1,10-Phenanthroline Complexes of Rhodium(I)

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The salts $[RhL(CO)_2][Rh(CO)_2Cl_2]$ [L = 1,10-phenanthroline (phen) or 2,2′-bipyridyl (bipy)] have been prepared from the reaction of the ligand L with $[(OC)_2Rh(\mu\text{-}Cl)_2Rh(CO)_2]$. The bipy salt was previously formulated as $[Cl(OC)_2Rh(\mu\text{-}bipy)Rh(CO)_2Cl]$. Chloride and perchlorate salts of the cation $[Rh(phen)(CO)_2]^+$ have also been prepared; the perchlorate is phototropic, being yellow in the dark and green in the light. Complexes previously formulated as [Rh(pd)(phen)] and [Rh(quin)(phen)] (pd = pentane-2,4-dionato and quin = quinolin-8-olato) are in fact both $[Rh(phen)(CO)_2Cl]$.

THE biological activity of complexes of rhodium(III) with *N*-heterocyclic ligands is apparently a consequence of the generation of substances containing rhodium(I). We recently studied the effects of adding such substances directly to growing cultures of *Escherichia coli.* Our choice of complexes of rhodium(I) was dictated by two considerations: (*i*) they should resemble as closely as possible the species produced by reduction of the biologically active [1] rhodium(III) complexes; (*ii*) they should be well characterised, air-stable, and water-soluble, behaving in a predictable manner in bacterial culture media. The obvious candidates, the actual reduction products of those complexes of rhodium(III) of biological interest, *e.g.* the recently isolated and characterised $[Rh(py)_4][ClO_4]$ [2] and $[Rh(tetmen)_2H(OH)]^+$ (ref. 3) (py = pyridine), decompose in air. Similarly unsuitable are complexes of the type $[Rh(bipy)_2]X$ ($X = ClO_4$ or NO_3; bipy = 2,2′-bipyridyl), reported [4] by Martin *et al.* following an observation [5] that intensely violet solutions were obtained by treating solutions of rhodium trichloride and bipy in methanol with zinc amalgam. Moreover, the true nature of these solids has now [6] been questioned.

The known chemistry of rhodium(I) is dominated by π-bonding ligands, and so is almost exclusively non-aqueous. Hence, in work [7] on catalysis by rhodium(I) of substitution at rhodium(III), complexes like $[(OC)_2Rh(\mu\text{-}Cl)_2Rh(CO)_2]$ and $[Rh(CO)(PPh_3)_2Cl]$ had to be used, the latter as a fine suspension. Although small amounts of hydrochloric acid stabilise solutions of $[(OC)_2Rh(\mu\text{-}Cl)_2Rh(CO)_2]$ through formation of the anion $[Rh(CO)_2Cl_2]^-$, neutral solutions discolour and within a few hours are completely decomposed [8] to rhodium metal. However, several papers [9-11] describe the synthesis of a series of air-stable complexes of rhodium(I), some of which, *e.g.* [Rh(quin)(phen)], supposedly contain only *N*-heterocyclic ligands like quinolin-8-ol (Hquin), 1,10-phenanthroline (phen), bipy, and py. Although these complexes are insoluble in most organic solvents, they are quite soluble and stable in water. We find that they display remarkable biological activity, interfering with cell division in bacteria. They have, however, been wrongly formulated, being, in fact, dicarbonyl complexes derived from such species as $[Rh(phen)(CO)_2]^+$.

This note reports the novel chemistry which has emerged as a result of the above reformulation. First, a more controlled and efficient synthesis of the biologically interesting species is described, followed by its full characterisation. Secondly, related reported reactions, including that which provided the first samples of $[Rh(phen)(CO)_2]^+$, are examined and reinterpreted in the light of the true nature of their respective products.

RESULTS AND DISCUSSION

The Cation $[Rh(phen)(CO)_2]^+$ *and its Derivatives.*—(a) *The reaction of phen with* $[(OC)_2Rh(\mu\text{-}Cl)_2Rh(CO)_2]$. This was examined at room temperature, in various solvents, using different ratios of phen to rhodium, after it had been discovered that a species of considerable biological interest, previously wrongly formulated, consisted of some combination of rhodium(I) with phen, carbon monoxide, and chlorine. A number of papers [12,13] discuss the products of the reaction, and one report [14] even states that there is no reaction. Previous workers always combined either equivalent amounts of phen and $[(OC)_2Rh(\mu\text{-}Cl)_2Rh(CO)_2]$, or equal weights (phen is then in 40% molar excess), and this probably explains the indefinite nature of their products. These papers are discussed in more detail later.

The reaction proceeded most smoothly in an inert solvent like benzene or hexane, the former being preferable as phen is not very soluble in hexane. Up to the point where the number of moles of phen added amounted to half the total number of moles of complexed rhodium present, mixing of the reactants gave an immediate brilliant blue-green amorphous precipitate,

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[1] R. J. Bromfield, R. H. Dainty, R. D. Gillard, and B. T. Heaton, *Nature*, 1969, **223**, 735.

[2] H. Shaw, Ph.D. Thesis, University of Kent at Canterbury, 1971.

[3] M. P. Hancock, Ph.D. Thesis, University of Kent at Canterbury, 1972.

[4] B. Martin, W. R. McWhinnie, and G. M. Waind, *J. Inorg. Nuclear Chem.*, 1961, **23**, 207.

[5] W. W. Brandt, F. P. Dwyer, and E. C. Gyarfas, *Chem. Rev.*, 1954, **54**, 960.

[6] E. D. McKenzie, *Co-ordination Chem. Rev.*, 1971, **6**, 187.

[7] J. V. Rund, *Inorg. Chem.*, 1968, **7**, 24.

[8] L. M. Vallarino, *Inorg. Chem.*, 1965, **4**, 161.

[9] Yu. S. Varshavskii and T. G. Cherkasova, *Russ. J. Inorg. Chem.*, 1971, **16**, 1384, and refs. therein.

[10] Yu. S. Varshavskii and T. G. Cherkasova, *Russ. J. Inorg. Chem.*, 1967, **12**, 899.

[11] Yu. S. Varshavskii, N. N. Knazeva, T. G. Cherkasova, N. V. Ivannikova, and T. I. Ionina, *Russ. J. Inorg. Chem.*, 1970, **15**, 367.

[12] W. Hieber, H. Heusinger, and O. Vohler, *Chem. Ber.*, 1957, **90**, 2425.

