The Interaction between Anionic and Cationic Rhodium(I) Complexes in Solution and in the Solid State

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U.v.–visible spectral studies show that in acetonitrile solution there is association between $[Rh(CO)_2(L–L)]^+$ or $[Rh(CO)_3(L–L)]^+$ [where L–L = 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen)] cations and $[RhX_2(CO)_2]^-$ (where X = Cl or Br) anions. The extent of the interaction depends on L–L and X and is most pronounced for $[Rh(CO)_3(phen)]^+$ and $[RhCl_2(CO)_2]^-$. The anion–cation compound formed by the reaction of L–L with $[(OC)_2Rh(\mu\text{-}Cl)_2Rh(CO)_2]$ has been shown to be $[Rh(CO)_3(L–L)][RhCl_2(CO)_2]$. All four compounds of the type $[Rh(CO)_3(L–L)][RhX_2(CO)_2]$ have been prepared in crystalline form by the action of CO on a solution of $[Rh(cod)(L–L)][BPh_4]$ (cod = cyclo-octa-1,5-diene) and $[RhX_2(CO)_2]^-$ in 1,2-dichlorobenzene, a new preparative method.

THE current interest in 'one dimensional' metal-atom chain compounds is based on their unusual and highly anisotropic physical properties, and the relationship of these properties to their chemical structures.[1,2] Much of the work on integral oxidation-state metal complexes has concentrated on the square coplanar d^8 ions of nickel(II), palladium(II), and particularly platinum(II). However, the greater spatial extension of the '*d*' orbitals on the isoelectronic rhodium(I) and iridium(I) ions due to their lower positive charge could result in greater metal–metal interactions in a columnar stacked structure. These systems are therefore worthy of a new and systematic study.

One of the earliest reported examples of a metal-atom chain compound was Magnus's Green Salt (MGS) in which a metal-atom chain is formed by a stack of alternating $[Pt(NH_3)_4]^{2+}$ and $[PtCl_4]^{2-}$ ions.[3] The interaction between adjacent platinum atoms at a distance of 3.25 Å results in the compounds having a characteristic green colour quite distinct from the colour of the constituent ions $[PtCl_4]^{2-}$ (pink) and $[Pt(NH_3)_4]^{2+}$ (colourless).[4] Electrical conduction studies have revealed a high extrinsic conductivity in the metal-atom chain direction with an anisotropy of *ca.* 100.[5] However, the palladium analogue $[Pd(NH_3)_4][PdCl_4]$, although isostructural with the same metal–metal separations, is pink and does not show any evidence of Pd–Pd interactions.[6] This is presumably due to the smaller spatial extension of the 4*d* orbitals of Pd compared to the 5*d* orbitals of platinum.

The work described here was initiated to study the interaction of rhodium(I) anions and cations and to ascertain whether a MGS type of compound can be formed in which Rh–Rh interactions occur through the overlap of the 4*d* orbitals on adjacent rhodium atoms. Suitable anions {*e.g.* $[RhX_2(CO)_2]^-$ where X = Cl, Br, or I} and cations {*e.g.* $[Rh(CO)_2(L–L)]^+$ where L–L = 1,10-phenanthroline (phen) or 2,2′-bipyridyl (bipy)} have been reported although the exact nature of the cations has caused confusion in the literature and will be discussed later.[7-11]

A brilliant blue-green precipitate has been reported to be obtained when phen is added to a solution of $[(OC)_2Rh(\mu\text{-}Cl)_2Rh(CO)_2]$ in benzene.[11] The compound was assigned the formula $[Rh(CO)_2(phen)][RhCl_2(CO)_2]$ and it was suggested that the colour indicated a chain structure with a metal–metal interaction. A similar compound with bipy has also been reported. However, both products were obtained in an amorphous state. For a detailed study of these systems single crystals of the products are required to enable a complete investigation of their structural and one-dimensional solid-state properties. We have therefore concentrated on a study of the interactions of the anions and cations in solution with the ultimate aim of finding the correct conditions for the growth of single crystals of these anion–cation compounds.

RESULTS AND DISCUSSION

Anions $[NBu_4][RhX_2(CO)_2]$ (*where* X = Cl, Br, *or* I).—These were prepared by the method described by Vallarino.[7] The ν(CO) of these compounds are listed in Table 1. These will be used diagnostically to detect the presence of these anions in the products to be discussed later.

Cations.—Tricarbonyl cations of the type $[Rh(CO)_3(L–L)]^+$ (where L–L = phen or bipy) were isolated as the perchlorate or tetrafluoroborate salts by two methods:[8,11]

$$\text{(a)}\ Rh[ClO_4]_3\cdot xH_2O + L–L \xrightarrow[CO]{EtOH} [Rh(CO)_3(L–L)][ClO_4] + xH_2O$$

$$\text{(b)}\ [Rh(cod)(L–L)][ClO_4] \xrightarrow[CO]{EtOH} [Rh(CO)_3(L–L)][ClO_4] + cod$$

Here cod = cyclo-octa-1,5-diene.

