

Metal basicity and cooperative effects in the reactions of dinuclear pyrazolato rhodium complexes

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Abstract: The complex $[\{\text{Rh}(\mu\text{-Pz})(\text{CNBu}^t)_2\}_2]$ (**1**) acts as a *supernucleophile* due to the strong basicity induced by the isocyanide ligands. It reacts rapidly with halocarbons (RX) such as PhCH_2Cl or MeI to give the cationic dirhodium(III) complexes of formula $[\{\text{Rh}(\mu\text{-Pz})(\text{R})(\text{CNBu}^t)_2\}_2(\mu\text{-X})]\text{X}$. These reactions are stereoselective since the single stereoisomer formed presents both organic groups (PhCH_2 or Me) outside the *pocket* of the complexes. However *gem*-dichloroderivatives, RCHCl_2 , react with **1** to give functionalised methylene bridged complexes $[\{\text{Rh}(\mu\text{-Pz})(\text{Cl})(\text{CNBu}^t)_2\}_2(\mu\text{-CHR})]$. The latter reactions involve an unusual three-fragment four-electron addition process. Bridged chloroalkyl $[\{\text{Rh}(\mu\text{-Pz})(\text{Cl})(\text{CNBu}^t)_2\}_2(\mu\text{-CClR})]$ complexes are also formed by reaction of **1** with *gem*-trichloroderivatives without β -hydrogen, but for 1,1,1-trichloroethane, which contains β -hydrogen, a further dehydrohalogenation reaction takes place to give the bridging vinylidene complex $[\{\text{Rh}(\mu\text{-Pz})(\text{Cl})(\text{CNBu}^t)_2\}_2(\mu\text{-C}=\text{CH}_2)]$. The latter reacts with O_2 in acid media to give the cationic dinuclear acyl-derivative $[\{\text{Rh}(\mu\text{-Pz})(\text{CNBu}^t)_2\}_2(\mu\text{-Cl})\text{Cl}(\eta^1\text{-COCH}_3)]\text{BF}_4$. These reactions could be a model for the degradation of alkyl chloro derivatives which are exogenous environmental pollutants.

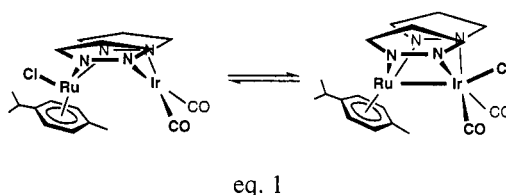
INTRODUCTION

The area of dimetallic complexes has aroused increased interest and great development in the field of organometallic chemistry. The central axis to this exploration has been the use of active metals such as rhodium and iridium together with binucleating ligands in search for a compromise between the stability of the dimetallic complexes and their reactivity. Among those, we have extensively studied the versatile azolate ligands, with particular emphasis in rhodium pyrazolato complexes. This type of ligands are of major interest because of their ability to yield dinuclear homo- or heterometallic, homo- or heterovalent complexes with interesting photochemical, redox and catalytic properties (ref. 1).

Our activity in this area begun in 1979 when we observed that pyrazolate-type anions react with a variety of cationic rhodium complexes such as $[\text{Rh}(\text{diolefin})\text{L}_2]^+$ ($\text{L} = \text{PPh}_3$ or Py , $\text{L}_2 = \text{bipy}$) to give markedly stable $[\{\text{Rh}(\mu\text{-Pz})(\text{diolefin})\}_2]$ compounds. The main structural feature of this type of complexes is the boatlike conformation of the "Rh(N-N)₂Rh" six-membered metallocycle as proved by the early crystallographic identification of $[\{\text{Rh}(\mu\text{-Pz})(\text{CO})\text{P}(\text{OPh})_3\}_2]$ and $[\{\text{Rh}(\mu\text{-3,5-Me}_2\text{Pz})(\text{CS})(\text{PPh}_3)\}_2]$ in the early 80's (ref. 2-3). Since then, we have developed an extensive chemistry on dinuclear rhodium azolato complexes in which the metal centres are joined by one or two exobidentate azolate ligands (ref. 4-10). Heterotrinnuclear complexes containing the metallocycles $\text{Rh}(\mu\text{-Pz})(\mu\text{-L})\text{Pd}(\mu\text{-Pz})(\mu\text{-L})\text{Rh}$ ($\text{L} = \text{Pz}$, S^tBu) (ref. 11-12) have also been prepared by controlled extension of the appropriate fragments. Related chemistry involving other bi- tri- or tetra-azolate ligands shows the formation of tetra- or tri-nuclear complexes, some of them with extended rhodium-rhodium interactions (ref. 13-15).

The intermetallic distance in dinuclear rhodium and iridium pyrazolato complexes results from a compromise of steric and electronic factors (ref. 16, 17), showing a wide range of values [Rh-Rh 2.581-3.889 Å; Ir-Ir 2.737-3.506 Å] due to the remarkable flexibility of the pyrazolate group in the boatlike conformation.

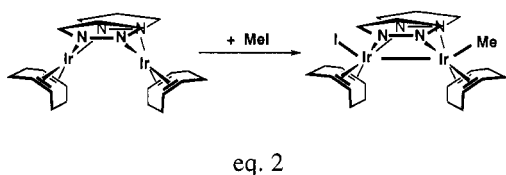
An interesting example of the flexibility of the six-membered metallocycle is provided by the reversible isomerization of the dinuclear complex $[(\eta^6\text{-p-cymene})\text{ClRu}(\mu\text{-Pz})_2\text{Ir}(\text{CO})_2]$ (eq. 1) that implies the migration of the chloride ligand from the ruthenium to the iridium accompanied by a strong compression along the Ru-Ir vector (from 3.66636(4) to 2.6962(6) Å) (ref. 18).



eq. 1

Interestingly, Stobart and coworkers have reported that the reaction of the $[\{\text{Ir}(\mu\text{-Pz})(\text{cod})\}_2]$ compound with methyl iodide leads to the formation of the metal-metal bonded complex $[(\text{cod})(\text{Me})\text{Ir}(\mu\text{-Pz})_2\text{Ir}(\text{I})(\text{cod})]$ (eq. 2).

