Oxidative-Addition of Organic Monochloro Derivatives to Dinuclear Rhodium Complexes: Mechanistic Considerations

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The addition of RCH_2Cl to the complex $[\{Rh(\mu\text{-}Pz)(CNBu^t)_2\}_2]$ (Pz = pyrazolate, **1**) occurs under mild conditions to yield the bis(alkyl)rhodium(III) complexes $[\{Rh(\mu\text{-}Pz)(\eta^1\text{-}CH_2R)(CNBu^t)_2\}_2(\mu\text{-}Cl)]Cl$ (R = Ph, CH=CH_2, CO_2Me, COMe). These reactions proceed through two separate steps, as evidenced by the observation of the intermediate mixed-valence complex $[(CNBu^t)_2Rh^I(\mu\text{-}Pz)_2Rh^{III}(\eta^1\text{-}CH_2Ph)(Cl)(CNBu^t)_2]$ resulting from the *trans*-addition of $PhCH_2Cl$ at a single metal center in **1**. Similar Rh(I)−Rh(III) complexes $[(cod)Rh(\mu\text{-}Pz)_2Rh(\eta^1\text{-}CH_2R)(Cl)(CNBu^t)_2]$ (R = Ph (**7**), CH=CH_2, CO_2Me) result from the addition of RCH_2Cl to the mixed-ligand complex $[(cod)Rh(\mu\text{-}Pz)_2Rh(CNBu^t)_2]$ (**6**). These exist in benzene and toluene as two interconverting conformers, differentiated by the location of the RCH_2 group either between the two metals in the pocket of the complexes (*endo* conformer) or at the *trans* position (*exo* conformer). An intramolecular boat-to-boat inversion accounts for this exchange. The thermodynamic parameters for complex **7** were $\Delta H^{\ddagger} = 16.2$ kcal·mol^{-1}, $\Delta S^{\ddagger} = 4.9$ eu, and $\Delta G_{293}{}^{\ddagger} = 14.9$ kcal·mol^{-1}. Primary alkyl bromides RCH_2Br react with **1** and with **6** to give the Rh(III) complexes $[\{Rh(\mu\text{-}Pz)(\eta^1\text{-}CH_2R)(CNBu^t)_2\}_2(\mu\text{-}Br)]Br$ (R = Ph, CO_2Me) and the mixed-valence complex $[(cod)Rh(\mu\text{-}Pz)_2Rh(\eta^1\text{-}CH_2Ph)(Br)(CNBu^t)_2]$. However, the secondary alkyl bromide PhCH(Me)Br reacts with **1** and with **6** to give the dirhodium(II) complexes $[\{Rh(\mu\text{-}Pz)(Br)(CNBu^t)_2\}_2]$ and $[(cod)(Br)Rh(\mu\text{-}Pz)_2Rh(Br)(CNBu^t)_2]$, respectively, along with 2,3-diphenylbutane and traces of styrene and ethylbenzene, suggesting free-radical pathways for these reactions. The thermal decomposition of the bis(alkyl)chloro complexes gives free isobutene and the cyanide complexes $[(CNBu^t)_2(\eta^1\text{-}CH_2R)Rh(\mu\text{-}Pz)_2(\mu\text{-}Cl)Rh(\eta^1\text{-}CH_2R)(CN)(CNBu^t)]$ (R = Ph, COMe, CO_2Me). Decomposition of the bis(alkyl)bromo derivatives occurs under sunlight irradiation and anaerobic conditions to give bibenzyl, *cis*- and *trans*-stilbene, and toluene.

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Introduction

The oxidative-addition of alkyl halides to metal complexes is a general synthetic method for metal−carbon σ bonds.[1] Most of the reported studies deal with alkyl iodides and bromides and rhodium,[2] iridium,[3] palladium,[4] platinum,[5] and gold[6] complexes. In particular, the addition of MeI to carbonyl rhodium complexes has been studied with mechanistic detail, since it is the key step in the catalyzed carbonylation of methanol on an industrial scale.[7] However, oxidative-addition reactions of the less reactive alkyl chlorides to metal centers are less common by far. A few mononuclear complexes are capable of cleaving alkyl C−Cl bonds by a conventional two-fragment, two-electron oxidative-addition reaction. Some examples are phosphino complexes of palladium,[8] platinum,[9] and rhodium[10] in low-oxidation state, cyclometalated complexes of platinum,[11b] and cyclopentadienyl derivatives of iridium.[12]

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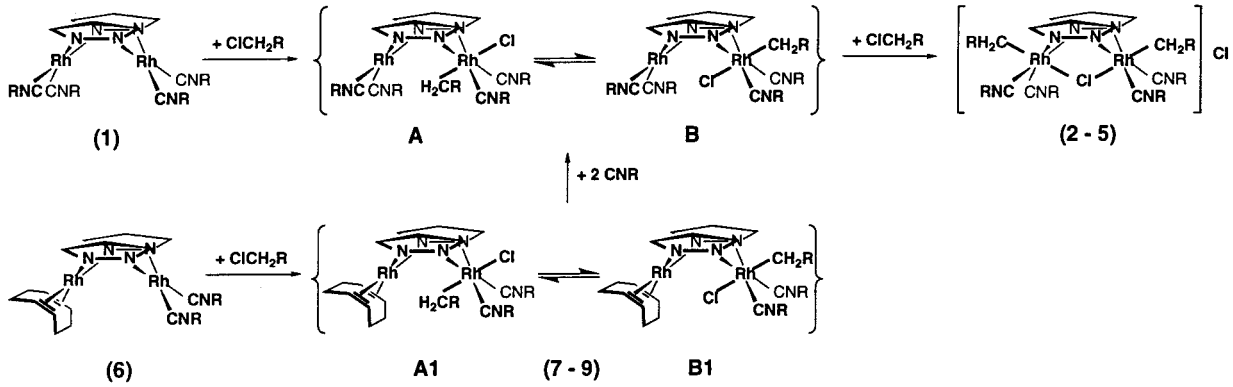
Scheme 1. Reactions of the Complexes 1 and 6, Showing the Proposed Intermediates A and B, and the Equilibria between Conformers



There is a no clear picture of the mechanism of the oxidative-addition of C−X bonds to metal complexes, since several pathways seem to be operative: an S_N2 mechanism,[1c,11] a concerted *cis*-addition, in which the metal inserts into the C−X bond,[2e] and mechanisms involving free alkyl radical intermediates.[13] In particular, paramagnetic organometallic intermediates have been detected in reactions of anionic iron(0) complexes with organic halides,[14] and halogen abstraction from RX by a metal-centered radical has been reported.[15] However, recent theoretical studies of the oxidative-addition of MeX (X = Cl, I) to Pd, Rh, and Ir complexes suggest that the preferred pathway is S_N2, either frontside[16] or backside.[17] Moreover, kinetic studies on the oxidative-addition of a wide range of alkyl halides to a Rh(I) complex suggest a general S_N2-like mechanism.[18]

Regarding the chemistry of dinuclear complexes, photoinduced C−Cl activation reactions have been reported for dinuclear gold[19] and iridium[20] complexes, and a thermal addition of dichloromethane to dinuclear rhodium complexes with P-donor ligands has been recently reported.[21] The general picture to date is that highly nucleophilic metal centers are required to overcome the relative inertness of the C−Cl bond toward reactions with metal complexes. An additional feature shown by dinuclear complexes is that cooperative effects between the metal center may facilitate C−Cl activations.[22] In this paper we focus our attention on the four-electron oxidative-addition reactions of monohaloalkyl compounds to dinuclear rhodium complexes.

