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Bimetallic Reactivity of Dirhodium Compounds Leading to Functionalized Methylene-Bridged Compounds[†]

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Reactions of $[\{Rh(\mu\text{-}Pz)(CNBu^t)_2\}_2]$ (Pz = pyrazolate, **1**) with dichloromethane, α,α-dichlorotoluene, 1,1-dichloroacetone, and methyldichloroacetate gave the functionalized methylene-bridged compounds $[\{Rh(\mu\text{-}Pz)(Cl)(CNBu^t)_2\}_2(\mu\text{-}CHR)]$ (R = H, Ph, COMe, CO_2Me), respectively. The molecular structure of $[\{Rh(\mu\text{-}Pz)(Cl)(CNBu^t)_2\}_2\{\mu\text{-}CH(CO_2Me)\}]$ was determined by an X-ray diffraction study. Similarly, the thiolate complex $[\{Rh(\mu\text{-}SBu^t)(CNBu^t)_2\}_2]$ was reacted with dichloromethane to give $[\{Rh(\mu\text{-}SBu^t)(Cl)(CNBu^t)_2\}_2(\mu\text{-}CH_2)]$. The *gem*-dichloroalkanes are formally broken in three fragments that become a methylene-bridging group and two terminal chloride ligands in these two-center four-electron oxidative-addition reactions. Decreasing the nucleophilicity of the metals via steric effects, while keeping the basicity of the metals constant, leads to a different type of product, as shown by reaction of dichloromethane with $[\{Rh(\mu\text{-}Me_2Pz)(CNBu^t)_2\}_2]$ to give $[\{Rh(\mu\text{-}Me_2Pz)(Cl)(CNBu^t)_2\}_2]$. A deeper insight into these reactions is provided by reactions of the complex $[(cod)Rh(\mu\text{-}Pz)_2Rh(CNBu^t)_2]$ with methyl dichloroacetate and dichloromethane to give the mixed-valence Rh(I)−Rh(III) complex $[(cod)Rh(\mu\text{-}Pz)_2Rh(Cl)\{\eta^1\text{-}CHCl(CO_2Me)\}(CNBu^t)_2]$ and the methylene-bridged complex $[(cod)(Cl)Rh(\mu\text{-}Pz)_2(\mu\text{-}CH_2)Rh(Cl)(CNBu^t)_2]$, respectively. The former evidences that the above rections take place in two steps and that the second step involves an internal oxidative-addition reaction following an S_N2 mechanism. The latter reaction is very suggestive of how cooperative effects can act in a dinuclear complex to induce an unusual reactivity.

Introduction

The oxidative-addition reaction of alkyl halides to low-valent transition metal complexes has been shown to be a key step for some catalytic processes[1] and a general synthetic method to form metal−carbon σ bonds.[2] The broad interest of this reaction has generated many studies of oxidative-addition reactions of alkyl iodides or bromides with mononuclear anionic or neutral complexes of the late transition metals.[3] However, reactions with chloroalkanes have been less frequently studied because stronger metal nucleophiles are usually needed. An increase in the electron density on the metal was particularly important in order to enhance the reactions with *gem*-dichloroalkanes[4] such as dichloromethane, and, for that reason, reports on these reactions have been limited. The nucleophilicity was found to be provided in rhodium(I) complexes by using polydentate N-donor ligands,[5] sulfur macrocycles,[6] and basic phosphines such as PMe_3.[7] Three types of compounds have previously been obtained: (a) Chloromethyl complexes, the most frequent products, have been the result of the addition of a C−Cl bond to a single metal center. These compounds show significant promise in developping a further reactivity, such as possible reagents in organic synthesis.[8] If the mononuclear complex contains a

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[†] Dedicated to Professor Rafael Usón on the occasion of his 75th birthday.

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nonmetal basic center, an insertion of the methylene group between the metal and this heteroatom has been observed,[9] providing evidence for the possibility of breaking both C−Cl bonds. (b) Methylene-bridged complexes also occur by an unusual two-center three-fragment oxidative-addition reaction[10] of dichloromethane to dinuclear complexes. (c) Schrock-type carbene complexes have been recently described as the product from a three-fragment oxidative-addition reaction on a single metal center in mononuclear ruthenium(0) complexes, with easily removable dihydrogen or dinitrogen ligands.[11]

We have recently described that the dinuclear complex $[\{Rh(\mu\text{-}Pz)(CNBu^t)_2\}_2]$ reacts with the organic monochloro compounds RCH_2Cl to give the double-addition products $[\{Rh(\mu\text{-}Pz)(\eta^1\text{-}CH_2R)(CNBu^t)_2\}_2(\mu\text{-}Cl)]Cl$.[12] We report now on the reactions of dinuclear rhodium complexes with organic *gem*-dichloro compounds, which offers an opportunity to study a different chemical behavior and to ascertain aspects of the cooperative effects between two metal centers in proximity. Aspects of these studies were published as a preliminary communication.[10b]

Results

(i) Oxidative-Addition Reactions of Organic *gem*-Dichlorocompounds with $[\{Rh(\mu\text{-}X)(CNBu^t)_2\}_2]$ (X = Pz, Me_2Pz, SBu^t). The simple dissolution of the yellow compound $[\{Rh(\mu\text{-}Pz)(CNBu^t)_2\}_2]$ (Pz = pyrazolate, **1**) in dichloromethane involves a reaction with the solvent evidenced when their spectroscopic properties were compared with similar yellow solutions using an inert solvent such as benzene. The resulting methylene-bridging compound $[\{Rh(\mu\text{-}Pz)(Cl)(CNBu^t)_2\}_2(\mu\text{-}CH_2)]$ (**2**) was isolated in good yield as white crystals, which showed a triplet for the carbon and protons in the $^{13}C\{^1H\}$ and ^1H NMR spectra, respectively, due to the coupling with the two active ^{103}Rh nuclei. Related methylene-bridging complexes with a functional group on the methylene carbon, $[\{Rh(\mu\text{-}Pz)(Cl)(CNBu^t)_2\}_2(\mu\text{-}CHR)]$ (R = Ph (**3**), COMe (**4**), CO_2Me (**5**)) (Scheme 1), were obtained by reaction of stoichiometric amounts of the organic *gem*-dichloro compounds $RCHCl_2$ (R = Ph, COMe, CO_2Me) with $[\{Rh(\mu\text{-}Pz)(CNBu^t)_2\}_2]$ (**1**). More importantly, an inert atmosphere and the absence of light were required to obtain pure samples of complexes **2**−**5**. For example, the addition of $PhCHCl_2$ to **1**, under air at room temperature, gave a mixture of compound **3** (40%) and the previously reported Rh(II) complex $[\{Rh(\mu\text{-}Pz)(Cl)(CNBu^t)_2\}_2]$ (**6**) (60%).