Both methods produced similar green solids. Previous workers have reported both a green and a yellow form of these compounds which had different ν(CO) stretching frequencies. From a study of the ν(CO) stretching frequencies we conclude that our products are a mixture of the two polymorphs reported previously. These compounds were initially reported to contain the dicarbonyl species $[Rh(CO)_2(L–L)]^+$,[8,11] but the positions of the ν(CO) stretching frequencies have subsequently identified them as tricarbonyl cations (see later).

TABLE 1

Infrared absorption bands (cm^{-1}) of solid samples as Nujol mulls

Compound	ν(CO)	ν(M–X)	ν(M–CO), δ(M–C–O)	Other bands	
[NBu$_4$][RhCl$_2$(CO)$_2$]	2 055s, 1 975br, 1 948vw	321s, 292s	622s, 500s	881w, 740w, 722w	
[NBu$_4$][RhBr$_2$(CO)$_2$]	2 050s, 1 985br	231vs, 209vs	607s, 495s, 485s, 533w, 400w	896w, 738w, 722w	
[NBu$_4$][RhI$_2$(CO)$_2$]	2 050vs, 2 035s, 1 985vs, 1 949s				
[Rh(CO)$_3$(phen)][BF$_4$]	2 108s, 2 100s, 2 060s, 2 041s		605s, 530(sh), 524s, 471s, 430s	1 050vs,br, 1 035vs, 856vs, 789w, 719vs, 1 524s, 1 519(sh)	Mixture of polymorphs
[Rh(CO)$_3$(bipy)][ClO$_4$]	2 105s, 2 095(sh), 2 045s, 2 020(sh)		604s	770s, 745w, 725s	Mixture of polymorphs
[Rh(CO)$_3$(phen)][RhCl$_2$(CO)$_2$]	2 099, 2 088, 2 062s, 2 057, 2 039, 2 019, 1 995, 1 982 all vs, 1 964vw, 1 956vw	315vs, 284vs, 245br,w	618(sh), 610w, 530w, 518w, 489w, 471w, 437s	1 530s, 1 525s, 848(sh), 843s, 728w, 720vs	Obtained from [{RhCl(CO)$_2$}$_2$] + phen in benzene
[Rh(CO)$_3$(bipy)][RhCl$_2$(CO)$_2$]	2 097, 2 088, 2 064, 2 058, 2 028, 2 016, 1 996, 1 985 all vs, 1 959vw	314vs, 284vs	612s, 528s, 489s, 479s, 462s, 440s, 412vs	1 608s, 1 613(sh), 769s, 727s	Obtained from [{RhCl(CO)$_2$}$_2$] + bipy in benzene
[Rh(CO)$_3$(phen)][RhBr$_2$(CO)$_2$]	2 097, 2 087, 2 062, 2 056, 2 039, 2 019, 1 997, 1 882 all vs, 1 967vw, 1 959vw	228vs, 204vs	605s, 660w, 530s, 512s, 475br, 436s	1 530s, 1 525s, 1 415w, 846s, 840vs, 775w, 728s, 717vs, 657w, 310s, 300w, 278w, 245s	Obtained from [Rh(cod)(phen)]-[BPh$_4$] + [NBu$_4$]-[RhBr$_2$(CO)$_2$] $\xrightarrow{CO}$
[Rh(CO)$_3$(bipy)][RhBr$_2$(CO)$_2$]	2 094, 2 085, 2 062, 2 055, 2 025, 2 015, 1 995, 1 983 all vs, 1 954vw	228s, 201s	601s, 526s, 497w, 482s, 463s, 440s, 410s	1 605s, 764vs, 723vs	Obtained from [Rh(cod)(bipy)]-[BPh$_4$] + [NBu$_4$]-[RhBr$_2$(CO)$_2$] $\xrightarrow{CO}$

TABLE 2

Details of $[Rh(CO)_3(phen)]^+ \underset{CO}{\overset{N_2}{\rightleftharpoons}} [Rh(CO)_2(phen)(solvent)]^+$ equilibrium in various solvents

