DALTON
FULL PAPER

Some studies of the substitution chemistry of $[Rh_2(OAc)_2(CH_3CN)_4][BF_4]_2$ with monodentate and bidentate tertiary phosphines †

Malcolm H. Chisholm,* John C. Huffman and Suri S. Iyer

Department of Chemistry and Molecular Structure Center, Indiana University, Bloomington, IN 47405, USA

Received 23rd December 1999, Accepted 23rd February 2000
Published on the Web 4th April 2000

The reactions between $[Rh_2(OAc)_2(CH_3CN)_4][BF_4]_2$ and each of the tertiary phosphines PMe_3, PCy_3 (Cy = cyclohexyl), $Me_2PCH_2CH_2PMe_2$ (dmpe), $Ph_2PCH_2CH_2PPh_2$ (dppe), $Me_2PCH_2PMe_2$ (dmpm) and $Ph_2PCH_2PPh_2$ (dppm) have been studied by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy in CD_3CN. The chelating phosphines dppe and dppm catalyze the exchange of coordinated CH_3CN for solvent CD_3CN exchange prior to any other observable substitution chemistry. The monodentate phosphines initially form kinetically labile biaxially ligated complexes, $[Rh_2(OAc)_2(CH_3CN)_4(PR_3)_2][BF_4]_2$ prior to substitution of the equatorial CH_3CN by PR_3. Over time, the biaxial complex rearranges to form the monoaxial, monoequatorial complex, involving displacement of a single equatorial CH_3CN ligand. For PCy_3 the complex $[Rh_2(OAc)_2(CH_3CN)_3(PCy_3)_2][BF_4]_2$ has been characterized by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. With time, a further reaction occurs leading to the cleavage of the Rh–Rh bond and the monomeric complex $[Rh(CH_3CN)_2(PCy_3)_2][BF_4]$ has been identified. Crystal data at +25 °C: space group $P2_1nm$, $a = 9.879(1)$ Å, $b = 13.275(1)$ Å, $c = 16.705(1)$ Å and $Z = 4$. A similar reaction sequence is observed with PMe_3 but more isomers of formula $[Rh_2(OAc)_2(CH_3CN)_3(PMe_3)_2][BF_4]_2$ are observed by $^{31}P\{^1H\}$ NMR spectroscopy. Reactions involving dppe lead to axial and equatorial Rh–P bonded complexes. Based on $^{31}P\{^1H\}$ NMR data, the bisequatorial complex formulated as $[Rh_2(OAc)_2(CH_3CN)_2(dppe)][BF_4]_2$ is formed. The formation of the latter, which has been followed from 35 to 80 °C, is evidently reversible since all attempts to crystallize the complex yielded only the acetonitrile salt $[Rh_2(OAc)_2(CH_3CN)_4][BF_4]_2$ and free dppe. With dppm, only axial ligation is observed while for dmpm and dmpe the substitutional behavior is more complex and has not been evaluated in detail. The activation parameters for the conversion of the biaxial $[Rh_2(OAc)_2(S)_4(L)_2][BF_4]_2$ to the monoaxial, monoequatorial $[Rh_2(OAc)_2(S)_3(L)_2][BF_4]_2$ complex (S = CH_3CN and L = phosphine) have been determined. For L = PMe_3, $\Delta H^{\ddagger} = 16(1)$ kcal mol^{-1} and $\Delta S^{\ddagger} = -9(3)$ cal K^{-1} mol^{-1} and for L = PCy_3, $\Delta H^{\ddagger} = 21(1)$ kcal mol^{-1} and $\Delta S^{\ddagger} = +2(3)$ cal K^{-1} mol^{-1}. For dppe, the 1 : 1 adduct shows only one type of ^{31}P signal for the initial axial complex indicative of rapid exchange of free and bound PPh_2 groups. The rearrangement to the equatorial–axial isomer $[Rh_2(OAc)_2(S)_3(dppe)][BF_4]_2$ occurs with $\Delta H^{\ddagger} = 26(1)$ kcal mol^{-1} and $\Delta S^{\ddagger} = +12(1)$ cal K^{-1} mol^{-1}. Collectively these data show that substitution at the Rh_2^{4+}-center proceeds *via* an initial reversible associative process followed by an interchange of labile axial for inert equatorial sites. These results are compared with earlier studies of the substitution of M_2^{4+}-containing complexes, where M = Mo, Ru and Rh.

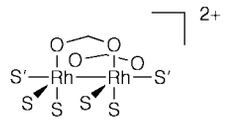
Introduction

A large number of dinuclear complexes containing a central M_2^{4+} core are known, many of which contain M–M bonds and have a common structural motif.[1] Such is the case for $M_2(O_2CR)_4$ compounds which are known for M = Cr, Mo, W, Ru, Rh and Cu with a common lantern or paddle wheel (D_{4h}) $M_2(O_2C)_4$ core. For M = Mo, W and Rh these compounds display a rich substitution chemistry and are often employed as starting materials in the synthesis of other dinuclear complexes.[1] Since the discovery by Bear *et al.*[2] that $Rh_2(OAc)_4$ shows antitumor activity for cancerous cells *in vitro* other workers have been attracted to the fundamental substitution chemistry of Rh_2^{4+}-containing compounds with nitrogen bases and purines.[3]

In comparing the reactivity of $Mo_2(O_2CR)_4$ and $Rh_2(O_2CR)_4$ compounds we have noted that the former may be characterized as labile and the latter as inert.[4] We suggested that the vast difference in rates of reactivity may reflect, in part, ground state effects associated with the M–M bond electronic configuration.[4] Thus the Mo_2^{4+} center with M–M $\sigma^2\pi^4\delta^2$ has low lying vacant metal based orbitals which may facilitate carboxylate group scrambling as seen in the reactions between $Mo_2(O_2CR)_4$ and $Mo_2(O_2CR')_4$ which occur upon mixing in a solvent such as benzene[4,5] or as in the fluxional nature of the $[Mo_2(\mu\text{-}O_2C^tBu)_4(\eta^1\text{-}O_2C^tBu)]^-$ anion by way of associative chemistry: bonds to Mo may be formed with or without sacrificing M–M bonding.[6] By contrast $Rh_2(O_2CR)_4$ compounds undergo carboxylate group scrambling only under more forcing conditions. The addition of $[Bu_4^nN][OAc]$ to $[Rh_2(O_2C^tBu)_4]$ reversibly forms a salt $[Bu_4^nN]_2[(\eta^6\text{-}C_6H_5Me)Rh_8(\mu\text{-}O_2C^tBu)_{16}(\mu\text{-}\eta^1,\eta^1\text{-}OAc)_2]$ in toluene, for example.[7] Here the Rh–Rh bonding electronic configuration is $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*4}$ and this may be compared with the kinetically inert t_{2g}^6 configuration seen in mononuclear octahedral complexes of Co^{3+}, Rh^{3+}, Ir^{3+} and Pt^{4+} which generally undergo substitution by dissociative, D, or interchange-dissociative, I_d, mechanisms.[8]