Results and Discussion

Reactions with Alkyl Chlorides. The dinuclear complex [{Rh(μ-Pz)(CNBu^t)$_2$}$_2$] (Pz = pyrazolate, **1**) adds a variety of alkyl monochloro derivatives (RCH_2Cl) under very mild conditions in the dark to give [{Rh(μ-Pz)(η^1-CH_2R)(CNBu^t)$_2$}$_2$(μ-Cl)]Cl (R = Ph (**2**); CH=CH_2 (**3**); CO_2Me (**4**); COMe (**5**)) in high isolated yield (Scheme 1). Noteworthy, complexes **2**−**5** were obtained as a single stereoisomer. The C_{2v} symmetry of this stereoisomer, deduced from the NMR spectra, is consistent with a structure formed by two face-sharing octahedra with two pyrazolate and one chloride bridging ligand. Moreover, the proximity between the methlylene group and the $H^{3,5}$ protons of the pyrazolate ligands is unambiguously detected through NOE experiments.

The above addition reactions, completed in a few minutes, involve the oxidation of both metallic centers. Direct evidence that the reactions occur in two separate steps was provided by monitoring the reaction of $PhCH_2Cl$ with **1** by ^{1}H NMR. On mixing equimolar amounts of **1** and $PhCH_2Cl$, one could observe the intermediate **A** (Scheme 1), which was found to be the mixed-valence

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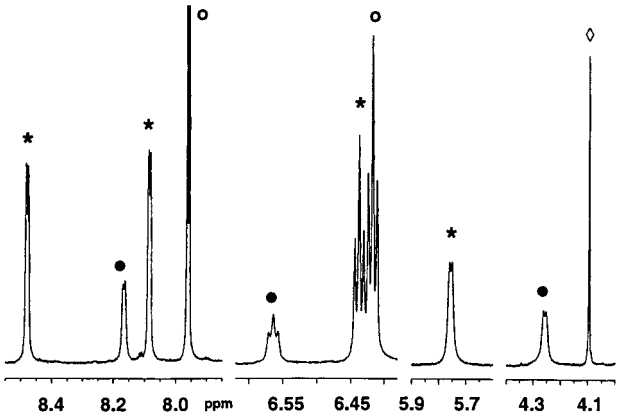

Figure 1. Selected regions of the ^{1}H NMR spectrum in C_6D_6 from the reaction mixture of [{Rh(μ-Pz)(CNBu^t)$_2$}$_2$] (**1**) with $PhCH_2Cl$ showing resonances for **1** (○), [{Rh(μ-Pz)(η^1-CH_2Ph)(CNBu^t)$_2$}$_2$(μ-Cl)]Cl (●), the intermediate [(CNBu^t)$_2$Rh^I(μ-Pz)$_2$Rh^{III}(η^1-CH_2Ph)(Cl)(CNBu^t)$_2$] (*), and $PhCH_2Cl$ (◊).

complex [(CNBu^t)$_2$Rh^I(μ-Pz)$_2$Rh^{III}(η^1-CH_2Ph)(Cl)(CNBu^t)$_2$] resulting from the *trans*-addition of the chloroalkane to a single metal center. Characterization of **A** relies on the C_s symmetry of the complex, shown by the ^{1}H NMR spectrum (Figure 1), the unusually low chemical shift for the methylene group (at $\delta = 5.76$), the lack of NOE between the Pz and the CH_2Ph protons since they are distant, and its preparation through a different route (vide infra). Addition of 1 molar equiv of $PhCH_2Cl$ to [(CNBu^t)$_2$Rh^I(μ-Pz)$_2$Rh^{III}(η^1-CH_2Ph)(Cl)(CNBu^t)$_2$] in the NMR tube gave quantitatively **2**.

Further evidence for this stepwise addition involving single metal centers comes from such additions to the mixed-ligand complex [(cod)Rh(μ-Pz)$_2$Rh(CNBu^t)$_2$] (**6**), which contains a less active "Rh(cod)" moiety. Complex **6** reacted with equimolar amounts of RCH_2Cl to give the neutral mixed-valence complexes [(cod)Rh(μ-Pz)$_2$Rh(η^1-CH_2R)(Cl)(CNBu^t)$_2$] (R = Ph (**7**); CH=CH_2 (**8**); CO_2Me (**9**)). These reactions involve the addition of the RCH_2Cl at the more nucleophilic rhodium atom with isocyanide ligands, confirmed by the shift of ν(CN) by ca. 115 cm^{-1} to higher frequencies, while the chemical shifts and coupling constants of the cod ligand in the $^{13}C\{^1H\}$ NMR spectra remained similar to those found in **6**.

Conformational Equilibria for Mixed-Valence Rh(I)−Rh(III) Complexes. Complexes **7**−**9** exist as an apparently single species in acetone-d_6 and $CDCl_3$ solution. NOE experiments at low temperature in $CDCl_3$ (Figure 2) conclusively established that the RCH_2 group is inside the pocket (*endo* position) of the complexes **7**−**9**. However, they exist as a mixture of two species in C_6D_6. Both species have an identical formulation by NMR, possess a symmetry plane between the two pyrazolate ligands, and are mixed-valence Rh(I)−Rh(III) complexes, judging from the $^{13}C\{^1H\}$ NMR chemical shifts and coupling constants of the cod carbons. The unique difference between them is the location of the alkyl group on the octahedral rhodium center; the species **A1** contain the RCH_2 group at the *endo* position, while it is placed at the *exo* position in the species **B1** (Scheme 1). Thus, the **A1** species give NOE results in toluene-d_8 at low temperature similar to those described for the solutions in $CDCl_3$, while the **B1** species show an

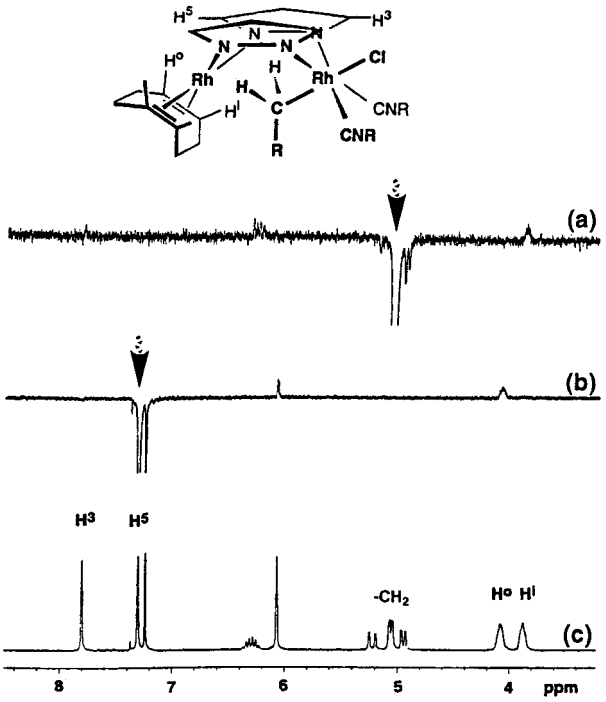

Figure 2. NOE difference spectra in $CDCl_3$ at −50 °C of [(cod)Rh(μ-Pz)$_2$Rh(η^1-CH_2CH=CH_2)(Cl)(CNBu^t)$_2$] (**8**) on irradiation at (a) the $-CH_2$ group, (b) H^5, (c) normal spectrum.

enhancement of the H^3 protons of the Pz ligands only upon irradiation of the RCH_2 group. Therefore, the mixed-valence Rh(I)−Rh(III) complexes **7**−**9** exist in benzene and toluene solution as the *endo* and *exo* conformers (**A1** and **B1**), respectively. The species **A1** and **B1** interconvert, which produced line broadening in the NMR spectra in benzene at room temperature. Accordingly, the coalescence of all pairs of resonances and a full picture for the exchange were observed on raising the temperature.