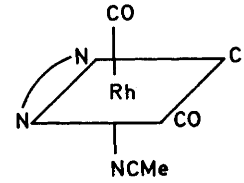
			Solution saturated with CO		Solution saturated with N$_2$	
Solvent	Anion	Solubility	Species present	$\tilde{\nu}$(CO)/cm^{-1}	Species present	$\tilde{\nu}$(CO)/cm^{-1}
Methanol–ethanol	[BF$_4$]$^-$, [ClO$_4$]$^-$	insoluble				
Acetone [a]	[BF$_4$]$^-$, [ClO$_4$]$^-$	very sparingly soluble	[Rh(CO)$_3$(phen)]$^+$	*b*	[Rh(CO)$_2$(phen)]$^+$ [b]	
Acetonitrile	[BF$_4$]$^-$, [ClO$_4$]$^-$	moderately soluble	[Rh(CO)$_3$(phen)]$^+$	2 103, 2 043	[Rh(CO)$_2$(phen)]$^+$	2 014, 1 979
Nitromethane	[BF$_4$]$^-$, [ClO$_4$]$^-$	moderately soluble	[Rh(CO)$_3$(phen)]$^+$	2 103, 2 043	[Rh(CO)$_3$(phen)]$^+$	2 103, 2 043
1,2-Dichlorobenzene	[BPh$_4$]$^-$	soluble	[Rh(CO)$_3$(phen)]$^+$	2 098, 2 041	[Rh(CO)$_3$(phen)]$^+$	2 098, 2 041
Benzyl alcohol	[BPh$_4$]$^-$	soluble	[Rh(CO)$_3$(phen)]$^+$	2 098, 2 041	[Rh(CO)$_3$(phen)]$^+$	2 098, 2 041

[a] Solubility too low for i.r. studies. [b] Based on changes in the u.v. spectrum of these solutions.

Mestroni *et al.*[10] showed that in acetonitrile solution a

$$[Rh(CO)_2(L\text{–}L)]^+ \underset{N_2}{\overset{CO}{\rightleftharpoons}} [Rh(CO)_3(L\text{–}L)]^+$$

reversible reaction occurs and is accompanied by characteristic changes in the i.r. spectrum. The green product [Rh(CO)$_3$(L–L)][ClO$_4$] when dissolved in acetonitrile gave rise to two ν(CO) absorptions at 2 103 and 2 043 cm^{-1}. On saturating the solution with N$_2$ these bands disappeared and two new bands appeared at 2 014 and 1 979 cm^{-1}. This process is completely reversible on resaturation of the solution with CO. This is in complete agreement with the results of Mestroni *et al.* and these frequencies will therefore be used diagnostically to detect the presence of the tricarbonyl or the dicarbonyl cations respectively in solution. It is probable that the solutions saturated with CO contain the species below since this would be expected to exhibit only two i.r.-active ν(CO) stretching frequencies whereas alternative configurations involving three CO groups and a bidentate ligand would exhibit three ν(CO) stretching frequencies.[12] It is this observation of only two ν(CO) bands which led to the original and erroneous description of the green product as a dicarbonyl.[8]



Although the green solid obtained from the above reactions contains the tricarbonyl cation it is obviously possible to produce the square-coplanar dicarbonyl cation in solution by removing the excess of CO with N$_2$. Attempts to isolate the dicarbonyl were only partially successful. Evaporation of a N$_2$-saturated acetonitrile solution containing [Rh(CO)$_2$(phen)][BF$_4$] under N$_2$ yielded a dark green solid which turned black in air. An i.r. spectrum recorded immediately after the solid had been prepared contained ν(CO) frequencies at 2 012 and

1 980 cm^{-1} confirming that it did contain the dicarbonyl cation. The remainder of the i.r. spectrum down to 650 cm^{-1} showed the presence of phen and $[BF_4]^-$. The conversion of the dicarbonyl cation into the tricarbonyl cation is also accompanied by a change in the position of the absorption edge of the intense Rh→CO π* transition from 450 to 500 nm.

A number of solvents were examined for the existence of a dicarbonyl $\rightleftharpoons$ tricarbonyl equilibrium to select the most appropriate solvent for the preparation of the anion–cation compounds. The results of this study are summarised in Table 2. It is clear from Table 2 that the dicarbonyl $\rightleftharpoons$ tricarbonyl equilibrium lies in favour of the dicarbonyl only in acetonitrile solution. Thus it seems likely that a polar σ-donor solvent is required to stabilise the dicarbonyl. In non-donor solvents the tricarbonyl remains the stable species even when all the excess of CO is removed from the solution by N_2.

Interaction of Rhodium(I) *Anions and Rhodium*(I) *Cations in Acetonitrile.*—A study has been made of the interaction of the cations $[Rh(CO)_x(phen)]^+$ or $[Rh(CO)_x(bipy)]^+$ ($x = 2$ or 3) with anions $[RhCl_2(CO)_2]^-$ or $[RhBr_2(CO)_2]^-$. There are large differences in behaviour between the phen and bipy cations and they will therefore be discussed separately.