In comparing the rates of solvent exchange in the $[M_2(OAc)_2(MeCN)_6][BF_4]_2$ complexes we again observed kinetic lability for M = Mo and the inertness of the Rh complex which undergoes exchange of CH_3CN for CD_3CN (solvent) very much more slowly.[4] Specifically, the $[Rh_2(OAc)_2(CH_3CN)_6][BF_4]_2$ complex, which has the structure shown in **A** below (S′ and S

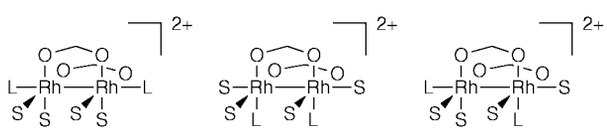
† Dedicated to Professor Jack Halpern on the occasion of his 70th birthday.



A

are the axial and equatorial CH_3CN's; O–O represents the acetate ligand) and was prepared originally by Garner and coworkers,[9–11] contains two types of coordinated CH_3CN ligands. S′ are axial ligands and S are equatorial with respect to the Rh–Rh bond and their exchange rates with CD_3CN vary greatly. S′ are labile as a result of the strong *trans*-influence and *trans*-effect of the Rh–Rh bond but S, the equatorial sites are inert as judged by the fact that it requires heating in CD_3CN to bring about any significant exchange with the solvent. Indeed, even at 100 °C the $t_{\frac{1}{2}}$ for CH_3CN for CD_3CN (solvent) exchange was of the order of 4 h and, from a study of the rate of CH_3CN for CD_3CN exchange over a temperature range, we estimated $\Delta H^{\ddagger} = 33$ kcal mol^{-1} and $\Delta S^{\ddagger} \approx +11$ cal K^{-1} mol^{-1}, which is consistent with a dissociative or interchange dissociative mechanism for the exchange of the equatorial CH_3CN solvent ligands S in **A**.[4]

In order to probe further the details of the substitution chemistry of Rh_2^{4+} centers we determined to study the reactions of $[Rh_2(OAc)_2(CH_3CN)_6][BF_4]_2$ with tertiary phosphines in CD_3CN solutions by NMR spectroscopy. This study takes advantage of the use of $^{31}P\{^1H\}$ and ^1H NMR spectroscopy, the occurrence of ^{103}Rh, $I = \frac{1}{2}$, 100% natural abundance and the prior work by Drago and coworkers[12] who classified bis(phosphine) complexes of dirhodium as Class I (biaxial), Class II (biequatorial) and Class III (monoaxial, monoequatorial) as depicted by **B**, **C** and **D** below, respectively (S = CH_3CN,



CLASS I CLASS II CLASS III

B C D

L = PR_3). The differentiation of **B**, **C**, **D** can be based on $^{13}P\{^1H\}$ chemical shifts. Of course, for compounds of type **C** and **D** more than one isomer is possible.

We describe here our findings of the substitution chemistry of $[Rh_2(OAc)_2(CH_3CN)_6][BF_4]_2$ in CD_3CN with the tertiary phosphines PMe_3, PBu^n_3, PCy_3 (Cy = cyclohexyl), $Me_2PCH_2CH_2PMe_2$ (dmpe), $Ph_2PCH_2CH_2PPh_2$ (dppe), $Me_2PCH_2PMe_2$ (dmpm) and $Ph_2PCH_2PPh_2$ (dppm).

Results and discussion

The reaction between $[Rh_2(OAc)_2(CH_3CN)_6][BF_4]_2$ and PMe_3 in CH_2Cl_2 or CH_3CN is extremely rapid at room temperature and leads to products of cleavage of the Rh–Rh bond, namely a black insoluble precipitate and a square planar Rh(I) complex $[Rh(PMe_3)_2(CH_3CN)_2][BF_4]$. The reaction with the extremely bulky PCy_3 ligand was significantly slower. However, this reaction too led to cleavage of the Rh–Rh bond and the bright yellow crystalline compound $[Rh(CH_3CN)_2(PCy_3)_2][BF_4]$ was isolated in *ca.* 40% yield based on Rh together with a black insoluble precipitate which was not characterized. However, an intermediate in this reaction, the green crystalline compound $[Rh_2(OAc)_2(CH_3CH)_3(PCy_3)_2][BF_4]_2$ was isolated and characterized, see Experimental section.

Solid-state structure

$[Rh(CH_3CN)_2(PCy_3)_2][BF_4]$. An ORTEP drawing of the square planar Rh(I) cation is shown in Fig. 1 and selected bond distances and bond angles are given in Table 1. There is nothing exceptional about the structural features of this d^8 Rh(I) cation and the P–Rh–P angle is close to 180° as expected. The Rh–P distances are similar to those seen in $[Rh(PPh_3)_3(CH_3CN)][BF_4]$[11] and $[Rh(PPh_3)_2(CO)(CH_3CN)][HC(SO_2CF_3)_2]$[12] as are the Rh–N distances of the coordinated acetonitrile ligands.