[13] J. V. Kingston, F. T. Mahmoud, and G. R. Scollary, *J. Inorg. Nuclear Chem.*, 1972, **34**, 3197.

[14] F. Calderazzo, R. Ercoli, and G. Natta in ' Organic Synthesis *via* Metal Carbonyls,' vol. 1, eds. I. Wender and P. Pino, Interscience–Wiley, 1968, p. 226.

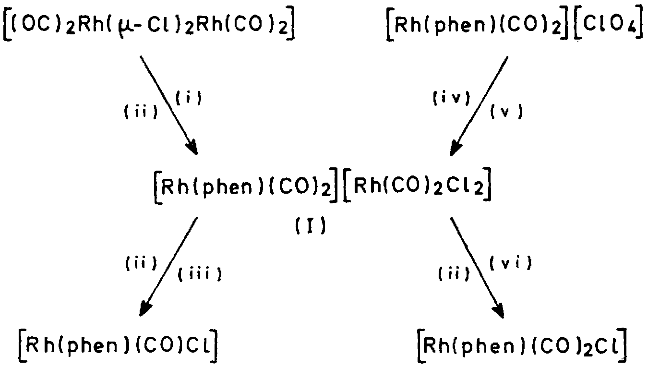
(I). At this stage, the supernatant liquid became quite colourless, indicating that all the rhodium had been precipitated. Addition of more phen consequently caused not more precipitation, but instead a change in the appearance and properties of the solid already produced, the exact nature of which depended on the polarity of the solvent employed. It is this process and not, as earlier suggested,[12] exposure to air of the blue-green solid (I) which leads to formation of indefinite mixtures of products by partial decomposition of the initial precipitate.

TABLE 1

Some properties of the carbonyl complexes of rhodium(I) and phen

Complex [a]	Colour	Solubility [b]	Conductivity [c] (Λ/S cm^2 mol^{-1})		$\tilde{\nu}$(CO) [d]/ cm^{-1}	$\tilde{\nu}$(Rh–Cl) [e]/ cm^{-1}	Analyses [f]/% Found				Calc.				Preparation
			H_2O	$MeNO_2$			C	H	N	Cl	C	H	N	Cl	
[Rh(phen)(CO)$_2$] [Rh(CO)$_2$Cl$_2$] [g,h]	Brilliant blue-green	Slightly soluble in H_2O, EtOH, Me_2CO, $MeNO_2$, *etc.*		**28·4**	2 101, 2 088, 2 061, 2 041, 2 021, 1 995, 1 981, 1 963, 1 955vw	284, 314	33·4	1·5	4·9	12·3	33·8	1·4	4·9	12·5	2[(OC)$_2$Rh(μ-Cl)$_2$Rh(CO)$_2$] + phen in C_6H_6
α-[Rh(phen)(CO)$_2$]-[ClO$_4$] [i,j]	Yellow	As above, except quite soluble in $MeNO_2$		84·2	2 104, 2 040		38·1	2·0	6·3	7·9	38·3	1·8	6·4	8·1	' Rh(ClO$_4$)$_3$ ' + phen + CO in EtOH
β-[Rh(phen)(CO)$_2$]-[ClO$_4$]	Green				2 114, 2 060										[Rh(phen)(cod)][ClO$_4$] + CO in MeOH
[Rh(phen)(CO)$_2$Cl] [g]	Yellow	Quite soluble in cold H_2O; more soluble in hot H_2O, with aquation	63·5 [k]	19·8	1 830, 1 810	246	45·5	2·5	7·6	9·3	44·9	2·2	7·5	9·5	[Rh(phen)(cod)]Cl + CO in Me_2CO [Rh(pd)(CO)$_2$] or [Rh(quin)(CO)$_2$] + phen + Cl$^-$ in dmf
[Rh(phen)(CO)Cl]	Brown				1 963br, 1 940		44·8	2·6	7·8		45·0	2·3	8·1		[Rh(phen)(CO)$_2$Cl], 240 °C, *in vacuo*

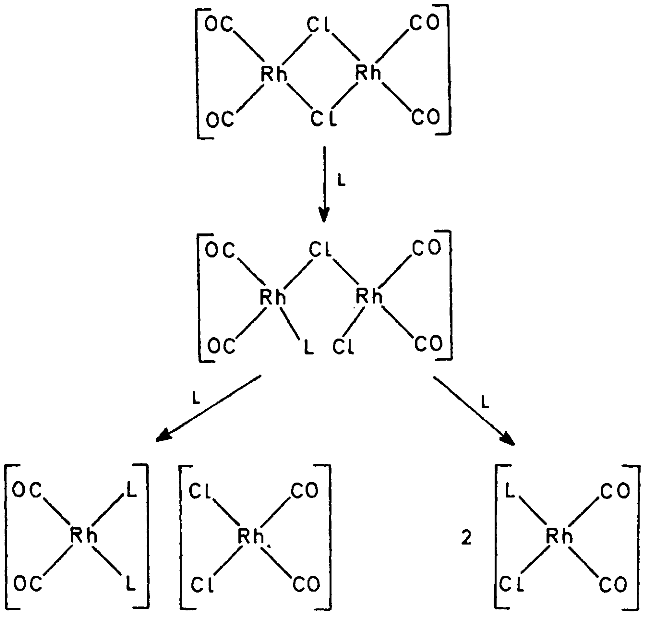
[a] None of the complexes decompose or melt below 300 °C, but become brown, lose CO, and gain H_2O. All are resistant to boiling concentrated acids (except perchloric acid). [b] All complexes dissolve in dmso and dmf (possibly with decomposition). [c] 10^{-3}M Solutions at 25 °C. [d] Nujol mulls, the complexes being too insoluble for solution spectra. [e] Polythene discs (*ca.* 10% complex w/w). [f] All products were crude because they were too insoluble for recrystallisation, chromatography, *etc.* and did not sublime. [g] Amorphous. [h] Over a period of several months' exposure to the air, CO was lost and replaced by H_2O (Found for starting complex: Rh, 34·3. Calc.: Rh, 36·2%). [i] Crystalline. [j] The yellow α form is converted to the green (β) in the light, the green to the yellow in the dark. [k] The solution was green {[Rh(phen)(CO)$_2$Cl] dissociates to [Rh(phen)(CO)$_2$]$^+$ + Cl$^-$ in water}.



