The Solution Behaviour of $[Rh_2(COMe)_2(CO)_2I_6]^{2-}$, its Reactions with CO, Pyridine, and Methanol, and the *X*-Ray Structure of $[AsPh_4][Rh(COMe)(CO)(NC_5H_5)I_3]$†

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It has been shown that the ion $[Rh_2(COMe)_2(CO)_2I_6]^{2-}$ in CD_2Cl_2 consists of at least six species. However, in methanol it is probably present as $[Rh(COMe)(CO)(MeOH)I_3]^-$. The nature of these species is discussed. Carbon monoxide reacts reversibly with this compound to give *mer-trans*-$[Rh(COMe)(CO)_2I_3]^{2-}$. The *trans* arrangement of the carbonyl ligands has been demonstrated by ^{13}CO–^{13}CO coupling in an enriched sample at −130 °C, when rotation about the Rh–COMe bond is slow. The lack of carbonyl scrambling in $[Rh_2(^{13}COMe)_2(^{12}CO)_2I_6]^{2-}$ demonstrates the irreversibility of its formation from $[RhMe(CO)_2I_3]^-$. Treatment of $[Rh_2(COMe)_2(CO)_2I_6]^{2-}$ with pyridine generates a species, probably $[I_3(OC)(MeCO)Rh(\mu\text{-}I)Rh(COMe)(CO)(NC_5H_5)I_2]^{2-}$, on slow addition and $[AsPh_4][Rh(COMe)(CO)(NC_5H_5)I_3]$ on rapid addition. The latter compound was characterised by *X*-ray crystallography.

The rhodium/iodine-catalysed carbonylation of methanol is now the industrially preferred process for acetic acid manufacture. Despite the importance of this process, little work has been done on the mechanism since the pioneering work of Forster.[1] It is well established that the catalyst is $[Rh(CO)_2I_2]^-$. When this compound is allowed to react with methyl iodide, then $[NMe_3Ph]_2[Rh_2(COMe)_2(CO)_2I_6]$ can be isolated. This compound was characterised by *X*-ray crystallography as (**1**).[2] It is dangerous to assume that in a labile system the species isolated from a solution fully characterises the species present in that solution. A preliminary i.r. investigation in CH_2Cl_2 had shown two acetyl CO stretches, indicating the presence of more than one species in solution.[3] The catalytic process is carried out in methanol, where solvated species could be present. It is believed that the next step of the catalytic cycle is the reaction with carbon monoxide to give $[Rh(COMe)(CO)_2I_3]^-$, but the stereochemistry of this material was not fully established due to its instability.[1] We have therefore carried out a detailed ^1H and ^{13}C n.m.r. investigation of the nature of these species. A preliminary report of the nature of $[Rh(COMe)(CO)_2I_3]^-$ and the lack of carbonyl scrambling in $[Rh_2(^{13}COMe)_2(^{12}CO)_2I_6]^{2-}$ has appeared.[4]

Experimental

The n.m.r. spectra were recorded on JEOL PFT-100, Bruker WP80-SY, AM 250, and WH 400 spectrometers, i.r. spectra on a Perkin-Elmer 257 spectrometer.

The compounds $[Rh_2(CO)_4Cl_2]$, $[Rh_2(CO)_4I_2]$, and $[AsPh_4]_2[Rh_2(COMe)_2(CO)_2I_6]$ were prepared according to literature methods.[5–8] 90% Enriched ^{13}CO and $^{13}CH_3I$ were purchased from Amersham International.

Crystal Data for $[AsPh_4][Rh(COMe)(CO)(NC_5H_5)I_3]\cdot C_6H_5Me$.—$C_{39}H_{36}AsI_3NO_2Rh$, $M = 1\,109.26$, crystallises from toluene–diethyl ether as purple needles, crystal dimensions $0.088 \times 0.150 \times 0.454$ mm, triclinic, $a = 11.17(3)$, $b = 11.58(4)$, $c = 15.87(4)$ Å, $\alpha = 103.72(5)$, $\beta = 98.34(11)$, $\gamma = 95.11(27)°$, $U = 1\,956(9)$ Å^3, $Z = 2$, $D_c = 1.883$ g cm^{-3}, space group $P\bar{1}$ (C_i, no. 2), Mo-K_α radiation ($\lambda = 0.710\,69$ Å), μ(Mo-K_α) = 36.43 cm^{-1}, $F(000) = 1\,060$.

Three-dimensional *X*-ray diffraction data were collected in the range $6.5 < 2\theta < 50°$ on a Stoe Stadi-2 diffractometer by the omega-scan method. The 3 184 independent reflections for which $I > 3.0\sigma(I)$ were corrected for Lorentz, polarisation and absorption effects. The structure was solved by standard Patterson and Fourier-transform techniques and refined by block-diagonal least-squares methods. Hydrogen atoms were detected and placed at calculated positions [C–H 0.97 Å, C–C–H(methyl) 112°]; their contributions were included in the structure-factor calculations ($B = 5.0$ Å^2) but no refinement of positional parameters was permitted. Refinement converged at R 0.0438 with allowance for anisotropic thermal motion of all non-hydrogen atoms and for the anomalous scattering of rhodium, iodine, and arsenic. Table 1 lists the atomic positional parameters with estimated standard deviations. Scattering factors were taken from the literature;[9] unit weights were used throughout the refinement. The computer programs used form part of the Sheffield *X*-ray system.

[^{13}C]*Tetracarbonyldichlorodirhodium*(I), $[Rh_2(^{13}CO)_4Cl_2]$.—The compound $[Rh_2(CO)_4Cl_2]$ (100 mg, 0.26 mmol) was dissolved in benzene (10 cm^3) and surface stirred under an atmosphere of ^{13}CO for *ca.* 8 h. The solution was then evaporated to dryness to yield orange crystals of $[Rh_2(CO)_4Cl_2]$ (90 mg, 0.23 mmol, 90%; *ca.* 80% ^{13}CO). I.r. (CH_2Cl_2): ν(CO) 2 085m, 2 048s, 2 004s, and 1 991s cm^{-1}. ^{13}C N.m.r. (CD_2Cl_2): δ 178.2 p.p.m., $^1J(^{103}Rh^{13}C) = 76$ Hz.

[^{13}C]*Tetracarbonyldi-iododirhodium*(I), $[Rh_2(^{13}CO)_4I_2]$.—The compound $[Rh_2(CO)_4I_2]$ (100 mg, 0.17 mmol) was dissolved in benzene (10 cm^3) and surface stirred under an atmosphere of ^{13}CO for *ca.* 8 h. The solution was then evaporated to dryness to yield dark orange crystals of $[Rh_2(^{13}CO)_4I_2]$ (88 mg, 0.15 mmol, 88%; *ca.* 80% ^{13}CO). I.r. (CH_2Cl_2): ν(CO) 2 093s, 2 081s, 2 069s, 2 025s, 1 997s, and 1 983 (sh) cm^{-1}. ^{13}C N.m.r. (CD_2Cl_2): δ 179.9 p.p.m., $^1J(^{103}Rh^{13}C) = 75$ Hz.