Table 1 Selected bond distances (Å) and angles (°) for $[Rh(CH_3CN)_2(PCy_3)_2][BF_4]$

Rh1–P2	2.342(2)	P13–C14	1.858(6)
Rh1–P13	2.340(2)	P13–C20	1.850(8)
Rh1–N24	1.984(4)	P2–C3	1.864(6)
N24–C25	1.134(6)	P2–C9	1.856(8)
C25–C26	1.459(7)		
P13–Rh1–P2	175.55(8)	Rh1–P13–C20	111.1(1)
P13–Rh1–N24	89.7(1)	Rh1–N25–C25	175.9(5)
P2–Rh1–N24	90.1(1)	Rh1–P2–C3	113.6(1)
N24–Rh1–N24	179.3(3)	Rh1–P2–C9	111.1(1)
Rh1–P13–C14	114.2(1)		

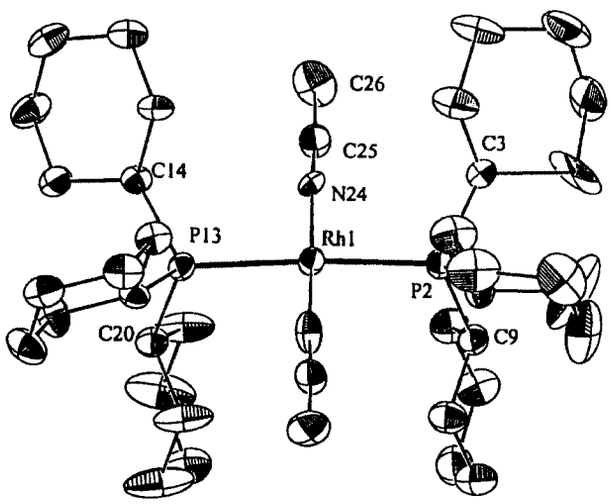


Fig. 1 An ORTEP[19] diagram of $[Rh(CH_3CN)_2(PCy_3)_2][BF_4]$ with thermal ellipsoids at the 50% probability level. The hydrogen atoms and the BF_4 anions are omitted for clarity.

$[Rh_2(OAc)_2(CH_3CN)_2(PCy_3)_2][BF_4]_2$. There was a disorder with one of the MeCN ligands and the two BF_4^- anions show a 50% site occupancy within the unit cell. These crystallographic problems prevent us from presenting any reliable structural information on this compound though there is little doubt that this is a dinuclear compound containing two bulky PCy_3 groups, one at each metal center with one being axially ligated and the other equatorial as demanded by the NMR studies presented below.

NMR studies

Because the reactions between $[Rh_2(OAc)_2(CH_3CN)_6][BF_4]_2$ and tertiary phosphines proceed so rapidly at room temperature they were followed by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy in CD_3CN as solvent in NMR tube reactions. In these studies the tertiary phosphine was added to a cooled or frozen solution of the Rh_2-cationic complex and the sample was introduced into the precooled probe of an NMR spectrometer. The reaction was then monitored with time and temperature.

Reactions involving PMe_3. The addition of PMe_3 to $[Rh_2(OAc)_2(CH_3CN)_6][BF_4]_2$ in CD_3CN solvent at −35 °C results in the formation of the biaxially ligated complex, **B**, or Class I complex. This is evidenced by the appearance of a single $^{31}P\{^1H\}$ signal at *ca.* δ −35.5, downfield from free PMe_3. The $^{31}P\{^1H\}$ signal of this bis adduct gives rise to an AA′XX′

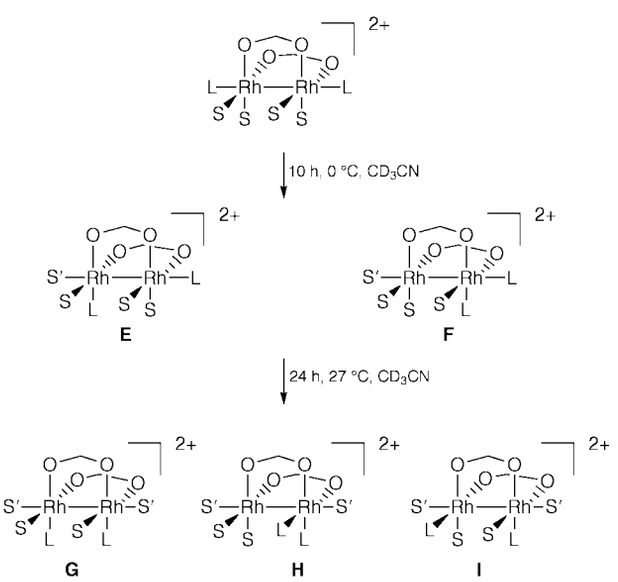
spectrum resulting from the ^{31}P–^{103}Rh–^{103}Rh–^{31}P connectivity and the spectrum was satisfactorily simulated with the following coupling constants $J_{RhRh} = 5$ Hz, $^1J_{RhP} = 55$ Hz, $^2J_{RhP} = 25$ Hz and $J_{PP} = 400$ Hz. These coupling constants are closely related to those reported by Drago *et al.*[12] for $[Rh_2(O_2CCF_3)_4(PPh_3)_2]$ and related complexes. The addition of an excess of PMe_3 (>2 equiv.) led to line broadening between the free and the coordinated PMe_3 ligands at −35 °C while when less than 2 equiv. of PMe_3 were added only the signal for the bis-ligated complex was seen. The latter finding indicates a cooperative binding of PMe_3 to the Rh_2^{4+} center is favored and that the monoligated complex is labile to disproportionation to give the Class I complex and the starting material, eqn. (1).

$$2[Rh_2(OAc)_2(CH_3CN)_4(PMe_3)][BF_4]_2 \rightleftharpoons [Rh_2(OAc)_2(CH_3CN)_4][BF_4]_2 + [Rh_2(OAc)_2(CH_3CN)_4(PMe_3)_2][BF_4]_2 \quad (1)$$

Class I

It is worth emphasizing at this point that the original Rh_2^{4+}-containing complex contained six CH_3CN ligands: four equatorial and two axial. The two axial CH_3CN ligands undergo essentially instantaneous exchange with the CD_3CN solvent and thus by ^1H NMR spectroscopy appear as free CH_3CN. At −35 °C the formation of the bis(phosphine) complex of Class I occurs without any detectable equatorial CH_3CN for solvent CD_3CN exchange.