Complexes **3**−**5** crystallized as the pale yellow hydrates by addition of a moist solvent and were characterized by analytical and spectroscopic methods, including a single-crystal X-ray analysis of complex **5** (Figure 1, see below). They were found to be dinuclear, while observing the molecular ions (M^+) via mass spectroscopy (FABS +). A general trend in these mass spectra was the detection of higher mass peaks, with isotopic profiles corresponding to $[\{Rh_2(Cl)(\mu\text{-}Pz)_2(\mu\text{-}CHR)(CNBu^t)_4\}_2(\mu\text{-}Cl)]^+$, conceivably emanating from the association of M^+ and $(M - Cl)^+$ through a chloride ligand (Scheme 2) occurring in the spectrometer. A tetranuclear complex, also formed in the MS spectrometer and isolated in a preparative scale, has been previously reported.[13]

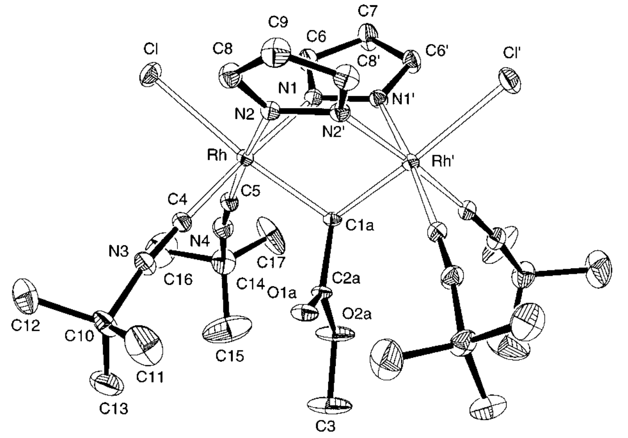
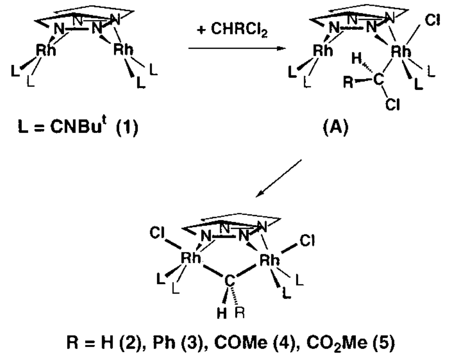
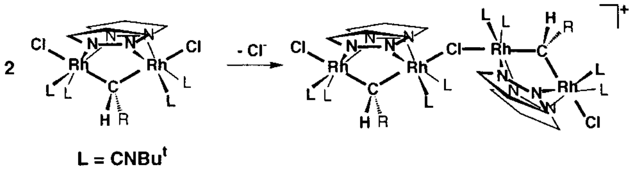


Figure 1. ORTEP view of the complex **5** together with the atomic numbering scheme. The ellipsoids for the atoms are drawn at the 30% probability level.

Scheme 1



Scheme 2



The molecular structure of $[\{Rh(\mu\text{-}Pz)(Cl)(CNBu^t)_2\}_2\{\mu\text{-}CH(CO_2Me)\}]$ (**5**) was determined by the X-ray analysis of the dihydrate complex **5**. A view of the structure of **5** is shown in Figure 1, together with the atomic numbering scheme. Selected bond distances and angles are given in Table 1. Complex **5** has an imposed crystallographic C_s symmetry, with the mirror passing through the midpoint of the Rh⋯Rh separation (3.341(1) Å) and the $CHCO_2Me$ ligand. The two Rh atoms are doubly bridged by two pyrazolates and symmetrically bridged by the C(1) atom from the $CHCO_2Me$ ligand.

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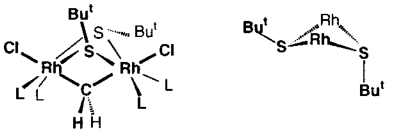
Table 1. Selected Bond Lengths (Å) and Angles (deg) for 5·2 H_2O

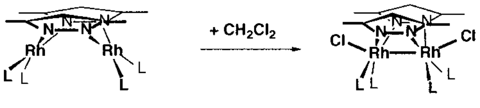
Rh−N1	2.056(2)	C1a−C2a	1.535(10)^{a}
Rh−N2	2.052(3)	C2a−O1a	1.180(11)^{a}
Rh−Cl	2.500(1)	C2a−O2a	1.360(14)^{a}
Rh−C1a	2.089(8)$^{\#}$	O2a−C3	1.415(10)^{a}
Rh−C1b	2.063(6)$^{\#}$	C1b−C2b	1.47(2)^{a}
Rh−C4	1.950(3)	C2b−O1b	1.254(18)^{a}
Rh−C5	1.951(4)	C2b−O2b	1.268(13)^{a}
N3−C4	1.141(4)	O2b−C3	1.386(10)^{a}
N4−C5	1.134(6)		
N1−Rh−N2	89.20(10)	Cl−Rh−C1b	170.42(3)
N1−Rh−Cl	92.66(7)	Cl−Rh−C4	91.65(10)
N1−Rh−C1a	78.03(7)$^{\#}$	Cl−Rh−C5	92.47(11)
N1−Rh−C1b	90.08(7)$^{\#}$	C1a−Rh−C5	83.66(10)^{a}
N1−Rh−C4	175.66(12)	C1a−Rh−C4	97.70(9)^{a}
N1−Rh−C5	89.63(13)	C1b−Rh−C5	96.73(10)^{a}
N2−Rh−Cl	91.90(8)	C1b−Rh−C4	85.59(9)^{a}
N2−Rh−C1a	91.88(8)$^{\#}$	C4−Rh−C5	90.65(14)
N2−Rh−C1b	78.96(8)^{a}	Rh−C4−N3	178.0(3)
N2−Rh−C4	90.19(12)	Rh−C5−N4	177.5(3)
N2−Rh−C5	175.53(13)	Rh−C1a−C2a	113.56(2)^{a}
Cl−Rh−C1a	169.90(3)	Rh−C1b−C2b	116.40(2)^{a}

[a] Atoms labeled with "a" or "b" represent the two disordered orientations of the bridging $CHCO_2Me$ group (see text and Supporting Information).

