$, where the bridging groups, X, are carboxylates, nitrate, thiocyanate, and sulphate, have been prepared from rhodium carbonyl chloride. A series of mononuclear amine complexes, $\text{RhXAm}(\text{CO})_2$, have also been prepared.

Bridged Rhodium Carbonyl Compounds.—Although in certain derivatives of rhodium carbonyl chloride, such as $(\text{dieneRhCl})_2$ ¹ and $\text{RhCO}(\text{PPh}_3)_2\text{Cl}$,² the chloride may be replaced by other monovalent anions in metathetical reactions, *e.g.*, with lithium bromide in acetone, such reactions have not been reported for rhodium carbonyl chloride itself. We have found that solutions of rhodium carbonyl chloride in petroleum, on shaking with solid silver salts at room temperature, give silver chloride and bridged derivatives of rhodium, $[\text{Rh}(\text{CO})_2\text{X}]_2$.

(a) *Bridged carboxylate compounds.* With silver acetate and with disilver phthalate, the complexes (I) and (II), respectively, are formed, both of which are soluble in organic



solvents, and are dimeric as indicated. With disilver terephthalate, a blue solid is formed; it is insoluble in common organic solvents, does not sublime, and is presumably polymeric. Under the same conditions, silver benzoate forms a blue solid with an infrared (i.r.) spectrum consistent with dicarbonylrhodium(I)- μ_2 -benzoatodicarbonylrhodium(I), but a satisfactory analysis could not be obtained, even after sublimation of the solid. Silver *p*-fluorobenzoate, however, gives blue needles of the expected complex.

¹ J. Chatt and L. M. Venanzi, *J.*, 1957, 4735.

² L. M. Vallarino, *J.*, 1957, 2287.

The carboxylate compounds are stable in dry air, but are sensitive to moisture. In the solid state, they (and the other bridged species) are generally dichroic, suggesting the presence of metal-metal bonding, as in rhodium carbonyl chloride itself;³ they dissolve in organic solvents, giving orange-yellow solutions. The main i.r. bands of the complexes are presented in Table I. The difference between the asymmetric and the symmetric carboxylate stretching frequencies is small, as expected,⁴ and much less than that in the complexes where the carboxylate acts as a monodentate ligand (see below).

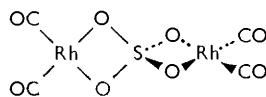
(b) *Other bridged compounds.* Under similar conditions, silver cyanide, fluoride,

TABLE I
Infrared bands (in cm^{-1}) of the bridged compounds (Nujol and hexachlorobutadiene mulls)

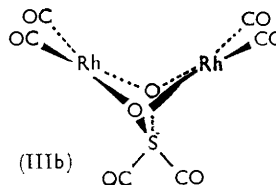
Compound	CO stretch	Asym. COO	Sym. COO	Other strong bands
$[\text{Rh}(\text{CO})_2\text{MeCO}_2]_2$	2083vs, 2067vs, 2027vs, 1980s	1560	1439	1422m, 1351m, 1261m, 690m
$[\text{Rh}(\text{CO})_2]_2\text{phthalate}$...	2094s, 2080vs, 2072vs, 2038vs, 2022vs, 2001s	1553	1408	1524m, 1515m, 1490m, 742m, 627m, 502m, 488m
$[\text{Rh}(\text{CO})_2\text{CF}_3\text{CO}_2]_2$	2101m, 2081s, 2031m	1686	1627	1180vs, 1176s, 1161m
$[\text{Rh}(\text{CO})_2\text{-}i\text{-}\text{C}_6\text{H}_4\text{CO}_2]_2$	2079vs, 2024vs, 1984w	1603	1546	1508m, 1408s, 1403s, 1379m, 1294m, 1227s, 1153s, 1145m, 1014m, 862m, 855s, 774s, 690m, 633m, 624s, 505s, 450s, b
$[\text{diene RhMeCO}_2]_2$ ¹ ...		1530	1419	
$[\text{Rh}(\text{CO})_2\text{NO}_3]_2$	2123vs, 2081m, 2037vs, 2000s, 1992m			1748m, 1639s, 1493m, 1374s, 1284vs, 1263m, 1096m, 1027s, 793, 621m
$[\text{Rh}(\text{CO})_2\text{SO}_4]$ *	2093vs, 2035s, 2014m			1198m, 1193sh, 1129sh (all vb)
$[\text{Rh}(\text{CO})_2\text{SCN}]_2$	2083vs, 2033vs			2092s
$[\text{Rh}(\text{CO})_2\text{Cl}]_2$ ⁶ †	2089, 2076, 2015			