At −35 °C further reaction is very slow requiring several days to give a mixture of two isomers of a Class III complex. At 0 °C in CD_3CN the formation of the two Class III isomers (monoaxial, monoequatorial) requires 10 h. The two possible isomers are shown in Scheme 1 as **E** and **F** and occur in the approximate



Scheme 1 Isomerizations of $[Rh_2(OAc)_2(CH_3CN)_4(PMe_3)_2][BF_4]_2$. S = CH_3CN, S′ = CD_3CN; L = PMe_3.

ratio 3:1. Evidence that these isomers are of the type Class III (**D** shown earlier) comes from the appearance of one $^{31}P\{^1H\}$ signal at *ca.* δ −40 and the other at *ca.* δ +12, corresponding to axial and equatorial Rh–PMe_3 groups, respectively. Regrettably the NMR data do not allow us to distinguish between the isomers **E** and **F** shown in Scheme 1. However, we can say that the formation of the Class III isomer occurs with the loss of only one CH_3CN equatorial ligand and thus the isomers have the formula $[Rh_2(OAc)_2(CH_3CN)_3(PMe_3)_2][BF_4]_2$.

At 0 °C, with further time new $^{31}P\{^1H\}$ signals grow in the region expected for Class II isomers (see **C** earlier) which have equatorial Rh–P bonds. Three isomers are possible for a Class II isomer (see Scheme 1). Regrettably from reactions between $[Rh_2(OAc)_2(CH_3CN)_4][BF_4]_2$ and PMe_3 we have not been able to isolate any compound in a pure state and with an excess of PMe_3 reactions evidently proceed rapidly to give cleavage of the Rh–Rh bond.

We have monitored the conversion of the biaxial PMe_3 complex to the isomers **E** and **F** in the temperature range −25 °C to +5 °C by following the disappearance of the $^{31}P\{^1H\}$ signal for the Class I complex, **B**, as a function of time. Slopes of $\ln[Rh_2(OAc)_2(CH_3CN)_4(BF_4)_2]$ *versus* time were linear for over three half-lives thus implicating at least a pseudo first order reaction for the disappearance of the Class I complex $[Rh_2(OAc)_2(CH_3CN)_4(PMe_3)_2][BF_4]_2$. From plots of $\ln(k_{obs})$ *versus* 1/temperature (Kelvin) we can estimate the activation parameters for the reaction shown in eqn. (2) to be $\Delta H^{\ddagger} = 16(1)$ kcal mol^{-1} and $\Delta S^{\ddagger} = -9(3)$ cal K^{-1} mol^{-1}.

$$[Rh_2(OAc)_2(CH_3CN)_4(PMe_3)_2][BF_4]_2 \xrightarrow[CD_3CN]{} [Rh_2(OAc)_2(CH_3CN)_3(PMe_3)_2][BF_4]_2 + CH_3CN \quad (2)$$

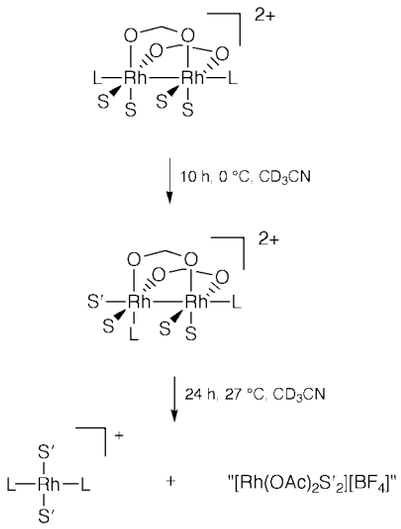
In the presence of an excess of PMe_3 (4 or more equivalents) the disappearance of $[Rh_2(OAc)_2(CH_3CN)_4][BF_4]_2$ was faster and the formation of products more complex. We take this as evidence for the reversible binding of PMe_3 in the biaxial complex, eqn. (1), and that once PMe_3 has acquired an equatorial site a further PMe_3 ligand can coordinate in the axial site to give compounds of the type $[Rh_2(OAc)_2(CH_3CN)_3(PMe_3)_3][BF_4]_2$ which are also labile toward CH_3CN ligand displacement and Rh–Rh bond rupture. A similar reaction sequence was seen in reactions involving PBu^n_3 but was not followed in detail.

Because of the facility of these reactions with PMe_3 and PBu^n_3, we turned our attention to the use of the bulky PCy_3 ligand (Cy = cyclohexyl) which has a Tolman cone angle[13] greater than 180°. For this monodentate tertiary phosphine the coordination of two PCy_3 ligands at the same metal center in a *cis* manner would be sterically impossible!

Reactions employing PCy_3. The addition of PCy_3 to $[Rh_2(OAc)_2(CH_3CN)_4][BF_4]_2$ in CD_3CN at −20 °C leads to a slower sequence of events wherein by $^{31}P\{^1H\}$ NMR spectroscopy we can observe the initial formation of a monoaxial adduct followed by formation of the biaxial Class I complex. The free PCy_3 appears at δ −4, the monophosphine complex at δ −23 and the biaxial Class I complex at δ −4.5. The conversion of the Class I biaxial complex to the monoaxial, monoequatorial Class III complex was followed with time in the temperature range −20 to +35 °C by monitoring the disappearance of the biaxial complex. From these studies we obtain an estimate of the activation parameters: $\Delta H^{\ddagger} = 21(1)$ kcal mol^{-1} and $\Delta S^{\ddagger} = +2(3)$ cal K^{-1} mol^{-1}. In view of the equilibria involving the biaxially ligated complex of Class I we cannot attempt to interpret these parameters beyond noting that enthalpically the conversion of the Class I to Class III compound is more demanding for the bulky PCy_3 ligand than for PMe_3. It is this $\Delta H^{\ddagger}$ term which leads to the notably lower rate of conversion. Also, in contrast to reactions employing PMe_3, we only observe one isomer of the monoaxial, monoequatorial complex $[Rh_2(OAc)_2(CH_3CN)_3(PCy_3)_2][BF_4]_2$. *Only one equatorial CH_3CN ligand is displaced in this substitution process.* There are three distinct CH_3CN signals of equal intensity for the bound CH_3CN ligands as expected from the structure of this compound seen in the solid state. With time, however, this compound decomposes at room temperature to give products of cleavage of the Rh–Rh bond, one of which has been characterized as $[Rh(CH_3CN)_2(PCy_3)_2][BF_4]$. The other compound is a black insoluble precipitate which has not been characterized.