(*a*) *Bipy system.* When equimolar solutions of $[RhCl_2(CO)_2]^-$ and $[Rh(CO)_3(bipy)]^+$ in acetonitrile are mixed together the i.r. spectrum of the resulting solution contains absorption bands at 2 040 and 2 103 cm^{-1} characteristic of the tricarbonyl cation. In addition there are peaks at 1 992 and 2 070 cm^{-1} which can be assigned to the anion,* and there is a shoulder at 2 092 cm^{-1}. When this solution is saturated with N_2 the peaks due to $[Rh(CO)_3(bipy)]^+$ disappear and are replaced by new peaks at 1 980 and 2 018 cm^{-1} characteristic of $[Rh(CO)_2(bipy)]^+$. The peaks at 1 992 and 2 070 cm^{-1} due to the anion remain and the shoulder observed initially at 2 092 cm^{-1} is now present as a strong peak. This new peak at 2 092 cm^{-1} could be a molecular mode arising from dimer or polymer formation between the dicarbonyl cation and the anion or it could be due to the formation of a tricarbonyl anion $[RhX_2(CO)_3]^-$. The same band at 2 092 cm^{-1} appears when solutions of $[Rh(CO)_2(bipy)]^+$ and $[RhCl_2(CO)_2]^-$ are mixed together.

The u.v.–visible spectra of 6×10^{-3} mol dm^{-3} acetonitrile solutions of $[Rh(CO)_3(bipy)]^+$ and $[RhCl_2(CO)_2]^-$ when saturated with CO and when saturated with N_2 are shown in Figure 1. These changes in the spectra are completely reversible. It can be seen from Figure 1 that the spectra of the CO-saturated solution which contains $[Rh(CO)_3(bipy)]^+$ and $[RhCl_2(CO)_2]^-$ is different from that of a simple combination of the spectra of the constituent ions. First, the band edge of the intense u.v. absorption has moved to much lower energy and secondly there is a small general increase in the absorption of the solution throughout the range 950—1 800 nm. When the solution is saturated with N_2 the u.v. absorption band edge moves to higher energy and there is a further rise in absorption in the region 950—1 800 nm.

The u.v.–visible and i.r. results can be explained by the formation of a dimer or cluster between the anion and either the dicarbonyl cation in N_2-saturated solution or the tricarbonyl cation in CO-saturated solutions. Indeed the spectral changes may simply result from the addition and removal of CO to and from an anion–cation dimer or cluster species in solution.

The behaviour of the bromide anion $[RhBr_2(CO)_2]^-$ with $[Rh(CO)_3(bipy)]^+$ is very similar to that of the chloride anion described above. The high-energy u.v. absorption edge occurs at higher energies than for the chloride and there is a smaller increase in the absorption in the 950—1 800 nm region on saturation with N_2. This suggests less interaction between the bromide anion and the cation than with the chloride anion and the cation. No precipitates were obtained in either system and attempts to obtain products by evaporation of the acetonitrile or addition of other solvents were not successful.

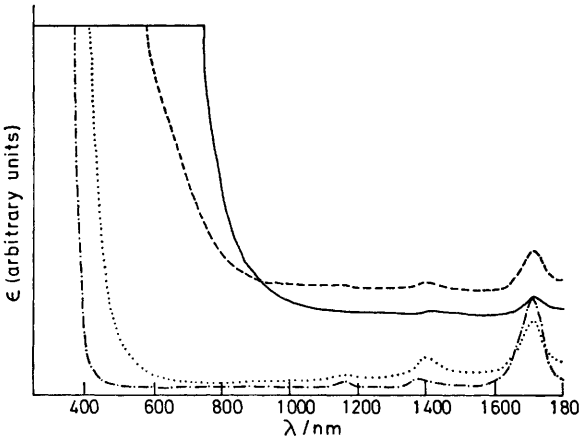


FIGURE 1 U.v.–visible spectra from 350 to 1 800 nm of *ca.* 6×10^{-3} mol dm^{-3} acetonitrile solutions of: (——) $[Rh(CO)_3(bipy)][BF_4]$ and $[NBu_4][RhCl_2(CO)_2]$ saturated with CO; (– – – –) $[Rh(CO)_2(bipy)][BF_4]$ and $[NBu_4][RhCl_2(CO)_2]$ saturated with N_2; (· · · ·) $[Rh(CO)_3(bipy)][BF_4]$ saturated with CO; and (— · — · —) $[NBu_4][RhCl_2(CO)_2]$ saturated with CO or N_2

(*b*) *Phen system.* The interaction of the phen cation $[Rh(CO)_x(phen)]^+$ ($x = 2$ or 3) and $[RhX_2(CO)_2]^-$ is quite different from that of the bipy complexes described above and is summarised below.