* In CHCl_3 . † In KBr disc.

molybdate, and perhenate do not react; silver carbonate gives an intractable black solid with no carbonyl stretching frequency in its i.r. spectrum, and silver chromate gives a solid which decomposed on attempted isolation. However, with silver nitrate, sulphate, and thiocyanate, binuclear species are formed. They are soluble in acetone and chloroform, giving stable yellow-orange non-conducting solutions. They are very sensitive to moisture. The i.r. bands of these complexes are presented in Table I. The nitrate shows bands at 1639, 1493, 1284, 1027, and 793 cm^{-1} , closely resembling those in other bidentate nitrates.⁵ The molecular weight of the complex shows that it is dimeric, and accordingly we formulate it as $[\text{Rh}(\text{CO})_2\text{NO}_3]_2$, with nitrate bridges. The i.r. spectrum of the sulphate, $\text{Rh}_2(\text{CO})_4\text{SO}_4$, has no bridging-carbonyl bands, and therefore there must be some form of sulphate bridge (IIIa or b) between the rhodium atoms.



(IIIa)



(IIIb)

As regards structure (IIIa), no other tetradentate sulphate complex appears to be known, so that direct comparison of i.r. spectra is not possible, but (IIIa) is supported by the

³ L. F. Dahl, C. Martell, and D. L. Wampler, *J. Amer. Chem. Soc.*, 1961, **83**, 1761.

⁴ T. A. Stephenson, E. Bannister, and G. Wilkinson, *J.*, 1964, 2538.

⁵ B. M. Gatehouse and A. E. Comyns, *J.*, 1958, 3965; J. G. Allpress and A. N. Hambly, *Austral. J. Chem.*, 1959, **12**, 569; J. E. Fleming and H. Lynton, *Chem. and Ind.*, 1960, 1415; C. C. Addison, *U.S. Dep. Comm., Office Tech. Serv. A.D.* 261, 382 (*Chem. Abs.*, 1963, **58**, 94).

resemblance of the single, very broad, band (centred at 1130 cm^{-1}) to that observed for ionic (tetrahedral) sulphate (centred at 1104 cm^{-1}).⁶ For bidentate sulphates, four well-resolved, broad bands are observed;⁶ however, such bands might be present under the broad profile of the rhodium carbonyl sulphate spectrum, and (IIIb) cannot be excluded.

The thiocyanate has an i.r. band at 2092 cm^{-1} , a typical value for a bridging thiocyanate,⁷ and no bridging-carbonyl stretching frequencies. This suggests that the compound is dimeric, with thiocyanate bridges, which is confirmed by its molecular weight.

Mononuclear Rhodium Carbonyl Compounds.—The halogen bridge in rhodium carbonyl chloride is readily split by phosphines, etc.,³ and by diketones,⁸ but aliphatic amines are reported⁹ to give only colourless, ill-defined products.

We have found that amines split the bridge, not only of rhodium carbonyl chloride, but also of the bridged carboxylates, giving dichroic, mononuclear species which are decomposed by moisture to ill-defined straw-coloured solids. Hydrazine and rhodium carbonyl chloride give a purple solid of high molecular weight.

The dichroism of the solid compounds suggests metal-metal bonding. Hydroxyl-aminechlorodicarbonylrhodium(I) was examined spectroscopically as an example. Its reflectance spectrum has maxima at 350, 402, and 600 $m\mu$. Its transmission spectrum (Nujol mull) has a broad band at 590 $m\mu$ with a shoulder at 410 $m\mu$, and its solution (acetone) transmission spectrum shows no bands in the visible region (except for a very weak band at 600 $m\mu$). Tail-end absorption from a strong ultraviolet band is the cause of the yellow colour.