The reaction between $[Rh_2(OAc)_2(CH_3CN)_4][BF_4]_2$ in CD_3CN and PCy_3 (4 or more equivalents) has been followed at 25 °C. The reaction proceeds more rapidly in the presence of

an excess of 2 equiv. of PCy_3 but only the biaxial complex, the monoaxial, monoequatorial complex and the mononuclear Rh^I complex are seen by $^{31}P\{^1H\}$ NMR spectroscopy and cleavage of the Rh–Rh bond is complete within 2 h. The reactions involving $[Rh_2(OAc)_2(CH_3CN)_4][BF_4]_2$ and PCy_3 are summarized in Scheme 2.

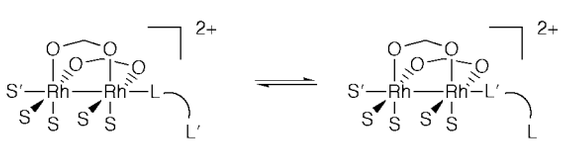


Scheme 2 $S' = CD_3CN$; $L' = PCy_3$.

For the reactions involving the monodentate PR_3 ligands described so far we can conclude the following. The substitution reaction of CH_3CN for PR_3 in the reaction between $[Rh_2(OAc)_2(CH_3CN)_4][BF_4]_2$ and PR_3 proceeds in a two step process. (1) The initial formation of a biaxial complex of formula $[Rh_2(OAc)_2(CH_3CN)_4(PR_3)_2][BF_4]_2$ is rapid and reversible. (2) The second step in the reaction is slower and involves an interchange mechanism wherein one of the axially bound PR_3 ligands displaces an equatorially bound CH_3CN ligand to form $[Rh_2(OAc)_2(CH_3CN)_3(PR_3)_2][BF_4]_2$ of Class III. This may, depending upon R, exist in more than one isomer and subsequent reactions lead to cleavage of the Rh–Rh bond. The overall rate of the reactions are dependent on both the concentrations of PR_3 and the nature of PR_3. Since these reactions proceed much faster than the rate of CD_3CN for CH_3CN exchange in the $[Rh_2(OAc)_2(CH_3CN)_4]^{2+}$ cation[4] it is evident that substitution of the equatorial CH_3CN ligand is promoted by the initial coordination of the PR_3 in the axial position. The PR_3 for CH_3CN substitution has the appearance of the associative interchange mechanism described previously in our studies of tertiary phosphine for tertiary phosphine exchange at M_2^{4+}-centers (M = Mo, W), eqn. (3).[14]

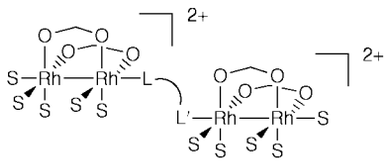
$$M_2Cl_4L_4 + L' \longrightarrow M_2Cl_4L_3L' + L \qquad (3)$$

Reactions with chelating tertiary diphosphines. With one equivalent of dmpe or dppe, $[Rh_2(OAc)_2(CH_3CN)_4][BF_4]_2$ in CD_3CN at −30 °C shows $^{31}P\{^1H\}$ signals, one at *ca.* δ −25, the other at *ca.* δ −10, both as 1:2:1 triplets. The interpretation of this observation is open to question. A monoaxial compound could be fluxional on the NMR time-scale as shown in eqn. (4)



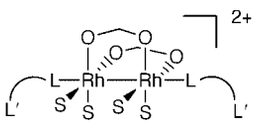
(4)

(S = CH_3CN, S′ = CD_3CN; L–L′ = dppe or dmpe). Fluxional η^1-dmpe and η^1-dppe ligands are known in mononuclear complexes[15] and no J_{RhP} coupling is observed at −30 °C. Alternatively one equivalent of the chelating phosphine could rapidly and reversibly link two Rh_2^{4+} centers as shown in **J**.



J

When more than one equivalent of the chelating phosphines is added then signals associated with bound and uncoordinated ^{31}P nuclei can be seen along with the signal of free dppe or dmpe. This suggests that adducts of the type **K** are formed



K

where exchange between bound and free ligands is relatively slow on the NMR time scale. Also in this instance the η^1-ligands are not fluxional on the NMR time-scale.

The most dramatic difference between the reactions involving dmpe and dppe in CD_3CN at −30 °C, as determined by NMR spectroscopy, is that the latter (dppe) but not the former (dmpe) causes a rapid exchange of bound equatorial CH_3CN for CD_3CN (solvent). This exchange is readily seen by ^1H NMR spectroscopy. This facile exchange of equatorial CH_3CN for CD_3CN (solvent) was also seen previously in reactions involving the addition of chelating ligands 2,2′-bipyridine, 1,10-phenanthroline and OAc^-.[4a] In each case the addition of the bidentate ligand effects CH_3CN (equatorial) for CD_3CN solvent exchange without any apparent reaction beyond a reversible axial coordination. Why this should be is quite puzzling, as is the fact that dmpe does not effect this reaction.

In the reaction between $[Rh_2(OAc)_2(CH_3CN)_4][BF_4]_2$ and dppe we can observe the conversion of the Class I compound to a Class III compound, a monoaxial, monoequatorial compound as evidenced by ^{31}P signals at δ −36 (axial Rh–P) and +59 (equatorial Rh–P). These occur in the integral ratio 1:1. The reaction with 1 equiv. of dppe was monitored in the temperature range +22 to +78 °C and an estimate of the activation parameters was obtained: $\Delta H^{\ddagger} = 26(1)$ kcal mol^{-1} and $\Delta S^{\ddagger} = +12(3)$ cal K^{-1} mol^{-1}.