The activation parameters for this process, $\Delta H^{\ddagger} = 16.2$ kcal·mol^{-1}, $\Delta S^{\ddagger} = 4.9$ eu, and $\Delta G_{293}{}^{\ddagger} = 14.9$ kcal·mol^{-1}, were obtained from the line shape analysis[23] of the variable-temperature ^{1}H NMR spectra of complex **7** in toluene-d_8 (Figure 3). The small value of $\Delta S^{\ddagger}$ along with the lack of line broadening effects upon dilution corroborates the intramolecular nature of the process. In addition, these parameters are similar to those found[24] for the boat−boat inversion of the "Rh(N−N)$_2$Rh" six-membered ring undergone by the precursor **6**. All these data provide evidence that the interconversion **A1**/**B1** proceeds through such a process. The *exo* conformers of **7**−**9** and complexes **2**−**5** show the chemical shifts of the CH_2 protons at high field at ca. 3−4 ppm, while it is at low field at ca. 6 ppm for the *endo* conformers. Thus, the chemical shift is a good diagnostic parameter to distinguish between these positions.

Addition of 2 molar equiv of CNBu^t to complex **7** resulted in the replacement of cod to give the complex [(CNBu^t)$_2$Rh(μ-Pz)$_2$Rh(η^1-CH_2Ph)(Cl)(CNBu^t)$_2$] (**A**). Although the *endo* and *exo* conformers were formed at the

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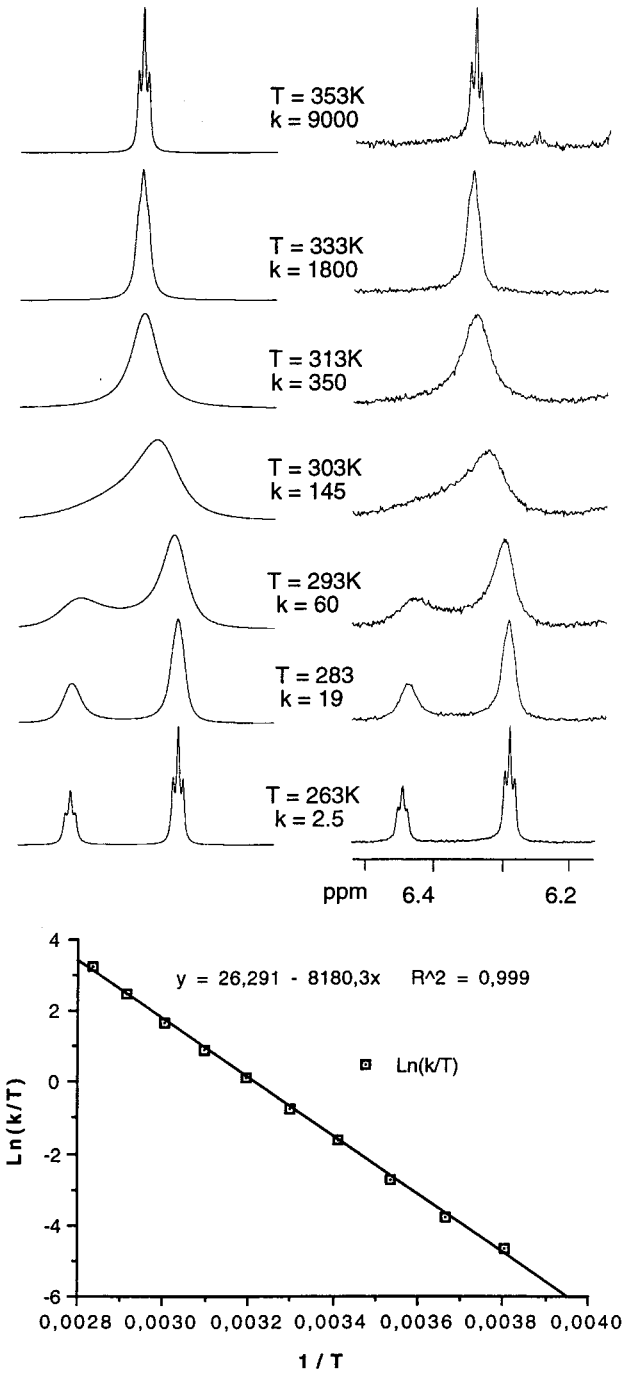
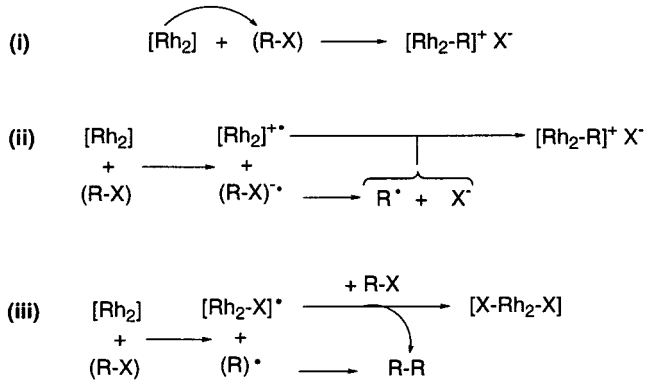


Figure 3. Simulated (left) versus experimental (right) variable-temperature ^{1}H NMR spectra in the region of the pyrazolate ligands for the interconversion of the conformers of complex **7** in toluene-d_8, and the corresponding Eyring plot.

beginning of the reaction, as shown by the chemical shifts for the CH_2Ph groups (5.77 (**A**), 4.31 (**B**), Scheme 1) in benzene-d_6, the equilibrium shifted to give the conformer **A** within 10 min.

The formation of complexes **7**−**9** starting from **6** indicated a close relation between the nucleophility of the rhodium center and the reactivity with primary alkyl chlorides, suggesting an S_N2 profile for these reactions (i, Scheme 2). In addition, attempts to add the secondary $MeCO_2CH(Me)Cl$ and tertiary Bu^tCl alkyl chlorides to **1** were unsuccessful. Both are particularly inappropriate for S_N2 type reactions because of the

Scheme 2



steric hindrance imposed on the α-carbon. Thus, while $MeCO_2CH_2Cl$ reacts with **1** to give **4**, the α-methyl-substituted $MeCO_2CH(Me)Cl$ is unreactive. These mixed-valence compounds could also result from an alternative and completely different mechanism. Thus, the transfer of one electron from **1** or **6** to RCl (ii, Scheme 2) would afford these products by coupling between the organic and inorganic radicals. However, the reduction potentials of the halo derivatives are too low to be reached by complex **1**, as shown by cyclic voltammetry measurements on **1**.[25] Finally, a halide abstraction mechanism involving the interaction between **1** and R−X to break the C−X bond homolytically into two radicals (iii, Scheme 2) also can be ruled out, since neither side-reactions nor C−C coupling products are detected in these reactions in the dark.