When CO-saturated solutions of $[Rh(CO)_3(phen)]^+$ and $[RhCl_2(CO)_2]^-$ are mixed together a clear yellow-brown solution is obtained. The i.r. spectrum of the solution contains only four absorption bands in the ν(CO) region at 1 992, 2 018, 2 070, and 2 092 cm^{-1}. The peaks at 2 070 and 1 992 cm^{-1} can be assigned to the $[RhCl_2(CO)_2]^-$ anion. The band at 2 092 cm^{-1} is in an identical position to the ' extra ' peak observed on saturating the bipy system with N_2 and was assigned to a band characteristic of some form of anion–cation associated species. The

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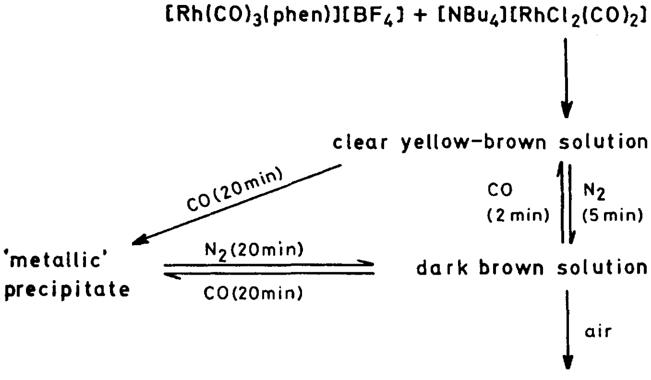
* In acetonitrile solution $[NBu_4][RhCl_2(CO)_2]$ has ν(CO) at 1 992 and 2 069 cm^{-1}.

remaining peak at 2 018 cm^{-1} is close to that of [Rh(CO)$_2$(phen)]$^+$ at 2 014 cm^{-1} but there is no second peak at 1 980 cm^{-1} characteristic of the dicarbonyl. The i.r. spectrum of the solution is unaffected by the passage of N_2 or CO although prolonged passage of CO produced a dark ' metallic ' precipitate which will be discussed later.



The u.v.–visible spectrum of the solution is similar to that of the bipy analogue except for a shoulder on the absorption edge at 750 nm (see Figure 2) and is strongly affected by the passage of N_2. The most prominent feature of the visible spectrum of the dark brown solution produced by saturating the solution with N_2 is the presence of a very broad strong absorption band stretching from 1 150 to >1 800 nm (Figure 2). The high-intensity u.v. absorption band edge also shifts to shorter wavelengths with a shoulder at >750 nm. It is hard to reconcile the i.r. and visible spectral data unless there is increased interaction between the anion and cation when the solution is purged with N_2. Similar behaviour is observed when the solution is purged with argon so that the N_2 is not playing any chemical role in this phenomena.

If CO is passed through the solution for *ca.* 20 min a very dark precipitate with a metallic lustre is produced. The precipitate will redissolve if the suspension is purged with N_2. It has an identical i.r. spectrum and elemental analysis to the product obtained by the action of phen on a solution of [(OC)$_2$Rh(μ-Cl)$_2$Rh(CO)$_2$] in benzene. The nature of this product, a rhodium(I) anion–cation compound, is discussed in detail later.

A mixture of equimolar solutions of the bromide [RhBr(CO)$_2$]$^-$ and [Rh(CO)$_3$(phen)]$^+$ behaves in a similar way except that the intensity of the low-energy band in the near-i.r. on saturating the solution with N_2 is less intense and no precipitate is obtained on prolonged saturation with CO.

Several important conclusions can be drawn from these studies. (*i*) The behaviours of [Rh(CO)$_x$(phen)]$^+$ and [Rh(CO)$_x$(bipy)]$^+$ (where $x = 2$ or 3) cations with [RhX$_2$(CO)$_2$]$^-$ (where X = Cl or Br) anions in acetonitrile solution are quite different. (*ii*) A rhodium(I) anion–cation compound is only precipitated from acetonitrile solution when the cation contains phen and the anion chloride. (*iii*) The anion–cation compound does not precipitate from solutions expected to contain the dicarbonyl cation but from solutions saturated with CO and therefore expected to contain the tricarbonyl cation.

Although the study of mixing rhodium(I) anions and cations in acetonitrile has shown that some form of association takes place, only in one case was a solid product obtained. This is therefore not a satisfactory method for obtaining solid complexes and single crystals for physical measurements. An alternative strategy is described below.

Preparation of Rhodium(I) *Anion–Cation Compounds from* [Rh(cod)(L–L)][BPh$_4$].—The reaction of [(OC)$_2$Rh(μ-Cl)$_2$Rh(CO)$_2$] with L–L in benzene precipitates anion–cation compounds in an amorphous form.[11] If either the anion or cation can be produced slowly *in situ* then there is a greater chance of obtaining crystalline products. We have found that, in dichlorobenzene, [Rh(cod)(L–L)][BPh$_4$] reacts with CO to give a solution which exhibits two ν(CO) absorptions at 2 098 and 2 041 cm^{-1} indicating the presence of [Rh(CO)$_3$(L–L)]$^+$. Previous studies (see Table 2) show that the tricarbonyl is the only stable cation in dichlorobenzene. The studies in acetonitrile solution suggest that the original formulation of the anion–cation compounds as containing the dicarbonyl cation may be wrong and that these compounds contain a tricarbonyl cation. If this is correct then the controlled preparation of [Rh(CO)$_3$(L–L)]$^+$ in dichlorobenzene may be a suitable route to crystals of the anion–cation compounds.

