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A spectroscopic study of halocarbonyl complexes of rhodium(I) and (III)

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Abstract

NMR studies (^{13}C and ^{103}Rh) show that mixing of equimolar amounts of $[RhX_2(CO)_2]^-$ and $[RhY_2(CO)_2]^-$ ($X \neq Y$ = Cl, Br, or I) results in approximately statistical X/Y exchange to give *cis*-$[RhXY(CO)_2]^-$. Products resulting from the addition of X_2 to $[RhX_2(CO)_2]^-$ (X = Cl, Br, or I) have been characterized by NMR and IR spectroscopic studies, and include the anions *cis*- and *trans*-$[RhX_4(CO)_2]^-$ which slowly lose CO to give the bis(halogen)-bridged dimer $[Rh_2X_8(CO)_2]^{2-}$; the dimer progressively reacts with halide to give the mono(halogen)-bridged dimer $[Rh_2X_9(CO)_2]^{3-}$, and this is followed by the formation of $[RhX_5(CO)]^{2-}$. The tendency for replacement of the halide *trans* to CO by methanol increases in the order X = Cl < Br < I.

1. Introduction

The preparations of the square-planar complex anions *cis*-$[RhX_2(CO)_2]^-$ have long been known [1] and because of the involvement of $[RhI_2(CO)_2]^-$ in the catalytic conversion of methanol to acetic acid, they continue to be investigated in some detail [2]. Up to now, the mixed halo-complex anions *cis*-$[RhXY(CO)_2]^-$ ($X \neq Y$ = Cl, Br or I) had not been reported, and we now describe their characterization through NMR studies together with a spectroscopic study of the products resulting from addition of X_2 to $[RhX_2(CO)_2]^-$, followed by a multinuclear NMR study of the products resulting from subsequent reaction of the rhodium(III) anions with halide.

2. Results and discussion

2.1. *The synthesis and properties of the salts A[RhXY(CO)$_2$] (A = NBu$_4$, Nhex$_4$)*

It was found that mixing of equimolar solutions of $[RhX_2(CO)_2]^-$ with $[RhY_2(CO)_2]^-$ ($X \neq Y$ = Cl, Br, I) in CH_2Cl_2 results in an approximately statistical redistribution of X and Y, eqn. (1) and similar behaviour is found on addition of $(NBu_4)Y$ to $[RhX_2(CO)_2]^-$. The

$$[RhX_2(CO)_2]^- + [RhY_2(CO)_2]^- \longrightarrow 2[RhXY(CO)_2]^- \quad (1)$$

disproportionation (eqn. (1)) occurs readily at room temperature, and, although ^{13}C NMR spectra at room temperature are relatively uninformative because of ligand inter-exchange, at low temperature two new and equally intense resonances appear due to the two inequivalent CO's in the mixed halo complex. At higher levels of ^{13}CO-enrichment, each of these resonances appears as a pseudo-triplet due to the coupling $^2J(^{13}CO–^{13}CO)$, and the relative intensities of the resonances due to the starting materials and the product (eqn. (1)) suggest in all cases an approximately statistical exchange of X and Y. These data, together with those for the starting materials, are summarized in Table 1. For $[RhX_2(CO)_2]^-$, there is little difference in either $\delta(^{13}CO)$ or $^1J(Rh–CO)$ on variation of the halogen, whereas for the mixed halo derivatives, there is a difference in both $\delta(^{13}CO)$ and $^1J(Rh–CO)$, but it is difficult to assign the inequivalent carbonyl resonances in $[RhXY(CO)_2]^-$ unambiguously. In order to do this, we have relied heavily upon the unambiguous ^{13}C, ^{31}P and ^{195}Pt NMR assignments found for $[PtX_xY_{3-x}(CO)]^-$ and $[PtX_xY_{3-x}(PEt_3)]^-$, ($X \neq Y$ = Cl, Br, or I; x = 0, 1, 2, or 3) [3,4]; in these cases, it is the ligand *cis*

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* This paper is dedicated to Professor M.F. Lappert FRS on the occasion of this 65th birthday and in recognition of his contributions to inorganic chemistry.