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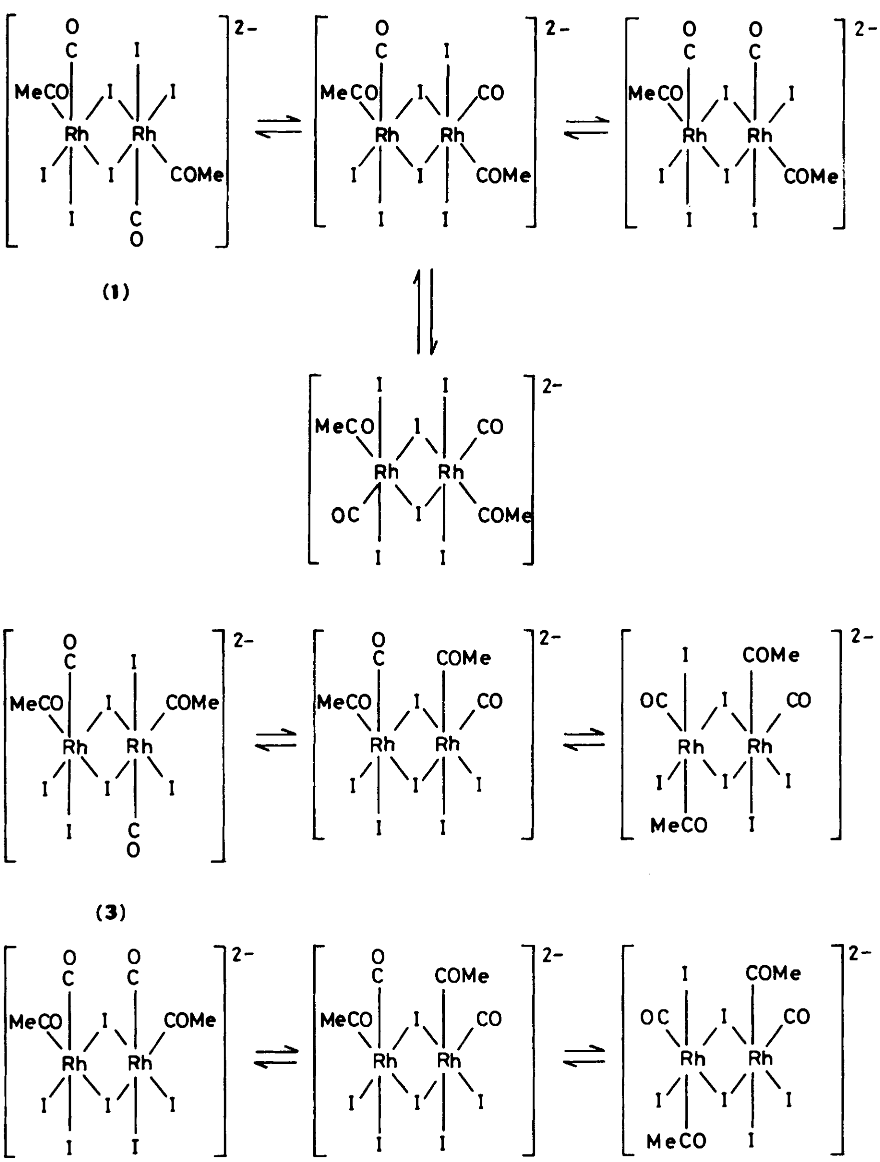
† Tetraphenylarsonium acetylcarbonyltri-iodo(pyridine)rhodate(III).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Non-S.I. unit employed: cal = 4.184 J.



(1)

(3)

(4)

Scheme 1. Proposed equilibria for $[Rh_2(COMe)_2(CO)_2I_6]^{2-}$ in solution

Tetraphenylarsonium Di[1-^{13}C]*acetyl*[^{13}C]*dicarbonyldi-μ-iodo-tetraiododirhodate*(III), $[AsPh_4]_2[Rh_2(^{13}COMe)_2(^{13}CO)_2I_6]$.—The compound $[Rh_2(^{13}CO)_4Cl_2]$ (64 mg, 0.16 mmol), $AsPh_4Cl$ (134 mg, 0.32 mmol), and LiI (0.43 g, 3.2 mmol) were stirred in nitromethane (2 cm^3) and methyl iodide (2 cm^3) for 40 min at 40 °C. The solution was then evaporated to dryness and the residue dissolved in dichloromethane (2 cm^3). This solution was then filtered through cellulose under vacuum and washed with more dichloromethane. Evaporation to dryness yielded $[AsPh_4]_2[Rh_2(^{13}COMe)_2(^{13}CO)_2I_6]$ (225 mg, 0.12 mmol, 75%) which was dried *in vacuo*. I.r. (CH_2Cl_2): ν(CO) 2 065m, 2 020s, 1 735vw, and 1 700m cm^{-1}.

Tetraphenylarsonium Di[1,2-$^{13}C_2$]*acetyl*[^{13}C]*dicarbonyldi-μ-iodo-tetraiododirhodate*(III), $[AsPh_4]_2[Rh_2(^{13}CO^{13}CH_3)_2(^{13}CO)_2I_6]$.—The compounds $[Rh_2(^{13}CO)_4I_2]$ (60 mg, 0.104 mmol) and $AsPh_4I$ (106 mg, 0.208 mmol) were mixed and cooled in liquid N_2. [^{13}C]Methyl iodide (1 g, 7 mmol) was distilled onto the mixture which was then stirred at room temperature for 1 h. The unreacted $^{13}CH_3I$ was removed under vacuum. The solid was recrystallised from dichloromethane (*ca.* 2 cm^3) and light petroleum (b.p. 40—60 °C, *ca.* 1 cm^3) to yield $[AsPh_4]_2[Rh_2(^{13}CO^{13}CH_3)_2(^{13}CO)_2I_6]$ (132 mg, 0.07 mmol, 68%) as a maroon powder.