Hieber *et al.*⁹ prepared a yellow solid of empirical formula $\text{Rh}(\text{CO})_2\text{py}_2\text{Cl}$ by the action of an excess of pyridine on the carbonyl chloride. On the basis of the diamagnetism of the compound, they suggested that it was dimeric, with chloro-bridges and six-co-ordinate rhodium(I). However, the five-co-ordinate monomer would also be diamagnetic, and would obey the Inert Gas Rule, and we see no reason to postulate a dimer. The evidence we present below supports a monomeric formula. (Molecular-weight determinations are impossible, as the compound decomposes in solution.) We have prepared the compound by dissolving pyridinechlorodicarbonylrhodium(I) in pyridine. The i.r. spectrum contains two carbonyl stretching frequencies between 1800 and 1850 cm^{-1} . Terminal carbonyl stretching frequencies have been reported¹⁰ as low as 1750 cm^{-1} in other compounds containing poor π -acceptors such as pyridine. Pyridinechlorodicarbonylrhodium reacts with excess of triphenylphosphine in benzene at room temperature, eliminating pyridine and carbon monoxide, and forming $\text{RhCO}(\text{PPh}_3)_2\text{Cl}$, identified by means of its i.r. spectrum and melting point.² The bispyridine complex gives the same compound when treated with fused triphenylphosphine, suggesting that the second pyridine molecule is loosely bound and may be readily lost.

The ammonia and methylamine complexes react with excess of the amine to form moisture-sensitive yellow solids, which revert to the purple $\text{Rh}(\text{CO})_2\text{Cl}(\text{Am})$ unless kept in an atmosphere of the amine. By preparing a mull in an ammonia atmosphere, it was possible to record the i.r. spectrum of the yellow ammine complex before it had all reverted to the purple complex. The spectrum has two strong bands in the 1800—1850 cm^{-1} region and, by analogy with the pyridine derivative, we formulate the complex as $\text{Rh}(\text{CO})_2(\text{NH}_3)_2\text{Cl}$.

With a $2\frac{1}{2}$ -fold excess of rhodium carbonyl chloride in benzene, 2,2'-bipyridyl gives a blue precipitate. In this complex the bipyridyl is merely acting as a bifunctional, and not as a chelating, ligand. However, when other proportions of the reagents are used, there is some evidence that $[\text{Rh}(\text{bipy})_2]\text{Cl}$, RhCObipyCl , and $[\text{Rh}(\text{CO})_2\text{bipy}]\text{Cl}$ are formed,

⁶ K. Nakamoto, J. Fujita, S. Tanaka, and M. Kobayashi, *J. Amer. Chem. Soc.*, 1957, **79**, 4904.

⁷ J. Chatt and L. A. Duncanson, *Nature*, 1956, **178**, 997.

⁸ F. Bonati and G. Wilkinson, *J.*, 1964, 3156.

⁹ W. Hieber, H. Heusinger, and O. Vohler, *Chem. Ber.*, 1957, **90**, 2425.

¹⁰ E. W. Abel, M. A. Bennett, and G. Wilkinson, *J.*, 1959, 2325.

TABLE 2
Infrared bands (in cm^{-1}) of the mononuclear compounds (Nujol and hexachlorobutadiene mulls)