The second step of the reactions of **1** with alkyl chlorides occurs at the "$Rh^I(CNBu^t)_2$" active center remaining in the intermediates $[(CNBu^t)_2Rh^I(\mu\text{-}Pz)_2\text{-}Rh^{III}(R)(Cl)(CNBu^t)_2]$ to give the isolated products **2**−**5** (Scheme 1). The stereoselectivity shown in these reactions, resulting in a single isomer, should not be accidental but a consequence of how the second step proceeds. Both conformers, **A** and **B**, are able to undergo nucleophilic attack on the alkyl halide. However, the bridging framework and the structure found for the products result straightforwardly if this step occurs on the minor conformer **B**. The most simple and reasonable proposal is that this addition takes place preferentially on the minor isomer followed by the conformational equilibrium **A**/**B** to account for the stereoselectivity of these reactions.

Reactions with Alkyl Bromides. The influence of the substrate and the reaction conditions on the reaction mechanism is exemplified by the reactions of alkyl bromides with **1** and **6**. Complex **1** reacted with the primary alkyl bromides RCH_2Br (R = Ph, CO_2Me) to give the Rh(III) complexes $[\{Rh(\mu\text{-}Pz)(\eta^1\text{-}CH_2R)(CNBu^t)_2\}_2(\mu\text{-}Br)]Br$ (R = Ph (**10**), CO_2Me (**11**)). In a similar way, complex **6** reacted with $PhCH_2Br$ to give the mixed-valence complex $[(cod)Rh(\mu\text{-}Pz)_2Rh(\eta^1\text{-}CH_2Ph)(Br)(CNBu^t)_2]$ (**12**). In general, the reactions proceed more rapidly and they are noticeably more sensitive to sunlight than those carried out with the analogous chlorides. Complexes **10** and **11** were obtained as pure samples only when working under strict darkness; otherwise, both complexes appeared to be contaminated

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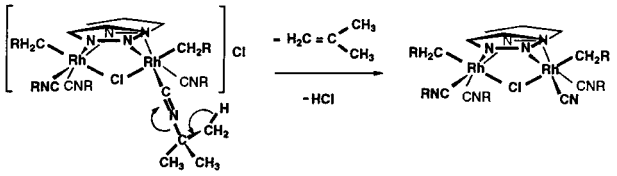
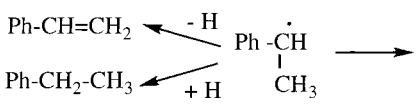
Scheme 3. Spontaneous Extrusion of Isobutene from an Isocyanide Ligand Leading to Cyanide Complexes



with variable amounts of the golden Rh(II) compound [{Rh(μ-Pz)(Br)(CNBu^t)$_2$}$_2$] (**13**). Therefore, the reactions of **1** and **6** with primary RCH$_2$Br substrates conform in general to the S$_N$2 pathway (i, Scheme 2), above proposed for the reactions with alkyl chlorides, if precautions to avoid free-radical initiators (light and oxygen) are taken. Complex **13** arises, probably, from a bromine abstraction reaction (iii, Scheme 3), which suggests the participation of two competitive reaction pathways: the S$_N$2 mechanism versus the radical bromine abstraction. A decisive test for this hypothesis is obtained from the results of the reaction of **1** and **6** with the substrate probe PhCH(Me)Br. Complex **1** reacted with PhCH(Me)Br under sunlight exposure and more slowly in the dark to give **13** in quantitative yield. Examination of the crystallization liquors revealed the formation of mainly an equimolar mixture of the two pairs of diastereoisomers of 2,3-diphenylbutane in almost quantitative yield, contaminated with traces of styrene and ethylbenzene.

Similarly, complex **6** reacted with PhCH(Me)Br giving the Rh(II) complex [(cod)(Br)Rh(μ-Pz)$_2$Rh(Br)(CNBu^t)$_2$] (**14**), isolated as a red crystalline solid, and mainly 2,3-diphenylbutane. Complex **14** was found to be diamagnetic and possessing a symmetry plane that makes the Pz ligands equivalent in the ^{1}H and ^{13}C{^{1}H} NMR spectra. Both metal centers were oxidized, as evidenced by the chemical shifts and coupling constants in the ^{13}C{^{1}H} NMR spectrum for the olefinic cod carbons. Therefore, complex **14** displays a Rh−Rh bond with the bromide ligands *trans* to this metal−metal bond. The formation of 2,3-diphenylbutane by a C−C coupling reaction and, more significantly, the observation of styrene and ethylbenzene as subproducts (eq 1) provide evidence for the participation of radicals PhCH(Me)$^\bullet$ in the process.[26] As noted above, the steric hindrance shown by the α-substituted alkyl chlorides disfavors S$_N$2 pathways, while it enhances in this case the stability of the possible radical PhCH(Me)$^\bullet$. Complex **13** should, hence, be the result of the halogen abstraction from the alkyl bromide, which generates the free radicals PhCH(Me)$^\bullet$ and [{Rh(μ-Pz)(CNBu^t)$_2$}$_2$Br]$^\bullet$, followed by the radical-chain propagation. Consequently, 2 molar equiv of PhCH(Me)Br are required to complete the reaction, as observed.



1/2 Ph-CH(Me)-CH(Me)-Ph (1)

Moreover, similar results from the reactions between the mixed-ligand complex **6** and alkyl bromides confirm these hypotheses. Thus, while the *trans*-addition of the primary alkyl bromide at a single metal center occurs in the reaction with PhCH$_2$Br, the dirhodium(II) complex [(cod)(Br)Rh(μ-Pz)$_2$Rh(Br)(CNBu^t)$_2$] (**14**) and 2,3-diphenylbutane result by bromine abstraction from the secondary alkyl bromide PhCH(Me)Br by **6**. Furthermore, these results show that the nucleophilicity of the metal center is the driving force for the reactions with primary bromides, while for the reactions with the secondary bromides a distinct reaction pathway involving the two metal centers is operative.

Further Reactions of the Alkyl Rhodium(III) Complexes. The sensitivity of the chloro complexes **2**−**5** to temperature, in particular of complex **2**, prompted us to study their stability. Complex **2** decomposes slowly but cleanly at room temperature in CDCl$_3$ to give a new complex, **15**, which has no symmetry and possesses only three isocyanide ligands according to the ^{1}H NMR spectrum of the reaction mixture. Isobutene was the second product of the reaction. This transformation, completed at 323 K in ca. 3 h in the NMR cavity, was reproduced in the laboratory to give the complex [(CNBu^t)$_2$(η^1-CH$_2$Ph)Rh(μ-Pz)$_2$(μ-Cl)Rh(η^1-CH$_2$Ph)-(CN)(CNBu^t)] (**15**). Complex **15** was isolated as a white crystalline solid in moderate yield and fully characterized by spectroscopic methods and by X-ray diffraction analyses (see below). The overall reaction involves a loss of the Cl and Bu^t groups as HCl and (CH$_3$)$_2$C=CH$_2$ from **2**, leaving a cyanide ligand (Scheme 3). Related fragmentations[27] in cationic complexes and rupture of an isocyanide ligand producing an oxidative-addition of the cyanide and alkyl groups to a low oxidation state metal center have been reported previously.[28] Although the complexes **4** and **5** are thermally more stable than **2**, they undergo a similar transformation into the complexes [(CNBu^t)$_2$(η^1-CH$_2$R)Rh(μ-Pz)$_2$(μ-Cl)Rh(η^1-CH$_2$R)-(CN)(CNBu^t)] (R = COMe, CO$_2$Me) upon heating in the darkness (^{1}H NMR evidence).

