366. iso*Cyano-complexes of Rhodium.** *Part I.* *Tetra*iso*cyanorhodium*(I) *Salts.*

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The preparation of rhodium(I) *iso*cyanide complexes, $[(R\cdot NC)_4Rh]X$ (where R = *p*-tolyl, *p*-chlorophenyl, or *p*-methoxyphenyl; X = chloride, perchlorate, or hexafluorophosphate), from hydrated rhodium trichloride and an excess of the *iso*cyanide is described. All the compounds prepared are diamagnetic and give conducting solutions in nitrobenzene. These complexes form addition compounds of different colours with water, alcohols, and chloroform.

*iso*CYANIDE complexes * of chromium [1], molybdenum [2], tungsten [3], manganese [4], iron [5], ruthenium [6], cobalt [7], nickel [8], palladium [9], copper, silver, and gold [10] have been prepared in these laboratories and this study has now been extended to rhodium. Also stable *iso*cyanide complexes of Co(I), in addition to those of Co(II) and Co(III), have been obtained.

In view of the analogy of complex-chemical behaviour between cobalt and rhodium, the existence of stable *iso*cyanide complexes of rhodium(I) could be predicted. These compounds have now been isolated.

The best method of preparation consists in treating an alcoholic solution of a rhodium compound, in the lowest possible oxidation state, with an alcoholic solution of an *iso*cyanide. The most convenient starting material is hydrated rhodium trichloride. The action of *p*-chlorophenyl *iso*cyanide on rhodium trichloride leads to the isolation of a stable,

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* *iso*Cyanide is I.U.P.A.C. nomenclature (cf. *J.*, 1952, 5069, rule 38), though these compounds have been termed *iso*nitriles in related papers.

[1] Malatesta, *Gazzetta*, 1952, **82**, 516; Malatesta and Sacco, *Atti Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat.*, 1952, **8**, (xii), 308.

[2] Malatesta, Sacco, and Gabaglio, *Gazzetta*, 1952, **82**, 548.

[3] Malatesta and Sacco, *Ann. Chim.* (*Italy*), 1953, **43**, 622.

[4] Sacco, *Gazzetta*, in the press; Sacco and Naldini, *ibid.*, in the press.

[5] Malatesta, *ibid.*, 1947, **77**, 240; Malatesta, Sacco, and Padoa, *Ann. Chim.* (*Italy*), 1953, **43**, 617; Malatesta and Sacco, *Z. anorg. Chem.*, 1953, **274**, 342; Malatesta, *Gazzetta*, 1953, **83**, 958.

[6] Malatesta, Padoa, and Sonz, *ibid.*, 1955, **85**, 1111.

[7] Malatesta and Sacco, *Z. anorg. Chem.*, 1953, **273**, 247; Malatesta, *Gazzetta*, 1953, **83**, 958, 499, 632; Malatesta and Sacco, *Atti Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat.* 1953, **8**, (xv), 93; Sacco, *ibid.*, p. 82.

[8] Malatesta and Sacco, *ibid.*, 1951, **6**, (xi), 379.

[9] Malatesta, *J.*, 1955, 3924.

[10] Sacco, *Gazzetta*, in the press; Sacco and Freni, *ibid.*, in the press.

crystalline, violet [(p-Cl·C_6H_4·NC)$_4$Rh]Cl, which is diamagnetic and gives a conducting solution in nitrobenzene. The action of other *iso*cyanides (phenyl, p-tolyl, and p-methoxyphenyl) on rhodium trichloride gives brown solutions which slowly become first green, and then violet, but do not give crystalline precipitates. Precipitation occurs on addition of anions such as perchlorate and hexafluorophosphate with formation of crystalline [(p-MeO·C_6H_4·NC)$_4$Rh][PF_6], [(p-MeO·C_6H_4·NC)$_4$Rh]ClO_4, and [(p-Me·C_6H_4·NC)$_4$Rh]ClO_4, which behave analogously to [(p-Cl·C_6H_4·NC)$_4$Rh]Cl.

The above experiments confirm the formulation of these compounds as tetra*iso*cyanorhodium salts.

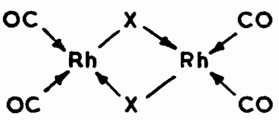
Rhodium(I)–*iso*cyanide complexes can also be obtained by treating $(CO)_4Rh_2Cl_2$ with the stoicheiometric amount of *iso*cyanide. They give crystals of different appearance, colour, and solubility, containing one molecule of solvent of crystallisation. The colour of these crystals varies greatly with the added molecule (see Table), but salts with different *iso*cyanides and different anions have similar colour when recrystallised from the same solvent. This can be taken to indicate that the solvent molecules are interacting within the co-ordination sphere, and the compounds are not clathrates, which, in turn, is an indication that the [(R·NC)$_4$Rh]$^+$ ion is co-ordinatively unsaturated.