SCHEME 1 Summary of the reactions described (properties of the products are given in Table 1): (*i*), C_6H_{14} or C_6H_6; (*ii*), phen; (*iii*), C_6H_{14}; (*iv*), Me_2CO; (*v*), [Rh(CO)$_2$Cl$_2$]$^-$; (*vi*), C_6H_6

The halogen bridge of [(OC)$_2$Rh(μ-Cl)$_2$Rh(CO)$_2$] is readily split by many nucleophiles, including [15] *N*-donor ligands (L) like primary amines and such heterocycles as pyridines and bipy. The reaction can be viewed as proceeding by one of the routes shown in Scheme 2. When L = py, the reaction leading to product (B) occurs.[15] However, when L is part of a chelating ligand like phen or bipy, formation of (A) should be favoured.*

The path for 2L = phen rationalises the properties of the initial deep green reaction product (I) in terms of structure (A). Analyses indicate an empirical formula Rh$_2$(phen)(CO)$_4$Cl$_2$. In nitromethane, the conductivity is comparable with values for other 1 : 1 electrolytes with two large complex ions (Table 2). (Any departure from the simplicity of, for example, chloride, as the counter-ion of the co-ordination complex is accompanied by a decrease in conductivity below the normal range [16] of 75—95 S cm^2 mol^{-1} for 1 : 1 electrolytes in nitromethane.) Other salt-like properties include insolubility in common organic solvents but sparing solubility in water, and a very high m.p. The far-i.r. spectrum



(A) (B)

SCHEME 2 Paths for reaction of unidentate or bidentate bases with [(OC)$_2$Rh(μ-Cl)$_2$Rh(CO)$_2$]

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* A closely similar finding is that by R. J. Irving and E. A. Magnusson (*J. Chem. Soc.*, 1956, 1860), who precipitated [Pt(bipy)(CO)Cl][Pt(CO)Cl$_3$] (often impure because of further reaction) by adding bipy to [{Pt(CO)Cl$_2$}$_2$] in benzene.

[15] D. N. Lawson and G. Wilkinson, *J. Chem. Soc.*, 1965, 1900.

[16] W. J. Geary, *Co-ordination Chem. Rev.*, 1971, **7**, 81.

suggested the presence of two *cis* terminal chlorine atoms bound to rhodium. There was a very intense and complicated absorption in the terminal carbonyl-stretching frequency region of the i.r. spectrum; the peaks can be assigned to superimposed individual carbonyl absorptions of $[Rh(phen)(CO)_2]^+$ and $[Rh(CO)_2Cl_2]^-$. Such complexity is characteristic of *cis*-dicarbonyl complexes of rhodium(I) with chelating ligands, as is the dichroism and intense colour of the complex when solid. These properties may indicate [17,18] a chain structure, with metal–metal interaction.

TABLE 2

Relevant properties of some related complexes

Complex	Colour	Λ [a]/S cm^2 mol^{-1}	$\bar{\nu}$(CO)/cm^{-1}	Preparation
$[Rh(bipy)(CO)_2][Rh(CO)_2Cl_2]$	Brilliant blue-green	21·7	2 085, 2 060, 2 026, 2 014, 1 993, 1 982, 1 956vw	$2[(OC)_2Rh(\mu\text{-}Cl)_2Rh(CO)_2]$ + bipy in C_6H_6
$[Rh(phen)_2Cl_2][Rh(phen)Cl_4],4H_2O$		41·9		*b*
$[Rh(bipy)_2Cl_2][Rh(bipy)Cl_4],3H_2O$		53·6		*b*

[a] In $MeNO_2$. [b] P. M. Gidney, Ph.D. Thesis, University of Kent at Canterbury, 1972.

The reaction of (I) with phen led to the production of chloride and of $[Rh(phen)(CO)_2]^+$ in excess over $[Rh(CO)_2Cl_2]^-$. The greater the polarity of the solvent, the weaker will be the interaction between the newly formed planar $[Rh(phen)(CO)_2]^+$ and its counter ion Cl^-. Thus, in benzene, there was a weak interaction resulting in co-ordination of chloride in the vacant fifth position. The reversible nature of this binding is such that in very polar solvents, such as water, equilibrium (1) is almost completely displaced to the right (see

$$[Rh(phen)(CO)_2Cl] \rightleftharpoons [Rh(phen)(CO)_2]^+ + Cl^- \quad (1)$$

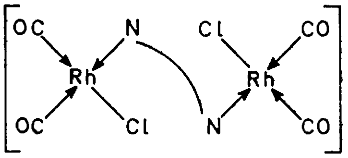
conductivities, Table 1). However, in the less-polar solvent hexane, chloride becomes firmly bound in one of the four co-ordination sites of the neutral square complex [Rh(phen)(CO)Cl]. Because of the insolubility of (I), and its derivatives, the reactions with phen under such heterogeneous conditions are far from complete. The final product of the interaction of $[(OC)_2Rh(\mu\text{-}Cl)_2Rh(CO)_2]$ and any molar quantity of phen larger than half the number of moles of rhodium present is always a mixture of at least two species.

The constituent ions of (I) are known species, so it is possible, finally, to verify the structure of (I) by isolating the dark green product of double decomposition in acetone, as in (2). The perchlorate of $[Rh(phen)(CO)_2]^+$

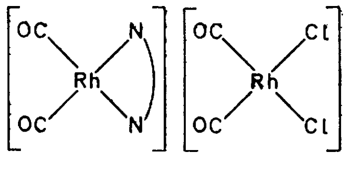
$$[Rh(phen)(CO)_2][ClO_4] + [Bu_4N][Rh(CO)_2Cl_2] \longrightarrow [Rh(phen)(CO)_2][Rh(CO)_2Cl_2] + [Bu_4N][ClO_4] \quad (2)$$

(prepared by the method [19] of Cocevar *et al.* described later) is almost as insoluble in acetone as the desired product of (2). However, the visible and i.r. spectra of the precipitate were identical, apart from contamination by perchlorate, with the corresponding spectra of (I). The coincidence of the very complex carbonyl-absorption pattern between 2 100 and 1 950 cm^{-1} was particularly striking.

A blue-green amorphous solid, (II), formed on interaction [15] of $[(OC)_2Rh(\mu\text{-}Cl)_2Rh(CO)_2]$ and bipy in benzene, when the rhodium complex was present in two-and-a-half-fold excess. These conditions are exactly analogous to those we employed using phen. Complex (II) was formulated as below on the basis of its empirical formula, since it was a non-conductor in nitromethane. {Such species as $[Rh(bipy)_2]Cl$, [Rh(bipy)Cl], and $[Rh(CO)_2(bipy)]Cl$ formed when more bipy was used in the reaction.} In a recent review,[20] (II) is the only example of a bridging bipy ligand cited for rhodium. Varshavskii *et al.* repeated and extended [21] that work finding an identical product (with a slightly better resolved i.r. spectrum) when the ratio of bipy to rhodium was less than 0·4 : 1.