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TABLE 1. ^{13}C and ^{103}Rh NMR data for $(NBu_4)[RhX_{2-x}Y_x(CO)_2]$ ($X \neq Y$ = Cl, Br, I; x = 0, 1, 2) in dichloromethane at −73°C. All coupling constant values are ±0.5 Hz

Complex	Assignment [a]/*trans*-ligand	$\delta(^{13}CO)$/ppm	^1J(Rh-CO)/Hz	^2J(CO-CO)/Hz	$\delta(^{103}Rh)$/ppm
$[RhCl_2(CO)_2]^-$	Cl	180.6	72.2	-	+73
$[RhBr_2(CO)_2]^-$	Br	181.1	72.7	-	−4
$[RhI_2(CO)_2]^-$	I	182.4	72.4	-	−221
$[RhClBr(CO)_2]^-$	Br	180.5	74.3	5.4	+35
	Cl	181.1	71.0		
$[RhClI(CO)_2]^-$	I	180.0	75.6	4.4	−46
	Cl	182.0	68.3		
$[RhBrI(CO)_2]^-$	I	181.0	74.0	4.1	−103
	Br	182.3	70.8		

[a] See text.

TABLE 2. Spectroscopic data for rhodium(III) halocarbonyl complexes in CH_2Cl_2. Chemical shifts are in ppm and J values in Hz (±0.5); ν(CO) are in cm^{-1}

Complex	X = Cl				Br				I			
	δ(CO)	J(Rh-CO)	δ(Rh)	ν(CO)	δ(CO)	J(Rh-CO)	δ(Rh)	ν(CO)	δ(CO)	J(Rh-CO)	δ(Rh)	ν(CO)
cis-$[RhX_4(CO)_2]^-$	168.5	52.7		2160,2130	169.5	53.3	1567 [b]	2146,2115	170.2	53.6		2123,2093
trans-$[RhX_4(CO)_2]^-$					172.2	48.6		2095	172.4	48.5		2094
$[Rh_2X_8(CO)_2]^{2-}$ [a]	170.0	61.3	4427 [b]	2115	174.9	59.9	2888 [c]	2095	180.9	54.8	2997 [c]	2072
$[Rh_2X_9(CO)_2]^{3-}$	172.7	61.5	3976 [b]						184.0	55.2		
$[RhX_5(CO)]^{2-}$	175.4	55.1	4047 [b]	2087	178.2	55.0	3158 [b]	2072	183.5	53.3		2050
$[RhX_4(CO)(MeOH)]^-$					175.2	58.4	3103 [b]	2072	178.6	55.7		2050

[a] Most abundant isomer. [b] Obtained via direct ^{103}Rh measurements. [c] Obtained via ^{13}C-{^{103}Rh} measurements.