Compound	CO stretch	Asym. COO	Sym. COO	Other strong bands
$\text{Rh}(\text{CO})_2\text{py}\cdot\text{MeCO}_2$	2062vs, 2041m, 2020s, 2000vs, 1957m	1567	1333	1621m, 1609s, 1600s, 1592s, 1558s, 1447s, 1225s, 1160m, 1073s, 1015s
$[\text{Rh}(\text{CO})_2\text{py}]_2\text{phthalate}$	2083vs, 2075s, 2049s, 2016vs, 2012vs	1626	1339 1321	3075m, 1605m, 1486m, 1447s, 1406m, 756m, 750m
$[\text{RhCO}(\text{PPh}_3)_2]_2\text{phthalate}$...	1969vs	1567	?	3049m, 1613m, 1585m, 1479m, 1433s, 1117m, 1095m, 743s, 693vs
$\text{RhCO}(\text{PPh}_3)_2\text{p}\cdot\text{F}\cdot\text{C}_6\text{H}_4\text{CO}_2$...	1965vs	1618	1477 1435	3049m, 1600m, 1587m, 1504m, 1351s, 1220m, 1136s, 1094s, 1037m, 998m, 854s, 774s, 751s, 746s, 740s, 706s, 693s, 521vs, 514vs, 499vs
$\text{Rh}(\text{CO})_2\text{Cl}\cdot\text{NH}_3$	2096s, 2063m, 2010vs			1610m, 1279m, b, 1255m, 1249m
$\text{Rh}(\text{CO})_2\text{Cl}\cdot\text{NH}_2\text{OH}$	2099vs, 2066s, 2012vs, 1988s			3311m, 1258s, 1236s, 495s
$\text{Rh}(\text{CO})_2\text{Cl}\cdot\text{NH}_2\text{Me}$	2092vs, 2064s, 2028vs, 1988s, 1980wsh, 1962w			3279s, 1567s, 1460m, 1393m, 1241m, 1230m, 1074s, 1063s, 1026s, 637s, 617s
$\text{Rh}(\text{CO})_2\text{Cl}\cdot\text{NH}_2\text{Ph}$	2096s, 2073s, 2019s, 2005s			3247m, 1600m, 1493m, 1116m, 1101s, 754m, 694m, 672m, 615m
$\text{Rh}(\text{CO})_2\text{Cl}\cdot\text{NH}_2\text{C}_6\text{H}_4\text{p}\cdot\text{Me}$...	2095s, 2066m, 2058m, 2037vs, 2000m			3347m, 3185m, 1515s, 1385m, 1122m, 814m, 617m
$\text{Rh}(\text{CO})_2\text{Cl}\cdot\text{py}$	2075s, 2060m, 2010vs, 1980m			1634m, 1484m, 1441m, 1220m, 1070m, 1063m, 1015m, 765m, 698m, 610m, 500m
$\text{Rh}(\text{CO})_2\text{Cl}(\alpha\text{-pic})$	2076vs, 2074s, 2010vs, 1976m			3040m, 1608s, 1565m, 1488s, 1449s, 1429m, 1379m, 1302s, 1248m, 1156m, 1302s, 1248m, 1156m, 1107m, 1055m, 962m, 763s, 758s, 724s, 667s
$[\text{Rh}(\text{CO})_2\text{Cl}]_2\text{bipy}$	2075s, 2053vs, 2008s, 1976vs			1600s, 1466m, 1445m, 1312m, 1242m, 1170m, 1157m, 766vs, 724s, 610m, 524m, 485m
$\text{RhCO}(\text{Me}_2\text{SO})_2\text{Cl}$	2008s			3003m, 2924m, 1117s, 1107s, 1131m, 1013s, 970m, 935m, 916m, 726m, 683m, 616m, 535m, 505m, 471m
$[\text{NMe}_2][\text{Rh}(\text{CO})_2\text{Cl}_2]$	2066vs, 2000vs			3030s, 1493s, 1486s, 1471m, 1412m, 1285m, 949vs, 621m, 481s

although they could not be isolated in a pure state. None of these complexes is unstable in air, as suggested by Hieber *et al.*⁹

The i.r. spectra of the mononuclear species are presented in Table 2. In the carboxylates, it may be seen that the symmetric carboxylate stretching frequency is displaced more than the asymmetric one on going from the bridged to the monodentate species, as predicted.⁴ As the electron-withdrawing power of other ligands in a complex increases, so the carbonyl stretching frequency increases. Thus, in order of increasing carbonyl stretching frequency, the bridged carboxylates display the order $p\text{-F}\cdot\text{C}_6\text{H}_4\text{CO}_2 < \text{CH}_3\text{CO}_2 < (\text{Cl}) < \text{phthalate} < \text{CF}_3\text{CO}_2$; the complexes $\text{Rh}(\text{CO})_2\text{Xpy}$, the order $\text{CH}_3\text{CO}_2 < \text{Cl} < \text{phthalate}$; and the complexes $\text{Rh}(\text{CO})_2\text{Cl}(\text{Am})$, the order $\text{bipy} \simeq \text{py} \simeq \alpha\text{-pic} < p\text{-Me}\cdot\text{C}_6\text{H}_4\text{NH}_2 < \text{C}_6\text{H}_5\text{NH}_2$, and $\text{MeNH}_2 < \text{C}_6\text{H}_5\text{NH}_2 \simeq \text{NH}_3 < \text{NH}_2\text{OH}$. The carbonyl chloride also reacts smoothly with dimethyl sulphoxide to give $\text{Rh}(\text{CO})(\text{Me}_2\text{SO})_2\text{Cl}$, which is monomeric in organic solvents and stable in air.