The structure of complex **15** is shown in Figure 4 along with the atom-numbering scheme used. Selected bond distances and angles are collected in Table 1. Both metals exhibit slightly distorted octahedral geometries: one rhodium center, Rh(1), completes its octahedral environment with two CNBu^t ligands, each *trans* to a bridging pyrazolate, and a benzyl group *trans*-disposed to the bridging chloride. The Rh···Rh intermetallic separation, 3.5594(8) Å, clearly indicates that there is no metal−metal bonding interaction. Along the metal−metal vector, the relative disposition of the terminal ligands is such that the two benzyl groups are eclipsed with respect to each other (C(1)−Rh(1)···Rh-(2)−C(12) 3.7(4)°); the Rh−C(benzyl) bond distances (mean 2.098(6) Å) are similar to those reported in related Rh(III)-η^1-benzyl complexes as in [(η^5-C$_5$Me$_5$)(η^1-CH$_2$Ph)Rh(μ-CH$_2$)$_2$Rh(η^4-C$_5$Me$_5$CH$_2$Ph)] (2.11(2) Å)[29] and [(tht)$_2$(η^1-CH$_2$Ph)Rh(μ-Cl)$_3$Rh(η^1-CH$_2$Ph)$_2$(tht)] (tht

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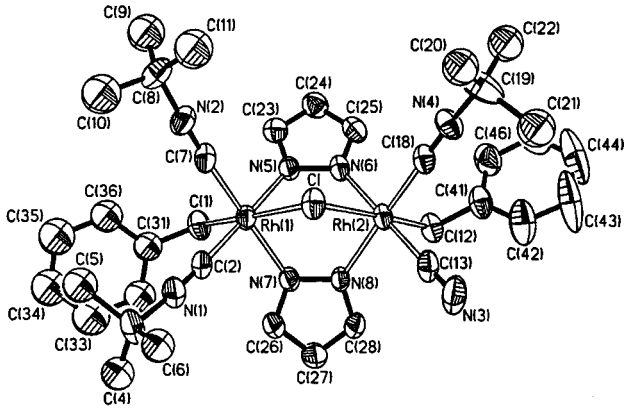

Figure 4. Molecular structure of complex **15**. For the disordered atoms (methyl groups and the phenyl ring C(31)−C(36)) only one group has been represented for clarity. The thermal ellipsoids are at the 50% probability level.

Table 1. Selected Bond Distances (Å) and Angles (deg) for Complex 15

Rh(1)···Rh(2)	3.5594(8)		
Rh(1)−Cl	2.507(2)	Rh(2)−Cl	2.522(2)
Rh(1)−N(5)	2.067(6)	Rh(2)−N(6)	2.094(6)
Rh(1)−N(7)	2.059(6)	Rh(2)−N(8)	2.067(5)
Rh(1)−C(1)	2.099(8)	Rh(2)−C(12)	2.096(8)
Rh(1)−C(2)	1.943(8)	Rh(2)−C(13)	1.982(9)
Rh(1)−C(7)	1.941(8)	Rh(2)−C(18)	1.920(8)
N(5)−N(6)	1.358(8)	N(7)−N(8)	1.356(8)
N(1)−C(2)	1.138(9)	N(3)−C(13)	1.114(10)
N(2)−C(7)	1.143(10)	N(4)−C(18)	1.142(9)
Cl−Rh(1)−N(5)	87.46(14)	Cl−Rh(2)−N(6)	85.96(14)
Cl−Rh(1)−N(7)	87.59(14)	Cl−Rh(2)−N(8)	86.86(13)
Cl−Rh(1)−C(1)	174.55(18)	Cl−Rh(2)−C(12)	175.75(18)
Cl−Rh(1)−C(2)	92.00(19)	Cl−Rh(2)−C(13)	94.11(19)
Cl−Rh(1)−C(7)	89.8(2)	Cl−Rh(2)−C(18)	90.70(18)
N(5)−Rh(1)−N(7)	91.23(19)	N(6)−Rh(2)−N(8)	90.73(19)
N(5)−Rh(1)−C(1)	87.4(2)	N(6)−Rh(2)−C(12)	91.1(2)
N(5)−Rh(1)−C(2)	178.1(2)	N(6)−Rh(2)−C(13)	179.5(2)
N(5)−Rh(1)−C(7)	89.8(2)	N(6)−Rh(2)−C(18)	92.0(2)
N(7)−Rh(1)−C(1)	90.8(2)	N(8)−Rh(2)−C(12)	90.1(2)
N(7)−Rh(1)−C(2)	90.5(2)	N(8)−Rh(2)−C(13)	89.8(3)
N(7)−Rh(1)−C(7)	177.1(2)	N(8)−Rh(2)−C(18)	176.2(2)
C(1)−Rh(1)−C(2)	93.2(3)	C(12)−Rh(2)−C(13)	88.8(3)
C(1)−Rh(1)−C(7)	91.9(3)	C(12)−Rh(2)−C(18)	92.5(2)
C(2)−Rh(1)−C(7)	88.4(3)	C(13)−Rh(2)−C(18)	87.5(3)
Rh(1)−C(1)−C(31)	121.2(5)	Rh(2)−C(12)−C(41)	117.8(4)
Rh(1)−C(2)−N(1)	177.6(6)	Rh(2)−C(13)−N(3)	179.1(6)
Rh(1)−C(7)−N(2)	175.8(6)	Rh(2)−C(18)−N(4)	175.6(6)
Rh(1)−Cl−Rh(2)	90.13(5)		

= tetrahydrothiophene) (mean 2.095(7) Å).[30] The Rh−C bond length for the terminal CN group (1.982(9) Å) is slightly shorter than those previously reported in Rh(III) cyanide complexes (range 2.000(6)−2.047(4) Å),[31] although in all these cases two relatively *trans*-disposed terminal CN groups compete for the electron density of the metal; the weaker *trans* influence of the bridging pyrazolate group could rationalize the short Rh−C separation observed in **15**. Bridging pyrazolate ligands show usual bond distances for rhodium−nitrogen contacts of this type,[2a,32] the Rh(2)−N(6) distance (*trans* to the cyanide ligand) being slightly longer.

Upon sunlight exposure, a colorless deoxygenated $CDCl_3$ solution of the bromo complex **10** becomes yellow and then orange. The coupled product Ph−CH_2−CH_2−Ph (50% relative to **10**) is the major component along with *cis* and *trans* stilbene (30%) and toluene (20%). Uncharacterized rhodium products were observed at the end of the reaction, although [{Rh(μ-Pz)(Br)($CNBu^t$)$_2$}$_2$] (**13**) appeared at the beginning. However, an independent experiment showed the decomposition of **13** under sunlight exposure. Attempts to obtain the cross-coupling product Ph−CH_2−CH_2−CO_2Me by irradiation of an equimolar mixture of complexes **10** and **11** were unsuccessful.