This oxidative-addition reaction to give a diiridium(II) complex is accompanied by a short contraction of the intermetallic distance from 3.216(1) to 3.112(1) Å, due to the steric hindrance of the cod ligands that precludes a closer distance (ref. 19).



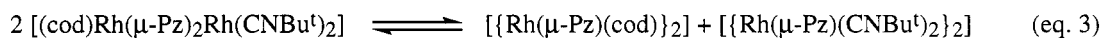
eq. 2

However the analogous $[\{\text{Rh}(\mu\text{-Pz})(\text{cod})\}_2]$ compound does not react with methyl iodide, most probably because the rhodium centres are not basic enough to promote the oxidative addition reaction, which it is more favoured for the diiridium(I) complex. Furthermore, the ancillary ligands frequently used in dinuclear $[\{\text{M}(\mu\text{-Pz})\text{L}_2\}_2]$ ($\text{M} = \text{Rh}, \text{Ir}$) complexes are π -acidic ligands such as the mentioned diolefins, carbon monoxide or phosphorous donor ligands. In this context, we became interested in the chemistry of new dinuclear pyrazolato rhodium complexes with alkyl isocyanide ligands. Isocyanides are strong σ -donor ligands that dramatically increase the electron density at the rhodium centres, in such a way that we can refer to the $[\{\text{Rh}(\mu\text{-Pz})(\text{CNBu}^t)_2\}_2]$ complex as a *supernucleophile* capable of some unusual reactions such as the activation of C-Cl bonds.

The oxidative addition reactions of halocarbons to low valent metal complexes are of paramount interest, particularly those involving organochloro volatile compounds that are environmental pollutants. In this context, it has been recently reported that nitrogen donor ligands make possible to form strongly nucleophilic rhodium complexes (ref. 20) capable of fast oxidative additions of C-Cl bonds. Furthermore, the combination of strong σ -donor ligands, such as the isocyanide ligands, with the binucleating pyrazolate nitrogen donor ligands should favour not only the nucleophilicity of the rhodium centres, but also the appearance of positive cooperative effects.

THE PYRAZOLATO ISOCYANIDE COMPLEXES: A STAR IS BORN

Isocyanides, such as CNBu^t , easily replace cod in the dinuclear complex $[\{\text{Rh}(\mu\text{-Pz})(\text{cod})\}_2]$. The replacement reaction is stepwise leading to $[\{\text{Rh}(\mu\text{-Pz})(\text{CNBu}^t)_2\}_2]$ (1) through the mixed-ligand complex $[(\text{cod})\text{Rh}(\mu\text{-Pz})_2\text{Rh}(\text{CNBu}^t)_2]$ (2). The iridium analogue $[\{\text{Ir}(\mu\text{-Pz})(\text{cod})\}_2]$ behaves in a similar way, confirming the already known stability of the "M(N-N)2M" metallocycle towards fragmentation. A result, apparently conflictive with this idea, is the ligand redistribution reaction (eq. 3) undergone by complex 2 in an inert solvent. However, this reaction is a general chemical equilibrium for dinuclear pyrazolato rhodium complexes, which can be reached from the right-hand side by mixing symmetrical complexes possessing different ancillary or bridging ligands.



Kinetic studies (ref. 16) on the equilibrium in eq. 3 show that the reaction follows a second order rate with a small activation entropy, which involve that the active species are dinuclear complexes, i.e., there is no fragmentation into mononuclear complexes. Moreover, this equilibrium is slow enough at $-20\text{ }^{\circ}\text{C}$ to maintain **2** unaltered for weeks.

Figure 1 shows a star-shaped molecular view of complex **1**, but this complex is also a *raising star* in the chemical sense since, along with complex **2**, has lead us to discover new observations concerning the dinuclear doubly bridged pyrazolato systems as well as some unusual new reactions. In particular, useful information on the reaction pathways for oxidative-addition reactions of halocarbons and diiodine can be obtained.

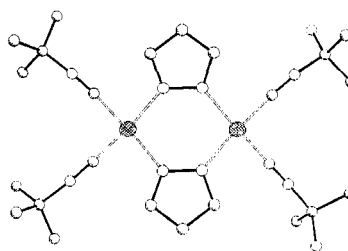
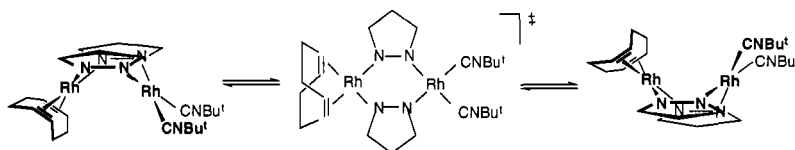


Figure 1

MOTIONS OF THE BRIDGES LEADING TO FLUXIONAL AND CHEMICAL PROCESSES

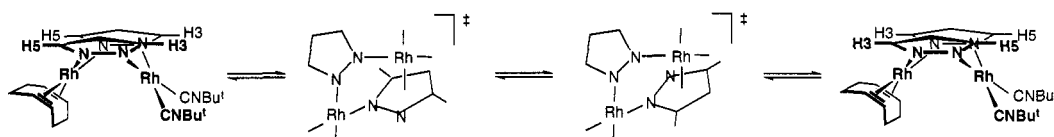
The study of the fluxionality of $[(\text{cod})\text{Rh}(\mu\text{-Pz})_2\text{Rh}(\text{CNBu}^t)_2]$ (**2**) provided us a rare opportunity to observe two independent intramolecular dynamic processes. One was confirmed to be the boat-boat inversion, previously suggested for these systems, (ref. 21) and the other a σ -1,2-metallotropic shift unprecedented for pyrazolato complexes.