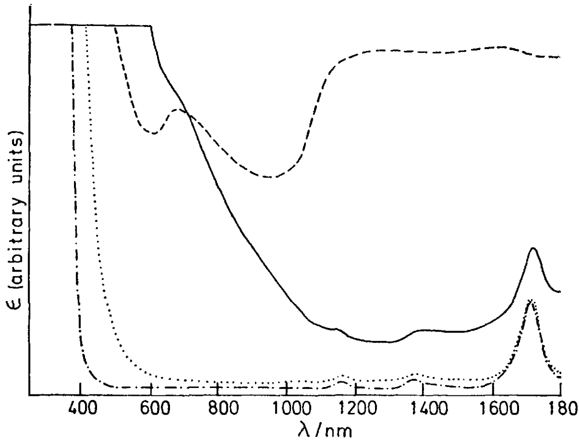


FIGURE 2 U.v.–visible spectra from 350 to 1 800 nm of *ca.* 6 × 10^{-3} mol dm^{-3} acetonitrile solutions of: (——) [Rh(CO)$_3$(phen)][BF$_4$] and [NBu$_4$][RhCl$_2$(CO)$_2$] saturated with CO; (– – – –) [Rh(CO)$_2$(phen)][BF$_4$] and [NBu$_4$][RhCl$_2$(CO)$_2$] saturated with N_2; (· · · ·) [Rh(CO)$_3$(phen)][BF$_4$] saturated with CO; and (— · — · —) [NBu$_4$][RhCl$_2$(CO)$_2$] saturated with CO or N_2

Solutions of [Rh(cod)(L–L)][BPh$_4$] and [RhX$_2$(CO)$_2$]$^-$ (where X = Cl or Br) in dichlorobenzene exposed to a CO atmosphere deposit dark precipitates. The products are microcrystalline but unfortunately the crystals obtained so far are too small for *X*-ray studies. The CO pressure over the solution has to be a compromise between too great a pressure which rapidly produces an

TABLE 3

Elemental analyses

Compound	Colour	Analysis (%) [a] C	H	N	Cl
$[AsPh_4][RhCl_2(CO)_2]$	Yellow	50.3 (50.95)	3.80 (3.30)		
$[NBu_4][RhCl_2(CO)_2]$	Yellow	45.6 (45.75)	7.40 (7.70)	3.05 (2.95)	
$[NBu_4][RhBr_2(CO)_2]$	Yellow	38.75 (38.5)	6.20 (6.40)	2.40 (2.50)	
$[NBu_4][RhI_2(CO)_2]$	Brown	32.8 (33.0)	5.20 (5.50)	2.20 (2.15)	
$[Rh(CO)_3(phen)][BF_4]$	Green	39.95 (38.45)	2.20 (2.00)	6.70 (6.90)	
$[Rh(CO)_3(bipy)][ClO_4]$	Green	35.75 (35.3)	2.00 (1.80)	6.90 (6.35)	
$[Rh(cod)(phen)][BPh_4]$	Red	73.55 (74.4)	5.40 (5.65)	3.95 (3.95)	
$[Rh(cod)(bipy)][BPh_4]$	Red	73.15 (37.5)	3.95 (5.85)	5.60 (4.10)	
$[Rh(CO)_3(phen)][RhCl_2(CO)_2]$					
(a) from $[\{RhCl(CO)_2\}_2]$ + phen [b]	Very dark brown	34.0 (34.2)	1.60 (1.35)	4.90 (4.70)	12.35 (12.45)
(b) from cod	Dark brown	34.5 (34.2)	1.90 (1.35)	4.95 (4.70)	
$[Rh(CO)_3(bipy)][RhCl_2(CO)_2]$					
(a) from $[\{RhCl(CO)_2\}_2]$ + bipy [b]	Very dark brown	31.3 (31.4)	1.60 (1.40)	5.10 (4.90)	12.7 (13.0)
(b) from cod	Dark brown	30.5 (31.45)	1.70 (1.40)	5.30 (4.40)	
$[Rh(CO)_3(phen)][RhBr_2(CO)_2]$	Dark brown	29.4 (29.75)	1.60 (1.20)	4.35 (4.10)	
$[Rh(CO)_3(bipy)][RhBr_2(CO)_2]$	Dark brown	27.5 (27.2)	2.20 (1.20)	4.50 (4.25)	

[a] Calculated values are given in parentheses. [b] The *X*-ray photoelectron spectrum confirms the presence of the Rh in oxidation state +1.

amorphous precipitate and too low a pressure which does not produce the desired product because of slow decomposition of the reactants with time. The analyses, the positions of the i.r. absorption bands, and the diffuse-reflectance spectra (350—1 800 nm) of the products are given in Tables **3** and 1 and Figure **3** respectively.