The formation of bibenzyl by a C−C coupling process could be explained in terms of an intramolecular reductive elimination of the two $PhCH_2$ fragments from **10** to give **13**. Hovewer, the observation of stilbene and toluene as products requires the participation of Ph−$CH_2^\bullet$ radicals in the process.[26] Both pathways could operate simultaneously in our case. Coupling reactions involving the intermediacy of benzyl radicals have been observed for the thermal reactions of $PhCH_2Br$ with dinuclear ruthenium[33] and mononuclear anionic iron complexes[14] and in photoinduced C−Cl activation by dinuclear gold complexes.[19]

When reproducing the above experiment, but using a solution of **10** in $CDCl_3$ under an oxygen atmosphere, the major organic product was benzaldehyde, along with small amounts of Ph−CH=N−Bu^t and Bu^t−NH−CO−NH−Bu^t. The former results from the oxidation of the Ph−$CH_2^\bullet$ fragments, a process also observed for light-induced reactions of certain organopalladium derivatives with oxygen.[34] Free *tert*-butylamine, produced from the decomposition of $CNBu^t$, is required to explain the formation of the organic nitrogen compounds.[35]

Concluding Remarks

The results reported in this paper show the complexity of the reactions of alkyl chlorides and bromides with nucleophilic dinuclear rhodium complexes. Several pathways are operative depending on the substrate, and they may compete depending on the reaction conditions. The influence of light and oxygen on the type of products resulting from these reactions requires a careful experimental procedure to reproduce and compare results. Moreover, the mechanism of the oxidative-addition of alkyl halides to metal complexes cannot be generalized, because the nature of the halide and subtle differences of the organic chain may produce significant changes in the reaction pathways.

Experimental Section

General Comments. All the reactions were carried out under argon using standard Schlenk techniques and protected from light with black photographic paper. The complexes [{Rh-

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(μ-Pz)(CNBu^t)$_2$}$_2$] (**1**) and [(cod)Rh(μ-Pz)$_2$Rh(CNBu^t)$_2$] (**6**) were prepared according to literature methods.[24] The alkyl halides were distilled under argon prior to use. In general, the products appear as pale yellow oils in dried solvents, which become white microcrystals that contain water of hydration upon addition of *moist* pentane. The formulas of the hydrates are indicated with the analytical data, and the water of crystallization was observed at 1.56 ppm in $CDCl_3$ and at 2.81 and 2.84 ppm in acetone-d_6 in their ^{1}H NMR spectra. They are light-sensitive and must be stored in the dark. Solvents were dried and distilled under argon before use by standard methods. Carbon, hydrogen, and nitrogen analyses were performed in a Perkin-Elmer 2400 microanalyzer. IR spectra were recorded with a Nicolet 550 spectrophotometer. Mass spectra were recorded in a VG Autospec double-focusing mass spectrometer operating in the FAB$^+$ mode. Ions were produced with a standard Cs^+ gun at ca. 30 kV, and 3-nitrobenzyl alcohol (NBA) was used as matrix. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker ARX 300 and on a Varian UNITY 300 spectrometer operating at 300.13 and 299.95 MHz for ^{1}H, respectively. Chemical shifts are reported in parts per million and referenced to $SiMe_4$ using the residual signal of the deuterated solvent as reference. NOE experiments were carried out using the standard NOE 1d pulse sequence on the Varian spectrometer. Conductivities were measured in 4−5 × 10^{-4} M acetone solutions using a Philips PW 9501/01 conductimeter.

Preparation of the Complexes. [{Rh(μ-Pz)(η^1-CH$_2$Ph)(CNBu^t)$_2$}$_2$(μ-Cl)]Cl (2). Neat $PhCH_2Cl$ (72 μL, 0.63 mmol) was added to a solution of [{Rh(μ-Pz)(CNBu^t)$_2$}$_2$] (**1**) (200 mg, 0.30 mmol) in benzene (5 mL) in the dark. After 30 min the solution was carefully layered with pentane (30 mL) to produce white crystals of **2** overnight, which were filtered, washed with cold pentane, and dried under vacuum. Yield: 248 mg (91%). Anal. Calcd for $C_{40}H_{56}N_8Cl_2Rh_2\cdot 2H_2O$: C, 49.96; H, 6.29; N, 11.65. Found: C, 49.52; H, 6.38; N, 11.96. IR (CH_2Cl_2, cm^{-1}): ν(CN) 2226 (s), 2205 (s). ^{1}H NMR (293 K, $CDCl_3$): δ 7.72 (d, 2.2 Hz, 4H, H^{3,5}Pz), 7.45 (d, 6.5 Hz, 4H, H^o Ph), 7.29 (t, 6.5 Hz, 4H, H^{m}Ph), 7.27 (t, 2H, H^{p}Ph), 6.40 (t, 2H, H^{4}Pz), 3.96 (d, $^2J_{H-Rh}$ = 3.2 Hz, 4H, CH_2), 1.34 (s, 36H, CNBu^t). ^{13}C{^{1}H} NMR (293 K, $CDCl_3$): δ 140.0 (C^{3,5}Pz), 149.3, 128.9, 128.8, and 125.8 (Ph), 106.2 (C^{4}Pz), 59.2 (*C*-(CH$_3$)$_3$), 29.9 (C−(*C*H$_3$)$_3$), 28.8 (d, $^1J_{C-Rh}$ = 21 Hz, CH_2). MS (FAB$^+$, CH_2Cl_2, *m*/*z*): 889, 100% (M$^+$). Λ_M (4.79 10^{-4} M in acetone): 81 S cm^2 mol^{-1}.

[{Rh(μ-Pz)(η^1-CH$_2$CH=CH$_2$)(CNBu^t)$_2$}$_2$(μ-Cl)]Cl (3) was prepared and isolated as described above for complex **2** starting from **1** (200 mg, 0.30 mmol) and allyl chloride (51 μL, 0.63 mmol) to yield white crystals. Yield: 217 mg (87%). Anal. Calcd for $C_{32}H_{52}N_8Cl_2Rh_2\cdot 2H_2O$: C, 46.61; H, 6.55; N, 13.00. Found: C, 44.44; H, 6.37; N, 13.21. IR (CH_2Cl_2, cm^{-1}): ν(CN) 2224 (s), 2203 (s). ^{1}H NMR (293 K, $CDCl_3$): δ 7.48 (d, 2.1 Hz, 4H, H^{3,5}-Pz), 6.26 (t, 2H, H^{4}Pz), 6.23 (m, 2H, CH_2CH=CH_2), 5.30 (dd, 15.8 and 1.1 Hz, 2H, CH_2CH=CH_2), 5.08 (dd, 9.8 and 1.1 Hz, 2H, CH_2CH=CH_2), 3.25 (dd, $^3J_{H-H}$ = 8.5 and $^2J_{H-Rh}$ = 2.5 Hz, 4H, CH_2CH=CH_2), 1.48 (s, 36H, CNBu^t). ^{13}C{^{1}H} NMR (293 K, $CDCl_3$) (assigned from the APT spectrum): δ 146.3 (CH_2CH=CH_2), 139.4 (C^{3,5}Pz), 112.1(CH_2CH=CH_2), 106.1 (C^{4}Pz), 59.1 (*C*−(CH$_3$)$_3$), 30.0 (C−(*C*H$_3$)$_3$), 28.2 (d, $^1J_{C-Rh}$ = 21 Hz, *C*H$_2$CH=CH_2). MS (FAB$^+$, CH_2Cl_2, *m*/*z*): 789, 100% (M$^+$). Λ_M (4.77 10^{-4} M in acetone): 82 S cm^2 mol^{-1}.