The low energy process ($\Delta G^{\ddagger 298} = 15.5\text{ Kcal}\cdot\text{mol}^{-1}$), that makes equivalent the olefinic carbons and protons of the cod ligand, is due to the inversion of the six-membered " $\text{Rh}(\text{N-N})_2\text{Rh}$ " metallocycle through a planar conformation (Scheme 1). Such a movement should be even more facile for complexes with sterically undemanding ancillary and bridging ligands such as $[\{\text{Rh}(\mu\text{-Pz})(\text{L})_2\}_2]$ ($\text{L} = \text{CO}, \text{CNBu}^t$), although undetectable by spectroscopic methods. However, the boat-to-boat inversion becomes a high-energy process for $[\{\text{Rh}(\mu\text{-Pz})(\text{cod})\}_2]$, and it is unfeasible for 3,5-disubstituted pyrazolato complexes due to a steric hindrance to reach the planar conformation of the excited state (ref. 16).



Scheme 1

The second dynamic process ($\Delta G^{\ddagger 298} = 18.3\text{ Kcal}\cdot\text{mol}^{-1}$) makes equivalent the H^3 - H^5 protons of the pyrazolate ring. This process involves the breaking of at least one Rh-N bond most probably followed by a η^5 -coordination of one pyrazolate ring. At this stage a σ -1,2-metallotropic shift on the π -coordinated pyrazolate followed by the re-formation of the Rh-N bond would produce the observed H^3 - H^5 exchange (Scheme 2). Support for this explanation comes from the observed interconversion between the head-to-head and head-to-tail isomers of $[\{\text{Rh}(\mu\text{-MePz})(\text{cod})\}_2]$ and from similar values of the activation energy for other σ -1,2-metallotropic shifts. Moreover, the η^5 -coordination of a pyrazolate ring to a metal has been recently reported (ref. 22).



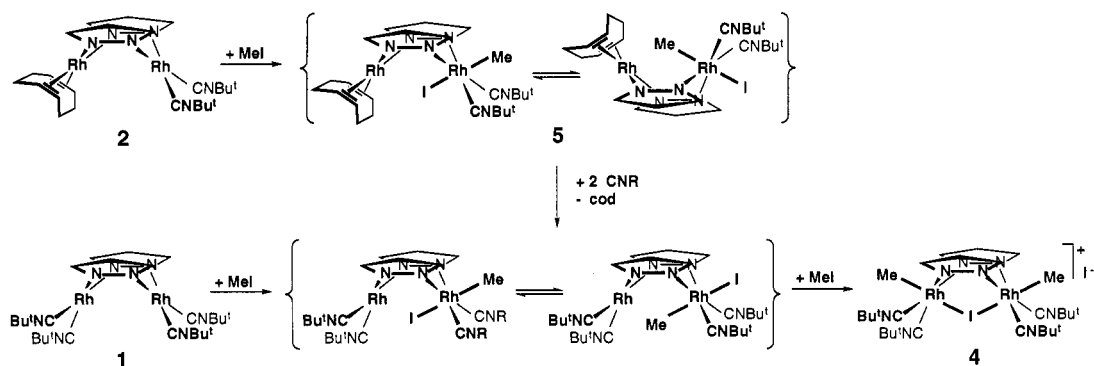
Scheme 2

Finally, although the chemical equilibrium that transforms **2** into **1** and $[\{\text{Rh}(\mu\text{-Pz})(\text{cod})\}_2]$ (eq. 3) is not observable on the NMR time scale, the value of $\Delta G^\ddagger_{298} = 24.0 \text{ Kcal}\cdot\text{mol}^{-1}$ -higher than for the high-energy fluxional process- suggests that the effective collisions probably involve at least one dinuclear species with a broken Rh-N bond (ref. 16).

A DIRHODIUM PYRAZOLATO COMPLEX WITH BASIC METAL CENTRES

Our star complex, $[\{\text{Rh}(\mu\text{-Pz})(\text{CNBu}^t)_2\}_2]$ (**1**) shows the influence of the electronic effects on the metal-metal separation. It possesses the longest intermetallic M-M distance ($3.8996(6) \text{ \AA}$) found for double-bridged pyrazolato complexes in a boat conformation. The high electron density at the rhodium atoms in **1** should be attributed to the CNBu^t ligands, and explains the long intermetallic distance as well as the feasibility of the reactions of **1** with electrophiles. Indeed, the electron rich complex **1** reacts with Me⁺ (as methyl triflate) to give $[\{\text{Rh}(\mu\text{-Pz})(\text{Me})(\text{CNBu}^t)_2\}_2(\mu\text{-CF}_3\text{SO}_3)]\text{CF}_3\text{SO}_3$, the product from the addition at both metal centres. In contrast, no reaction is observed between the related carbonyl complex $[\{\text{Rh}(\mu\text{-Pz})(\text{CO})_2\}_2]$ (**3**) and Me⁺, evidencing the higher basicity of **1**. Moreover, complex **1** reacts immediately with a poorer electrophile such MeI, *in the dark*, to give the ionic Rh(III)-Rh(III) compound $[\{\text{Rh}(\mu\text{-Pz})(\text{Me})(\text{CNBu}^t)_2\}_2(\mu\text{-I})\text{I}]$ (**4**). These reactions show the enhancement in the reactivity due to the ancillary ligands, since complex **1** undergoes a double oxidative-addition reaction while $[\{\text{Rh}(\mu\text{-Pz})(\text{cod})\}_2]$ does not react with MeI (ref. 23).