Colour of products obtained from various solvents.

			Solvent		
Complex	Benzene	Methanol	Ethanol	Aq. methanol	Chloroform
[(p-MeO·C_6H_4·NC)$_4$Rh]ClO_4	Green	Orange	Red	†	Violet
[(p-MeO·C_6H_4·NC)$_4$Rh]PF_6	Green	Violet	Red-violet	Red	Violet
[(p-Me·C_6H_4·NC)$_4$Rh]ClO_4	Yellow	Blue	Violet	Red	Violet
[(p-Cl·C_6H_4·NC)$_4$Rh]Cl	*	Light blue	Violet	†	Violet

* Too insoluble in benzene to be recrystallised. † Decomposed by this solvent.

The fact that rhodium(I), unlike cobalt(I) and manganese(I), does not give a compound with an effective atomic number corresponding to that of the next inert gas is not surprising. Rhodium(I) is isoelectronic with palladium(II), and the latter gives almost exclusively tetraco-ordinated complexes with square planar configuration and dsp^2 hybridisation. The only well-established rhodium(I) complexes, $(CO)_4Rh_2X_2$ (X = Cl, Br, I),[12] have almost certainly the tetraco-ordinated structure shown in the inset. The formation of the π-type bonds between the filled $4d$ orbitals of the rhodium atom and the p_π orbitals on the carbon of the *iso*cyanide molecule will enhance the electron affinity of the metal and facilitate the attachment of a suitable solvent molecule by the vacant $5p_z$ orbital on the rhodium atom. This would explain the strong tendency of rhodium(I)–*iso*cyanide complexes to form solvates.



Experimental

p-Methoxyphenyl, p-tolyl, and p-chlorophenyl *iso*cyanides were prepared, purified, and analysed as described by Malatesta.[11] The alcohol-soluble rhodium trichloride was prepared as follows: powdered metallic rhodium mixed with four parts, by weight, of sodium chloride was heated for 2 hr. at 600—700° in a stream of dry chlorine. The mass thus obtained was extracted with hot water, affording a red solution of Na_3RhCl_6. This was made faintly alkaline with sodium hydroxide, and the precipitate of gelatinous yellow-brown rhodium(III) hydroxide was washed free from alkali and dissolved in hydrochloric acid. The solution was then taken to dryness. The red residue, consisting of $RhCl_3,xH_2O$ and a small amount of Na_3RhCl_6, was dissolved in anhydrous ethanol, which dissolves only the former. This solution is stable in the cold for some time, but on long standing or warming it deposits metallic rhodium as a black powder.

Tetra-p-*chlorophenyl*iso*cyanorhodium Chloride*.—Excess of the *iso*cyanide (5—6 mol. per atom of rhodium) was gradually added with gentle warming to an alcoholic solution of rhodium trichloride. A brown gelatinous precipitate was formed; this became first black and then brown, and on prolonged boiling with excess of *iso*cyanide became crystalline and violet. This

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[11] Malatesta, *Gazzetta*, 1947, **77**, 238.
[12] Hieber and Lagally, *Z. anorg. Chem.*, 1943, **251**, 98.

violet product is insoluble in ether, benzene, chloroform, and methylene chloride. It is moderately soluble in boiling anhydrous methanol, from which it separates on cooling in a different crystal form and blue colour. This blue product, which is moderately soluble in methylene chloride and chloroform, can be reconverted into the violet form by prolonged boiling with ethanol. Both products are diamagnetic and electrolytes in nitrobenzene solution. The blue *solvate* (from methanol) (Found: Rh, 14·2; Cl, 24·7; N, 8·0. $C_{28}H_{16}N_4Cl_5Rh,CH_4O$ requires Rh, 14·3; Cl, 24·65; N, 8·0%) had m. p. 140° (decomp.), $\chi_M = -50 \times 10^{-6}$, $\Lambda_\infty = 28$ ohm^{-1} cm.^{3} at 20° in nitrobenzene (these conditions apply to all later conductivity data). The violet *salt* (from ethanol) (Found: Rh, 14·6; Cl, 25·1; N, 8·25. $C_{28}H_{16}N_4Cl_5Rh$ requires Rh, 14·9; Cl, 25·7; N, 8·3%) had m. p. 137° (decomp.), $\chi_M = -35 \times 10^{-6}$, $\Lambda_\infty = 29$ ohm^{-1} cm.^{2}.

Both products can also be obtained as follows: A solution of $(CO)_4Rh_2Cl_2$ [12] in chloroform, cooled in ice-water, is treated with the stoicheiometric amount (or a slight excess) of *iso*cyanide in chloroform solution. Carbon monoxide is evolved and the solution becomes violet. The solution is taken to dryness under reduced pressure, and the residue, when boiled in ethanol or methanol, affords products identical with the foregoing.