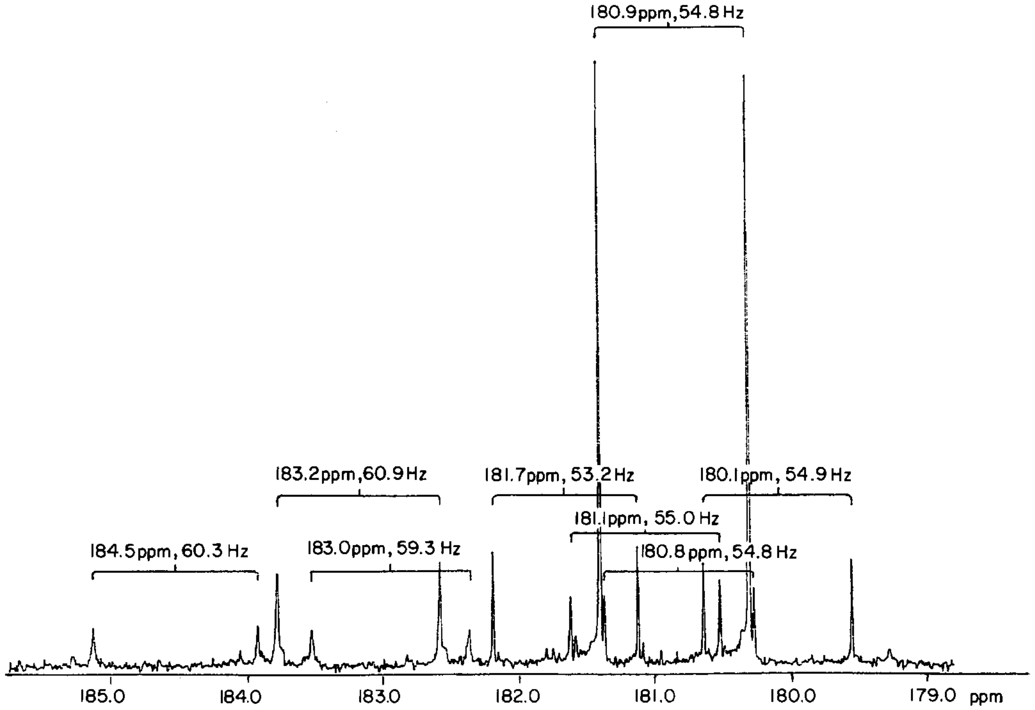


Fig. 1. ^{13}C NMR spectrum of $(Nhex_4)_2[Rh_2I_8(CO)_2]$ in dichloromethane at room temperature.

to CO or PEt_3 that has the greatest effect on both $\delta(^{13}CO)$ or $\delta(^{31}P)$ and $^1J(Pt{-}^{13}CO)$ or $^1J(Pt{-}PR_3)$, respectively. In terms of this assumption, there is generally a smooth progression of both $\delta(^{13}CO)$ and $^1J(Rh{-}CO)$ in $[RhXY(CO)_2]^-$ on varying the *trans* group while retaining the same *cis* ligands. The values of $\delta(Rh)$ for the mixed halo complexes occur close to the mean value for the starting materials, except in the case of the chloro/iodo complex.

It is noteworthy that variable temperature ^{13}C NMR measurements for all the combinations of X and Y in eqn. (1) always show that the rate of ligand exchange as shown by the broadening of the resonances associated with the various complexes is Rh–I > Rh–Br > Rh–Cl, with no preferential broadening of either of the two resonances associated with the mixed halo complexes. This is in accord with the known tendency of the least electronegative halide in the square-planar complex $[PtX_xY_{3-x}(CO)]^-$, ($X \neq Y = Cl, Br, I$, $x = 0, 1, 2, 3$) to avoid the site *trans* to CO [4].

2.2. *Oxidative-addition of halogen to rhodium(I) complexes and reactions of halo carbonyl rhodium(III) complexes*

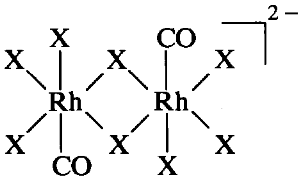
Oxidative-addition of halogen to $[RhX_2(CO)_2]^-$ has previously been studied by Forster [5], who found that the first product formed is *cis*-$[RhX_4(CO)_2]^-$, which isomerizes in solution to the *trans*-isomer. Those studies relied heavily upon infrared spectroscopy and, when X = I it was possible to isolate crystals of $[RhI_4(CO)_2]^-$ which was characterized by X-ray crystallography and shown to be the *trans*-isomer [6]. Nevertheless, Forster found that the nature of the products from the above oxidative-addition reactions depends heavily upon the choice of solvent and cation, and we now report a systematic IR and NMR study of the products resulting from these oxidative addition reactions in dichloromethane together with compounds formed from them through loss of CO and subsequent reactions with halide and methanol.