The above mentioned reactions are stereoselective since the single stereoisomer formed presents both methyl groups outside the *pocket* of the complexes. As kinetic measurements are unavailable because the reactions are completed immediately upon mixing, the use of the mixed-ligand complex $[(\text{cod})\text{Rh}(\mu\text{-Pz})_2\text{Rh}(\text{CNBu}^t)_2]$ (**2**) allow us to disclose the mechanism and the origin of the stereoselectivity. Complex **2** can be viewed as formed from two halves of **1** and the unreactive $[\{\text{Rh}(\mu\text{-Pz})(\text{cod})\}_2]$ and, therefore, it presents one of the metal centres unfavoured for an oxidative-addition reaction. As expected, MeI reacts with **2** to give the Rh(I)-Rh(III) mixed-valence complex $[(\text{cod})\text{Rh}(\mu\text{-Pz})_2\text{Rh}(\text{Me})(\text{I})(\text{CNBu}^t)_2]$ (**5**) (Scheme 3). Complex **5** exists in solution as two conformers, which interconvert on the NMR time scale through a boat-to-boat inversion.



Scheme 3

The reaction of **2** with MeI to give complex **5** is a model for the first step in the reaction of **1** with MeI, and the proposed intermediate $[(\text{CNBu}^t)_2\text{Rh}(\mu\text{-Pz})_2\text{Rh}(\text{Me})(\text{I})(\text{CNBu}^t)_2]$ is formed by replacing cod by CNBu^t in **5** to give the corresponding conformers (Scheme 3). A further addition of MeI to give **4** replicates the second step. We believe that the reaction between **2** and MeI probably takes place in two sequential and well-differentiated steps, as shown in Scheme 3, following a S_N pathway.

A similar stereochemistry is observed for the single isomer of the type $[\{M(\mu\text{-L})(\text{Me})(\text{CNBu}^t)_2\}_2(\mu\text{-I})\text{I}]$, obtained from the reactions of $[\{\text{Ir}(\mu\text{-Pz})(\text{CNBu}^t)_2\}_2]$ and $[\{\text{Rh}(\mu\text{-SBU}^t)(\text{CNBu}^t)_2\}_2]$ with MeI. Thus, the origin of the observed stereoselectivity in the reactions of these three dinuclear open-book complexes with MeI is a consequence of the simultaneous occurrence of several factors: the relatively small cavity in the pocket of the intermediate M(I)-M(III) complex leading to an incipient pentacoordination, the S_N

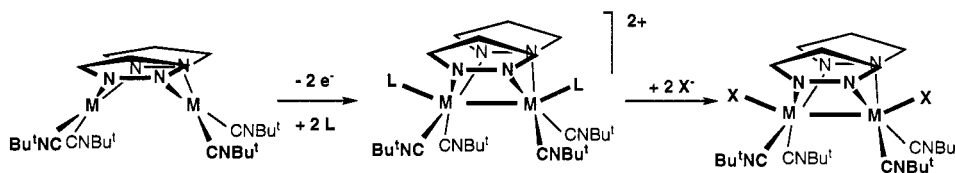
mechanism in the second step, and the fluxional motions associated to the framework of the metals and bridging ligands, such as the boat-boat inversion of the double-bridged dinuclear pyrazolato complexes.

METAL-METAL BOND FORMATION VERSUS REACTIONS AT SINGLE CENTRES

The iridium analogues $[\{\text{Ir}(\mu\text{-Pz})(\text{CNBu}^t)_2\}_2]$ (**6**) and $[\{\text{Ir}(\mu\text{-Pz})(\text{cod})\}_2]$ (**7**) display noticeable differences in their reactions with MeI. Thus, while **7** gives the metal-metal bonded diiridium(II) complex $[(\text{cod})(\text{Me})\text{Ir}(\mu\text{-Pz})_2\text{Ir}(\text{I})(\text{cod})]$ and no further reaction with MeI is observed, complex **6** gives the double oxidative-addition product $[\{\text{Ir}(\mu\text{-Pz})(\text{Me})(\text{CNBu}^t)_2\}_2(\mu\text{-I})\text{I}]$ *in the dark*. The result of the reaction of MeI with the mixed-ligand complex $[(\text{cod})\text{Ir}(\mu\text{-Pz})_2\text{Ir}(\text{CNBu}^t)_2]$ (**8**) is unpredictable *a priori*, since this compound is made of two halves of **6** and **7**. In the practice, **8** behaves as **6** to give the diiridium (III) compound $[(\text{cod})(\text{Me})\text{Ir}(\mu\text{-Pz})_2(\mu\text{-I})\text{Ir}(\text{Me})(\text{CNBu}^t)_2]\text{I}$, which suggests the influence of one metal on the reactivity of the other. Complexes **6** and **8** seems to break the general tendency of dinuclear complexes of iridium to form a stable metal-metal bond, as shown by the reactivity of **7** and related $[\{\text{Ir}(\mu\text{-Pz})(\text{CO})(\text{L})\}_2]$ complexes (ref. 17, 19).

To address further the possible differences between rhodium and iridium complexes we have examined the reactions of $[\{\text{Rh}(\mu\text{-Pz})(\text{CO})_2\}_2]$ (**3**), $[\{\text{Rh}(\mu\text{-Pz})(\text{CNBu}^t)_2\}_2]$ (**1**) and $[\{\text{Ir}(\mu\text{-Pz})(\text{CNBu}^t)_2\}_2]$ (**6**) with one molar equiv. of diiodine. Dirhodium and diiridium metal-metal bonded complexes $[\{\text{M}(\mu\text{-Pz})(\text{I})(\text{L})_2\}_2]$ were obtained in all cases. Thus, these complexes behave in a similar way independently of the electron density on the metals. Even complex **2** gives the dirhodium(II) complex $[(\text{cod})(\text{I})\text{Rh}(\mu\text{-Pz})_2\text{Rh}(\text{I})(\text{CNBu}^t)_2]$. The metal-metal bond formation is thus a result of the behaviour of the dinuclear complex as a whole, since there is not differentiation of the individual centres. Moreover, the nucleophilicity of the metals seems not to be involved in these reactions with diiodine, while it is a crucial factor for the reactions with MeI.