A mononuclear species of a different type is obtained by treating rhodium carbonyl chloride with tetramethylammonium chloride. Well-defined yellow needles of the salt $\text{Me}_4\text{N}[\text{Rh}(\text{CO})_2\text{Cl}_2]$ are obtained; this salt is soluble in acetone and nitromethane, giving conducting solutions, the conductivities corresponding to a 1:1 electrolyte. The solutions and the salts are hydrolysed by water. The anion $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$ is also formed by dissolution of rhodium carbonyl chloride in strong hydrochloric acid, from which it can be precipitated by large cations. The anion is clearly square-planar with *cis* carbon monoxide groups.

EXPERIMENTAL

Microanalyses were by the Microanalytical Laboratory, Imperial College. Molecular weights were by the Mechrolab Osmometer method. Solvents were dried over molecular sieves. The petroleum had b. p. 40–60°. Rhodium carbonyl chloride (tetracarbonyl- μ -dichlorodirrhodium(I)) was prepared by the usual method.¹¹ Colours of dichroic solids are reported by reflected/transmitted light. Infrared spectra were obtained with a Grubb-Parsons "Spectromaster" instrument. Analyses are reported in Table 3.

Dicarbonylrhodium(I)- μ_2 -acetatodicarbonylrhodium(I).—Rhodium carbonyl chloride (0.4 g.) and solid silver acetate (an excess) were shaken in petroleum (50 ml.), for 2 hr. at room temperature. The *acetate* was deposited as a green-red solid (approx. quantitative yield), decomp. 160°, on cooling the filtrate to –80°. It is soluble in organic solvents, to give orange solutions, and may be sublimed *in vacuo* at ca. 100°.

Acetatodicarbonylpyridinerhodium(I).—The acetate, in petroleum, was treated with the stoichiometric amount of dry pyridine. The mixture was cooled to 0° for 1 hr., and the resulting fine orange needles of the *complex* were collected (approx. quantitative yield), decomp. 110°. The complex is soluble in acetone and benzene, and sparingly soluble in petroleum.

Dicarbonylrhodium(I)- μ_2 -trifluoroacetatodicarbonylrhodium(I).—Rhodium carbonyl chloride and excess of silver trifluoroacetate were shaken, in petroleum, at room temperature for 12 hr. The collected deposit was extracted with acetone, giving an orange solution which, at –80°, deposited the *trifluoroacetate* as a dark blue solid, decomp. 100–120°. It is soluble in benzene, acetone, chloroform, and ethanol, giving orange solutions, but is insoluble in petroleum.

Dicarbonylrhodium(I)- $\mu\mu'$ -phthalatodicarbonylrhodium(I).—Rhodium carbonyl chloride and an excess of disilver phthalate were shaken, in benzene, at room temperature for 3 hr. The orange filtrate was evaporated to dryness *in vacuo*. The *phthalate* crystallised from petroleum as a purple-brown solid, decomp. 160–170°, soluble in common organic solvents.

μ -Phthalatotetracarbonyldipyridinedirrhodium(I).—The *complex* was obtained, in a manner analogous to that used for acetatodicarbonylpyridinerhodium(I), as yellow crystals, decomp. 130–140°. It is soluble in acetone and benzene, but is insoluble in petroleum.

μ -Phthalatotetrakis(triphenylphosphine)dicarbonyldirrhodium(I).—Rhodium carbonyl phthalate and triphenylphosphine (an excess) reacted together, in benzene, carbon monoxide being

¹¹ J. A. McCleverty and G. Wilkinson, *Inorg. Synth.*, 1965, **8**, in the press.