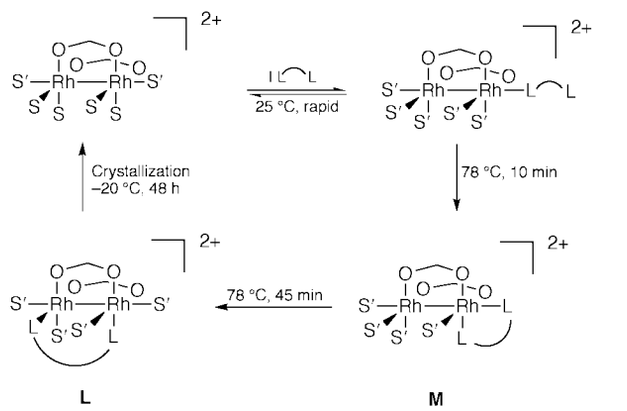
A further reaction occurs as evidenced by the disappearance of the signal at δ −36 and the growth of the signal at δ +59. This is believed to be a biequatorially substituted isomer, or Class II compound. Of the three possible isomers for such a compound the one shown in Scheme 3 is believed to be most likely as this one has the dppe ligand bridging the Rh–Rh bond in a staggered manner which is well known for dppe ligands at dinuclear metal centers.[1]

While it is quite evident from $^{31}P\{^1H\}$ NMR studies that a single isomer of formula $[Rh(OAc)_2(dppe)(CD_3CN)_x][BF_4]_2$ is formed all attempts to isolate this compound by crystallization failed. Indeed, cooling to −20 °C leads to the *slow* crystallization of $[Rh_2(OAc)_2(CD_3CN)_6][BF_4]_2$ and free dppe. Thus we believe that compound **L** shown in Scheme 3 must be formed reversibly and that the less soluble acetonitrile complex crystallizes from solution preferentially. The reactions shown in Scheme 3 have been recycled several times in selected NMR tube reactions and in no instance has Rh–Rh bond cleavage been observed.

Reactions involving the methylene bridged diphosphines $Me_2PCH_2PMe_2$ (dmpm) and $Ph_2PCH_2PPh_2$ (dppm) were also studied but proved to yield a myriad of products as judged by

Table 2 Summary of activation parameters for equatorial CH_3CN substitution in $[Rh_2(OAc)_2(CH_3CN)_4]^{2+}$ in CD_3CN solution

Ligand (L)	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}
PMe_3	16(1)	−9(3)
PCy_3	21(1)	+2(3)
dppe	26(1)	+12(3)
CD_3CN	33(1)	+11(3)



Scheme 3 Reaction of $[Rh_2(OAc)_2(CH_3CN)_6][BF_4]_2$. S = CH_3CN; S′ = CD_3CN; L–L = dppe.

$^{31}P\{^1H\}$ NMR spectroscopy and no single compound was obtained by crystallization. At low temperatures, *ca.* −30 °C, the initial formation of axially bound phosphine complexes occurs as evidenced by $^{31}P\{^1H\}$ chemical shifts of δ −25 (dmpm) and −26 (dppm). Subsequent to this ^{31}P signals in the region δ +10 to +60 grow in and these are taken as evidence for the formation of equatorial Rh–P bonds. However, we cannot determine that the Rh–Rh bond remains intact.

Concluding remarks

This work shows that the $[Rh_2(OAc)_2(CH_3CN)_4]^{2+}$ cation reacts with monodentate tertiary phosphines in a sequential manner. The formation of the axially ligated Class I compounds is rapid and reversible and is followed by a slower reaction to form a monoaxial, monoequatorial compound, Class III compound, by the displacement of a single CH_3CN equatorial ligand in CD_3CN as solvent. The rate of this reaction is markedly dependent upon the PR_3 ligand (R = Me ≈ Bu^n > Cy). In the case of the chelating diphosphine dppe this event occurs in a stepwise manner and the chelating effect does not facilitate the substitution of the Rh–S equatorial site, Scheme 3. A summary of the activation parameters for equatorial CH_3CN substitution is given in Table 2. The increase in $\Delta H^{\ddagger}$ within the series PMe_3 < PCy_3 < dppe < CD_3CN is understandable in terms of the basicity of the entering ligand in the axial position facilitating a bond dissociation in the equatorial site. The entropic term becomes more positive along this series which suggests that bond dissociation or a more disordered transition state is more important as we progress from PMe_3 to PCy_3 to dppe to CD_3CN. The data clearly support an interchange mechanism for equatorial CH_3CN bond substitution involving prior coordination of the entering ligand at the axial site. In this regard the mechanism is similar to that for M–PR_3 substitution by PR_3' ligands in $M_2Cl_4(PR_3)_4$ compounds described previously in this journal.[14]

The ability of certain chelating ligands such as dppe, dppm, 2,2′-bipyridine, 1,10-phenanthroline to catalyze the exchange of equatorial CH_3CN ligands for CD_3CN solvent molecules implies the rapid and reversible formation of an activated complex that is kinetically labile yet not directly on the path of the substitution chemistry described here. We have previously suggested the possibility of the reversible formation of a mixed valence complex Rh^{III}–Rh^{I} wherein the Rh(I) center is kinetically labile.[4] Obviously this possibility and other details of the substitution behavior of Rh_2^{4+} centers remain to be investigated.

Experimental

Physical techniques

^1H NMR spectra were recorded on a Varian XL-300 spectrometer at 300 MHz in the appropriate dry and oxygen-free solvents. $^{31}P\{^1H\}$ NMR spectra were recorded on a Nicolet 360 MHz spectrometer, all samples being referenced to external H_3PO_4. All chemical shifts are reported in ppm relative to the protio impurity signals of the solvents. Elemental analyses were carried out by Atlantic Microlabs, Norcross, GA.

Synthesis and chemicals

All reactions were carried out under an atmosphere of dry, oxygen-free nitrogen using standard Schlenk and glovebox techniques. All solvents were distilled, degassed, and stored over 4 Å sieves before use. Anhydrous CH_3CN was purchased from Aldrich. CD_3CN was purchased from Cambridge Isotopes. PCy_3, dppm, dppe, dmpm and dmpe were purchased from Strem Chemicals. PCy_3, dppm and dppe were purified by sublimation before use. $Rh_2(OAc)_4$ was synthesized using the procedures of Wilkinson *et al.*[16] $[Rh_2(OAc)_2(CH_3CN)_4][BF_4]_2$ was synthesized by the method of Garner *et al.*[9] PMe_3 was made using the standard procedure of Fackler *et al.*[17] and purified by distillation.