By carefully monitoring the IR and NMR spectra simultaneously it was possible to obtain the NMR data for the complexes shown in Table 2 and to confirm that the first product formed on oxidative addition of iodine to $[RhI_2(CO)_2]^-$ is *cis*-$[RhI_4(CO)_2]^-$, which slowly isomerizes in solution to the *trans*-isomer. Thus, addition of iodine to a solution of either the $(NBu_4)^+$ or $(Nhex_4)^+$ (hex = hexyl) salt of $[RhI_2(CO)_2]^-$ in CH_2Cl_2 at −78°C, followed by immediate measurement of the low temperature ^{13}C NMR spectrum showed only the presence of the doublet that was assigned to the *cis*-isomer on the basis of the IR spectrum; with time, and on warming to room temperature, this was slowly replaced by a new doublet corresponding to the *trans*-isomer, which has only one ν(CO) band in the IR spectrum. This tendency to isomerize to the *trans*-isomer is much less pronounced when X = Cl, Br (probably because of steric and electronic effects), and we only have IR and NMR evidence for the presence of trace amounts of *trans*-$[RhBr_4(CO)_2]^-$. When X = Cl, Br, there is a strong tendency for $[RhX_4(CO)_2]^-$ to undergo reductive elimination of halogen, and so the NMR measurements were all carried out in a sealed NMR tube containing an excess (*ca.* 30%) of halogen.

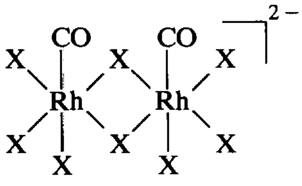
In all cases, $[RhX_4(CO)_2]^-$ loses CO, either spontaneously (X = Cl) or on refluxing in MeOH (X = Br, I), to give $[Rh_2X_8(CO)_2]^{2-}$, and this reaction is reversed under CO (1 atm) in CH_2Cl_2, eqn. (2). Some of these observations have been made previously, and the di-

$$2[RhX_4(CO)_2]^- \rightleftharpoons [Rh_2X_8(CO)_2]^{2-} \qquad (2)$$

meric formulation, rather than the solvated monomer $[RhX_4(CO)S]^-$ (S = solvent), was suggested on the basis of far-IR vibrational data [7]. Our NMR and analytical data support the dimeric structure, and NMR spectra provide evidence for the existence of all five possible isomers, **I** to **V**, behaviour similar to that found for $[Rh_2I_6(COMe)_2(CO)_2]^{2-}$ in solution [8].



(I)



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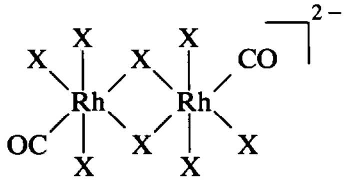

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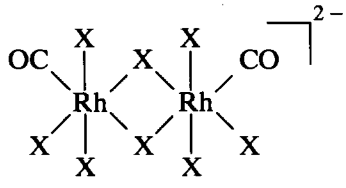
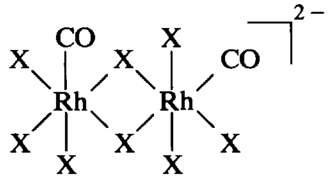


(IV)

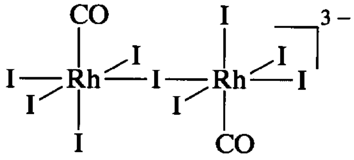


(V)