Chart 1. Two Views of the Anti Conformation of the Bu^t Groups in Complex 8



Scheme 3



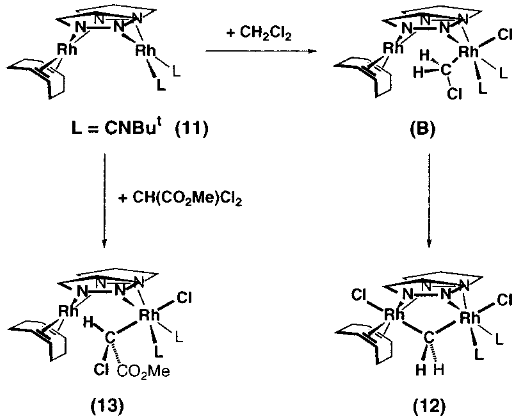
L = CNBu^t (9)

(10)

The octahedral coordination about each Rh atom is completed by a Cl atom and by two C atoms from terminal isocyanide ligands. It is noteworthy that the $CHCO_2Me$ ligand was found disordered and distributed in two positions (both on the mirror and with equal occupancy factor) having the terminal methyl in common.

The analogous thiolate complex **7** reacted with dichloromethane to give white crystals of [{Rh(μ-SBu^t)(Cl)(CNBu^t)$_2$}$_2$(μ-CH_2)] (**8**). The analytical data agree with the incorporation of one molecule of dichloromethane, and the presence of a methylene bridging group was evidenced by a triplet (J_{C-Rh} = 20 Hz) in the $^{13}C\{^1H\}$ NMR spectrum. Moreover, the anti stereochemistry of the bridging SBu^t ligands (Chart 1) was detected by the inequivalence of the methylenic protons in the single species observed in the ^1H NMR spectrum. However, the dimethylpyrazolate complex [{Rh(μ-Me_2Pz)(CNBu^t)$_2$}$_2$] (**9**) dissolves in dichloromethane to give a yellow solution, from which yellow crystals of the product, [{Rh(μ-Me_2Pz)(Cl)(CNBu^t)$_2$}$_2$] (**10**), separate. Complex **10** (Scheme 3) was isolated in high yield and was characterized as the dirhodium(II) complex on the basis of analytical and spectroscopic data (see Experimental Section). In contrast with the reactions described above, the dichloromethane does not add to complex **9**, but an oxidation of the rhodium centers with abstraction of chloride from dichloromethane was found to occur.

Scheme 4



(ii) Oxidative-Addition Reactions of *gem*-Dichloro Compounds to [(cod)Rh(μ-Pz)$_2$Rh(CNBu^t)$_2$] (11). The results of the reactions of two selected *gem*-dichloro derivatives, CH_2Cl_2 and $CH(CO_2Me)Cl_2$, with the mixed-ligand complex [(cod)Rh(μ-Pz)$_2$Rh(CNBu^t)$_2$] (**11**) containing two rhodium atoms of different nucleophilicity are summarized in Scheme 4. The reaction with the simplest *gem*-dichloro alkane, CH_2Cl_2, gave the methylene-bridged complex [(cod)(Cl)Rh(μ-Pz)$_2$(μ-CH_2)Rh(Cl)(CNBu^t)$_2$] (**12**), in which the two Rh atoms were oxidized. The bridging methylene group was unequivocally confirmed by the expected triplet in the ^1H and $^{13}C\{^1H\}$ NMR spectra. A consequence of the oxidation of the "Rh(cod)" moiety was the chemical shift at lower field and the smaller coupling constants $^1J_{Rh-C}$ for the olefinic cod carbons, when compared with those in the starting material, **11**. As shown in Table 2, this effect can be used as a tool to establish whether the "Rh(cod)" moiety was oxidized.

The product of the reaction of **11** with $CH(CO_2Me)Cl_2$ was [(cod)Rh(μ-Pz)$_2$Rh(Cl){η^1-CHCl(CO_2Me)}(CNBu^t)$_2$] (**13**), a mixed-valence Rh(I)−Rh(III) complex, which resulted from the oxidative-addition reaction of only one C−Cl bond at a single rhodium center. Moreover, the ^1H and $^{13}C\{^1H\}$ NMR spectra consisted of broad signals at room temperature, corresponding to possible fluxional species. The low-temperature ^1H NMR and $^{13}C\{^1H\}$ NMR spectra showed one single species in the slow-exchange region with the −CHCl(CO_2Me) group bonded to a single rhodium atom, since the methylenic proton and carbon gave a doublet due to coupling with only one ^{103}Rh nucleus, in both spectra. The resonances for the olefinic cyclooctadiene carbons (Table 2) were similar to those of **11**, according to the presence of a Rh$^{(I)}$(cod) center. Moreover, the lack of symmetry of the molecule due to the chiral carbon was evidenced by the inequivalence of all the pyrazolate protons for example. Furthermore, the −CHCl(CO_2Me) group was inside the pocket of the complex, i.e., far away from the pyrazolate bridging groups, since there was no NOE enhancements upon irradiation at the pyrazolate protons on the proton of the −CHCl(CO_2Me) group. Finally, it is remarkable that a very low chemical shift (δ 9.74 ppm), possibly due to the magnetic anisotropic effect of the pyrazolyl groups in a deshielding region, was found for the proton on the substituted

