The Solution Structure of $[Rh(COMe)(CO)_2I_3]^-$ and the Absence of Methyl Migration in $[Rh_2(COMe)_2(CO)_2I_6]^{2-}$

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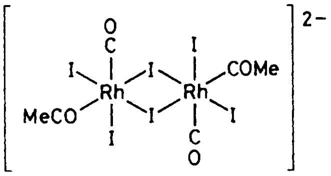
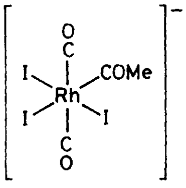
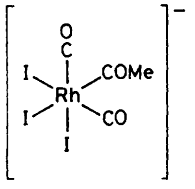
The observation of inequivalent CO groups at −130 °C for $[Rh(COMe)(CO)_2I_3]^-$ is due to restricted rotation about the Rh–COMe bond with $\Delta G^\ddagger$ 7.6 kcal mol^{-1},† $^2J(^{13}CO,^{13}CO)$ 59 Hz showing that the carbonyls are mutually *trans*; the lack of $^{13}COMe/^{12}CO$ exchange in $[Rh_2(^{13}CO^{13}CH_3)_2(^{12}CO)_2I_6]^{2-}$ demonstrates that its preparation from $[Rh(^{13}CH_3)(^{12}CO)(^{13}CO)I_3]^-$ is not reversible.

The $[Rh(CO)_2I_2]^-/I^-$ catalysed reaction of methanol with carbon monoxide to give acetic acid is now a major industrial process.[1,2] Apart from the pioneering work of Forster,[2] very little attention has been paid to the mechanism of this reaction. The only intermediate that has been isolated from the reaction is $[Me_3PhN]_2[Rh_2(COMe)_2(CO)_2I_6]$, for which the crystal structure has been established.[3,4] Little work appears to have been done on the chemisty of this acyl intermediate, although a number of related rhodium-acyls have been examined.[5—8] Most acyl-rhodium complexes readily isomerise to the alkyl rhodium carbonyl complex, and in favourable cases, the equilibrium can be investigated. Thus for $RhCl_2(COMe)(PAr_3)_2$ and $RhMeCl_2(CO)(PAr_3)_2$ the equilibrium constant has been determined,[5] and for $[RhCl(COMe)(PMe_2Ph)_3]^+$ the rate was determined.[7] It has been recently shown that $Rh(COMe)I_2(PPh_3)_2$ decomposes with elimination of methyl iodide to form $RhI(CO)(PPh_3)_2$.[9] This and similar work implies the *reversible* formation of


(I)


(II)


(III)

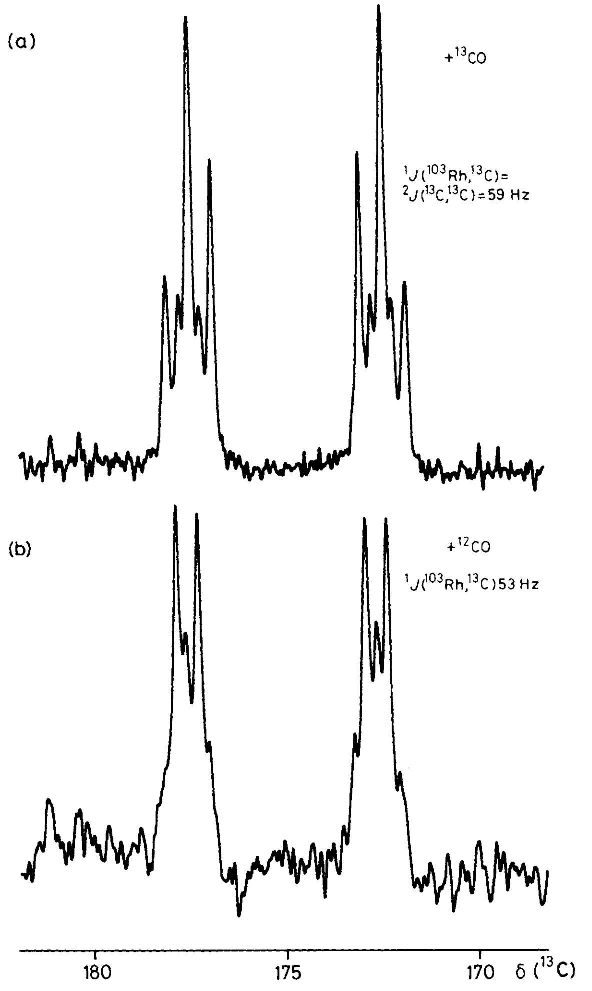


Figure 1. A partial ^{13}C n.m.r. spectrum of $[Rh(COMe)(^{13}CO)_2I_3]^-$, (II), in CD_2Cl_2–$CHFCl_2$, 1 : 1, at −130 °C (^{13}CO region): (a) *ca.* 80% enriched in ^{13}CO, (b) *ca.* 40% enriched in ^{13}CO.

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† kcal = 4.184 kJ.