As diiodine is an oxidising agent, we turned our attention to electron transfer reactions of these complexes. In particular, **1** and **6** are easily oxidised to the cationic complexes $[\{\text{M}(\mu\text{-Pz})(\text{CNBu}^t)_2(\text{NCMe})\}_2]^{2+}$ by a mild oxidant such as $[\text{FeCp}_2]^+$ in acetonitrile. The labile acetonitrile ligands (L) *trans* to the metal-metal bond in these complexes are readily replaceable by nucleophiles. Thus, further treatment with soluble halide (X^-) salts results in the complexes $[\{\text{M}(\mu\text{-Pz})(\text{X})(\text{CNBu}^t)_2\}_2]$, ($\text{X} = \text{Cl}, \text{I}$) (Scheme 4). The diiodo products obtained in this way are identical to those obtained from the reactions of **1** and **6** with diiodine. This observation evidences that the metal-metal bond formation results from an electron transfer (ET) reaction.

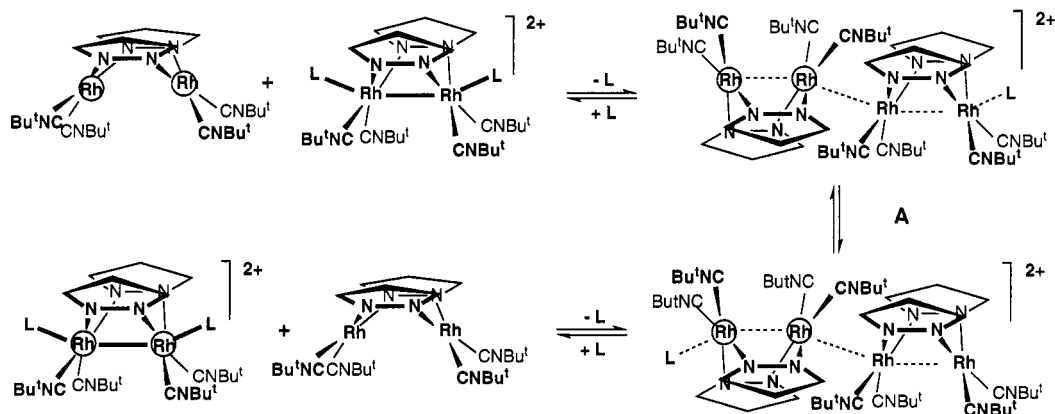


Scheme 4

It is now clear that the origin of the similarity of results for the reactions of diiodine with quite different complexes comes from a single type of reaction. The two electrons removed should come from the HOMO orbital of the starting complexes. As this HOMO is a metal centred antibonding orbital, the electron transfer inevitably leads to the metal-metal bond formation. At this point, what makes the reactions of the rhodium and iridium complexes with iodine and MeI so different? Methyl iodide has the possibility to act either as a very weak one-electron oxidant or as an electrophile. Clearly, the reactions of MeI with the rhodium complexes occur at individual centres and involve the nucleophilic attack of the metal to the polar I-C bond. Therefore, these features fit in a Lewis acid-base scheme, operative for the proposed S_{N} -like mechanism. On the other hand, the strong photoreductor character of the iridium complex **7** shifts the balance toward an ET mechanism, while the strong nucleophilic character of the iridium complex **6** could tip the balance toward a S_{N} -like mechanism.

POLYNUCLEAR BLUE COMPLEXES

Interestingly, beautiful deep blue or purple solutions were obtained by mixing equimolar amounts of the yellow rhodium and iridium complexes **1** and **6** and the corresponding pale-yellow oxidised complexes. It should be mentioned that $[\{\text{Rh}(\mu\text{-Pz})(\text{CNBu}^t)_2\}_2]$ and $[\{\text{Rh}(\mu\text{-Pz})(\text{CNBu}^t)(\text{L})\}_2](\text{PF}_6)_2$ ($\text{L} = \text{MeCN}$) are not as such in this mixture, but as fluxional species. When this solution is cooled down the process becomes slow, allowing the interception of the tetranuclear species **A** responsible for the blue colour and the fluxional motion observed. Taking into account the lability of the nitrile ligands in $[\{\text{Rh}(\mu\text{-Pz})(\text{CNBu}^t)_2(\text{NCMe})\}_2](\text{PF}_6)_2$ and the nucleophilic character of the rhodium metals in **1**, it is possible to explain the formation of an unusual **A** adduct, according to Scheme 5. A delocalization of the metal-metal bond through the metal atoms chain in **A** would give account for the deep colours. The entry of acetonitrile at the axial positions of this species would break it into the starting dinuclear species.

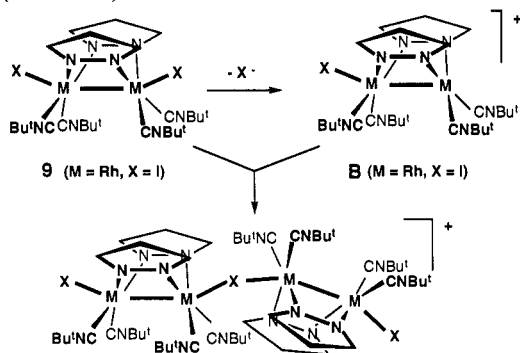


Scheme 5

Notice however, that an internal two-electron electron transfer, facilitated by the metal-metal bond delocalization, should occur in the tetranuclear species in such way that $[\{\text{Rh}(\mu\text{-Pz})(\text{CNBu}^t)_2\}_2]$ and $[\{\text{Rh}(\mu\text{-Pz})(\text{CNBu}^t)_2(\text{NCMe})\}_2]^{2+}$ interconvert, as observed for the fluxional process.