TABLE 3
Analyses

Compound	Found (%)					Required (%)					M			
	C	H	Hal	N	O	S	M (solvent)	C	H	Hal		N	O	S
[Rh(CO) ₂ MeCO ₂] ₂	22.0	1.5			29.3		441 Me ₂ CO	22.0	1.4			29.4		436
[Rh(CO) ₂ CF ₃ CO ₂] ₂	18.0	0.0	20.8		26.4		532 Me ₂ CO	17.6	0.0	21.0		26.6		544
[Rh(CO) ₂ phthalate].....	30.1	1.1					487 C ₆ H ₆	29.9	0.8					482
[Rh(CO) ₂ p-F-C ₆ H ₄ CO ₂] ₂	35.9	1.4	6.8				562 C ₆ H ₆	36.2	1.3	6.4				596
[Rh(CO) ₂ NO ₂] ₂	10.6	0.0		6.0	36.0		438 CHCl ₃	10.9	0.0		6.3	36.2		442
[Rh(CO) ₂ SO ₄] ₂	12.2	0.0			31.0	7.2	423 CHCl ₃	11.6	0.0			31.0	7.7	414
[Rh(CO) ₂ SCN] ₂	16.4	0.0		6.4	14.6	14.3	424 CHCl ₃	16.6	0.0		6.5	14.7	14.7	434
Rh(CO) ₂ MeCO ₂ py.....	36.3	3.0		4.7	22.1		284 Me ₂ CO	36.4	2.7		4.7	21.6		297
[Rh(CO) ₂ py] ₂ phthalate.....	41.3	2.6		4.5	20.2		681 Me ₂ CO	41.3	2.2		4.4	20.0		640
[RhCO(PPh ₃) ₂] ₂ phthalate.....	66.6	4.5	[P, 7.9]		6.7		1449 C ₆ H ₆	66.7	4.4	[P, 8.3]		6.5		1452
RhCO(PPh ₃) ₂ p-F-C ₆ H ₄ CO ₂	66.6	4.8	[P, 7.2]				791 CHCl ₃	66.2	4.4	[P, 7.8]		6.5		794
Rh(CO) ₂ Cl-NH ₂	11.6	1.7	16.4	6.4				11.4	1.4	16.7	6.7			
Rh(CO) ₂ Cl-MeNH ₂	16.3	2.4	15.8	6.5				16.1	2.2	15.8	6.2			
Rh(CO) ₂ Cl-NH ₂ OH.....	11.4	1.4		6.2	21.6		232 CHCl ₃	10.8	1.3		6.2	21.3		227
Rh(CO) ₂ Cl-NH ₂ Ph.....	33.8	2.7	12.7	4.9			292 C ₆ H ₆	33.8	2.4	12.4	4.9			287
Rh(CO) ₂ Cl-NH ₂ C ₆ H ₄ p-Me.....	35.8	3.2	11.8	4.7			299 C ₆ H ₆	36.0	3.0	11.8	4.7			301
Rh(CO) ₂ Cl-py.....	31.0	2.0	13.2	5.2			274 Me ₂ CO	30.8	1.8	13.0	5.1			273
Rh(CO) ₂ Cl-C ₆ H ₄ N.....	33.2	2.5	12.8				291 Me ₂ CO	33.2	2.4	12.4				288
Rh(CO) ₂ Clpy ₂	41.1	3.1	10.4	8.1	8.8			40.8	2.8	10.0	8.0	9.0		
[Rh(CO) ₂ Cl] ₂ bipy.....	30.9	2.67		5.4			546 Me ₂ CO	30.9	1.47		5.2			544
RhCO(Me ₂ SO) ₂ Cl.....	18.8	3.8					322 CHCl ₃	18.6	3.7					322
NMe ₄ ⁺ [Rh(CO) ₂ Cl] ₂ ⁻	23.9	3.9	23.4	4.5				23.7	4.0	23.4	4.6			

evolved. The *complex* was precipitated as a yellow solid, m. p. 127—128° (decomp.), by the addition of petroleum, and was recrystallised from benzene. It is soluble in benzene and acetone, but insoluble in petroleum.

Dicarbonylrhodium(1)- μ_2 -*p*-fluorobenzoato*rhodium*(1).—Rhodium carbonyl chloride and an excess of silver *p*-fluorobenzoate were shaken, in petroleum, at room temperature for 3 hr., The deep brown filtrate was cooled to -80° , and the *complex* was deposited as dark blue needles m. p. 144°. It is soluble in all common organic solvents.

p-Fluorobenzoatobis(triphenylphosphine)*dicarbonylrhodium*(1).—Rhodium carbonyl *p*-fluorobenzoate and an excess of triphenylphosphine reacted together in petroleum, carbon monoxide being evolved. The *complex* was precipitated as yellow needles, m. p. 173—175° (decomp.). It is freely soluble in methylene chloride and chloroform, and sparingly soluble in benzene, acetone, and carbon tetrachloride.

Dicarbonylrhodium(1)- μ_2 -nitratod*icarbonylrhodium*(1).—Rhodium carbonyl chloride and dried silver nitrate (an excess), shaken together in petroleum at room temperature, deposited a solid. From this, the *nitrate* could be sublimed at 80° *in vacuo* as a purple solid, decomp. 100—105°. It is soluble in acetone and chloroform, giving orange solutions.