Table 2. Chemical Shifts δ (in ppm) and Coupling Constants $^1J_{C-Rh}$ (in Hz) for the Olefinic cod Carbons in the $^{13}C\{^1H\}$ NMR Spectra

complex	δ (J)
11, $[(cod)Rh(\mu\text{-}Pz)_2Rh(CNBu^t)_2]$	80.4 (13) and 79.7 (11)
13, $[(cod)Rh(\mu\text{-}Pz)_2Rh(Cl)\{\eta^1\text{-}CHCl(CO_2Me)\}(CNBu^t)_2]$	81.2 (13) and 80.6 (11)
12, $[(cod)(Cl)Rh(\mu\text{-}Pz)_2(\mu\text{-}CH_2)Rh(Cl)(CNBu^t)_2]$	109.6 (6) and 103.1 (7)

chloromethyl group. Most probably the fluxional process is due to a boat-to-boat inversion of the six-membered "$Rh(N-N)_2Rh$" ring, an effect that was not observed for **12**, since the methylene bridge prevents this conformational equilibrium. Supporting the proposed boat-to-boat inversion, which takes the $-CHCl(CO_2Me)$ group outside the pocket of the complex and places it in proximity to the pyrazolate rings, weak NOE enhancements of the two pyrazolate doublets at low field were observed on irradiation at the proton on the $-CHCl(CO_2Me)$ group in the ^1H NMR spectrum at room temperature.

It is noteworthy that the addition of $CNBu^t$ to the mixed-valence complex **13** produced the methylene-bridged complex **5** immediately.

Discussion

From our previous studies on the reactivity of dinuclear isocyanide rhodium and iridium complexes, we have shown them to be easily oxidized,[13] to act as donors through one metal center,[14] and to be nucleophiles.[15] In this study, our attention was focused on the reactions with *gem*-dichloroalkanes, which are attractive as a formal source of carbene ligands. However, this transformation has been scarcely observed,[11,16] since it involves the cleavage of two C−Cl bonds and the bonding of the three fragments to the metal, increasing the electron count in four units. Our 32 valence electron dinuclear complexes are especially appropriate for this kind of transformation, because they fulfill both requirements: high nucleophilicity and accessibility to 36 valence electron compounds if the three fragments became attached to both metals.

It is now well established that the nucleophilic complex $[\{Rh(\mu\text{-}Pz)(CNBu^t)_2\}_2]$ reacts with *gem*-dichloroalkanes to give methylene-bridged complexes $[\{Rh(\mu\text{-}Pz)(Cl)(CNBu^t)_2\}_2(\mu\text{-}CHR)]$. Moreover, the formation of the methylene-bridged complex $[\{Rh(\mu\text{-}SBu^t)(Cl)(CNBu^t)_2\}_2(\mu\text{-}CH_2)]$ from the dinuclear compound $[\{Rh(\mu\text{-}SBu^t)(CNBu^t)_2\}_2]$ indicates that N-donors are not strictly necessary to achieve highly reactive complexes, but the isocyanide ligands play the key role in enhancing the reactivity of these compounds. These reactions can be classified as two-center four-electron oxidative-addition reactions in which the *gem*-dichloroalkanes are formally broken in three fragments that appear as a carbene- or methylene-bridging group and two terminal chloride ligands in the products. As the overall reaction involves the cleavage of two C−Cl bonds, most probably it occurs in two separate steps. The first one would lead to complexes containing chloride and chloromethyl groups, and the second one would involve the cleavage of the C−Cl bond from the $Rh-(\eta^1\text{-}CHRCl)$ moiety. We believe that the intermediate species in these reactions are the Rh(I)−Rh(III) complexes $[(CNBu^t)_2Rh(\mu\text{-}L)_2Rh(Cl)(\eta^1\text{-}CHRCl)(CNBu^t)_2]$ (A, Scheme 1) with the organic group in the endo position. This stereochemistry, systematically found in related mixed-valence rhodium complexes,[15a,d] places the Rh(I) center and the organic substrate in proximity and facilitates the second intramolecular C−Cl bond oxidative-addition reaction. In fact, if the second step occurs slower than the first one, the double-addition products of formula $[\{Rh(\mu\text{-}L)(\eta^1\text{-}CHRCl)(CNBu^t)_2\}_2(\mu\text{-}Cl]Cl$ can be expected by addition of an excess of substrate. Indeed, the reactions of **1** and **7** with CH_2Cl_2 exclusively produce the methylene-bridged complexes **2** and **8**. This fact strongly supports the second step going much faster than the first one, and therefore, the complex resulting from the first C−Cl bond cleavage evolves so fast to the products that the addition of a second molecule of dichloromethane is prevented.

In addition, we have studied the reactions of the mixed-ligand complex $[(cod)Rh(\mu\text{-}Pz)_2Rh(CNBu^t)_2]$ (**11**) with two selected *gem*-dichloro organics. It is noteworthy that recent reactivity studies of complex **11** with organic monochloro compounds always yielded Rh(I)−Rh(III) compounds, maintaining the Rh(cod) center intact.[12] Moreover, no reaction of $[\{Rh(\mu\text{-}Pz)(cod)\}_2]$ with halocarbons has been previously observed. The reaction of **11** with $CH(CO_2Me)Cl_2$ produces the mixed-valence Rh(I)−Rh(III) complex $[(cod)Rh(\mu\text{-}Pz)_2Rh(Cl)\{\eta^1\text{-}CHCl(CO_2Me)\}(CNBu^t)_2]$ (**13**) (Scheme 4) even if an excess of substrate was used. However, the reaction of **11** with CH_2Cl_2 does not stop at this stage (**B**, Scheme 4), but evolves further to the methylene-bridged complex $[(cod)(Cl)Rh(\mu\text{-}Pz)_2(\mu\text{-}CH_2)Rh(Cl)(CNBu^t)_2]$ (**12**) (Scheme 4). At first glance, the results from these reactions seems to be reversed, since methyldichloroacetate, which contains the electron-withdrawing CO_2Me group, must be more reactive than dichloromethane. However, the reactions of **11** with the former appears to give the mixed-valence complex **13,** while the reaction with the latter provides the methylene-bridged compound **12**. On the other hand, assuming that cooperative effects between the metals enhance the reactivity of the Rh(cod) center, there was no apparent electronic reason to exclude them for the reaction with $CH(CO_2Me)Cl_2$, and therefore the difference points to steric reasons. In this context, it is interesting to remark on the anomalous chemical shift for the $-CHCl(CO_2Me)$ proton in the ^1H NMR spectrum of **13**. The origin of the large deshielding for this proton was its location in proximity to the line where the two deshielding cones of both pyrazolate rings bisect; this reinforces the shielding effect. Moreover, molecular models indicated that the