REACTIONS OF METAL-METAL BONDED COMPLEXES WITH ELECTROPHILES

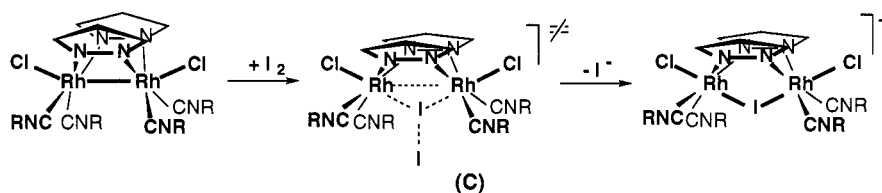
The metal-metal bonded complexes $[\{\text{M}(\mu\text{-Pz})(\text{X})(\text{CNBu}^t)_2\}_2]$ present two reactive sites for electrophilic attack: the metal-metal bond accessible from the endo site, and the iodide ligands *trans* to this metal-metal bond. Reaction at this exo site occurs on addition of MeCF_3SO_3 to $[\{\text{Rh}(\mu\text{-Pz})(\text{I})(\text{CNBu}^t)_2\}_2]$ (**9**) to give the cationic complex $[\text{Rh}_2(\mu\text{-Pz})_2(\text{I})(\text{CNBu}^t)_4]\text{CF}_3\text{SO}_3$ (**[B]** CF_3SO_3). (Scheme 6).



Scheme 6

The abstraction of the iodide ligand *trans* to the metal-metal bond by the strong electrophile Me^+ (as MeCF_3SO_3) is a method to create vacant coordination sites at this position, which can be occupied by nucleophiles. Thus, the unusual tetranuclear cation $[\{\text{Rh}_2(\mu\text{-Pz})_2(\text{I})(\text{CNBu}^t)_4\}_2(\mu\text{-I})]^+$ was prepared by reacting **9** with **[B]** $^+$. The latter cation **[B]** $^+$ presents a polarised Rh-Rh bond that could be described as a dative bond from the pentacoordinated Rh(I) to the octahedral Rh(III) centre (ref. 24).

The metal-metal bond in the complexes $[\{M(\mu\text{-Pz})(\text{I})(\text{CNBu}^t)_2\}_2]$ is cleaved by diiodine to give the double addition product $[\{M(\mu\text{-Pz})(\text{I})(\text{CNBu}^t)_2\}_2(\mu\text{-I})\text{I}]$. Cyclic voltammetry experiments on $[\{\text{Rh}(\mu\text{-Pz})(\text{Cl})(\text{CNBu}^t)_2\}_2]$ show that a pure oxidation by diiodine is chemically inaccessible. A key observation to understand the pathway for the cleavage of the metal-metal bond in the $M(\text{II})\text{-}M(\text{II})$ complexes is the addition of diiodine to the chloro complex $[\{\text{Rh}(\mu\text{-Pz})(\text{Cl})(\text{CNBu}^t)_2\}_2]$ to give $[\{\text{Rh}(\mu\text{-Pz})(\text{Cl})(\text{CNBu}^t)_2\}_2(\mu\text{-I})\text{I}]$. The result evidences the role of the halide ligand (Cl) and the added halogen and the site where the reaction occurs. While the added iodine atom bridges the metals formerly bonded in the starting material, the chloride ligands remain at the exo sites. The observation of the bridging iodide in the product provides strong chemical evidence in favour of the involvement of the electronic density at the metal-metal bond in the reaction. A reasonable mechanism requires the interaction of the diiodine molecule with the $M\text{-}M$ metal bond, as shown in Scheme 7.



Scheme 7

This hypothetical transition state (C) could lead to the heterolytic cleavage of the I-I bond resulting in an iodide ligand bridging two rhodium atoms, i.e., the cation $[\{M(\mu\text{-Pz})(\text{X})(\text{CNBu}^t)_2\}_2(\mu\text{-I})]^+$ and an iodide anion. This proposal involves the actuation of both metals in a cooperative way, such that the metal-metal bond is acting as a nucleophile, and this transition intermediate resembles to the transition state proposed for the electrophilic additions of iodine to carbon-carbon double bonds.

A definitive support for the nucleophilic attack by the metal-metal bond to the diiodine molecule leading to heterolytic rupture of the I-I bond comes from the reactions of the complexes $[\{M(\mu\text{-Pz})(\text{X})(\text{CNBu}^t)_2\}_2]$ with the cationic complex $[\text{I}(\text{py})_2]\text{BF}_4$, which possesses a positive iodine atom. They give the complexes $[\{M(\mu\text{-Pz})(\text{X})(\text{CNBu}^t)_2\}_2(\mu\text{-I})\text{BF}_4]$ quantitatively, in which the added iodine (I) bridges the rhodium atoms, and pyridine. As expected from this mechanism, $[\{\text{Rh}(\mu\text{-Pz})(\text{I})(\text{CNBu}^t)_2\}_2]$ does not react with MeI *in the dark*, since the iodine atom supports a partial negative charge in the I-C_{sp^3} bond and the methyl group is not electrophilic enough to interact.

The preference for the exo site by the strong electrophilic methyl group such as MeCF_3SO_3 should be attributed to the polar Rh-I bond, that facilitates the reaction. This reaction results in the halogen abstraction, maintaining intact the metal-metal bond. The endo site, i.e. the metal-metal bond in $[\{M(\mu\text{-Pz})(\text{X})(\text{CNBu}^t)_2\}_2]$ is the preferred position for the attack of iodine and electrophilic iodine compounds, which leads to the cleavage of the metal-metal bond.