Because of the exact parallel between this reaction and our own preparation of (I), a sample of (II) was obtained by the prescribed route. It had the same conductivity in nitromethane as (I), and a virtually identical absorption pattern in the carbonyl-stretching region of the i.r. spectrum. There is no way in which a phen molecule can act as a bridge, and we propose, on the basis of the exact equivalence of (I) and (II), that the structure of both may be represented schematically as below. This suggestion, by extension, casts doubt on the formulation of two 'analogous' complexes said to support the structure for (II) involving the bridging heterocycle. These are (*i*) the corresponding complex



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[17] N. A. Bailey, E. Coates, G. B. Robertson, F. Bonati, and R. Ugo, *Chem. Comm.*, 1967, 1041.

[18] C. G. Pitt, L. K. Montkeith, L. F. Ballard, J. P. Collman, J. C. Morrow, W. R. Roper, and D. Ulkü, *J. Amer. Chem. Soc.*, 1966, **88**, 4286.

[19] C. Cocevar, G. Mestroni, and A. Camus, *J. Organometallic Chem.*, 1972, **35**, 389.

[20] W. R. McWhinnie and J. D. Miller, *Adv. Inorg. Chem. Radiochem.*, 1969, **12**, 135.

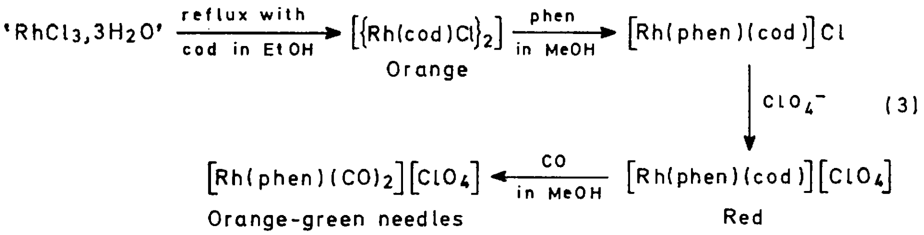
[21] Yu. S. Varshavskii, N. V. Kiseleva, and N. A. Buzina, *Russ. J. Inorg. Chem.*, 1971, **16**, 863.

with 4,4′-bipyridyl,[21] where the only properties mentioned (bright orange and two intense CO absorptions) actually differ from those of (II), and (*ii*) the orange product[22] of the reaction of $[\{\mathrm{Pt(CO)Cl_2}\}_2]$ and bipy formulated as $[\mathrm{Cl_2(OC)Pt(\mu\text{-}bipy)Pt(CO)Cl_2}],x\mathrm{dmf}$ (x = 1—1·5, dmf = *NN*-dimethylformamide), which is probably a mixture of $[\mathrm{Pt(CO)Cl(bipy)}][\mathrm{Pt(CO)Cl_3}]$ and its derivatives with excess of bipy.

(b) *The synthesis and properties of* $[\mathrm{Rh(phen)(CO)_2}]X$ ($X = \mathrm{Cl}$ *or* $\mathrm{ClO_4}$) *and its derivatives.* Section (a) illustrates the difficulty of obtaining any salt of $[\mathrm{Rh(phen)(CO)_2}]^+$ other than (I) by direct reaction of phen and $[\mathrm{(OC)_2Rh(\mu\text{-}Cl)_2Rh(CO)_2}]$. However, there are two indirect preparative routes to such complexes, involving as the final step (*i*) substitution by carbon monoxide, and (*ii*) substitution by phen.

(*i*) *Using gaseous carbon monoxide.* There are two reported preparations of this type, both giving the cation as its perchlorate salt. In the account[23] of Reddy and Susheelamma the yellow desired product [*] (m.p. 190—200 °C) is said to separate from an alcoholic solution of 'rhodium(III) perchlorate' and phen on saturation with carbon monoxide. In our experience, the initial precipitation of yellow rhodium(III)–phen species was but slowly reversible, to give, eventually, bright green and yellow products; both, from analyses and spectra, are slightly hydrated samples of $[\mathrm{Rh(phen)(CO)_2}][\mathrm{ClO_4}]$. Initially, the solid contained very little carbonyl (i.r. spectrum), and moreover it is only this initial substance which has m.p. 190—200 °C.

The second synthesis, our modification of that for $[\mathrm{Rh(bipy)(CO)_2}][\mathrm{ClO_4}]$ given[19] by Cocevar *et al.*, is more satisfactory since it proceeds smoothly in several stages [reaction (3)], in each of which the product can be isolated and purified. Because $[\mathrm{Rh(phen)(CO)_2}][\mathrm{ClO_4}]$ is insoluble, we tried to make the chloride. This would be more useful in double decompositions to give (I). The salt $[\mathrm{Rh(phen)(cod)}]\mathrm{Cl}$ (cod = η-cyclo-octa-1,5-diene) formed as a bright red precipitate, when acetone was used instead of methanol (which of course solvates chloride much better) as the solvent for the reaction of phen with $[\{\mathrm{Rh(cod)Cl}\}_2]$. Reaction of $[\mathrm{Rh(phen)(cod)}]\mathrm{Cl}$ with carbon monoxide was carried out in methanol, in which the complex is soluble. As when perchlorate was present, there was an immediate colour change from red to green on bubbling carbon monoxide through the solution. The main product was a lime-green powder, (X), which contained no $[\mathrm{Rh(phen)(CO)_2}]^+$, and was useless as a substitute for $[\mathrm{Rh(phen)(CO)_2}][\mathrm{ClO_4}]$. The reaction was therefore repeated in other solvents. The product in acetone, $[\mathrm{Rh(phen)(CO)_2Cl}]$, might have been predicted since equilibrium (1) should be displaced to the left where chloride is poorly solvated. Stoicheiometric loss of one molecule of carbon monoxide to give the brown four-co-ordinate complex $[\mathrm{Rh(phen)(CO)Cl}]$ (see Table 1) can be achieved by heating yellow $[\mathrm{Rh(phen)(CO)_2Cl}]$ to 240 °C *in vacuo*.