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free rotation around the Rh−{η^1-CHCl(CO_2Me)} bond is hindered by the cod ligand, and the proton on the carbon atom was just in the deshielding cone. This is the main difference found between complexes **13** and **B** (Scheme 4), since the formal replacement of the CO_2Me group by a proton would allow a larger rotational freedom around the Rh−(η^1-CH_2Cl) bond. As an internal S_N2 reaction was found to be sensitive to steric effects, this proposal may account for the results. The correct orientation for this reaction was probably difficult to achieve with **13**, and therefore the reaction ceases at this stage. The rotamer appears to be easily achieved in the case of **B**, and therefore this reaction goes to completion. Furthermore, the addition of $CNBu^t$ to **13** produced the replacement of the cod ligand at the Rh(cod) center and the addition of the C−Cl bond of the −CHCl(CO_2Me) group to the Rh(I) center to give **5**. These observations suggest that mixed-valence Rh(I)−Rh(III) complexes are intermediates in the double oxidative-addition reactions described herein and that an internal S_N2 mechanism is the logical pathway for the second step in the reactions leading to methylene-bridged complexes.

Furthermore, the enhanced reactivity of the Rh(cod) moiety in **11** to give the methylene-bridged complex **12** was remarkable. This reaction represents an interesting example of bimetallic cooperativity, since one of the rhodium atoms "Rh($CNBu^t$)$_2$" adds dichloromethane and places the chloromethyl group in close proximity to the second rhodium center and *in the correct orientation* that possibly allows the further reaction of the otherwise "inert" Rh(cod) moiety.

A final comment on the nucleophilicity of the metals comes from the comparison of the reactions of complexes [{Rh(μ-Pz)($CNBu^t$)$_2$}$_2$] (**1**) and [{Rh(μ-Me_2Pz)($CNBu^t$)$_2$}$_2$] (**9**) with dichloromethane. The former gave the methylene-bridged compound [{Rh(μ-Pz)(Cl)($CNBu^t$)$_2$}$_2$(μ-CH_2)] (**2**), while the latter provided the Rh(II) complex [{Rh(μ-Me_2Pz)(Cl)($CNBu^t$)$_2$}$_2$] (**10**). These differences could be explained by the nucleophilic character of the rhodium atoms in both complexes. From an electronic point of view, the incorporation of two methyl groups on the pyrazolate ring enhances the basicity of this ligand, and thus, the rhodium atoms in **9** are more basic than in **1**. However, the nucleophilicity of the metals in **9** was considerably reduced, since these puckered structures contain substituents at the 3 and 5 positions of the pyrazolate ligands that block the access to the d_{z^2} metal orbitals to act as nucleophiles. Indeed, the effect of the substituents on the pyrazolate rings has been observed to produce a dramatic decrease of the reaction rate for the addition of methyl iodide to dinuclear iridium carbonyl complexes, driving the reaction toward an electron transfer (ET) mechanism.[17] In our case, the consequence of the lower nucleophilicity of the complex with substituted pyrazolates **9**, relative to **1**, tilts the reaction to a different product, which is indicative of a mechanism that surplants the associative process.

Experimental Section

Starting Materials and Physical Methods. All reactions were carried out under argon using standard Schlenk techniques and protected from light with black photographic paper. The starting rhodium dinuclear pyrazolato and *tert*-butylthiolato complexes were prepared according to literature methods.[15d,18] The organochlorinated compounds were distilled under argon prior to use. Solvents were dried and distilled under argon by standard methods. Complexes **3**−**5** require the addition of a *moist* solvent to crystallize, and they are isolated as the hydrates. The formulas of the hydrates are indicated with the analytical data, and the water of crystallization was observed at 1.56 ppm in $CDCl_3$ in their ^1H NMR spectra. The new complexes described herein are light sensitive and should be stored in the dark. Physical measurements were carried out on the apparatus described previously.[12] NOE experiments were carried out using the standard CYCLENOE pulse sequence on the Varian spectrometer.

Preparation of the Complexes. [{Rh(μ-Pz)(Cl)($CNBu^t$)$_2$}$_2$(μ-CH_2)] (2). [{Rh(μ-Pz)($CNBu^t$)$_2$}$_2$] (100 mg, 0.15 mmol) was dissolved in 5 mL of CH_2Cl_2 in the dark. After 1 h of reaction, the yellow solution was evaporated to dryness and the residue recrystallized from acetone−diethyl ether. The solid was filtered, washed with pentane, and vacuum-dried. Yield: 111 mg (98%). Anal. Calcd for $C_{27}H_{44}N_8Cl_2Rh_2$: C, 42.82; H, 5.85; N, 14.79. Found: C, 43.04; H, 5.95; N, 14.93. IR (CH_2Cl_2, cm^{-1}): ν(CN) 2216 (s), 2193 (s), 2166 (s). ^1H NMR (298 K, $CDCl_3$): δ 7.81 (d, 4H), $H^{3,5}Pz$; 5.97 (t, 2H), H^4Pz; 3.45 (t, J_{H-Rh} = 1.4 Hz, 2H), μ-CH_2; 1.46 (s, 36H), CNC*Me*$_3$. ^{13}C-{^1H} NMR (298 K, $CDCl_3$): δ 139.2 $C^{3,5}Pz$; 134.3 (d, J_{C-Rh} = 56 Hz) *C*NCMe$_3$; 103.7 C^4Pz; 58.1 CN*C*Me$_3$; 30.4 CNC*Me*$_3$; 26.3 (t, J_{C-Rh} = 22 Hz) μ-CH_2. MS (FAB$^+$, CH_2Cl_2, *m*/*z* for ^{35}Cl): 756 (M^+, 7%), 721($M^+ - Cl$, 100%).