A distinctive reaction pathway should be operative for the slow addition of MeI to $[\text{B}]^+$ and to $[\{\text{Rh}(\mu\text{-Pz})(\text{I})(\text{CNBu}^t)_2\}_2]$ to give the cation $[(\text{CNBu}^t)_2(\text{I})\text{Rh}(\mu\text{-Pz})_2(\mu\text{-I})\text{Rh}(\text{Me})(\text{CNBu}^t)_2]^+$, since these reactions require the irradiation with the direct sun light or with an intense visible lamp. A high selectivity and yield is observed for these photochemical reactions. Absorption bands in the visible region, as shown by $[\text{B}]^+$ and $[\{\text{Rh}(\mu\text{-Pz})(\text{I})(\text{CNBu}^t)_2\}_2]$, seem to be due to a $d\sigma\text{-}d\sigma^*$ transition from the $d\sigma^2$ ground state of the d^7_2 configuration systems. Therefore the triplet excited state $d\sigma^1d\sigma^{*1}$ is easily reached on irradiation, and this excited species should react with MeI . The metal-metal bond is broken in the excited state and hence a structure with a large metal-metal separation should be the reactive species.

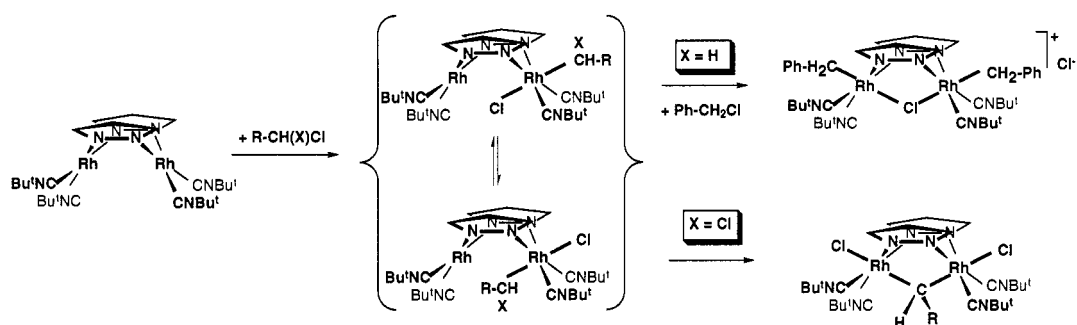
C-Cl ACTIVATION: SUPERNUCLEOPHILE ISOCYANIDE PYRAZOLATO COMPLEXES

The activation of alkyl iodides by oxidative-addition to metal complexes is a key reaction in a number of industrially important catalytic processes (ref. 25). However, the oxidative addition of the less reactive alkyl chlorides has been scarcely studied. A few mononuclear complexes containing electron-rich metal centres are capable to activate alkyl C-Cl bonds by a conventional two-fragment two-electron oxidative-

addition reactions (ref. 20). Complexes **1** and **2** proved to be two unusual binuclear complexes capable to react with a variety of mono-, di- and tri-chloroderivatives.

Monochloroderivatives such as benzyl chloride react with **1** under very mild conditions *in the dark* to give bisalkyl-rhodium(III) complexes. Thus, $[\{\text{Rh}(\mu\text{-Pz})(\text{CH}_2\text{Ph})(\text{CNBu}^t)_2\}_2(\mu\text{-Cl})]\text{Cl}$ can be isolated in high yield. Complex **1** reacts faster with the bromo analogue PhCH_2Br leading to $[\{\text{Rh}(\mu\text{-Pz})(\text{CH}_2\text{Ph})(\text{CNBu}^t)_2\}_2(\mu\text{-Br})]\text{Br}$, as expected from the weaker C-Br bond relative to the C-Cl bond.

Although kinetic measurements are usually unavailable because the reactions are fast, an useful mechanistic information is obtained starting from the mixed-ligand complex $[(\text{cod})\text{Rh}(\mu\text{-Pz})_2\text{Rh}(\text{CNBu}^t)_2]$ (**2**). All these reactions take place in two-steps occurring each at a single rhodium centre (Scheme 8), as above commented for MeI. For instance, we have been able to detect the mixed-valence Rh(I)-Rh(III) complex $[(\text{CNBu}^t)_2\text{Rh}(\mu\text{-Pz})_2\text{Rh}(\text{CH}_2\text{Ph})(\text{Cl})(\text{CNBu}^t)_2]$ in the course of the reaction as the addition product of PhCH_2Cl to one of the rhodium atoms in **1**. Moreover, the related complex $[(\text{cod})\text{Rh}(\mu\text{-Pz})_2\text{Rh}(\text{CH}_2\text{Ph})(\text{Cl})(\text{CNBu}^t)_2]$, which is model for the first step, is easily available starting from **2** and PhCH_2Cl . As expected, replacement of *cod* by CNBu^t leads to $[(\text{CNBu}^t)_2\text{Rh}(\mu\text{-Pz})_2\text{Rh}(\text{CH}_2\text{Ph})(\text{Cl})(\text{CNBu}^t)_2]$, which reacts with additional benzyl chloride to give the expected bisbenzyl-rhodium complex. Therefore the second step occurs on the mixed-valence Rh(I)-Rh(III) complex $[(\text{CNBu}^t)_2\text{Rh}(\mu\text{-Pz})_2\text{Rh}(\text{CH}_2\text{Ph})(\text{Cl})(\text{CNBu}^t)_2]$.