Tetraphenylarsonium Acetylcarbonyltri-iodo(*pyridine*)*rhodate*(III), $[AsPh_4][Rh(COMe)(CO)(NC_5H_5)I_3]$.—Pyridine (4.4 μl, 4.2 mg, 0.054 mmol) was added to a solution of $[AsPh_4]_2[Rh_2(COMe)_2(CO)_2I_6]$ (50 mg, 0.027 mmol) in dichloromethane (2.0 cm^3) with rapid stirring, which was maintained for 30 min. The solution was then evaporated to dryness *in vacuo*. The resulting oil was dissolved in a minimum volume of toluene–dichloromethane (3:1 v/v) and left to

Table 1. Atomic positional parameters with estimated standard deviations (e.s.d.s) for $[AsPh_4][Rh(COMe)(CO)(NC_5H_5)I_3]\cdot C_6H_5Me$

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
I(1)	−0.042 55(10)	−0.192 08(9)	0.173 77(7)
I(2)	−0.090 27(12)	0.205 61(10)	0.408 40(7)
I(3)	−0.337 27(10)	−0.057 33(11)	0.242 49(8)
Rh	−0.078 92(11)	0.009 42(10)	0.284 01(7)
As	−0.592 51(13)	−0.664 39(13)	0.299 71(9)
O(1)	−0.103 0(12)	−0.134 9(12)	0.412 2(8)
O(2)	0.157 3(10)	0.113 8(12)	0.287 3(8)
N	−0.085 4(10)	0.108 3(9)	0.187 1(7)
C(1)	−0.093 9(16)	−0.077 2(14)	0.365 7(10)
C(2)	0.114 4(12)	0.048 4(11)	0.321 5(9)
C(3)	0.172 0(16)	−0.008 5(17)	0.377 9(13)
C(4)	−0.171 4(15)	0.182 2(13)	0.180 5(9)
C(5)	−0.181 5(17)	0.242 3(16)	0.117 2(12)
C(6)	−0.105 0(19)	0.230 9(17)	0.057 9(11)
C(7)	−0.018 6(17)	0.157 3(15)	0.062 5(11)
C(8)	−0.009 9(13)	0.098 3(13)	0.127 5(9)
C(9)	−0.717 7(14)	−0.567 0(12)	0.317 3(9)
C(10)	−0.690 4(13)	−0.453 6(14)	0.377 1(10)
C(11)	−0.780 7(14)	−0.384 4(14)	0.393 6(11)
C(12)	−0.897 0(15)	−0.423 8(15)	0.352 0(13)
C(13)	−0.924 6(15)	−0.534 3(16)	0.296 4(13)
C(14)	−0.837 6(13)	−0.607 7(14)	0.274 5(10)
C(15)	−0.447 1(12)	−0.558 9(12)	0.301 8(9)
C(16)	−0.457 0(14)	−0.481 9(14)	0.248 0(10)
C(17)	−0.354 5(16)	−0.407 6(12)	0.245 9(10)
C(18)	−0.245 5(15)	−0.416 9(15)	0.293 0(12)
C(19)	−0.234 7(15)	−0.494 8(16)	0.345 1(14)
C(20)	−0.339 4(16)	−0.568 3(15)	0.351 0(12)
C(21)	−0.563 3(12)	−0.737 7(13)	0.394 8(9)
C(22)	−0.473 4(13)	−0.809 9(13)	0.399 7(9)
C(23)	−0.451 5(15)	−0.860 5(14)	0.469 6(11)
C(24)	−0.518 5(15)	−0.835 8(14)	0.536 1(11)
C(25)	−0.609 9(16)	−0.766 6(14)	0.532 0(9)
C(26)	−0.634 0(14)	−0.716 8(13)	0.460 0(9)
C(27)	−0.628 7(12)	−0.775 5(12)	0.186 1(8)
C(28)	−0.628 1(16)	−0.894 7(14)	0.175 8(10)
C(29)	−0.643 1(21)	−0.974 2(14)	0.094 6(11)
C(30)	−0.667 7(18)	−0.929 7(16)	0.023 3(10)
C(31)	−0.674 1(16)	−0.813 4(18)	0.030 5(10)
C(32)	−0.656 9(16)	−0.734 7(13)	0.110 0(9)
C(33)	−0.610 8(16)	−0.335 2(17)	0.076 1(12)
C(34)	−0.634 9(20)	−0.422 6(18)	0.000 5(13)
C(35)	−0.731 1(21)	−0.506 0(20)	−0.022 1(14)
C(36)	−0.812 7(23)	−0.504 4(16)	0.038 0(15)
C(37)	−0.794 7(19)	−0.414 7(18)	0.113 4(15)
C(38)	−0.694 8(18)	−0.330 3(16)	0.134 5(11)
C(39)	−0.675 6(23)	−0.232 7(25)	0.218 2(16)

The atoms As(1), C(9)—C(14), C(15)–C(20), C(21)–C(26), and C(27)–C(32) comprise the tetraphenylarsonium cation, C(33)—C(39) the toluene molecule of solvation.

crystallise at −20 °C to yield maroon crystals of $[AsPh_4][Rh(COMe)(CO)(NC_5H_5)I_3]$ (22 mg, 0.022 mmol, 41%), m.p. 116—119 °C (decomposes) (Found: C, 41.25; H, 3.25; I, 34.3; N, 1.15. Calc. for $C_{32}H_{28}AsI_3NO_2Rh$: C, 41.1; H, 3.25; I, 34.35; N, 1.25%). I.r. (CH_2Cl_2): ν(CO) 2 060s and 1 709m cm^{-1}.

Tetraphenylarsonium Acetyldicarbonyltri-iodorhodate(III), $[AsPh_4][Rh(COMe)(CO)_2I_3]$.—A stream of CO was bubbled through a solution of $[AsPh_4]_2[Rh_2(COMe)_2(CO)_2I_6]$ (150 mg, 0.08 mmol) in dichloromethane (5 cm^3) for 30 s. Light petroleum (b.p. 40—60 °C, *ca.* 2 cm^3) was added to the solution until it became cloudy and then CO was passed through the solution for a further 30 s. Standing at −20 °C afforded bright orange crystals of $[AsPh_4][Rh(COMe)(CO)_2I_3]$ (120 mg, 0.13 mmol, 80%) which were filtered off and dried *in vacuo* (Found: C, 34.9; H, 2.70; I, 41.35. Calc. for $C_{28}H_{23}AsI_3O_3Rh$: C, 34.8; H, 2.40; I, 39.45%). I.r. (CH_2Cl_2); ν(CO) 2 085s and 1 703m cm^{-1}.

Results

The i.r. spectrum of $[AsPh_4]_2[Rh_2(COMe)_2(CO)_2I_6]$ in CH_2Cl_2 shows a broad carbonyl stretch at 2 065 cm^{-1}, while the acyl stretch consists of a strong signal at 1 734 cm^{-1} with a shoulder at 1 712 cm^{-1}, see Figure 1. The intensity ratio of the shoulder to the main acetyl signal was batch independent. The doubling of the acetyl signal also occurs in the ^1H n.m.r. spectrum in CD_2Cl_2, with signals at δ 3.08 and 3.10. Magnetisation-transfer measurements showed that two species were interconverting slowly at room temperature with a rate of *ca.* 1 s^{-1}, corresponding to $\Delta G^‡ = 17$ kcal mol^{-1}.