[{Rh(μ-Pz)(η^1-CH$_2$CO$_2$Me)(CNBut)$_2$}$_2$(μ-Cl)]Cl (4) was prepared and isolated as described above for complex **2** starting from **1** (200 mg, 0.30 mmol) and $MeCO_2CH_2Cl$ (59 μL, 0.63 mmol) to render white crystals. Yield: 217 mg (82%). Anal. Calcd for $C_{32}H_{52}N_8O_4Cl_2Rh_2\cdot 2H_2O$: C, 42.35; H, 6.00; N, 12.35. Found: C, 42.35; H, 5.76; N, 12.17. IR (CH_2Cl_2, cm^{-1}): ν(CN) 2235 (s), 2217 (s); ν(CO) 1713 (s). ^{1}H NMR (293 K, $CDCl_3$): δ 7.74 (d, 2.2 Hz, 4H, H^{3,5}Pz), 6.35 (t, 2H, H^{4}Pz), 3.75 (s, 6H, CH_3OOC), 2.87 (d, $^2J_{H-Rh}$ = 3.2 Hz, 4H, CH_2), 1.55 (s, 36H, CNBu^t). ^{13}C{^{1}H} NMR (293 K, $CDCl_3$): δ 179.5 (CO), 140.3 (C^{3,5}Pz), 106.6 (C^{4}Pz), 59.8 (*C*-(CH$_3$)$_3$), 51.2 (*C*H$_3$CO$_2$), 29.9 (C−(*C*H$_3$)$_3$), 17.9 (d, $^1J_{C-Rh}$ = 22 Hz, CH_2). MS (FAB$^+$, CH_2Cl_2, *m*/*z*): 853, 100% (M$^+$). Λ_M (5.17 10^{-4} M in acetone): 113 S cm^2 mol^{-1}.

[{Rh(μ-Pz)(η^1-CH$_2$COMe)(CNBu^t)$_2$}$_2$(μ-Cl)]Cl (5) was prepared as described above for complex **2** starting from **1** (200 mg, 0.30 mmol) and $MeCOCH_2Cl$ (51 μL, 0.63 mmol) to render pale yellow crystals. Yield: 240 mg (94%). Anal. Calcd for $C_{32}H_{52}N_8O_2Cl_2Rh_2\cdot 2H_2O$: C, 43.01; H, 6.32; N, 12.54. Found: C, 42.91; H, 6.30; N, 12.35. IR (CH_2Cl_2, cm^{-1}): ν(CN) 2232 (s), 2210 (s); ν(CO) 1676 (s). ^{1}H NMR (293 K, $CDCl_3$): δ 7.74 (d, 2.2 Hz, 4H, H^{3,5}Pz), 6.30 (t, 2H, H^{4}Pz), 3.10 (d, $^2J_{H-Rh}$ = 3.1 Hz, 4H, CH_2), 2.25 (s, 6H, CH_3CO), 1.51 (s, 36H, CNBu^t). ^{13}C-{^{1}H} NMR (293 K, $CDCl_3$): δ 213.3 (CO), 140.5 (C^{3,5}Pz), 106.6 (C^{4}Pz), 60.1 (*C*−(CH$_3$)$_3$), 30.4 (*C*H$_3$CO), 30.1 (C−(*C*H$_3$)$_3$), 29.2 (d, $^1J_{C-Rh}$ = 22 Hz, CH_2). MS (FAB$^+$, CH_2Cl_2, *m*/*z*): 821, 100% (M$^+$). Λ_M (4.99 10^{-4} M in acetone): 111 S cm^2 mol^{-1}.

[(cod)Rh(μ-Pz)$_2$Rh(η^1-CH$_2$Ph)(Cl)(CNBut)$_2$] (7). $PhCH_2Cl$ (56 μL, 0.49 mmol) was added to a suspension of [(cod)Rh-(μ-Pz)$_2$Rh(CNBu^t)$_2$] (**6**) (250 mg, 0.41 mmol) in pentane (15 mL) and stirred overnight in the dark. The resulting suspension was decanted and the residue washed with cold pentane and dried under vacuum. Yield: 270 mg (89%). Anal. Calcd for $C_{31}H_{43}N_6ClRh_2\cdot 2H_2O$: C, 47.92; H, 5.58; N, 10.82. Found: C, 48.24; H, 5.71; N, 10.59. IR (CH_2Cl_2, cm^{-1}): ν(CN) 2222 (s), 2199 (s). ^{1}H NMR (223 K, $CDCl_3$): δ 7.81 (d, 1.8 Hz, 2H, H^3-Pz), 7.36 (d, 2H, H^{5}Pz), 7.29 (d, 7.0 Hz, 2H, H^{o}Ph), 7.20 (t, 7.0 Hz, 2H, H^{m}Ph), 7.16 (t, 1H, H^{p}Ph), 6.11 (t, 2H, H^{4}Pz), 5.83 (d, $^2J_{H-Rh}$ = 3.2 Hz, 2H, CH_2), 4.13 and 3.96 (m, 2H + 2H, =CH cod), 2.55 and 2.24 (m, 2H + 2H, H$_2$C^{exo} cod), 1.82 and 1.68 (m, 2H + 2H, H$_2$C^{endo} cod), 1.39 (s, 18H, CNBu^t). ^{13}C{^{1}H} NMR (223 K $CDCl_3$): δ 142.0 (C^{3}Pz), 137.7 (C^{5}Pz), 152.2, 128.3, 128.1, and 124.2 (Ph), 104.6 (C^{4}Pz), 81.1 (d, $^1J_{C-Rh}$ = 13 Hz, =CH cod), 80.3 (d, $^1J_{C-Rh}$ = 12 Hz, =CH cod), 57.9 (*C*-(CH$_3$)$_3$), 30.4 and 30.2 (H$_2$C cod), 29.9 (C−(*C*H$_3$)$_3$), 29.4 (d, $^1J_{C-Rh}$ = 23 Hz, CH_2). MS (FAB$^+$, CH_2Cl_2, *m*/*z*): 740, 5% (M$^+$); 705, 90% (M − Cl$^+$); 649, 10% (M − CH_2Ph^+); 614, 100% (M − CH_2Ph − Cl$^+$). Λ_M (4.50 10^{-4} M in acetone): 3 S cm^2 mol^{-1}.