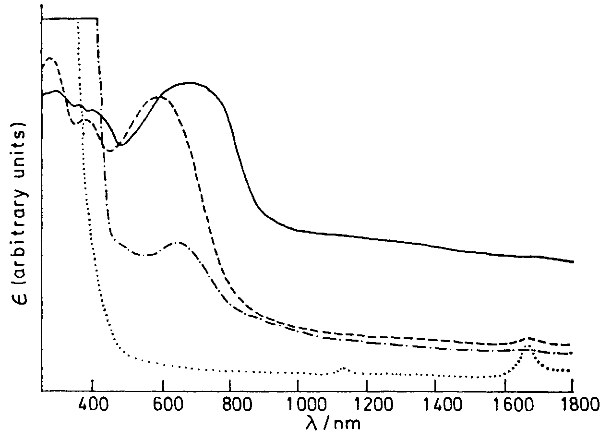


FIGURE 3 Diffuse-reflectance spectra from 350 to 1 800 nm of: (——) $[Rh(CO)_3(phen)][RhX_2(CO)_2]$ (where X = Cl or Br); (– – – –) $[Rh(CO)_3(bipy)][RhX_2(CO)_2]$ (where X = Cl or Br); (— · — · —) $[Rh(CO)_3(phen)][BF_4]$; and (· · · ·) $[NBu_4]$-$[RhCl_2(CO)_2]$

The product formed from $[Rh(CO)_3(phen)]^+$ and $[RhCl_2(CO)_2]^-$ has identical analysis, i.r., and diffuse-reflectance spectra to the products obtained from the reaction of phen with $[(OC)_2Rh(\mu\text{-}Cl)_2Rh(CO)_2]$ in benzene, and to the ' metallic precipitate ' obtained from acetonitrile solution (see above). All three very different preparations give the same product and this, therefore, appears to be the most stable rhodium(I) anion–cation compound that can be formed.

Anion–Cation Compounds.—The i.r. spectrum of all four anion–cation compounds exhibit the same complex pattern of eight absorption bands in the ν(CO) region (see Table 1). The spectrum is therefore much more complex than that of a combination of the spectra of the individual anions and cations for which only four absorption bands would be expected. The observation of absorption bands at >2 080 cm^{-1} indicates the presence of a tricarbonyl cation and is not compatible with the presence of a dicarbonyl cation. At lower frequencies two ν(CO) absorption bands which are close to those for $[RhX_2(CO)_2]^-$ are observed. The presence of $[RhX_2(CO)_2]^-$ is confirmed by the observation of two ν(M–X) absorption bands very close to those observed for $[NBu_4][RhX_2(CO)_2]$ (see Table 1). The occurrence of eight rather than the expected four absorption bands in the ν(CO) range is probably due to the splitting of the fundamental bands of the anions and cations due to solid-state interaction. There is no evidence from the positions of the ν(CO) stretching absorption bands of bridging carbonyl groups.

We consider that these anion–cation compounds should be reformulated as $[Rh(CO)_3(L\text{–}L)][RhX_2(CO)_2]$ for several reasons: (*a*) the presence of ν(CO) bands at >2 080 cm^{-1} is indicative of a tricarbonyl cation; (*b*) the compounds are obtained from dichlorobenzene solutions which contain the tricarbonyl but not the dicarbonyl cation; (*c*) the ' metallic ' compound of identical properties is obtained from acetonitrile solution saturated with CO and in which $[Rh(CO)_3(phen)]^+$ has been proved to be present in the absence of the anion.

The diffuse-reflectance spectra from 300 to 1 800 nm of the four anion–cation compounds (see Figure **3**) are in general very similar but differ from one another in the intensity of the broad absorption band stretching from 950 to <1 800 nm.

The movement of the absorption bands present in the constituent ions to lower energies and the greater intensity of lower-energy absorption bands in these products is similar to the properties of MGS and the columnar stacked anion compounds such as the cyanoplatinum species. The electronic spectra of both these series of compounds have been discussed in terms of an axial perturbation of the out-of-plane *d* and *p* orbitals of the anion by the adjacent metal atoms in the chain.[13,14] Since the rhodium anion–cation compounds contain a five-co-ordinate cation a MGS-type columnar structure can be ruled out. The failure to obtain MGS-type compounds with the square coplanar cation $[Rh(CO)_2(L{-}L)]^+$ is probably a reflection of the lower lattice energy of the MGS-type structure involving a uninegative anion and a unipositive cation compared with $[Pt(NH_3)_4]^{2+}[PtCl_4]^{2-}$.