In order to get a complex more soluble than $(NBu_4)[RhI_4(CO)_2]$, it was necessary to prepare $(Nhex_4)[RhI_4(CO)_2]$, which can be converted to $(Nhex_4)_2[Rh_2I_8(CO)_2]$ by refluxing in methanol for 30 min; although the carbonyl regions of the IR spectra of *trans*-$[RhI_4(CO)_2]^-$ and of $[Rh_2I_8(CO)_2]^{2-}$ are identical, NMR measurements clearly show that the reaction can be cleanly reversed by stirring a solution of $[Nhex_4]_2[Rh_2I_8(CO)_2]$ in CH_2Cl_2 under CO (*ca.* 1.5 atm) for one minute. The IR spectrum of $[Rh_2I_8(CO)_2]^{2-}$ shows just one ν(CO) band, suggesting a centrosymmetric structure, but it is impossible to distinguish **I** from **III** on the basis of spectroscopic measurements, and unfortunately the crystals of $(NBu_4)_2[Rh_2I_8(CO)_2]$ were twinned, preventing X-ray analysis. The ^{13}C NMR spectrum of $(Nhex_4)_2[Rh_2I_8(CO)_2]$ is shown in Fig. 1 and consists of a major doublet at 180.9 ppm with ^1J(Rh–CO) 54.8 Hz (see Table 2), together with seven minor doublets. It is impossible to make detailed assignments of these resonances, but, for the isomers **I** to **V**, there are six inequivalent CO's, and additional resonances could arise from the presence of $[Rh_2I_{8-x}(MeOH)_x(CO)_2]^{(2-x)-}$ ($x = 1$ or 2), since it is well known that iodide *trans* to CO can be easily replaced by methanol [8,9]. Although crystals of $(Nhex_4)_2[Rh_2I_8(CO)_2]$ could not be obtained, the analytical data for $(NBu_4)_2[Rh_2I_8(CO)_2]$, which was obtained by recrystallization from dichloromethane solution, were entirely consistent with this formulation; as mentioned earlier $(NBu_4)_2[Rh_2I_8(CO)_2]$ is not very soluble, but the NMR spectrum also consists of a single doublet at 180.9 ppm. It thus seems unlikely that the major species in Fig. 1 contains methanol.

Incremental (1 to 10 molar equivalents) addition of iodide to $[Rh_2I_8(CO)_2]^{2-}$ (Fig. 1) results in the sequential loss of the major resonance at 180.9 ppm and appearance of a new doublet at 184.0 ppm (Table 2), which we attribute to $[Rh_2I_9(CO)_2]^{3-}$, followed by loss of intensity of this resonance and the appearance of a doublet at 183.5 ppm (Table 2) due to the formation of $[RhI_5(CO)]^{2-}$, and this is also consistent with the presence of a single low frequency ν(CO) band in the IR spectrum. It was impossible to monitor the change of the minor species on addition of iodide, but it is noteworthy that, in contrast to the cleavage of the chloro- and bromo-bridges of the analogous dimers by chloride and bromide ion respectively, cleavage of both the above iodo-bridged species required more than the stoichometric amount of iodide.

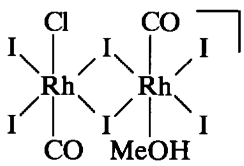
It is appropriate to comment on the structure of $[Rh_2I_9(CO)_2]^{3-}$, which has not hitherto been reported. We assume that the structure, which is in accord with the NMR data, is as shown in **VI**; free rotation about the Rh–I–Rh bonds would be expected and also substitution *cis* to the bridging iodide would be expected on a statistical basis.



(VI)

Titration of the dichloromethane solution in Fig. 1 gave rise to the appearance of only one doublet at 178.6 ppm (Table 2) which we attribute to *trans*-$[RhI_4(MeOH)(CO)]^-$; this is consistent with the presence of a single ν(CO) band in the IR spectrum, at 2050 cm^{-1}.

The structure of $PPN[Rh_2ClI_6(MeOH)(CO)_2]$ was reported previously, [9] and is schematically represented as **VII**. It is of interest that this compound, which was prepared by oxidation of $PPN[RhCl_2(CO)_2]$ with an excess of iodine (6 molar equivalents) followed by refluxing in methanol for 6 h, does *not* contain iodide *trans* to CO and was obtained exclusively on crystallization. The ^{13}C NMR spectrum of **VII** in CH_2Cl_2 contains two equally intense resonances due to the inequivalent CO's, at 181.9 and 180.2 ppm with ^1J(Rh–CO) values of 59.9 and 53.8 Hz, respectively, and, in CH_2Cl_2 solution there is only one sharp band due to ν(CO) in the IR spectrum, at 2085 cm^{-1}. Other mixed halorhodium(III) carbonyls can be prepared in solution by addition of a different halide to the rhodium(III) halo-derivatives reported in Table 2, but their identification through spectroscopic measurements has so far proved to be impossible.