The multiplicity is best observed in the ^{13}C n.m.r. spectrum of $[Rh_2(^{13}COMe)_2(^{13}CO)_2I_6]^{2-}$, see Figure 2. The ^{13}C n.m.r. spectrum at room temperature shows two carbonyl signals at δ 181.06 p.p.m., $^1J(^{103}Rh^{13}C) = 71$ Hz and δ 180.83 p.p.m., $^1J(^{103}Rh^{13}C) = 67$ Hz, with an impurity signal due to rhodium(I) at δ 182.71 p.p.m., $^1J(^{103}Rh^{13}C) = 72$ Hz, and two poorly resolved acetyl carbonyl signals at δ 202.44 p.p.m., which is too broad to show ^{103}Rh coupling, and δ 210.16 p.p.m., $^1J(^{103}Rh^{13}C) = 18$ Hz. In view of the broadness of the acetyl carbonyl signals, it is probable that a dynamic process is occurring. On cooling to −60 °C, one set of signals splits into four pairs, with the carbonyl resonances at δ 180.55 [$^1J(^{103}Rh^{13}C) = 74$], 180.68 [$^1J(^{103}Rh^{13}C) = 67$], 181.45 [$^1J(^{103}Rh^{13}C) = 71$], and 184.15 p.p.m. [$^1J(^{103}Rh^{13}C) = 66$ Hz], and the acetyl carbonyl at δ 211.06 [$^1J(^{103}Rh^{13}C) = 21$], 211.89 [$^1J(^{103}Rh^{13}C) = 23$], 212.12 [$^1J(^{103}Rh^{13}C) = 23$], and 227.44 p.p.m. [$^1J(^{103}Rh^{13}C) = 18$ Hz]. The other set of signals broadens considerably, with the acetyl carbonyl signal still being at δ 207.5 p.p.m., but the carbonyl is obscured by the other carbonyl resonances. On further cooling to −90 °C, the broad

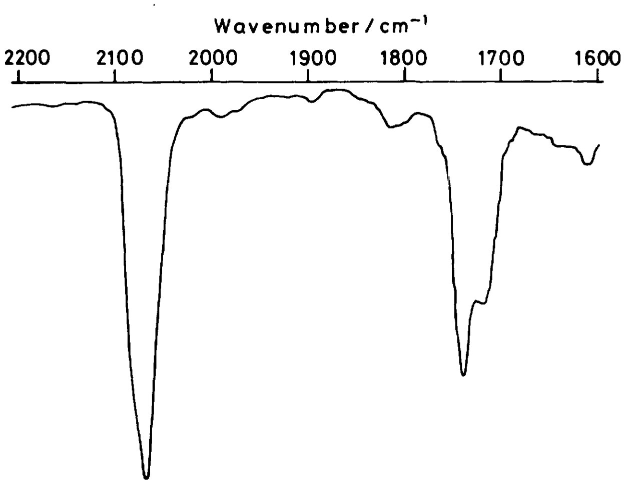


Figure 1. Partial i.r. spectrum of $[AsPh_4]_2[Rh_2(COMe)_2(CO)_2I_6]$ in CH_2Cl_2 (2 200—1 600 cm^{-1})

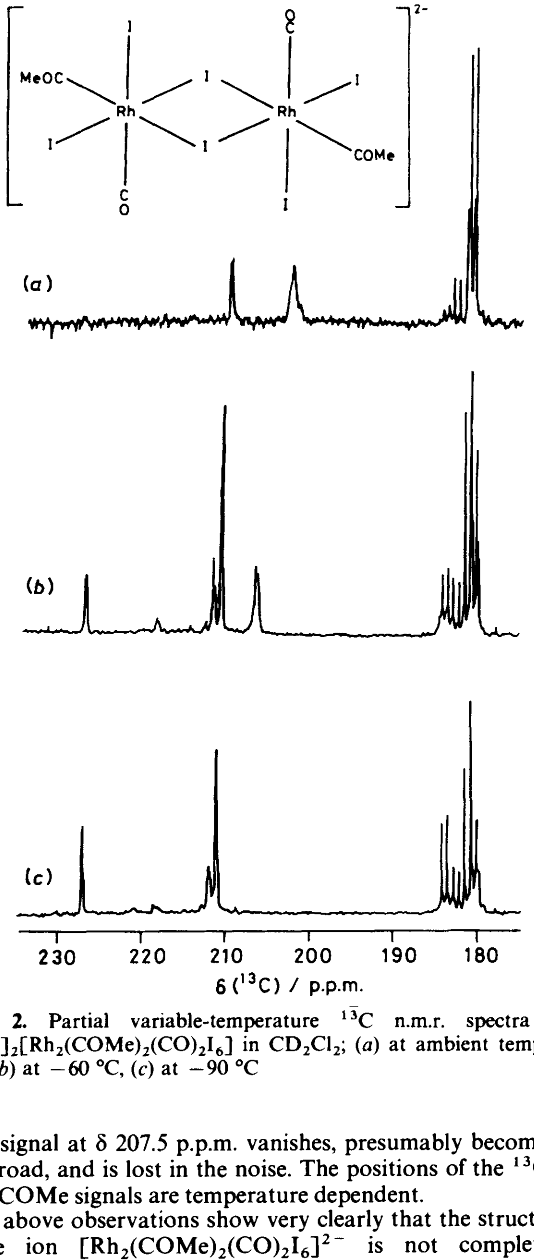


Figure 2. Partial variable-temperature ^{13}C n.m.r. spectra of $[AsPh_4]_2[Rh_2(COMe)_2(CO)_2I_6]$ in CD_2Cl_2; (*a*) at ambient temperature, (*b*) at −60 °C, (*c*) at −90 °C

Table 2. Selected bond lengths (Å) and angles (°) with e.s.d.s for $[AsPh_4][Rh(COMe)(CO)(NC_5H_5)I_3]{\cdot}C_6H_5Me$

Rh–I(1)	2.666(8)	C(2)–C(3)	1.356(24)
Rh–I(2)	2.659(8)	As–C(9)	1.884(15)
Rh–I(3)	2.857(8)	As–C(15)	1.934(13)
Rh–N	2.121(11)	As–C(21)	1.901(14)
Rh–C(1)	1.834(17)	As–C(27)	1.915(13)
Rh–C(2)	2.132(13)	O(2) ··· N(1)	2.924(17)
O(1)–C(1)	1.116(22)	O(2) ··· C(8)	2.880(20)
O(2)–C(2)	1.141(18)	O(2) ··· H(8)	2.49
I(1)–Rh–I(2)	172.4(2)	I(3)–Rh–C(2)	175.2(4)
I(1)–Rh–I(3)	91.2(2)	N–Rh–C(1)	172.9(6)
I(1)–Rh–N	93.8(4)	N–Rh–C(2)	93.5(5)
I(1)–Rh–C(1)	87.8(5)	C(1)–Rh–C(2)	93.4(6)
I(1)–Rh–C(2)	87.5(5)	Rh–C(1)–O(1)	176.5(16)
I(2)–Rh–I(3)	94.4(2)	Rh–C(2)–O(2)	113.5(11)
I(2)–Rh–N	91.1(4)	Rh–C(2)–C(3)	118.6(12)
I(2)–Rh–C(1)	88.1(5)	O(2)–C(2)–C(3)	127.9(15)
I(2)–Rh–C(2)	86.4(5)	Rh–N–C(4)	120.2(9)
I(3)–Rh–N	91.2(4)	Rh–N–C(8)	123.2(9)
I(3)–Rh–C(1)	81.9(5)		