NMR studies

Typical samples were made by dissolving 10 mg (0.0134 mmol) of $[Rh_2(OAc)_2(CH_3CN)_6][BF_4]_2$ in 0.5 ml of CD_3CN. The sample was cooled to −30 °C. Appropriate quantities (0.0134/0.0268 mmol) of PMe_3, dmpm and dmpe were added using a microliter syringe at −30 °C. Solid PCy_3/dppe/dppm were added directly to the solution containing $[Rh_2(OAc)_2(CH_3CN)_6][BF_4]_2$ under a helium atmosphere; the NMR tubes were sealed by following the normal freeze–pump–thaw procedure at −178 °C.

The samples thus prepared were transferred to a pre-equilibrated NMR probe for studies of kinetics. The delay *d*1 used for $^{31}P\{^1H\}$ NMR was 5 s, 400 scans were accumulated and then Fourier transformed to give a suitable spectrum. The concentrations of various species present in solution were estimated by the integration of their $^{31}P\{^1H\}$ signals.

Estimates of the activation parameters and determination of rate constants were carried out according to procedures described previously in this journal. A summary of $^{31}P\{^1H\}$ NMR data for the various compounds described herein is given in Table 3.

Reactions

Of $[Rh_2(OAc)_2(CH_3CN)_4][BF_4]_2$ with $2PCy_3$. Two equivalents of PCy_3 (37.5 mg, 0.134 mmol) in 20 ml of degassed CH_3CN was added to a purple colored solution of $[Rh_2(OAc)_2(CH_3CN)_6][BF_4]_2$ (50 mg, 0.67 mmol) in 20 ml of degassed CH_3CN at 25 °C. This resulted in a deep red colored solution. The reaction mixture was allowed to stir overnight (≈12 h) to give a greenish red color. The solvent was removed *in vacuo* and 20 ml of anhydrous methanol were added to the sticky paste and the solution was cooled to −20 °C. Deep reddish green crystalline material was obtained in near quantitative yield (75 mg, 92%) overnight. Suitable crystals were submitted for X-ray analysis. ^1H NMR: δ 2.61 (s, 1H), 2.43 (s, 1H), 2.38 (s, 1H), 2.12 (s, 1H), 2.09 (s, 1H), 1.95 (s, 3H), 1.80 (m), 1.3 (m). IR/cm^{-1}: 2976 (s), 2941 (s), 1688 (w), 1522 (s),

Table 3 $^{31}P\{^{1}H\}$ NMR data for Rh_2^{4+}–phosphine complexes[a]

	Axial P (δ)	Equatorial P (δ)
1. $[Rh_2(OAc)_2(CH_3CN)_4(PMe_3)_2]$		
Class I (biaxial) isomer	−35.5 (dd, J_{Rh-Rh} = 5 Hz, $^1J_{Rh-P}$ = 55 Hz, $^2J_{Rh-P}$ = 25 Hz, J_{P-P} = 400 Hz)	
Class III (monoaxial, monoequatorial) isomers (A)	−44.0 (m)	+10.6 (dd, $^1J_{Rh-P}$ = 152 Hz, $^2J_{Rh-P}$ = 17 Hz)
(B)	−35.8 (m)	+17.0 (dd, $^1J_{Rh-P}$ = 145 Hz, $^2J_{Rh-P}$ = 15 Hz)
Class II (biequatorial) isomer		+ 2 (d, $^1J_{Rh-P}$ = 153 Hz), +12.8 (d, $^1J_{Rh-P}$ = 135 Hz)
2. $[Rh_2(OAc)_2(CH_3CN)_4(PCy_3)_2]$		
Class I (biaxial) isomer	−4.4 (m)	
Class III (monoaxial, monoequatorial) isomers	−6.0 (m)	+42.0 (dd, $^1J_{Rh-P}$ = 146 Hz, $^2J_{Rh-P}$ = 14 Hz)
3. $[Rh_2(OAc)_2(CH_3CN)_4(dmpe)]$		
Class I (biaxial) isomer	−26 (br, m)	
Class III (monoaxial, monoequatorial) isomers	−27.0 (m)	+37.1 (d, $^1J_{Rh-P}$ = 79 Hz)
4. $[Rh_2(OAc)_2(CH_3CN)_4(dppe)]$		
Class I (biaxial) isomer	−10 (br, m)	
Class III (monoaxial, monoequatorial) isomers	−36.1 (m)	+59.0 (d, $^1J_{Rh-P}$ = 132 Hz)
Class II		+59.0 (d, $^1J_{Rh-P}$ = 132 Hz)
5. $[Rh_2(OAc)_2(CH_3CN)_4(dmpm)]$		
Class I (biaxial) isomer	−25 (br, m)	
6. $[Rh_2(OAc)_2(CH_3CN)_4(dppm)]$		
Class I (biaxial) isomer	−26 (br, m)	

[a] All spectra were referenced to external H_3PO_4. Only one monoaxial monoequatorial isomer is seen for entry 2. There were a number of peaks seen for entries 5 and 6. However, it was not possible to determine whether or not the Rh–Rh remained intact in these reactions and so the $^{31}P\{^{1}H\}$ NMR values for the Class II and Class III isomers are not reported.

Table 4 Summary of crystal data

	$[Rh(CH_3CN)_2(PCy_3)_2][BF_4]$	$[Rh_2(OAc)_2(CH_3CN)_3(PCy_3)_2][BF_4]_2$[a]
Empirical formula	$C_{40}H_{72}BF_4N_2P_2Rh$	$C_{46}H_{81}N_3B_2F_8O_4P_2Rh_2$
Color of crystal	Yellow	Red
Crystal dimensions/mm	0.30 × 0.30 × 0.45	0.28 × 0.25 × 0.42
Space group	$P2_1nm$	$P\bar{1}$
Crystal system	Orthorhombic	Triclinic
T/°C	25	−170
a/Å	9.879(1)	14.638(2)
b/Å	13.275(1)	16.055(3)
c/Å	16.705(1)	12.507(2)
α/°		94.55(1)
β/°		90.41(1)
γ/°		72.13(1)
Z	4	2
V/Å^3	2190.76	2788.12
d_{calcd}/g cm^{-3}	2.367	1.407
Molecular weight	832	1181.53
μ/cm^{-1}	9.278	7.042
2θ range/°	6–45	6–45
Total no. of reflections collected	3159	7850
No. of unique intensities	1589	7261
No. with $F > 0.0$	1575	6770
No. with $F > 2.33\sigma(F)$	1554	5405
$R(F)$	0.0271	0.0508
$R_w(F)$	0.0270	0.0499
Goodness of fit for last cycle	1.644	1.600
Maximum δ/σ for last cycle	0.09	0.05

[a] Due to problems with crystallographic disorder, full structural data are not being reported for this structure.