$[RhMe(CO)_2I_3]^-$ from $[Rh_2(COMe)_2(CO)_2I_6]^{2-}$, but in contrast $[Rh(COMe)(CO)_2I_3]^-$ decomposes to give acetyl iodide.[2]

When $[Rh_2(^{13}COMe)_2(^{13}CO)_2I_6]^{2-}$, (I),[‡] is treated with ^{13}CO, then $[Rh(^{13}COMe)(^{13}CO)_2I_3]^-$ is formed. The ^{13}C n.m.r. spectrum in CD_2Cl_2 at −30 °C shows $^{13}COMe$ at δ 216.42, $^1J(^{103}Rh,^{13}C)$ 18 Hz and ^{13}CO at δ 177.11, $^1J(^{103}Rh,^{13}C)$ 54 Hz. On cooling to −90 °C, the $^{13}COMe$ signal remains sharp, but there is extreme broadening of the ^{13}CO signal. In CD_2Cl_2–$CHFCl_2$, 1 : 1, at −130 °C, the spectrum shows one $^{13}COMe$ signal at δ 216.60, $^1J(^{103}Rh,^{13}C)$ 18 Hz and two ^{13}CO signals at δ 177.79 and 173.03, both triplets, with underlying doublets; $^1J(^{103}Rh,^{13}C) = {}^2J(^{13}C,^{13}C) = 59$ Hz, see Figure 1. The attribution of one 59 Hz coupling to $^2J(^{13}C,^{13}C)$ is confirmed by treating $[Rh_2(^{13}COMe)_2(^{13}CO)_2I_6]^{2-}$ with ^{12}CO, when predominantly $[Rh(^{13}COMe)(^{13}CO)(^{12}CO)I_3]^-$ is formed, and the ^{13}CO n.m.r. signal consists of two doublets, with underlying triplets. The value of 59 Hz for $^2J(^{13}C,^{13}C)$ demonstrates a *trans* carbonyl arrangement, (II). As many rhodium acyl complexes are 5-co-ordinate it is possible that this compound is also square-pyramidal with the vacant site *trans* to COMe. The carbonyl inequivalence arises from restricted rotation about the Rh–COMe bond with $\Delta G^{\ddagger}$ 7.6 kcal mol^{-1}.[†] This compound has been previously reported,[3] but a *fac*-structure, (III), was suggested. $[Rh(^{13}COMe)(^{13}CO)_2I_3]^-$ slowly decomposes at room temperature to give $[Rh(^{13}CO)_2I_2]^-$ and various organic acetyl species. It is improbable that (II) with its *trans*-carbonyls will decompose directly to give $[Rh(CO)_2I_2]^-$ with *cis*-carbonyls. Therefore, the mechanism probably consists of isomerisation of (II) to (III), which rapidly loses CH_3COI, and is not detected.

When N_2 is passed through a solution of $[Rh(COMe)(CO)_2I_3]^-$, $[Rh_2(COMe)_2(CO)_2I_6]^{2-}$ is generated. Hence repeated treatment[§] of $[Rh_2(^{13}CO^{13}CH_3)(^{13}CO)_2I_6]^{2-}$ with alternately ^{12}CO and N_2 generates $[Rh_2(^{13}CO^{13}CH_3)_2(^{12}CO)_2I_6]^{2-}$. The $^{13}CH_3$ n.m.r. spectrum has a doublet, δ 46.07, $^1J(^{13}C,^{13}C)$ 35 Hz with a singlet due to the $^{13}CH_3{}^{12}CO$ group, and provides a monitor of the $^{12}CO^{13}CH_3 : {}^{13}CO^{13}CH_3$ ratio. After 1 week in CH_2Cl_2 this ratio does not change, remaining at 1 : 4 as it was in the initial $[Rh_2(^{13}CO\ ^{13}CH_3)_2(^{13}CO)_2I_6]^{2-}$. Therefore $[Rh_2(^{13}CO^{13}CH_3)_2(^{12}CO)_2I_6]^{2-}$ does not give $[Rh(^{13}CH_3)(^{12}CO)(^{13}CO)I_3]^-$ at a significant rate to permit $^{12}C/^{13}C$ scrambling, yielding $[Rh_2(^{12}CO^{13}CH_3)_2(^{13}CO)_2I_6]^{2-}$, even though the formation of $[Rh_2(COCH_3)_2I_6]^{2-}$ from $[Rh(CO)_2I_2]^-$ and CH_3I is believed to go *via* $[Rh(CH_3)(CO)_2I_3]^-$.[2] This is surprising in view of the facile formation of rhodium-methyls from other rhodium-acetyls, and indicates an unusual chemistry for $[Rh_2(COCH_3)_2(CO)_2I_6]^{2-}$.

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[‡] $Rh_2(CO)_4Cl_2$ in CH_2Cl_2 readily exchanges with ^{13}CO. Subsequent reaction with MeI, $AsPh_4Cl$, and LiI yields $[AsPh_4]_2[Rh_2(^{13}COMe)_2(^{13}CO)_2I_6]$, ref. 3.

[§] Synthesised as $[AsPh_4]_2[Rh_2(^{13}COMe)_2(^{13}CO)_2I_6]$, using $^{13}CH_3I$.