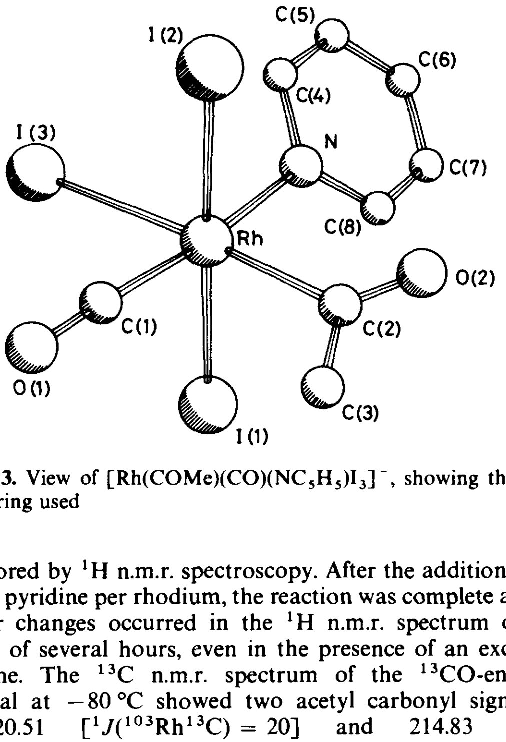


Figure 3. View of $[Rh(COMe)(CO)(NC_5H_5)I_3]^-$, showing the atom numbering used

acetyl signal at δ 207.5 p.p.m. vanishes, presumably becoming very broad, and is lost in the noise. The positions of the ^{13}CO and ^{13}COMe signals are temperature dependent.

The above observations show very clearly that the structure of the ion $[Rh_2(COMe)_2(CO)_2I_6]^{2-}$ is not completely represented by the crystal structure.[2] There must be two species present at room temperature which interconvert, showing that they are very closely related. Each of these species must be a mixture of isomers. One gives four separate signals on cooling, while the signals of the other broaden prior to splitting into two or more separate sets of signals at very low temperature. In view of the temperature dependence of the chemical shifts, it is probable that other equilibria are occurring. Consequently $[Rh_2(COMe)_2(CO)_2I_6]^{2-}$ is not a single species in solution but a mixture of at least six species. Unfortunately, these experiments do not give sufficient information to characterise these species. Further reactions were performed in order to throw more light on the nature of these species.

When 1 molar equivalent of pyridine per rhodium is added to $[AsPh_4]_2[Rh_2(COMe)_2(CO)_2I_6]$ in CH_2Cl_2, then $[AsPh_4][Rh(COMe)(CO)(NC_5H_5)I_3]$ is isolated, and its structure was established by *X*-ray crystallography (see below). In contrast, when the reaction is performed as a slow titration, adding 0.05 molar equivalent aliquots, in an n.m.r. tube, different results are produced. The course of the reaction was monitored by ^{1}H n.m.r. spectroscopy. After the addition of 0.5 mol of pyridine per rhodium, the reaction was complete and no further changes occurred in the ^{1}H n.m.r. spectrum over a period of several hours, even in the presence of an excess of pyridine. The ^{13}C n.m.r. spectrum of the ^{13}CO-enriched material at −80 °C showed two acetyl carbonyl signals at δ 220.51 [$^1J(^{103}Rh^{13}C) = 20$] and 214.83 p.p.m. [$^1J(^{103}Rh^{13}C) = 18$ Hz], and two carbonyl signals at δ 185.79 [$^1J(^{103}Rh^{13}C) = 57$] and 183.28 p.p.m. [$^1J(^{103}Rh^{13}C) = 58$ Hz]. At room temperature a dynamic process caused these pairs of signals to average to give one acetyl carbonyl signal at δ 219.65 [$^1J(^{103}Rh^{13}C) = 20$] and one carbonyl signal at 185.89 p.p.m. [$^1J(^{103}Rh^{13}C) = 57$]. Attempts to isolate this species only yielded the monomer $[AsPh_4][Rh(COMe)(CO)(NC_5H_5)I_3]$. The species formed with one pyridine per two rhodium atoms is presumably $[I_3(OC)(MeCO)Rh(\mu\text{-}I)Rh(COMe)(CO)(NC_5H_5)I_2]^{2-}$ with a single iodide bridge. The stereochemistry at each rhodium atom is unknown.

The structure of the anion $[Rh(COMe)(CO)(NC_5H_5)I_3]^-$ is shown in Figure 3. The co-ordination around the rhodium is a distorted octahedron with a *mer* arrangement of iodides and with pyridine *trans* to the carbonyl group. Also present in the unit cell is a tetrahedral tetraphenylarsonium cation and one

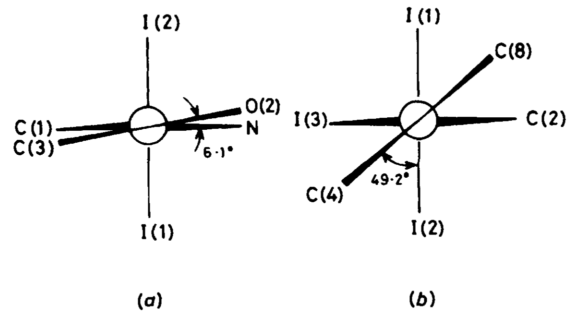


Figure 4. Torsion angles and orientations in $[Rh(COMe)(CO)(NC_5H_5)I_3]^-$: (*a*) along the Rh–C(2) bond; (*b*) projection along the Rh–N bond

molecule of toluene per anion. Selected bond lengths and angles are given in Table 2.

The plane of the acetyl group lies approximately parallel to the equatorial plane which contains itself, the carbonyl and pyridine ligands, and I(3). The torsion angle O(2)–C(2)–Rh–N is only +5.5° [see Figure 4(*a*)], although, since the rhodium atom lies 0.10 Å out of the acetyl plane, this torsion angle does not merely represent a twist of the ligand about the Rh–C bond. This approximate coplanarity may either be due to steric repulsion by the iodide ligands I(1) and I(2) or to an electronic interaction. The pyridine is substantially twisted [approximately 45°, see Figure 4(*b*)] with respect to the same equatorial plane with a similar deviation of the rhodium atom from the mean plane: the torsion angle C(2)–Rh–N–C(8) is +47.0°. The contact between O(2) and the pyridyl ligand, particularly O(2) ··· C(8), is considerably less than the sum of the van der Waals radii and the directions of bend and twist of these two ligands are such as to maximise this distance. The site of the acetyl group with two *cis* and one *trans* iodides is best satisfied by a minimal out-of-equatorial-plane displacement. However, the pyridine is *cis* to all three iodides as well as to an in-plane-bulky acetyl, and a 45° twist probably represents an optimum compromise in a sterically congested environment.