(VII)

The addition of bromine to $[RhBr_2(CO)_2]^-$ in dichloromethane immediately gives *cis*-$[RhBr_4(CO)_2]^-$ with evidence from the ^{13}C NMR spectrum for the presence of only a trace of the *trans*-isomer and, in contrast to the behaviour of the iodo-analogue there is no evidence for *cis* → *trans* isomerization. In the absence of an excess of bromine, there is a strong tendency for $[RhBr_4(CO)_2]^-$ to lose bromine more readily than CO. As a result, decarbonylation of $(NBu_4)[RhBr_4(CO)_2]$ was carried out by refluxing in methanol for 10 min in the presence of bromine (*ca.* 0.3 molar equivalents). The IR and ^{13}C NMR spectra of the resulting product were very similar to those found for $[Rh_2I_8(CO)_2]^{2-}$, and the ^{13}C NMR spectrum consists of an intense doublet at 174.9 ppm, with ^1J(Rh–CO) 59.9 Hz, together with seven minor doublets at the following positions (with coupling constants in parentheses) 175.1 (59.1), 174.4 (54.5), 174.2 (61.6), 173.5 (62.1), 172.3 (60.9), 172.2 (61.9), 171.5 (59.4).

Addition of bromide (one molar equivalent) to $[Rh_2Br_8(CO)_2]^{2-}$ results in a slow reaction, and the appearance only of a doublet at 178.2 ppm (^1J(Rh–CO) 55.0 Hz); no other new resonances appeared on addition of a large excess of bromide. We therefore attribute the observed doublet to $[RhBr_5(CO)]^{2-}$ (Table 2), and we found no evidence for the presence of the mono-bromo bridged dimer, $[Rh_2Br_9(CO)_2]^{3-}$. Addition of an excess of methanol to a solution of $(NBu_4)_2[Rh_2Br_8(CO)_2]$ in dichloromethane resulted in the disappearance of the intense doublet at 174.9 ppm, and the appearance of two new resonances, at 175.2 and 175.8 ppm (with ^1J(Rh–CO) 58.4 and 58.2) in the ratio 30:1, the stronger resonance being assigned to *trans*-$[RhBr_4(MeOH)(CO)]^-$ (Table 2); the minor species could be due to either *cis*-$[RhBr_4(MeOH)(CO)]^-$, or (more probably) $[Rh_2Br_6(MeOH)_2(CO)_2]$ with methanol *trans* to CO, analogous to the structure found for **VII**.

Addition of chlorine to a solution of $[RhCl_2(CO)_2]^-$ in dichloromethane gave only *cis*-$[RhCl_4(CO)_2]^-$, and there was no evidence for isomerization with time. In the presence of a slight excess (*ca.* 30%) of chlorine this solution slowly loses CO to give $[Rh_2Cl_8(CO)_2]^{2-}$ and, monitoring of the IR spectrum on bubbling CO through this solution showed that the reverse reaction occurred cleanly, with eventual reformation of $[RhCl_2(CO)_2]^-$. The ^{13}C NMR spectrum of $[Rh_2Cl_8(CO)_2]^{2-}$ formed from the above transformation in CH_2Cl_2, consists of an intense doublet at 170.0 ppm (with ^1J(Rh–CO) 61.3 Hz) together with five minor doublets—172.1 (53.8), 171.6 (54.3), 171.5 (62.2), 171.1 (56.5), 170.1 (61.3). Since methanol cannot be associated with this sample, the above ^{13}C NMR spectrum is entirely consistent with the presence of all five isomers, **I** to **V**.