Tetra-p-*tolyl*iso*cyanorhodium Perchlorate*.—When rhodium trichloride and the *iso*cyanide were treated as described above, a violet solution was obtained from which no crystalline product could be isolated, but on addition of alcoholic sodium perchlorate a crystalline violet product separated. This is extremely soluble in methylene chloride and chloroform, rather soluble in boiling methanol, and insoluble in all other solvents. A hot methanol solution deposits a crystalline blue product on cooling, but from methylene chloride, on addition of benzene or ethyl acetate, a pale-yellow salt is obtained. A red salt is obtained by adding a little water to a hot solution in anhydrous methanol. A chloroform solution on evaporating and cooling gives a red-violet product. The last two products change composition on drying. The yellow *salt* (from benzene or ethyl acetate) (Found: Rh, 15·5; Cl, 5·3; N, 8·5. $C_{32}H_{28}O_4N_4ClRh$ requires Rh, 15·35; Cl, 5·3; N, 8·3%), had m. p. 198^c (decomp.), $\chi_M = -50 \times 10^{-6}$, $\Lambda_\infty = 30$ ohm^{-1} cm.^{2}. The violet *solvate* (from ethanol) (Found: Rh, 14·5; Cl, 5·15; N, 8·0. $C_{32}H_{28}O_4N_4ClRh,C_2H_6O$ requires Rh, 14·3; Cl, 4·9; N, 7·8%), m. p. 207° (decomp.), $\chi_M = -60 \times 10^{-6}$, $\Lambda_\infty =$ 31 ohm^{-1} cm.^{2}. The blue *solvate* (from methanol) (Found: Rh, 14·7; Cl, 5·3; N, 8·1. $C_{32}H_{28}O_4N_4ClRh,CH_4O$ requires Rh, 14·6; Cl, 5·05; N, 8·0%) had m. p. 200° (decomp.), $\chi_M = -80 \times 10^{-6}$, $\Lambda_\infty = 31$ ohm^{-1} cm.^{2}. The products obtained from chloroform and aqueous methanol alter their composition on drying in a vacuum desiccator.

Tetra-p-*methoxyphenyl*iso*cyanorhodium perchlorate* was prepared analogously to the *p*-tolyl derivative. The green salt (from benzene) (Found: Rh, 13·9; Cl, 4·75; N, 7·8. $C_{32}H_{28}O_8N_4ClRh$ requires Rh, 14·0; Cl, 4·8; N, 7·6%) had m. p. 180° (decomp.) and was diamagnetic: $\Lambda_\infty = 30$ ohm.$^{-1}$ cm.^{2}. The other products, red (from ethanol), orange (from methanol), and violet (from chloroform), on drying *in vacuo* gave a diamagnetic brown product (Found: Rh, 13·9; N, 7·5%).

Tetra-*p*-methoxyphenyl*iso*cyanorhodium hexafluorophosphate was obtained by reaction between rhodium trichloride and the *iso*cyanide as described above and treating the violet solution thus obtained with ammonium hexafluorophosphate. A red precipitate was obtained which, on recrystallisation from various solvents, gave the following compounds: Brilliant green *salt* (from benzene) (Found: Rh, 13·0; P, 3·8; N, 7·4. $C_{32}H_{28}O_4N_4F_6PRh$ requires Rh, 13·2; P, 4·0; N, 7·2%), m. p. 230° (decomp.), $\chi_M = -90 \times 10^6$, $\Lambda_\infty = 28$ ohm^{-1} cm.^{2}. Red *hydrate* (from aqueous methanol) (Found: Rh, 13·0; P, 3·75; N, 7·0. $C_{32}H_{28}O_4N_4F_6PRh,H_2O$ requires Rh, 12·9; P, 3·9; N, 7·0%), m. p. 215° (decomp.), $\chi_M = -70 \times 10^{-6}$. Red-brown *solvate* (from methylene chloride and ethanol) (Found: Rh, 12·6; P, 4·0; N, 6·6; Cl, 0. $C_{32}H_{28}O_4N_4F_6PRh,C_2H_6O$ requires Rh, 12·4; P, 3·75; N, 6·8%), diamagnetic. Violet *solvate* (from chloroform) (Found: Rh, 11·6; P, 3·9; N, 6·2; Cl, 10·5. $C_{32}H_{28}O_4N_4F_6PRh,CHCl_3$ requires Rh, 11·45; P, 3·4; N, 6·2; Cl, 10·7%), m. p. 237° (decomp.), $\chi_M = -60 \times 10^{-6}$.

It was not possible to determine the molecular weight of any of these compounds because those solvents in which they are sufficiently soluble cause decomposition.

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