[{Rh(μ-Pz)(Cl)($CNBu^t$)$_2$}$_2$(μ-CHPh)] (3). To a solution of [{Rh(μ-Pz)($CNBu^t$)$_2$}$_2$] (**1**) (150 mg, 0.22 mmol) in ethyl acetate (9 mL) at −30 °C was added $CHPhCl_2$ (32.5 μL, 0.25 mmol) to give a navy blue solution, which was left in the freezer for 24 h. During this period pale yellow crystals were deposited, which were separated by filtration, washed with diethyl ether, and dried under vacuum (115 mg). The filtrate was concentrated up to 2 mL, and diethyl ether (10 mL) was added to give a second crop of crystals. Total yield: 134 mg (73%). Anal. Calcd for $C_{33}H_{48}N_8Cl_2Rh_2 \cdot H_2O$: C, 46.55; H, 5.92; N, 13.16. Found: C, 46.61; H, 6.12; N, 13.15. IR (CH_2Cl_2, cm^{-1}): ν(CN) 2235 (s), 2195 (s). ^1H NMR (295 K, $CDCl_3$): δ 7.83 (m, 4H), $H^{3,5}Pz$; 6.93 (m, 3H) and 6.77 (br s, 2H), μ-CH*Ph*; 6.14 (t, 2.10 Hz, 1H) and 6.06 (t, 2.10 Hz, 1H), H^4Pz; 5.54 (t, $^2J_{H-Rh}$ = 2.1 Hz, 1H), μ-C*H*Ph, 1.483 and 1.19 (s, 2 × 18H), CNC*Me*$_3$. ^{13}C-{^1H} NMR (295 K, $CDCl_3$): δ 161.3, 135.2, 127.5 and 123.9 (μ-CH*Ph*); 139.6 and 139.4 ($C^{3,5}Pz$); 104.33 and 104.28 (C^4Pz); 58.1 and 57.5 (CN*C*Me$_3$); 51.7 (t, J_{C-Rh} = 24 Hz) (μ-*C*HPh); 30.5 and 29.8 (CNC*Me*$_3$). MS (FAB$^+$, CH_2Cl_2, *m*/*z*) for ^{35}Cl: 1629, 75% ($2M - Cl^+$); 832, 30% (M^+); 797, 100% ($M - Cl^+$). If the reaction is carried out in the air and under the usual day lighting, the crude product of the reaction contains **3** (40%) and **6** (60%).

[{Rh(μ-Pz)(Cl)($CNBu^t$)$_2$}$_2$(μ-CHCOMe)] (4). To a solution of **1** (200 mg, 0.30 mmol) in ethyl acetate (9 mL) at −30 °C was added CH(COMe)Cl_2 (34.0 μL, 0.35 mmol), and the reaction mixture was left at this temperature for 1 h to give pale yellow crystals. The suspension was concentrated to 3 mL, and diethyl ether (10 mL) was added to complete the crystallization in the freezer overnight. The microcrystalline solid was separated by filtration and washed with cold hexane. Yield: 189 mg (80%). Anal. Calcd for $C_{29}H_{46}N_8Cl_2ORh_2 \cdot H_2O$: C, 42.61; H, 5.92; N, 13.71. Found: C, 42.12; H, 5.69; N, 13.61. IR (CH_2Cl_2, cm^{-1}): ν(CN) 2240 (s), 2200 (s). ^1H NMR (295 K, $CDCl_3$): δ 7.86 (d, 2.2 Hz, 2H) and 7.77 (d, 2.2 Hz, 2H), $H^{3,5}Pz$; 6.10 (t, 2.2 Hz, 1H) and 6.08 (t, 2.2 Hz, 1H), H^4Pz; 4.46 (t, $^2J_{H-Rh}$ = 1.7 Hz, 1H), μ-C*H*COMe; 1.82 (s, 3H), μ-CHCO*Me*; 1.50 and

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1.47 (s, 2 × 18H), CNC*Me*$_3$. ^{13}C{^{1}H} NMR (295 K, CDCl$_3$): δ 211.9 (μ-CH*C*OCH$_3$); 139.6 and 139.3 (C^{3,5}Pz); 104.6 and 104.8 (C^{4}Pz); 58.4 and 58.2 (CN*C*Me$_3$); 49.5 (t, $J_{\mathrm{C-Rh}}$ = 23 Hz) (μ-*C*HCOCH$_3$); 30.2 and 30.1 (CNC*Me*$_3$); 28.8 (μ-CHCO*C*H$_3$). MS (FAB$^+$, CH$_2$Cl$_2$, *m/z*) for ^{35}Cl: 1561, 10% (2M − Cl$^+$); 798, 7% (M$^+$); 763, 60% (M − Cl$^+$); 680, 95% (M − CNBu^t − Cl$^+$).

[{Rh(*μ*-Pz)(Cl)(CNBu^t)$_2$}$_2$(*μ*-CHCO$_2$Me)] (5) was prepared as described for **4** from [{Rh(μ-Pz)(CNBu^t)$_2$}$_2$] (**1**) (200 mg, 0.30 mmol) and CH(CO$_2$Me)Cl$_2$ (40.0 μL, 0.39 mmol). The solution was concentrated to 1 mL, mixed with 10 mL of diethyl ether, and left in the freezer overnight to give a pale yellow solid. The solid was separated by decantation, washed with 2 × 5 mL of hexane, and dried under vacuum. Yield: 207 mg (85%). Anal. Calcd for $C_{29}H_{46}N_8Cl_2O_2Rh_2\cdot H_2O$: C, 41.79; H, 5.80; N, 13.44. Found: C, 41.93; H, 5.81; N, 13.67. IR (CH$_2$Cl$_2$, cm^{-1}): ν(CN) 2223 (s), 2202 (s). ^{1}H NMR (295 K, CDCl$_3$): δ 7.82 (d, 2.0 Hz, 2H) and 7.75 (d, 2.0 Hz, 2H), H^{3,5}Pz; 6.06 (t, 2.0 Hz, 1H) and 6.04 (t, 2.0 Hz, 1H), H^{4}Pz; 4.15 (t, $^2J_{\mathrm{H-Rh}}$ = 2.20 Hz, 1H), μ-C*H*CO$_2$Me; 3.52 (s, 3H), μ-CHCO$_2$*Me*; 1.47 (s, 36H), CNC*Me*$_3$. ^{13}C{^{1}H} NMR (295 K, CDCl$_3$): δ 181.7 (μ-CH*C*O$_2$CH$_3$); 139.5 and 138.9 (H^{3,5}Pz); 104.2 and 103.8 (H^{4}Pz); 58.3 and 58.1 (CN*C*Me$_3$); 50.2 (μ-CHCO$_2$*C*H$_3$); 32.2 (t, $J_{\mathrm{C-Rh}}$ = 24 Hz, μ-*C*HCO$_2$CH$_3$); 30.35 and 30.27 (CNC*Me*$_3$). MS (FAB$^+$, CH$_2$Cl$_2$, *m/z*) for ^{35}Cl: 1593, 17% (2M − Cl$^+$); 814, 35% (M$^+$); 779, 95% (M − Cl$^+$); 696, 100% (M − CNBu^t − Cl$^+$).