The rhodium–iodine bond *trans* to the acetyl ligand is 0.2 Å longer than those to the mutually *trans* pair of iodides. The pyridine ligand is planar; the carbonyl co-ordination is essentially linear. The geometries of the cation and solvent are unexceptionable. There are no significant intermolecular contacts.

When $[Rh_2(^{13}COMe)_2(^{13}CO)_2I_6]^{2-}$ is treated with ^{13}CO, $[Rh(^{13}COMe)(^{13}CO)_2I_3]^-$ is generated, as would be expected on the basis of Forster's work.[1] The ^{13}C n.m.r. spectrum in CD_2Cl_2 at −30 °C shows an acetyl carbonyl signal at δ 216.42 $[^1J(^{103}Rh^{13}C) = 18]$ and a carbonyl signal at 177.11 p.p.m. $[^1J(^{103}Rh^{13}C) = 54$ Hz]. On cooling to −95 °C, the $^{13}COMe$ signal remains sharp, but there is extreme broadening of the ^{13}CO signal. Addition of $CHFCl_2$ (1:1 v/v) permitted measurement of the spectrum at −130 °C, when two ^{13}CO and one acetyl signals are observed, see Figure 5(*a*). The two ^{13}CO signals are triplets due to an ABX pattern, X being ^{103}Rh. There is an underlying doublet, which is dominant when the solution is prepared from $[Rh_2(^{13}COMe)_2(^{13}CO)_2I_6]^{2-}$ and natural-abundance CO, see Figure 5(*b*). This removal of the triplet structure when the ^{13}CO enrichment is reduced clearly demonstrates that the extra coupling arises from $^2J(^{13}C^{13}C)$ = *ca.* 60 Hz. The full analysis of the spectrum gives the carbonyl signals at δ 177.79 $[^1J(^{103}Rh^{13}C) = 53]$ and 173.03 p.p.m. $[^1J(^{103}Rh^{13}C) = 53$ Hz]. The dynamic process giving rise to the two carbonyl signals is characterised by $\Delta G^\ddagger = 7.6$ kcal mol^{-1}.

The salt $[AsPh_4][Rh(COMe)(CO)_2I_3]$ can easily be isolated from dichloromethane and light petroleum as long orange needles, which are moderately stable at −20 °C in an atmosphere of CO. Attempts at determining the *X*-ray structure of this material failed. At room temperature the crystals decomposed rapidly in the *X*-ray beam, while on cooling to −150 °C the crystal became amorphous, possibly due to a phase change.

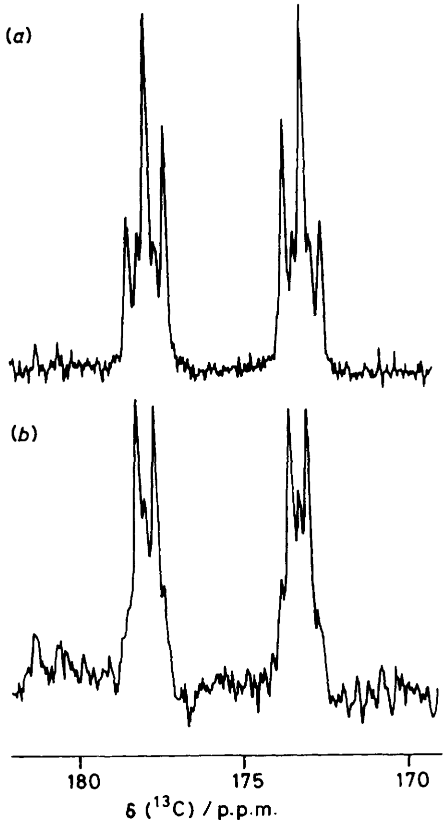
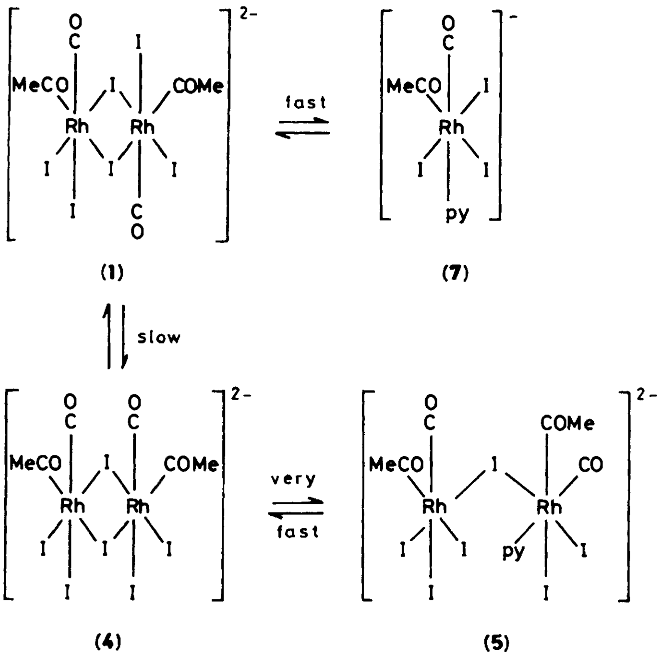


Figure 5. Partial ^{13}C n.m.r. spectrum of the reaction mixture of $[Rh_2(^{13}COMe)_2(^{13}CO)_2I_6]^{2-}$ with (*a*) ^{13}CO and (*b*) ^{12}CO in CD_2Cl_2–$CHFCl_2$

When a solution of $[Rh(COMe)(CO)_2I_3]^-$ in dichloromethane is purged with dinitrogen for *ca.* 3 h then $[Rh_2(COMe)_2(CO)_2I_6]^{2-}$ is regenerated. This provides a route to $[Rh_2(^{13}COMe)_2(^{12}CO)_2I_6]^{2-}$ from $[Rh_2(^{13}COMe)_2(^{13}CO)_2I_6]^{2-}$ and provides a method to investigate methyl migration between the acetyl and terminal carbonyl groups. As ^{13}C n.m.r. intensities are notoriously unreliable, in order to put the work on a sound basis, $[Rh_2(^{13}CO^{13}CH_3)_2(^{13}CO)_2I_6]^{2-}$ was synthesised. The ^{13}C n.m.r. spectrum shows a doublet for the $^{13}CH_3$ group at δ 46.07 p.p.m. $[^1J(^{13}C^{13}C) = 35$ Hz], with a singlet due to the $^{13}CH_3{}^{12}CO$ group. This ratio of the doublet to the singlet provides a reliable determination of the ^{13}CO content of the acyl group, as apart from a minor contribution from ^{13}C–^{13}C dipolar relaxation, the relaxation behaviour of both isotopomers will be identical. Repeated treatments of $[Rh_2(^{13}CO^{13}CH_3)_2(^{13}CO)_2I_6]^{2-}$ with CO and N_2 reduced the ^{13}CO content of the carbonyl group to *ca.* 20%, without affecting the ^{13}CO content of the acetyl group. This ratio did not change even on standing in solution for 7 d, even though considerable decomposition occurred during this time.