1398 (vs, br), 1267 (s), 1170 (w), 1036 (br, vs). Found: C = 46.74, H = 6.86, N = 3.56. Calc. for $[Rh_2(OAc)_2(CH_3CN)_4(PCy_3)_2][BF_4]_2$: C = 46.29, H = 7.02, N = 3.39%.

If the reaction mixture was left to stir for 24 h it resulted in a light orange colored solution with black insoluble material at the bottom of the flask. This solution was filtered, concentrated and kept at −20 °C. Bright yellow crystals were obtained in approximately 40% yield (18 mg) after 2 d. IR/cm^{-1}: 2941 (s, br), 2741 (s), 1477 (s), 1267 (s), 1171 (w), 1036 (br, vs, d). Found: C = 57.49, H = 8.55, N = 3.30. Calc. for $[Rh(CH_3CN)_2(PCy_3)_2][BF_4]$: C = 57.70, H = 8.66, N = 3.37%.

Of $[Rh_2(OAc)_2(CH_3CN)_6][A]_2$ (A = BF_4 or PF_6) with $2PMe_3$. Two equivalents of PMe_3 (0.134 mmol) were added to a purple colored solution of $[Rh_2(OAc)_2(CH_3CN)_6][A]_2$ (0.067 mmol) in 20 ml of degassed CH_3CN at −30 °C. This resulted in a deep red colored solution. The temperature was slowly brought to 25 °C and the reaction was stirred for 1 h. The color of the

solution changes from deep red to light orange. Cooling to −20 °C resulted in a light orange colored powder. Unfortunately, X-ray quality crystals could not be obtained from these reactions.

Of $[Rh_2(OAc)_2(CH_3CN)_4][BF_4]_2$ with dppe. To an acetonitrile solution containing $[Rh_2(OAc)_2(CH_3CN)_4][BF_4]_2$ (50 mg, 0.67 mmol) solid dppe (26 mg, 0.67 mmol) was added. The purple colored solution turned deep red within 5 min. This solution was heated to 80 °C for 1 h; the solution was concentrated and cooled to −20 °C. After 2 d, purple crystals were obtained, the analysis of which showed it to be the starting material.

Single crystal X-ray studies

General operating procedures and listings of programs have been previously reported.[18] A summary of crystal data is given in Table 4.

CCDC reference number 186/1870.

See http://www.rsc.org/suppdata/dt/b0/b001444n/ for crystallographic files in .cif format.

Acknowledgements

We thank the National Science Foundation for support.

References

1 F. A. Cotton and R. A. Walton, in *Multiple Bonds Between Metal Atoms*, Oxford University Press, 2nd edn., 1993.
2 R. G. Hughes, Jr., J. L. Bear and A. P. Kimbell, *Proc. Am. Assoc. Cancer Res.*, 1972, **13**, 120.
3 (*a*) C. A. Crawford, J. H. Matonic, W. E. Streib, J. C. Huffman, K. R. Dunbar and G. Christou, *Inorg. Chem.*, 1993, **32**, 3125; (*b*) C. A. Crawford, *Synthesis, Characterization and Reactivity of Dinuclear Rhodium(II) Complexes Containing Nitrogen Donor Ligands: A Model Approach to Antitumor Activity*, Ph.D. Thesis, Indiana University, 1995.
4 (*a*) J. M. Casas, R. H. Cayton and M. H. Chisholm, *Inorg. Chem.*, 1991, **30**, 358; (*b*) M. H. Chisholm and A. M. Macintosh, *J. Chem. Soc., Dalton Trans.*, 1999, 1205.
5 H. Chen and F. A Cotton, *Polyhedron*, 1995, **14**, 2221.
6 R. H. Cayton, S. Chacon, M. H. Chisholm and K. Folting, *Polyhedron*, 1995, **12**, 415.
7 M. H. Chisholm, K. Folting, K. G. Moodley and J. L. Wesemann, *Polyhedron*, 1996, **15**, 1903.
8 F. Basolo and R. G. Pearson, in *Mechanisms of Inorganic Reactions. A Study of Metal Complexes in Solution*, John Wiley Publishers, New York, 2nd edn., 1968.
9 G. Pimblett and C. D. Garner, *J. Chem. Soc., Dalton Trans.*, 1986, 1257.
10 G. Pimblett, C. D. Garner and W. Clegg, *J. Chem. Soc., Dalton Trans.*, 1985, 1977.
11 A. R. Siedle, W. B. Gleeson, R. A. Newmark, R. P. Skarjune, P. A. Lyon, G. C. Markell, K. O. Hodgson and A. L. Roe, *Inorg. Chem.*, 1990, **29**, 1667.
12 J. Telser and R. S. Drago, *Inorg. Chem.*, 1986, **25**, 2989.
13 C. A. Tolman, *Chem. Rev.*, 1977, **77**, 313.
14 M. H. Chisholm and J. M. McInnes, *J. Chem. Soc., Dalton Trans.*, 1997, 2735.
15 (*a*) V. Riena, M. A. Ruiz, F. Villafare, C. Bois and Y. Jeanin, *Organomet. Chem.*, 1990, **382**, 407; (*b*) F. A. Cotton and M. Matsusz, *Polyhedron*, 1987, **6**, 261.
16 G. A. Rempel, P. Legzdins, H. Smith and G. Wilkinson, *Inorg. Synth.*, 1972, **13**, 90.
17 M. L. Luetkins, Jr., A. P. Sattelberger, H. H. Murray, J. D. Basil and J. P. Fackler, Jr., *Inorg. Synth.*, 1982, **22**, 7.
18 M. H. Chisholm, K. Folting, J. C. Huffman and C. C. Kirkpatrick, *Inorg. Chem.*, 1984, **23**, 1021.
19 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.