[{Rh(*μ*-SBu^t)(Cl)(CNBu^t)$_2$}$_2$(*μ*-CH$_2$)] (8) was prepared and isolated as described for **2** starting from [{Rh(μ-SBu^t)(CNBu^t)$_2$}$_2$] (**7**) (77 mg, 0.107 mmol) and dichloromethane as substrate and solvent (5 mL). Yield: 70 mg (81%). Anal. Calcd for $C_{29}H_{56}N_4Cl_2S_2Rh_2$: C, 43.48; H, 7.05; N, 6.99. Found: C, 43.75; H, 6.96; N, 6.78. IR (CH$_2$Cl$_2$, cm^{-1}): ν(CN) 2196 (s), 2177 (s). ^{1}H NMR (295 K, CDCl$_3$): δ 3.32 (br s, 1H) and 2.654 (br s, 1H), μ-CH$_2$; 1.66 (s, 9H) and 1.55 (s, 9H), SC*Me*$_3$; 1.51 (s, 36H), CNC*Me*$_3$. ^{13}C{^{1}H} NMR (295 K, CDCl$_3$): δ 57.8 and 57.6 (CN*C*Me$_3$), 49.4 and 42.7 (S*C*Me$_3$), 32.9 and 32.4 (SC*Me*$_3$), 30.6 and 30.3 (CNC*Me*$_3$), 22.1 (t, $J_{\mathrm{C-Rh}}$ = 20 Hz, μ-CH$_2$). MS (FAB$^+$, CH$_2$Cl$_2$, *m/z*) for ^{35}Cl: 800, 5% (M$^+$); 765, 70% (M − Cl$^+$); 682, 100% (M − CNBu^t − Cl$^+$).

[{Rh(*μ*-Me$_2$Pz)(Cl)(CNBu^t)$_2$}$_2$] (10). Solid [{Rh(μ-Me$_2$Pz)(CNBu^t)$_2$}$_2$] (**9**) (138 mg, 0.19 mmol) was dissolved in dichloromethane, and the solution was left at room temperature for 24 h in the dark. Evaporation to ca. 1 mL and addition of pentane (15 mL) rendered the product as a yellow microcrystalline solid. The solid was filtered, washed with pentane, and vacuum-dried. Yield: 110 mg (70%). Anal. Calcd for $C_{30}H_{50}N_8Cl_2Rh_2$: C, 45.06; H, 6.32; N, 14.02. Found: C, 44.59; H, 6.49; N, 13.81. IR (CH$_2$Cl$_2$, cm^{-1}): ν(CN) 2203 (s), 2177 (s). ^{1}H NMR (298 K, CDCl$_3$): δ 5.25 (s, 2H), H^{4}Me$_2$*Pz*; 2.43 (s, 12H), *Me*$_2$Pz; 1.49 (s, 36H), CNC*Me*$_3$. ^{13}C{^{1}H} NMR (298 K, CDCl$_3$): δ 148.7 (C^{3,5}Me$_2$*Pz)*; 139.1 (d, $J_{\mathrm{C-Rh}}$ = 54 Hz, *C*NCMe$_3$); 105.4 (C^{4}Me$_2$*Pz)*; 58.3 (CN*C*Me$_3$); 30.9 (CNC*Me*$_3$); 13.3 (*Me*$_2$Pz). MS (FAB$^+$, CH$_2$Cl$_2$, *m/z* for ^{35}Cl): 798 (M$^+$, 23%); 763 (M$^+$ − Cl, 100%); 728 (M$^+$ − 2Cl, 63%).

[(cod)(Cl)Rh(*μ*-Pz)$_2$(*μ*-CH$_2$)Rh(Cl)(CNBu^t)$_2$] (12). To a solution of [(cod)Rh(μ-Pz)$_2$Rh(CNBu^t)$_2$] (75.0 mg, 0.12 mmol) in pentane (15 mL) at −40 °C was added CH$_2$Cl$_2$ (2 mL). After stirring for 20 min, the solution was evaporated to ca. 1 mL, layered with diethyl ether (15 mL), and left at room temperature for 2 days in the dark. Yellow crystals were deposited during this period, which were separated by decantation, washed with cold pentane, and vacuum-dried. Yield: 60 mg (70%). Anal. Calcd for $C_{25}H_{38}N_6Cl_2Rh_2$: C, 42.65; H, 5.48; N, 12.05. Found: C, 42.93; H, 5.49; N, 12.02. IR (CH$_2$Cl$_2$, cm^{-1}): ν(CN) 2217 (s), 2195 (s). ^{1}H NMR (298 K, CDCl$_3$): δ 7.78 (d, 1.8 Hz, 2H) and 7.68 (d, 1.9 Hz, 2H), H^{3,5}Pz; 6.02 (t, 1.9 Hz, 2H), H^{4}Pz; 5.62 (m, 2H) and 4.30 (m, 2H), HC = cod; 5.44 (t, $J_{\mathrm{H-Rh}}$ = 1.2 Hz, 2H), μ-CH$_2$; 3.29 (m, 2H) and 2.70 (m, 2H), H$_2$C exo cod; 2.17 (d, 8.8 Hz, 2H) and 2.08 (d, 7.3 Hz, 2H), H$_2$C endo cod; 1.49 (s, 18H), CNC*Me*$_3$. ^{13}C{^{1}H} NMR (298 K, CDCl$_3$): δ 139.8 and 139.6 (C^{3,5}Pz); 104.8 (C^{4}Pz); 109.3 (d, $J_{\mathrm{C-Rh}}$ = 6 Hz) and 103.1 (d, $J_{\mathrm{C-Rh}}$ = 7 Hz, HC= cod); 51.2 (t, $J_{\mathrm{C-Rh}}$ = 20 Hz, μ-CH$_2$); 58.6 CN*C*Me$_3$; 30.1 and 28.9 (H$_2$C cod); 30.5 (CNC*Me*$_3$). MS (FAB$^+$, CH$_2$Cl$_2$, *m/z* for ^{35}Cl): 663 (M$^+$ − Cl, 100%).