Due to its insolubility, it proved impossible to study $[AsPh_4]_2[Rh_2(COMe)_2(CO)_2I_6]$ in methanol. However, as methanol is the solvent used in the industrial process, it is important to characterise the species present. A solution of

$[AsPh_4]_2[Rh_2(^{13}COMe)_2(^{13}CO)_2I_6]$ in CD_2Cl_2 was titrated with methanol and monitored by ^{13}C n.m.r. spectroscopy. A new set of signals appeared at δ 183.1 p.p.m. [$^1J(^{103}Rh^{13}C) = 67$ Hz] for the carbonyl group and at 229.9 p.p.m. [$^1J(^{103}Rh^{13}C) = 17$ Hz] for the acetyl group. After the addition of 1 equivalent of methanol per rhodium all the starting dimer had been consumed, and only three new signals were detected. The addition of further methanol up to 2 molar equivalents produced no further change in the spectrum. Hence the species formed is $[Rh(COMe)(CO)(MeOH)I_3]^-$.

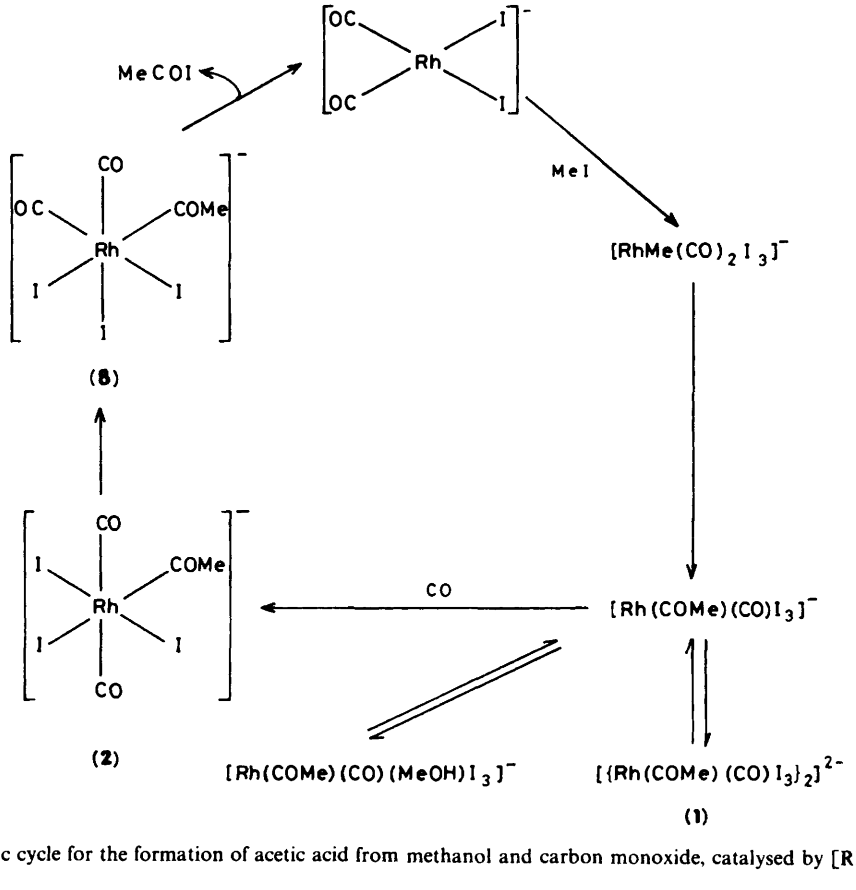


Scheme 2. The reaction between $[Rh_2(COMe)_2(CO)_2I_6]^{2-}$ and pyridine

Discussion

A number of *X*-ray structure determinations have been reported for rhodium acyl complexes.[2,10–21] The Rh–COMe bond length is relatively long, 2.132 Å, in $[Rh(COMe)(CO)(NC_5H_5)I_3]^-$, compared with most other rhodium acyl complexes, which generally have bond lengths around 2.00 Å. Even $[Rh_2(COMe)_2(CO)_2I_6]^{2-}$ has a Rh–COMe bond length of 2.062 Å. The long Rh–COMe bond must reflect a large *trans* influence of the terminal iodide, and is consistent with the ready loss of acetyl iodide in $[Rh(COMe)(CO)_2I_3]^-$. The Rh–CMe=O bond angle of 113.5° is approximately the same as that previously observed for $[Rh_2(COMe)_2(CO)_2I_6]^{2-}$, as are the Rh–I bond lengths for the iodide *trans* to iodide. The low Rh–CMe=O bond angle, coupled with the relatively high $\Delta G^\ddagger$ for acetyl rotation in $[Rh(COMe)(CO)_2I_3]^-$, raises the possibility of η^2-COMe bonding, but the relatively high values of ν(C=O) in these complexes makes this highly unlikely. The restricted rotation of the acetyl probably arises from predominantly steric effects, with the interaction between the acetyl and the iodide ligands inhibiting rotation.

The structure of the carbon monoxide adduct $[Rh(COMe)(CO)_2I_3]^-$ is proven unambiguously from the low-temperature ^{13}C n.m.r. spectrum. The observation of $^2J(^{13}C^{13}C) =$ *ca.* 60 Hz for the two carbonyl ligands is only consistent with them being mutually *trans*. It is well established that large coupling constants are found for rhodium(III) complexes when the



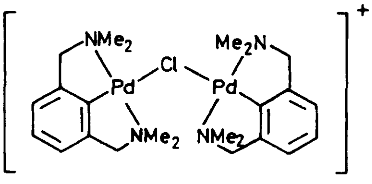
Scheme 3. Revised catalytic cycle for the formation of acetic acid from methanol and carbon monoxide, catalysed by $[Rh(CO)_2I_2]^-$

ligands are mutually *trans*, while small coupling constants are found for mutually *cis* ligands.[22] Hence the stereochemistry must be (**2**). The inequivalence of the carbonyl groups must arise from restricted rotation of the acetyl group. The acetyl group is trapped between the two large iodide ligands. Using the bond lengths derived for $[Rh(COMe)(CO)(NC_5H_5)I_3]^-$, simple rotation of the acetyl group would involve an overlap of the acetyl oxygen atom with the iodide ligand of 0.65 Å, based on van der Waals radii. It is therefore probable that the major cause of the restricted rotation is steric. This structure with *trans* carbonyl groups is consistent with the observation of only one strong v(CO) at 2 084 cm^{-1} with a very weak signal at 2 141 cm^{-1}.[1] This structure does not appear in the mechanistic schemes in the literature where the carbonyls are placed *cis*. The placement of the carbonyls *cis* is necessary to facilitate the elimination of acetyl iodide to give *cis*-$[Rh(CO)_2I_2]^-$ in the final step of the catalytic cycle. We have shown that when PMe_2Ph is used instead of carbon monoxide as the added ligand there is a sequence of reactions, giving initially ligand *trans* to acetyl, then *trans* to carbonyl as in (**2**), and finally *trans* to iodide.[23] It is therefore probable that (**2**) is detected because it cannot directly eliminate acetyl iodide, as the resulting complex would have the structure *trans*-$[Rh(CO)_2I_2]^-$. It can slowly isomerise to *fac*-$[Rh(COMe)(CO)_2I_3]^-$ which can then rapidly eliminate acetyl iodide. If this conclusion is correct, the kinetic investigations[24] on the decomposition of (**2**) have actually measured the rate of its isomerisation to *fac*-$[Rh(COMe)(CO)_2I_3]^-$.