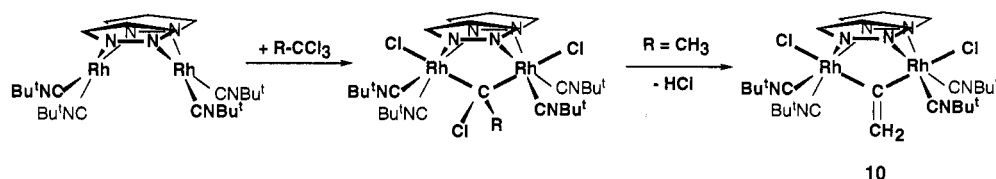


Scheme 8

Gem-dichloroderivatives, RCHCl_2 , react with **1** to give functionalised methylene bridged complexes $[\{\text{Rh}(\mu\text{-Pz})(\text{Cl})(\text{CNBu}^t)_2\}_2(\mu\text{-CHR})]$ ($\text{R} = \text{H}, \text{CO}_2\text{Me}, \text{Ph}$). These reactions involve an unusual three-fragment four-electron addition scheme, which can be easily explained on the mechanistic scenario proposed for the monochloroderivatives. We can assume that the first step for these reactions should be similar (Scheme 8), leading to the mixed-valence Rh(I)-Rh(III) complexes. The main difference now is the presence of a coordinated RCHCl ligand. Therefore, two possible reactions can take place on this intermediate: an internal addition of the C-Cl bond of the RCHCl group or the addition of a second molecule of *gem*-dichloroderivative. The former is clearly the preferred process versus the latter because the chlorocarbonyl fragment is just brought in the nearby of the second metal centre for the endo conformer, facilitating the intramolecular nucleophilic attack by the metal. This constitutes an outstanding example of positive cooperative effects. It should be mentioned that when the preferred conformer reacts, the boat-to-boat inversion of the six membered "Rh(N-N)₂Rh" ring regenerates this active endo conformer to bring the reaction to completion.

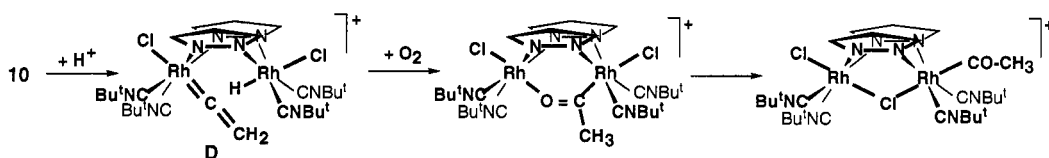
Gem-trichloroderivatives reproduce the reactions of their homologues *gem*-dichloroderivatives with **1**. Two distinctive cases have been observed. For *gem*-trichloroderivatives without β -hydrogen, such as chloroform and methyl trichloroacetate, the bridged $[\{\text{Rh}(\mu\text{-Pz})(\text{Cl})(\text{CNBu}^t)_2\}_2(\mu\text{-CClR})]$ complexes are obtained (Scheme 9). However, for 1,1,1-trichloroethane, which contains β -hydrogen, a further dehydrohalogenation reaction takes place to give the bridging vinylidene complex $[\{\text{Rh}(\mu\text{-Pz})(\text{Cl})(\text{CNBu}^t)_2\}_2(\mu\text{-C}=\text{CH}_2)]$ (**10**). The reaction of **1** with 1,1,1-trichloroethane constitutes a complete dechlorination of a *gem*-trichloroalkane by a dinuclear complex. In a formal sense, two of the abstracted

Cl atoms end up as chloride ligands, while the third is lost as HCl and the hydrocarbyl moiety remains bonded to the metal atoms.



Scheme 9

Reaction of **10** with HBF_4 gives an air-sensitive dark-green solution of the rhodium hydride complex $[\{\text{Rh}(\mu\text{-pz})\text{Cl}(\text{CNBu}^t)_2\}_2\text{H}(\eta^1\text{-C}=\text{CH}_2)]^+$ (**D**) (Scheme 10). Further reaction of this intermediate with O_2 gives the cationic dinuclear acyl-derivative $[\{\text{Rh}(\mu\text{-Pz})(\text{CNBu}^t)_2\}_2(\mu\text{-Cl})\text{Cl}(\eta^1\text{-COCH}_3)]\text{BF}_4$. The reaction involves the oxidation of a vinylidene ligand by molecular oxygen although neither complex **10** reacts with O_2 nor vinylidene ligands are easy to oxidise (ref. 26).



Scheme 10

The search of catalytic models for the degradation and oxidation of halogenated volatile organic compounds is an area of current interest. In this context, if we combine the steps in Schemes 9 and 10, i.e., the four-electron two-centres oxidative-addition of 1,1,1-trichloroethane to **1** with the associated elimination of HCl and the oxidation of **10** by molecular oxygen in presence of H^+ to give $[\{\text{Rh}(\mu\text{-Pz})(\text{CNBu}^t)_2\}_2(\mu\text{-Cl})\text{Cl}(\eta^1\text{-COCH}_3)]\text{BF}_4$, we have an example of binuclear reactivity where a *gem*-trichloroderivative is dechlorinated and oxidised to an acetyl group.

CONCLUDING REMARKS

The use of *supernucleophile* dinuclear complexes for cooperative activation of halocarbons is an area in an initial stage of investigation. The tuning of the metal basicity induced by the isocyanide ligands favour the reaction of dinuclear pyrazolato rhodium isocyanide complexes not only with alkyl iodides and bromides, but also with chlorocarbons to give dialkyl and functionalised bridging alkylidene dirhodium(III) complexes easily and quickly. From our results is apparent that intramolecular motions are decisive to allow the existence of cooperative effects in oxidative-addition reactions, which direct the pathways to products with specific stereochemistries. Moreover, several reaction types such as the S_{N} , occurring at individual centres, may compete with ET and free-radical, for which both metals act as a whole, depending on the nature of the metal and on the substrates. It is clear from our work that this approach has a great potential for a better understanding of the degradation of alkyl chloro derivatives by dinuclear complexes.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the efforts to the coworkers cited in the references for their many important contributions. This work was financially supported by DGICYT (Spain) (Projects 94-1186 and 95-221-C1) and the European Commission.

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