The progressive addition of incremental amounts of chloride to $(NBu_4)_2[Rh_2Cl_8(CO)_2]$ in dichloromethane is entirely consistent with the progressive formation of $[Rh_2Cl_9(CO)_2]^{3-}$ followed by $[RhCl_5(CO)]^{2-}$ (see Table 2). However, we have no evidence in the chlorocarbonyl rhodium(III) series for the formation of methanol-solvated complexes.

3. Experimental section

NMR spectra were obtained with the following spectrometers: ^{13}C, Bruker WM 200 and AMX 400; ^{103}Rh, Bruker WH 360 and AMX 400; ^{13}C-{^{103}Rh}, JEOL PS-100 and Bruker WM 200 as described previously [10]. $\delta(^{13}C)$ is referenced to external TMS and $\delta(^{103}Rh)$ is referenced to 3.16 MHz at such a magnetic field that the protons in TMS resonate at exactly 100 MHz. IR spectra were measured as solutions in cells containing CaF_2 windows on either a Perkin Elmer 683 or 1720-X FT spectrometer on nonenriched complexes. Simultaneous reactions were carried out on complexes which had been enriched with ^{13}CO (*ca.* 30%) using standard vacuum line techniques; the most convenient precursor for measurements requiring ^{13}CO-enrichment was $[RhX_2(CO)_2]^-$. Enriched samples were used for ^{13}C and ^{13}C-{^{103}Rh} NMR measurements, and the analogous unenriched sample for direct ^{103}Rh NMR and IR measurements. Accurate transfer of chlorine and bromine to the reaction vessel/NMR tube was made on a vacuum line.

$(NR_4)[RhX_2(CO)_2]$ (R = Bu, hex; X = Cl, Br, I). These were prepared by a procedure similar to that described by Vallarino [1].

$(NR_4)[RhX_4(CO)_2]$ (R = Bu, hex; X = Cl, Br, I). These were prepared by addition of the appropriate halogen (1.3 mmol) to a dichloromethane solution of the corresponding halo complex, $(NR_4)[RhX_2(CO)]$ (1 mmol). IR spectra showed that the oxidative-addition was instantaneous, and in the case of $(NBu_4)[RhI_4(CO)_2]$ it was possible to isolate black crystals of the product from dichloromethane solution in 77% yield. (Analysis found: C, 23.78; H, 3.99; N, 1.54. $C_{18}H_{36}I_4NO_2Rh$ calc: C, 23.75, H, 3.99; N 1.54%).

$(NR_4)_2[Rh_2X_8(CO)_2]$ (R = Bu, hex; X = Cl, Br, I). For X = Br, I, these were prepared by addition of methanol to the above solution of $(NR_4)_2[Rh_2X_8(CO)_8]$ followed by refluxing for 10 min. Evaporation of the solvent gave a red (X = Br) or black (X = I) oil, which was dried under high vacuum for 2 h, redissolved in CH_2Cl_2, and characterized by IR and NMR spectroscopy. For X = Cl, the solution of $(NBu_4)[RhCl_4(CO)_2]$ in dichloromethane containing an excess of Cl_2, was repeatedly (*ca.* × 5) evaporated to dryness and redissolved in CH_2Cl_2 until the IR spectrum consisted of only a single band, at 2115 cm^{-1}, arising from the $(NBu_4)_2[Rh_2X_8(CO)_2]$ formed.

$(NR_4)_2[RhX_5(CO)]$ (R = Bu, hex; X = Cl, Br, I). Monitoring of the IR and NMR spectra of a dichloromethane solution of $(NR_4)_2[Rh_2X_8(CO)_2]$ during incremental additions of $(NR_4)X$ provided spectroscopic evidence for the stepwise formation of $[Rh_2X_9(CO)_2]^{3-}$ (X = Cl, I) and $[RhX_5(CO)]^{2-}$ (X = Cl, Br, I).

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NMR measurements, and also for financial support to CJ.

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