The preparation from rhodium(III) perchlorate gave rise mainly to yellow products, but a bright green species was produced in the final stages, after removal of earlier solid products. Cocevar's method, on the other hand, always resulted in formation of a fine green solid. All these samples (except the initial precipitates from the perchlorate) are formulated (Table 1) as $[\mathrm{Rh(phen)(CO)_2}][\mathrm{ClO_4}]$ on the basis of elemental analyses, i.r. spectra, and conductivities. Intermediate samples from rhodium(III) perchlorate (presumably mixtures of the yellow and green products) had i.r. spectra in which a number of peaks were split into two distinct components, most marked being the carbonyl peak just above 2 100 cm^{-1}, and the peak due to phen at 850 cm^{-1}. This splitting disappeared in later samples and the position of the peaks depended on whether the sample was yellow or green. Yellow samples left standing in a vacuum became green on exposed surfaces, and the unexposed bulk of green samples became yellow under the same conditions. There was a concomitant shift in the frequency of the carbonyl and some of the phen absorptions.

There are then at least two polymorphs of $[\mathrm{Rh(phen)(CO)_2}][\mathrm{ClO_4}]$, one yellow and one green, with slightly different i.r. absorption frequencies for the carbonyl and phen groups (Table 1). The two forms are probably related by phototropy, and since the yellow form is produced in the dark this is likely to be thermodynamically the more stable. The salt $[\mathrm{Rh(bipy)(CO)_2}][\mathrm{ClO_4}]$ is yellow according to Cocevar.[19] Since the carbonyl-absorption spectrum is rather simple and since neither polymorph is strongly coloured, metal–metal interaction in the solid state is probably not so important for $[\mathrm{Rh(phen)(CO)_2}][\mathrm{ClO_4}]$ as for (I),

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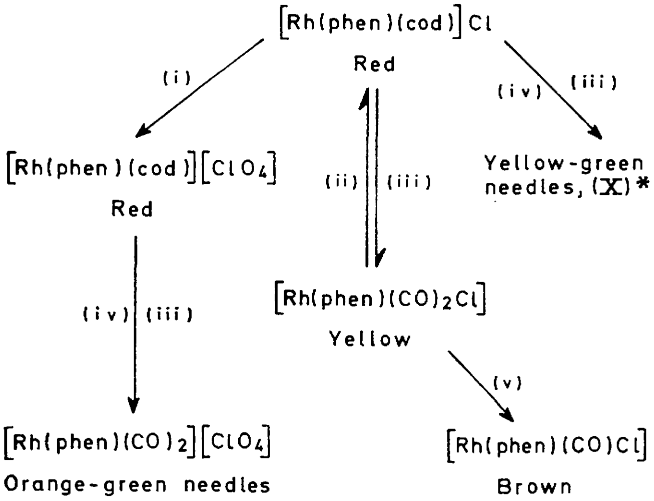
[*] *Added at proof:* In a recent extension to ref. 23, G. K. N. Reddy and B. R. Ramesh (*J. Organometallic Chem.*, 1974, **67**, 443) describe $[\mathrm{Rh(CO)_2L}][\mathrm{ClO_4}]$ as yellow but $[\mathrm{Rh(CO)_2L}][\mathrm{BF_4}]$ as green (L = bipy or phen). All four complexes were made by passing CO through alcoholic solutions of rhodium(III) salts. The i.r. frequencies recorded agree well with ours.

[22] I. B. Bondarenko, N. A. Buzina, Yu. S. Varshavskii, M. I. Gel'fman, V. V. Razumovskii, and T. G. Cherkasova, *Russ. J. Inorg. Chem.*, 1971, **16**, 1629.

[23] G. K. N. Reddy and C. H. Susheelamma, *Chem. Comm.*, 1970, 54.

$[Rh(quin)(CO)_2]$, $[Rh(pd)(CO)_2]$ (pd = pentane-2,4-dionate), *etc.* McKenzie and Plowman studied[24] the polymorphs of $[Rh(phen)_2Cl_2]Cl$. A drab green sample became yellow when exposed to moist air, but since that work all forms of $[Rh(phen)_2Cl_2]Cl$ have been shown to be yellow unless contaminated with such impurities as rhodium metal. The polymorphs[25] of $[Ir(phen)_2Cl_2]Cl$ are also of interest in this context, and the red and yellow dimorphs[26] of $[Pt(bipy)Cl_2]$ particularly so.



SCHEME 3 Reactions of $[Rh(phen)(cod)]Cl$ with carbon monoxide: with some $[\{Rh(phen)(CO)_2\}_n]^{n+}$ salt(s); (*i*), ClO_4^-; (*ii*), Me_2CO; (*iii*), CO; (*iv*), MeOH; (*v*), 240 °C, *in vacuo*

(ii) *Addition of phen to* cis-*dicarbonyl complexes of rhodium*(I). This alternative synthetic route was discovered during reformulation of the products of a series of reactions described[9,27] by Varshavskii *et al.* When 'soluble rhodium(III) trichloride' is heated under reflux in dmf for *ca.* 20 min a yellow solution containing *cis*-dicarbonyl derivatives of rhodium(I) is produced.[10,22] This solution can be used directly for the synthesis[28] of many dicarbonyl complexes of rhodium(I). For example, addition of such potentially bidentate anions as quin and pd results in formation of the well characterised $[Rh(quin)(CO)_2]$[29] and $[Rh(pd)(CO)_2]$[30] respectively. These can be isolated on addition of water, but if instead phen or bipy is added to their orange solutions there is an immediate colour change to dark brown; a green resinous mass can be precipitated out on addition of diethyl ether. The Russian workers formulated the products variously as [Rh(pd)(phen)], (III), [Rh(pd)(bipy)], [Rh(quin)(phen)], (IV), and [Rh(quin)(bipy)].

However, there is much against these formulations. (1) There was generally no evolution of gas on addition of phen or bipy; gas was evolved when the reaction products were dissolved in hot water. (2) There is an error in the translation from the Russian whereby acetylacetone is translated as acetone. Actually, however, the use of acetone in the synthesis made little difference to the final product! (3) The products '[Rh(pd)(phen)],' (III), and '[Rh(quin)(phen)],' (IV), gave identical analyses for carbon, hydrogen, and nitrogen (all in considerable disagreement with theoretical values), and both contained *ca.* 10% chlorine. (4) I.r. spectra of (III) and (IV) were very similar, the only significant peaks being characteristic of phen and two *cis*-carbonyl groups, the latter mainly at an unusually low frequency, found previously[15] in five-co-ordinate complexes of rhodium(II). (5) Samples of (III) and (IV) recovered from boiling water, or heated to 300 °C under nitrogen, lost all absorption in the carbonyl-stretching region. However, a sample heated to 240 °C *in vacuo* retained one carbonyl absorption, shifted by over 100 cm^{-1} in accordance with its altered involvement in back bonding to the metal atom. The loss of carbon monoxide was not accompanied by any heat change, neither were there any phase changes up to 500 °C (differential-scanning calorimeter).