Dicarbonylrhodium(1)- μ_2 -sulphatod*icarbonylrhodium*(1).—Rhodium carbonyl chloride and silver sulphate (an excess), shaken together in petroleum at room temperature for 12 hr., deposited a purple solid. The orange acetone-extract at -80° deposited the *sulphate* as a green-purple solid, decomp. *ca.* 50°. It is soluble in acetone and chloroform.

Dicarbonylrhodium(1)- μ_2 -thiocyanatod*icarbonylrhodium*(1).—Rhodium carbonyl chloride and silver thiocyanate (an excess), shaken together in chloroform for 24 hr. at room temperature, deposited a blue solid. This was extracted with carbon disulphide, and, from the orange extract, the *complex* was obtained as a brown solid, decomp. 120—130°, by evaporation of the solvent. It is soluble in carbon disulphide and tetrahydrofuran, and is slightly soluble in acetone and chloroform.

Amminechlorodcarbonylrhodium(1).—Dry ammonia gas, passed into a solution of rhodium carbonyl chloride in petroleum, precipitated the *ammine*. This sublimed at 100° *in vacuo* as a green-purple solid, decomp. 110°, which was slightly soluble in acetone and chloroform.

Methylaminechlorodcarbonylrhodium(1).—The *complex* was prepared, by a method analogous to that used for the *ammine*, as a green-purple solid, decomp. 135°, which was slightly soluble in acetone and chloroform.

Hydroxylaminechlorodcarbonylrhodium(1).—Hydroxylamine in petroleum, added to rhodium carbonyl chloride, precipitated the *complex*, decomp. 135°. This sublimed *in vacuo* as a green-purple solid, which is soluble in chloroform and acetone.

Anilinechlorodcarbonylrhodium(1).—Rhodium carbonyl chloride reacted with an excess of aniline in benzene. The *complex* was precipitated from the orange solution, by addition of petroleum, as green-brown needles, decomp. 140°; it is soluble in benzene, chloroform, and acetone.

p-Toluidinechlorodcarbonylrhodium(1).—An excess of *p*-toluidine was added to rhodium carbonyl chloride in benzene. The *complex* was precipitated, by addition of petroleum, as a yellow, microcrystalline solid, decomp. 147°. It is soluble in benzene, acetone, and chloroform.

Pyridinechlorodcarbonylrhodium(1).—The stoichiometric amount of pyridine was added to rhodium carbonyl chloride in petroleum. On cooling the mixture at 0° for 30 min., orange-red needles, m. p. 68°, of the *complex* separated. It is soluble in common organic solvents.

α -Picolinechlorodcarbonylrhodium(1).—The *complex* was prepared, by a method analogous to that used for pyridinechlorodcarbonylrhodium(1), as lemon-yellow needles, m. p. 95°; it is soluble in common organic solvents.

Bispyridinechlorodcarbonylrhodium(1).—Pyridinechlorodcarbonylrhodium(1) was dissolved in an excess of dry pyridine and cooled in ice for 3 hr. The resulting yellow solid was washed with ether and dried under nitrogen.

Chlorodcarbonylrhodium(1)- μ_2 -2,2'-bipyridylchlorodcarbonylrhodium(1).—Rhodium carbonyl (0.2 g., 0.005 moles) reacted with 3 ml. of a 1% solution of 2,2'-bipyridyl (0.002 moles) in benzene, depositing the *complex* as an amorphous blue-green solid, decomp. 130—140°. It is soluble in nitromethane, giving a non-conducting solution, and is slightly soluble in acetone, chloroform, and dichloromethane.

Chlorobis(dimethyl sulphoxide)carbonylrhodium(1).—Rhodium carbonyl chloride (0.2 g.) was dissolved in freshly distilled dimethyl sulphoxide (10 ml.). After the evolution of gas had

ceased, the volume of the solutions was reduced to 2 ml. (38°; 0.1 mm.), and the *complex* was precipitated as yellow crystals, m. p. 117—119° (decomp.), by addition of ethanol. It is soluble in acetone and chloroform.

Tetramethylammonium Dichlorodicarbonylrhodium(I).—To a solution of tetramethylammonium chloride and an excess of rhodium carbonyl chloride in tetrahydrofuran at 0°, was slowly added petroleum; after 1 hr., yellow needles of the *salt*, m. p. 102°, were collected. It is soluble in tetrahydrofuran and acetone. In nitromethane, $\Lambda_M (10^{-3}M) = 79.3$.

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