An anion–cation dimeric structure might also produce the observed spectral changes due to the Rh–Rh interaction and an alternative structure based on a columnar stack of square-planar $[RhCl_2(CO)_2]^-$ ions is also possible. Although there is clearly some form of Rh–Rh interaction in these anion–cation compounds this does not lead to the relatively high electrical conductivities observed in MGS or the cyanoplatinum species. Compressed pellets of $[Rh(CO)_3(phen)][RhCl_2(CO)_2]$ and $[Rh(CO)_3(bipy)][RhCl_2(CO)_2]$ both exhibit a room-temperature specific conductivity of $<10^{-9}\ \Omega^{-1}\ cm^{-1}$. A full understanding of the structure and spectral properties of these interesting compounds must await a detailed crystal-structure determination.

EXPERIMENTAL

The compounds $[NBu_4][RhCl_2(CO)_2]$, $[NBu_4][RhBr_2(CO)_2]$, $[\{RhCl(cod)\}_2]$, and $[Rh(cod)(L{-}L)]X$ (where $X = BF_4$, ClO_4, or BPh_4) were prepared as previously described.[7,8,15]

$[Rh(CO)_3(L{-}L)]X$ (*where* $X = BF_4$ *or* ClO_4).—Carbon monoxide was bubbled through a suspension of finely ground $[Rh(cod)(L{-}L)]X$ in methylated spirit for several hours. The green product was filtered off and washed with methylated spirit.

$[Rh(CO)_3(L{-}L)][RhX_2(CO)_2]$ (*where* $X = Cl$ *or* Br).—These were prepared by two different methods.

(*a*) A benzene solution of the chelate (up to 0.4 times the number of moles of Rh present) was added dropwise to a benzene solution of $[\{RhCl(CO)_2\}_2]$. The product was filtered off and washed with benzene and diethyl ether.[16]

(*b*) Equimolar solutions of $[Rh(cod)(L{-}L)][BPh_4]$ and $[NBu_4][RhX_2(CO)_2]$ ($X = Cl$ or Br) in 1,2-dichlorobenzene were combined and allowed to stand in an atmosphere of carbon monoxide overnight. The product was filtered off and washed with 1,2-dichlorobenzene and methylated spirit.

Physical Measurements.—Infrared spectra were obtained using a Perkin-Elmer 225 spectrometer, diffuse-reflectance spectra and u.v.–visible solution spectra using a Beckman DK-2A spectrometer. The microanalysis was carried out by Mr. E. Lewis (U.C.N.W., Bangor). Chloride analyses were by Dr. F. B. Strauss, Microanalytical Laboratory, Oxford. *X*-Ray photoelectron spectra were determined by Mrs. S. A. Wass (Johnson, Matthey & Co. Ltd.).

We thank the S.R.C. for a CASE award (to P. N. A. S.) and Johnson, Matthey & Co. Ltd. for their collaboration in this work and for the loan of rhodium compounds.

[8/1830 *Received*, 19*th October*, 1978]

REFERENCES

[1] J. S. Miller and A. J. Epstein, *Progr. Inorg. Chem.*, 1976, **20**, 1.

[2] A. E. Underhill and D. J. Wood, *Ann. New York Acad. Sci.*, 1979, **313**, 516.

[3] M. Atoji, J. W. Richardson, and R. E. Rundle, *J. Amer. Chem. Soc.*, 1957, **79**, 3017.

[4] D. S. Martin, R. M. Rush, R. F. Kroening, and P. E. Fanwick, *Inorg. Chem.*, 1973, **12**, 301.

[5] P. S. Gomm, T. W. Thomas, and A. E. Underhill, *J. Chem. Soc.* (*A*), 1971, 2154.

[6] A. E. Underhill and T. W. Thomas, *Chem. Comm.*, 1969, 725.

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

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

[9] G. K. N. Reddy and B. R. Ramesh, *J. Organometallic Chem.*, 1974, **67**, 443.

[10] G. Mestroni, A. Camus, and G. Zassinovich, *J. Organometallic Chem.*, 1974, **65**, 119.

[11] R. D. Gillard, K. Harrison, and I. H. Mather, *J.C.S. Chem. Comm.*, 1975, 133.

[12] L. M. Haines and M. H. B. Stiddard, *Adv. Inorg. Chem. Radiochem.*, 1969, **12**, 53.

[13] L. V. Interante and F. B. Bundy, *Inorg. Chem.*, 1971, **10**, 1169.

[14] M. Stock and H. Yersin, *Chem. Phys. Letters*, 1976, **40**, 423.

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

[16] Yu. S. Varsharskii, N. V. Kiseleva, and N. A. Buzina, *Russ. J. Inorg. Chem.*, 1971, **16**, 862.