Further, positive evidence for revising the formulation is as follows. (6) One phen per molecule (*M ca.* 375) was indicated by the position and absorption coefficient of the peaks in the u.v. absorption spectrum of (III) and (IV). (7) The unusual thermal stability of (III) and (IV) made the likelihood of seeing the parent ion in the mass spectrum very small; the highest *m/e* peak was at 180 (phen). The presence of carbon monoxide was also indicated by the size of the peak at 28 (too large for background nitrogen). (8) Product (III) was diamagnetic. (9) Products (III) and (IV) behaved as 1 : 1 electrolytes in water, and in nitromethane showed behaviour intermediate between that of 1 : 1 and non-electrolytes. The addition of perchlorate and nitrate to aqueous solutions, or placing of the products on a cation-exchange column, resulted in complete removal of the coloured species from solution. Silver(I) nitrate produced a precipitate of silver chloride.

All these results are consistent with our reformulation of the major component of both (III) and (IV) as $[Rh(phen)(CO)_2Cl]$. The complex obviously dissociates in polar solvents, according to equation (1). In summary, the initial formation of $[Rh(phen)(CO)_2]^+$ is followed by its reaction with chloride already present [*]

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[*] Varshavskii also reported the reaction of $[Rh(quin)(CO)_2]$ and $[Rh(pd)(CO)_2]$ with phen in chloroform to give products identical with (III) and (IV). This presumably involved some solvent decomposition in the presence of base to give the chloride counter ions. Abstraction of hydrogen ion produces the carbanion CCl_3^-, which is known to eliminate chloride, forming highly reactive dichlorocarbene. It is thus understandable that from our experiments in such non-halogenated solvents as hexane and benzene the products were black intractable solids, whose i.r. spectra suggested that they were composed mainly of polymeric species like $[\{Rh(phen)(CO)_2\}_n]^{n+}$ with bridging carbonyl groups.

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[29] R. Ugo, G. La Monica, S. Cenini, and F. Bonati, *J. Organometallic Chem.*, 1968, **11**, 151.

[30] F. Bonati and G. Wilkinson, *J. Chem. Soc.*, 1964, 3156.

in the dmf solution, to give a neutral precipitate on addition of diethyl ether. This reaction can take place in at least four ways, resulting in the production of, for example, [Rh(phen)(CO)$_2$]Cl, [Rh(phen)(CO)$_2$Cl], [Rh(phen)(CO)Cl], or [{Rh(phen)Cl}$_2$], or any combination of these. What does in fact occur in a solvent of the polarity of dmf appears to be critically dependent on factors which have not been investigated under controlled conditions, such as temperature, presence of impurities, *etc.* There is no precipitation of (I) in dmf because the complex is soluble in this solvent. However, the utility of any of these reactions in making carbonyl derivatives of rhodium(I) and phen is very limited by contamination of the products with the extremely persistent solvent and the occurrence of the numerous side-reactions.

The Assignment of Carbonyl-stretching Frequencies in Various Derivatives of Rhodium(I) *and phen.*—We used the stretching frequencies of the carbonyl groups both to confirm the formation of species for which the spectrum was known, and to predict the structure of products by extrapolation and comparison with the absorptions of known species (see Table 3). This application is complicated, for many of the reactions studied, by formation of mixed products containing several different carbonyl species.

TABLE 3

(*a*) Assignment of characteristic CO stretching frequencies of carbonyl derivatives of rhodium(I) and phen

Rhodium-containing species	Average $\tilde{\nu}$(CO) [a]/cm^{-1}	Colour
[Rh(phen)(CO)$_2$]$^+$	2 109, 2 050	Green
[Rh(phen)(CO)$_2$Cl]	1 830, 1 810	Yellow
[Rh(phen)(CO)Cl]	1 963br, 1 940	Brown
[{Rh(phen)(CO)$_2$}$_n$]$^{n+}$	1 800—1 740br	Black

(*b*) Carbonyl-stretching frequencies of some related complexes

		Source
[(OC)$_2$Rh(μ-Cl)$_2$Rh(CO)$_2$]	2 100, 2 085, 2 038, 2 025	*b*
[Bu$_4$N][Rh(CO)$_2$Cl$_2$]	2 058, 1 974	8
[Me$_4$N][Rh(CO)$_2$Cl$_2$]	2 066, 2 000	15
[Rh(CO)$_2$Cl(py)]	2 075, 2 060, 2 010, 1 980	15
[Rh(CO)$_2$Cl(py)$_2$]	two peaks between 1 800 and 1 850	15
[Rh(quin)(CO)$_2$]	2 067, 2 055, 1 992, 1 984	*b*, 11
[Rh(pd)(CO)$_2$]	2 063, 2050(sh), 2 000, 1 992w, 1 963w	*b*
[Rh(phen)(CO)$_2$][ClO$_4$]	2 105, 2 042	23
[Rh(bipy)(CO)$_2$][ClO$_4$]	2 103, 2 044	19
[Cl(OC)$_2$Rh(μ-bipy)Rh(CO)$_2$Cl]	2 075, 2 053, 2 008, 1 976	15
	2 095, 2 088, 2 063, 2 056, 2 028, 2 015, 1 995, 1 984	21
[Rh(pd)(CO)(PPh$_3$)]	1 981	11
[Rh(quin)(CO)(PPh$_3$)]	1 950	11

[a] From Nujol mull. [b] This work.

It has been said[31] that a terminal carbonyl group absorbs at 2 100—2 000 cm^{-1}, whereas a bridging carbonyl group absorbs at 1 900—1 800 cm^{-1}. However, there have been reports of terminal carbonyl-stretching frequencies as low as 1 750 cm^{-1} in complexes[32] with ligands like py which are poor π-acceptors, and Adams summarises[33] the true position; *i.e.* absorption in the range 1 898—1 785 cm^{-1} can be taken as diagnostic of bridging carbonyl groups only when the spectrum of the same complex also exhibits terminal ν(CO) absorption at substantially higher frequency.