Table 3. Experimental Data for the X-ray Diffraction Study of 5·2H$_2$O

formula	$C_{29}H_{46}Cl_2N_8O_2Rh_2\cdot 2H_2O$
cryst syst	monoclinic
space group	$P2_1/m$
cell params at 295 K	
a, Å	8.962(5)
b, Å	21.543(5)
c, Å	11.014(5)
β, deg	110.13(2)
V, Å^3	2001(2)
Z	2
D_{calcd}, g cm^{-3}	1.413
F(000)	872
mol wt	851.48
linear abs coeff, cm^{-1}	9.98
2θ range, deg	6−60
index ranges	$-3 \le h \le 12$ $-30 \le k \le 28$ $-15 \le l \le 15$
no. of measd reflns	6263
no. of unique reflns	5980 (R_{int} = 0.0201)
no. of obsd reflns [$I > 2\sigma(I)$]	4627
no. of params, restraints	263, 0
wR_2 (all data)[a]	0.1656
R_1 [a]	0.0356

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$.

[(cod)Rh(*μ*-Pz)$_2$Rh(Cl){*η*^{1}-CHCl(CO$_2$Me)}(CNBu^t)$_2$] (13). Methyldichloroacetate (30 μL, 0.24 mmol) was added to a solution of [(cod)Rh(μ-Pz)$_2$Rh(CNBu^t)$_2$] (150 mg, 0.24 mmol) in pentane (15 mL) at −40 °C. Most of the product crystallizes in 40 min. The reaction mixture was concentrated to ca. 3 mL, and the solid was filtered, washed with cold pentane, and vacuum-dried. The crude product was recrystallized from CH$_2$Cl$_2$−pentane to render yellow microcrystals. Yield: 112 mg (60%). Anal. Calcd for $C_{27}H_{40}N_6Cl_2O_2Rh_2$: C, 42.81; H, 5.33; N, 11.10. Found: C, 42.65; H, 5.23; N, 11.28. IR (CH$_2$Cl$_2$, cm^{-1}): ν(CN) 2234 (s), 2212 (s). ^{1}H NMR (243 K, CDCl$_3$): δ 9.74 (d, $J_{\mathrm{H-Rh}}$ = 4.0 Hz, 1H), C*H*Cl(CO$_2$Me); 7.77 (d, 2.0 Hz, 1H), 7.63 (d, 2.0 Hz, 1H), 7.37 (d, 1.7 Hz, 1H) and 7.31 (d, 1.7 Hz, 1H), H^{3,5}Pz; 6.16 (t, 2.0 Hz, 1H) and 6.08 (t, 2.0 Hz, 1H), H^{4}Pz; 4.27 (m, 1H), 4.16 (m, 1H) and 4.07 (m, 2H), HC = cod; 3.65 (s, 3H), CHCl(CO$_2$*Me)*; 2.63 (m, 1H), 2.46 (m, 1H) and 2.37 (m, 2H), H$_2$C exo cod; 1.97 (m, 1H) and 1.73 (m, 3H), H$_2$C endo cod; 1.58 (s, 9H) and 1.58 (s, 9H), CNC*Me*$_3$. ^{13}C{^{1}H} NMR (243 K, CDCl$_3$): δ 177.3 (CHCl(*C*O$_2$Me)); 141.6, 137.8 and 137.7 (C^{3,5}Pz); 105.0 (C^{4}Pz); 83.5 (d, $J_{\mathrm{C-Rh}}$ = 13 Hz), 83.1 (d, $J_{\mathrm{C-Rh}}$ = 11 Hz), 82.2 (d, $J_{\mathrm{C-Rh}}$ = 11 Hz) and 81.1 (d, $J_{\mathrm{C-Rh}}$ = 13 Hz) (HC = cod); 58.9 (d, $J_{\mathrm{C-Rh}}$ = 21 Hz, *C*HCl(CO$_2$Me); 51.7 (CHCl(CO$_2$*Me*)); 51.1 and 50.7 (CN*C*Me$_3$); 31.1 and 29.9 (H$_2$C cod); 30.2 and 29.7 (CNC*Me*$_3$). MS (FAB$^+$, CH$_2$Cl$_2$, *m/z* for ^{35}Cl): 756 (M$^+$, 38%), 721 (M$^+$ − Cl, 100%), 614 (M$^+$ − Cl − CHClCO$_2$Me, 67%).

Crystal Structure Determination of Complex 5·2H$_2$O. The intensity data were collected at room temperature (293(2) K) on a Siemens AED single-crystal diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and the $\theta/2\theta$ scan technique. Crystallographic and experimental details are summarized in Table 3. No correction for absorption was made. The structure was solved by direct methods and refined by full-matrix least-squares procedures (based on F_o^2) with anisotropic thermal parameters in the last cycles of refinement for all non-hydrogen atoms. All hydrogen atoms were placed at their geometrically calculated positions and refined riding on their parent atoms, except those of the pyrazolate ligands, which were clearly localized in the final ΔF map and refined isotropically. A weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.2P)^2]$ was used in the last cycles of refinement, where $P = (F_o^2 + 2F_c^2)/3$. All calculations were carried out on the DIGITAL Alpha Station 255 computers of the "Centro di Studio per la Strutturistica Diffrattometrica" del CNR, Parma, using the SHELX-97 systems of crystallographic computer programs.[19]

The details of the crystal structure investigation are deposited to the Cambridge Crystallographic Data Center as supplementary publications no. CCDC-159670. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: int. code + 44-(1223)336-033, e-mail: deposit@ccdc.cam.ac.uk].

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Supporting Information Available: A listing of full experimental details of the structure determination, atomic coordinates, thermal parameters, hydrogen coordinates, and bond distances and angles for **5**$\cdot 2H_2O$. This material is available free of charge via the Internet at http://pubs.acs.org.

OM000946H

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