The reversal of the reaction of $[Rh_2(COMe)_2(CO)_2I_6]^{2-}$ with CO to give (**2**) by the passage of dinitrogen clearly demonstrates the weakness of the Rh^{III}–CO bond in these complexes. However this reaction provides a facile synthesis of $[Rh_2(^{13}CO^{13}CH_3)_2(^{12}CO)_2I_6]^{2-}$. Even over a period of 7 d at room temperature there is no exchange between the carbonyl and acetyl CO groups. This observation is very surprising in view of the facile formation of rhodium methyl complexes from other rhodium acetyls.[10,14,18,20,24–29] In favourable cases the equilibrium has been investigated.[14] The dimer is very easily cleaved with PMe_2Ph even at −80 °C. Hence the bridge-opening reaction of $[Rh_2(COMe)_2(CO)_2I_6]^{2-}$ is facile.[23] Despite the easy formation of $[Rh(COMe)(CO)I_3]^-$, the rearrangement to $[RhMe(CO)_2I_3]^-$ equilibrating the carbonyl groups does not occur. The reverse reaction is believed to be a key step in the catalytic pathway.

Clearly from the observed temperature dependence of the ^{13}C n.m.r. spectrum, see Figure 2, the solution structure of $[Rh_2(COMe)_2(CO)_2I_6]^{2-}$ is complicated. As all the species present are interconverting, it can be assumed that they are all closely related to (**1**). There are three possible dynamic processes to explain temperature-dependent ^{13}C n.m.r. spectra: restricted rotation about the Rh–COMe bond, breakage of one iodide bridge, and breakage of both iodide bridges. Restricted rotation about the Rh–COMe bond is considered to be unlikely in view of the low activation energy determined for acetyl rotation in $[Rh(COMe)(CO)_2I_3]^-$. In $[Rh(COMe)(CO)_2I_3]^-$, the acetyl group is sandwiched between two large iodide atoms, which probably provide the steric barrier for acetyl rotation. In $[Rh_2(COMe)_2(CO)_2I_6]^{2-}$, the acetyl group is *cis* to three iodide atoms, providing a lower barrier to acetyl rotation. However the interconversion of rotamers may account for the temperature dependence of the ^{13}C chemical shifts. It is known that $[Rh_2(COMe)_2(CO)_2I_6]^{2-}$ reacts rapidly with tertiary phosphines,[23] pyridine, and CO at low temperature, implying that the iodide bridge is very labile. It is therefore proposed that the two species observed at room temperature are interconverting by cleavage of both iodide bridges, with $\Delta G^\ddagger = 17$ kcal mol^{-1}, while the low-temperature process involves cleavage of one iodide bridge. For the group of species that is static at −60 °C, $\Delta G^\ddagger = ca.$ 14 kcal mol^{-1}, while for the other group which is not frozen out $\Delta G^\ddagger$ must be less than 9 kcal mol^{-1}. Scheme 1 presents a possible group of interconverting isomers. It is proposed that the fast process involves the cleavage of the rhodium–iodine bond *trans* to acetyl or carbonyl. The slow interconversion of isomers at room temperature arises from cleavage of the rhodium–iodine bond *trans* to iodine. As the mechanism goes *via* five-co-ordinate intermediates, where a rapid Berry pseudo-rotation is plausible, many more isomers are possible. Indeed the interconversion of the two species observed at room temperature could involve a single bridge breaking, coupled with a Berry pseudo-rotation. The two species observed at room temperature are proposed to differ by isomerism about the bridge. Such isomerism is now well established.[30] There is one problem associated with Scheme 1. There should be three, not two, sets of averaged signals at room temperature. The sets based on (**3**) and (**4**) differ only in the relative axial orientation of the carbonyl groups. This may be insufficient to produce a measurable chemical shift difference, or the two sets may be interconverting by the Berry pseudo-rotation mechanism.

The reaction between $[Rh_2(COMe)_2(CO)_2I_6]^{2-}$ and pyridine to give $[I_3(OC)(MeCO)Rh(\mu\text{-}I)Rh(COMe)(CO)(NC_5H_5)I_2]^{2-}$ (**5**), is surprising. There are a few examples of a single iodide bridge in the literature. A similar species has been reported for (**6**), involving a chloride bridge.[31] The iodide bridge is very labile, preventing the isolation of (**5**). The formation of (**5**) with an iodide bridge when pyridine addition is slow, but of the monomer, (**7**), when the addition is fast can be rationalised using species (**1**) and (**3**),(**4**) from Scheme 2. In view of the *trans*-labilising effect of the acetyl group, it is improbable that a single iodide bridge which is *trans* to acetyl would be stable. A consistent interpretation is given by proposing a slow equilibrium observed for two species of $[Rh_2(COMe)_2(CO)_2I_6]^{2-}$ as given in Scheme 2. When pyridine is added rapidly to this mixture then both species react as there is insufficient time for the equilibrium to be established. When pyridine is added very slowly, then the most reactive species (**3**),(**4**), reacts quickly, but the equilibrium is re-established, allowing the production of a single product, see Scheme 2.



(**6**)

The mechanism of rhodium/iodide-catalysed methanol carbonylation in methanol can now be modified in the light of these investigations, see Scheme 3. The $[RhMe(CO)_2I_3]^-$ formed isomerises *irreversibly* to give $[Rh(COMe)(CO)(MeOH)I_3]^-$. The presence of methanol of co-ordination is probable from the reaction between $[Rh_2(COMe)_2(CO)_2I_6]^{2-}$ and methanol. As in many catalytic processes, the isolated species, $[Rh_2(COMe)_2(CO)_2I_6]^{2-}$, is not on the true catalytic cycle. Subsequent reaction with carbon monoxide gives *mer-trans*-$[Rh(COMe)(CO)_2I_3]^-$. As the elimination of acetyl iodide from this isomer would generate *trans*-$[Rh(CO)_2I_2]^-$, it is proposed that there is isomerisation to *mer-cis*-$[Rh(COMe)(CO)_2I_3]^-$ (**8**). Elimination of acetyl iodide then proceeds rapidly to complete the catalytic cycle.

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