It appears, for the carbonylrhodium(I) species studied here, that the largest shift in ν(CO) (*ca.* 200 cm^{-1}) results from the change in co-ordination number of rhodium(I) from four to five [equation (4)]. Any factor which

$$[\mathrm{Rh(phen)(CO)_2}]^+ + \mathrm{Cl}^- \longrightarrow [\mathrm{Rh(phen)(CO)_2Cl}]$$
$$(\textit{cf.}\ [\mathrm{Rh(py)(CO)_2Cl}] + \mathrm{py} \longrightarrow [\mathrm{Rh(py)_2(CO)_2Cl}]\ ^{15}) \quad (4)$$

increases the σ-donation of electrons to rhodium without a concomitant increase in the π-acceptor ability of the surrounding ligands will presumably result in lowering of the carbonyl-stretching frequency. Similarly, when some CO groups are replaced by ligands which are poorer π-acceptors, the remaining CO groups must accept d_π electrons from the metal atom to a greater extent. This reasoning was used to assign the absorptions at *ca.* 1 965 cm^{-1} to species containing only one CO group. A number of products contained species absorbing diffusely between 1 800 and 1 740 cm^{-1}. Since all the likely structures with terminal absorptions have already been assigned higher absorption frequencies, this lowest broad peak probably arises from polymeric species with bridging carbonyl groups.

EXPERIMENTAL

Analyses.—*Chlorine.* The given complex (*ca.* 0·1 g) was weighed accurately into a nickel crucible and covered with layers of sodium carbonate, sodium carbonate–sodium peroxide (1 : 1), and sodium peroxide (total weight of sodium carbonate and sodium peroxide was *ca.* 5 g). The crucible was then heated gradually to a dull red heat, taking care to prevent vigorous evolution of gases, and covered with a lid when the solids had melted, to prevent spitting. When cool, the crucible was immersed in boiling water to leach out the contents. The resulting black colloidal solution was centrifuged and the supernatant filtered through a no. 4 porosity sinter. The solid was washed several times with water and the combined filtrate plus filtered washings were made just acid with concentrated nitric acid. This solution was analysed for chloride gravimetrically by precipitation of silver chloride. It is interesting that perchlorate ions were completely decomposed in the strongly oxidising conditions prevalent in the alkaline melt.

Rhodium.[34] A known weight of the complex (*ca.* 0·05 g) was dissolved in concentrated nitric acid (50 cm^3). Aliquot portions (1—5 cm^3) of this solution were heated to dryness and the residue dissolved in concentrated hydrochloric acid (5 cm^3). A solution of tin(II) chloride [5 cm^3; 20% in HCl–H$_2$O (1 : 3)] was added and the mixture heated at 90 °C on a water-bath. A raspberry-red colour gradually developed. The volume of the solution was held roughly

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[31] K. Nakamoto, 'Infra-red Spectra of Inorganic and Co-ordination Compounds,' Wiley, 1963, p. 180.

[32] E. W. Abel, M. A. Bennett, and G. Wilkinson, *J. Chem. Soc.*, 1959, 2325.

[33] D. M. Adams, 'Metal–Ligand and Related Vibrations,' Arnold, 1967.

[34] E. B. Sandell, 'Colorimetric Determination of Traces of Metals,' 3rd edn., Interscience, p. 769.

constant by the addition of $HCl–H_2O$ (1 : 5). After several hours it was made up to 25 cm^3 with $HCl–H_2O$ (1 : 5) and its optical density at 470 nm measured using 1 cm cells. There is a linear relation between the optical density at 470 nm and concentration in the range 0—30 p.p.m. rhodium. This was established using *trans*-$[Rh(py)_4Cl_2]Cl,5H_2O$ as a standard (ϵ_{470} 3·95 × 10^3 l mol^{-1} cm^{-1}), and was used to calculate the amount of rhodium present in solutions.

Complexes of rhodium(I) containing phen were not fully decomposed by boiling nitric or sulphuric acids. It was necessary to heat these complexes either in an alkaline melt or in concentrated perchloric acid to effect complete decomposition. The former procedure resulted in formation of rhodium metal, which, insoluble in all acids, could be solubilised for analysis only by heating in molten potassium hydrogensulphate. Digestion of the complex with boiling concentrated nitric and perchloric acids in turn was more convenient and gave more reproducible results. The residue on heating the perchloric acid solution to dryness was dissolved in concentrated hydrochloric acid and analysed spectrophotometrically as described above. This difficulty in causing the release of rhodium from its complexes with phen or bipy casts doubt on a formulation[13] of products from $[(OC)_2Rh(\mu\text{-}Cl)_2Rh(CO)_2]$ + L (in ethanol; *cf.* our syntheses in benzene) as $[HRh(CO)(L)X_2]$, based chiefly on a Rh : Cl analytical ratio of 1 : 2. The products probably contain rhodium(I).

Preparation of Rhodium(I) *Complexes*.—The complexes $[(OC)_2Rh(\mu\text{-}Cl)_2Rh(CO)_2]$, $[\{Rh(cod)Cl\}_2]$, $[Bu_4N][Rh(CO)_2Cl_2]$, $[Rh(pd)(CO)_2]$, $[Rh(quin)(CO)_2]$, and $[Rh(phen)(cod)][ClO_4]$ were prepared by the methods described in refs. 35, 36, 8, 10, 11, and 19 respectively.

Dicarbonyl(1,10-*phenanthroline*)*rhodium*(I) *dicarbonyldichlororhodate*(I), $[Rh(phen)(CO)_2][Rh(CO)_2Cl_2]$, (I).—A solution of phen (0·04 g) in sodium-dried benzene was added slowly, dropwise with stirring, at room temperature, to a solution of $[(OC)_2Rh(\mu\text{-}Cl)_2Rh(CO)_2]$ (0·1 g) in sodium-dried benzene. The resulting brilliant green *precipitate* was collected, washed thoroughly with benzene and diethyl ether, and dried *in vacuo*. I.r. absorptions (Nujol mull): 3 045w; 2 101s; 2 088s; 2 061s; 2 041s; 2 021s; 1 995s; 1 981s; 1 963vw; 1 955vw; 1 633vw; 1 606w; 1 585w; 1 529m; 1 525m; 1 435m; 1 413w; 1 368w; 1 342vw; 1 303vw; 1 223w; 1 139w; 1 109vw; 1 095vw; 1 040w; 847 (sh); 843m; 775w; 723 (sh); 718m; 654w; 612 (sh); 610m; 537m; 521w; 492w; and 488w cm^{-1}. All the carbonyl absorption associated with $[Rh(phen)(CO)_2]^+$ was lost when the dry sample was finely ground. Carbon monoxide is easily lost from several of the rhodium(I) species containing phen.

(2,2′-*Bipyridyl*)*dicarbonylrhodium*(I) *dicarbonyldichlororhodate*(I), $[Rh(bipy)(CO)_2][Rh(CO)_2Cl_2]$, (II). The preparation was exactly analogous to that of the complex (I), except that the starting material was bipy (Found: C, 30·3; H, 2·0; N, 5·1. Calc. for $C_{14}H_8Cl_2N_2O_4Rh_2$: C, 30·9; H, 1·5; N, 5·1%). I.r. absorptions (Nujol mull): 3 080w; 3 052w; 2 085s; 2 060s; 2 026s; 2 014s; 1 993s; 1 982s; 1 956w; 1 610m (sh); 1 605m; 1 500w; 1 438m; 1 368w; 1 319w; 1 245w; 1 170w; 1 159w; 1 105vw; 1 075vw; 1 035vw; 769m; and 726 cm^{-1}.

(η-*Cyclo-octa*-1,5-*diene*)(1,10-*phenanthroline*)*rhodium*(I) *chloride*, $[Rh(phen)(cod)]Cl$. Filtered solutions of $[(OC)_2Rh(\mu\text{-}Cl)_2Rh(CO)_2]$ (0·1 g) and phen (0·12 g) in acetone were mixed with stirring. The resulting bright red *precipitate* was collected, washed thoroughly with acetone, and dried *in vacuo*, yield 0·17 g (Found: C, 55·5; H, 4·7; N, 6·5. Calc. for $C_{20}H_{20}ClN_2Rh$: C, 56·3; H, 4·7; N, 6·5%). I.r. absorptions (Nujol mull): 1 700w,br; 1 624w; 1 598w; 1 583w; 1 517m; 1 505 (sh); 1 488w; 1 432s; 1 410m; 1 328m; 1 297w; 1 221m; 1 170w; 1 143w; 1 080w,br; 1 034w; 997m; 981w; 880w; 852s; 842 (sh); 825w; 775w; 735w; 718s; and 645w cm^{-1}.

Dicarbonyl(1,10-*phenanthroline*)*rhodium*(I) *perchlorate*, $[Rh(phen)(CO)_2][ClO_4]$. Carbon monoxide was bubbled through a deaerated suspension of finely ground $[Rh(phen)(cod)][ClO_4]$ in methanol for several minutes. The dark green, flakey, crystalline *product* (which has a metallic lustre) was collected, washed thoroughly with methanol, and dried *in vacuo*. On standing *in vacuo* the metallic lustre disappeared. I.r. absorptions (Nujol mull): 3 100w; 3 060w; 2 114s; 2 060s; 1 632w; 1 605w; 1 522m; 1 434m; 1 418w; 1 370w; 1 225w; 1 160w; 1 086s,br; 1 040w; 852m; and 775w cm^{-1}. This reaction was readily reversible in the presence of an excess of cyclo-octa-1,5-diene. It may be photocatalysed, since it appears to be rapid only in the light.

Dicarbonylchloro(1,10-*phenanthroline*)*rhodium*(I), $[Rh(phen)(CO)_2Cl]$. (*a*) Carbon monoxide was bubbled through a deaerated suspension of finely ground $[Rh(phen)(cod)]Cl$ in acetone for several minutes. The pinkish yellow, finely crystalline, *product* was filtered off, washed thoroughly with acetone, and dried *in vacuo*. I.r. absorptions (Nujol mull): 3 075w; 3 040w; 1 980w,br; 1 942w; 1 830s; 1 810s; 1 790 (sh); 1 700w,br; 1 623w; 1 601w; 1 588w; 1 578w; 1 517m; 1 509 (sh); 1 495w; 1 432m; 1 413m; 1 370w; 1 341m; 1 308vw; 1 225m; 1 191vw; 1 143w; 1 106vw; 1 090vw,br; 1 057vw; 963vw; 870w; 852vw; 810vw; 783m; 733s; 723s; 645m; and 580m cm^{-1}. Grinding a sample of the solid induced a change in the i.r. spectrum, presumably through intense local heating causing either loss of CO or adoption of an ionic structure. The resulting, almost black, material is, from its i.r. spectrum, a mixture of $[Rh(phen)(CO)Cl]$ and $[Rh(phen)(CO)_2]Cl$.

(*b*) The complex was also obtained by treating rhodium trichloride, which had reacted with dmf, with phen. However, formation of the five-co-ordinate species *via* this synthetic path is very sensitive to the slightest alteration in the conditions of reaction, as the following examples illustrate.

The preparation was carried out in one instance with anhydrous starting materials, to avoid a possible source of contamination. The product was a markedly darker green than previously, and its carbonyl-absorption spectrum (completely above 2 000 cm^{-1}) indicated the presence of considerable amounts of $[Rh(phen)(CO)_2]^+$. It has been postulated[37] that a co-ordinated water molecule may be required for the reduction of rhodium(III) by carbon monoxide under mild conditions, so it is perhaps not surprising that the use of anhydrous rhodium trichloride should slightly alter the course of the reaction. During another preparation, it was necessary to boil the solution of rhodium trichloride in dmf with charcoal before filtration to obtain a clear yellow filtrate. On addition of phen, gas

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[36] J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 1957, 4735.

[37] B. R. James, *Co-ordination Chem. Rev.*, 1966, **1**, 517 and refs. therein.

was evolved, though the final product, after 'recrystallisation' from aqueous solution, was identical with previous samples which had been similarly purified.

Carbonylchloro(1,10-*phenanthroline*)*rhodium*(I), [Rh(phen)(CO)Cl]. The complex [Rh(phen)$(CO)_2$Cl] was heated at 240 °C *in vacuo* for *ca.* 15 min, to give a chocolate-brown product. I.r. absorptions (Nujol mull): 3 050w; 1 962s,br; 1 941s; 1 915 (sh)w; 1 630w; 1 600w; 1 578w; 1 510w; 1 496w; 1 438m; 1 412w; 1 370w; 1 341w; 1 252vw; 1 224w; 1 212w; 1 201vw; 1 150w; 1 092w; 971w; 915w; 841s; 830w; 770w; 725 (sh); 713s; 650w; and 598w cm^{-1}.

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