[(cod)Rh(μ-Pz)$_2$Rh(η^1-CH$_2$CH=CH$_2$)(Cl)(CNBu^t)$_2$] (8) was prepared as described above for complex **7** starting from **6** (100 mg, 0.16 mmol) and allyl chloride (17 μL, 0.20 mmol). Yield: 88 mg (80%). Anal. Calcd for $C_{27}H_{41}N_6ClRh_2\cdot H_2O$: C, 45.74; H, 6.11; N, 11.85. Found: C, 45.99; H, 5.61; N, 11.56. IR (CH_2Cl_2, cm^{-1}): ν(CN) 2228 (s), 2201 (s). ^{1}H NMR (223 K, $CDCl_3$): δ 7.79 (br s, 2H, H^{3}Pz), 7.30 (br s, 2H, H^{5}Pz), 6.29 (m, 1H, CH_2CH=CH_2), 6.07 (br s, 2H, H^{4}Pz), 5.22 (br d, 16.7, 1H, CH_2-CH=CH_2), 5.05 (br t, $^3J_{H-H}$ and $^2J_{H-Rh}$ = 5.8 Hz, 2H, CH_2-CH=CH_2), 4.95 (dd, 9.7 and 2.3 Hz, 1H, CH_2CH=CH_2), 4.08 and 3.88 (m, 2H + 2H, =CH cod), 2.52 and 2.38 (m, 2H + 2H, H$_2$C^{exo} cod), 1.78 (m, 4H, H$_2$C^{endo} cod), 1.53 (s, 18H, CNBu^t). ^{13}C{^{1}H} NMR (223 K $CDCl_3$) (asigned form APT spectrum): δ 148.1 (CH_2CH=CH_2), 141.9 (C^{3}Pz), 137.6 (C^{5}Pz), 132.5 (d, $^1J_{C-Rh}$ = 54 Hz, CN), 109.9 (CH_2CH=CH_2), 104.5 (C^{4}Pz), 80.9 (d, $^1J_{C-Rh}$ = 13 Hz, =CH cod), 80.3 (d, $^1J_{C-Rh}$ = 11 Hz, =CH cod), 57.8 (*C*−(CH$_3$)$_3$), 30.4 and 30.2 (H$_2$C cod), 30.0 (C−(*C*H$_3$)$_3$), 28.4 (d, $^1J_{C-Rh}$ = 21 Hz, CH_2). MS (FAB$^+$, CH_2Cl_2, *m*/*z*): 690, 7% (M$^+$); 655, 95% (M − Cl$^+$); 614, 100% (M − CH_2CH=CH_2 − Cl$^+$).

[(cod)Rh(μ-Pz)$_2$Rh(η^1-CH$_2$CO$_2$Me)(Cl)(CNBu^t)$_2$] (9) was prepared as described above for complex **7** starting from **6** (100 mg, 0.16 mmol) and $MeCO_2CH_2Cl$ (19 μL, 0.20 mmol). Yield: 88 mg (75%). Anal. Calcd for $C_{27}H_{41}N_6O_2ClRh_2\cdot H_2O$: C, 43.76; H, 5.85; N, 11.34. Found: C, 43.46; H, 6.16; N, 10.97. IR (CH_2Cl_2, cm^{-1}): ν(CN) 2233 (s), 2211 (s); ν(CO) 1706 (s). ^{1}H NMR (223 K, $CDCl_3$): δ 7.78 (d, 1.9 Hz, 2H, H^{3}Pz), 7.30 (d, 1.6 Hz, 2H, H^{5}Pz), 6.08 (t, 2H, H^{4}Pz), 4.53 (d, $^2J_{H-Rh}$ = 3.2 Hz, 2H, CH_2), 4.08 and 3.93 (m, 2H + 2H, =CH cod), 3.66 (s, 3H, CH_3-OOC), 2.52 and 2.40 (m, 2H + 2H, H$_2$C^{exo} cod), 1.78 (m, 4H, H$_2$C^{endo} cod), 1.56 (s, 18H, CNBu^t). ^{13}C{^{1}H} NMR (223 K $CDCl_3$): δ 181.5 (CO), 142.2 (C^{3}Pz), 138.1 (C^{5}Pz), 104.6 (C^4-Pz), 81.2 (d, $^1J_{C-Rh}$ = 13 Hz, =CH cod), 80.6 (d, $^1J_{C-Rh}$ = 11 Hz, =CH cod), 58.5 (*C*−(CH$_3$)$_3$), 50.7 (*C*H$_3$OOC), 30.8 and 30.7

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(H_2C cod), 30.3 (C−(CH_3)$_3$), 17.7 (d, $^1J_{C-Rh}$ = 21 Hz, CH_2). MS (FAB$^+$, CH_2Cl_2, *m/z*): 723, 25% (M^+); 687, 100% (M − Cl)$^+$.

[{Rh(μ-Pz)(η^1-CH$_2$Ph)(CNBu^t)$_2$}$_2$(μ-Br)]Br (10) was prepared as described above for complex **2** starting from **1** (200 mg, 0.30 mmol) and $PhCH_2Br$ (78 μL, 0.63 mmol) to render pale yellow crystals. Yield: 285 mg (92%). Anal. Calcd for $C_{32}H_{52}N_8O_4Br_2Rh_2\cdot 2H_2O$: C, 45.73; H, 5.75; N, 10.66. Found: C, 45.40; H, 5.46; N, 10.97. IR (CH_2Cl_2, cm^{-1}): ν(CN) 2226 (s), 2203 (s). ^{1}H NMR (293 K, $CDCl_3$): δ 7.75 (d, 2.2 Hz, 4H, H^{3,5}-Pz), 7.50 (d, 7.7 Hz, 4H, H^{o}Ph), 7.32 (m, 6H, H^{m,p} Ph), 6.42 (t, 2H, H^{4}Pz), 4.00 (d, $^2J_{H-Rh}$ = 3.3 Hz, 4H, CH_2), 1.41 (s, 36H, CNBu^t). ^{13}C{^{1}H} NMR (293 K, $CDCl_3$): δ 140.3 (C^{3,5}Pz), 149.2, 128.9, 128.8 and 125.8 (Ph), 106.3 (C^{4}Pz), 59.2 (*C*−(CH_3)$_3$), 29.9 (C−(*C*H$_3$)$_3$), 31.1 (d, $^1J_{C-Rh}$ = 21 Hz, CH_2). MS (FAB$^+$, CH_2Cl_2, *m/z*): 935, 100% (M^+). Λ_M (4.79 10^{-4} mol·L^{-1} in acetone): 100 S cm^2 mol^{-1}.

[{Rh(μ-Pz)(η^1-CH$_2$CO$_2$Me)(CNBu^t)$_2$}$_2$(μ-Br)]Br (11) was prepared as described above for complex **2** starting from **1** (100 mg, 0.15 mmol) and $MeCO_2CH_2Br$ (31 μL, 0.31 mmol) to render white crystals. Yield: 126 mg (86%). Anal. Calcd for $C_{32}H_{52}N_8O_4Br_2Rh_2\cdot 2H_2O$: C, 37.88; H, 5.56; N, 11.04. Found: C, 37.62; H, 5,20; N, 11.25. IR (CH_2Cl_2, cm^{-1}): ν(CN) 2234 (s), 2216 (s); ν(CO) 1732 (s). ^{1}H NMR (293 K, $CDCl_3$): δ 7.69 (d, 2.1 Hz, 4H, H^{3,5}Pz), 6.29 (t, 2H, H^{4}Pz), 3.72 (s, 6H, CH_3OOC), 2.87 (d, $^2J_{H-Rh}$ = 3.2 Hz, 4H, CH_2), 1.53 (s, 36H, CNBu^t). ^{13}C{^{1}H} NMR (293 K, $CDCl_3$): δ 179.4 (CO), 140.6 (C^{3,5}Pz), 106.7 (C^{4}Pz), 59.8 (*C*−(CH_3)$_3$), 51.3 (*C*H$_3$OOC), 30.2 (C−(*C*H$_3$)$_3$), 20.1 (d, $^1J_{C-Rh}$ = 22 Hz, CH_2). MS (FAB$^+$, CH_2Cl_2, *m/z*): 897, 100% (M^+). Λ_M (4.92 10^{-4} mol·L^{-1} in acetone): 91 S cm^2 mol^{-1}.

[(cod)Rh(μ-Pz)$_2$Rh(η^1-CH$_2$Ph)(Br)(CNBu^t)$_2$] (12) was prepared as described above for complex **7** starting from **6** (100 mg, 0.16 mmol) and $PhCH_2Br$ (21.3 μL, 0.18 mmol). Yield: 108 mg (85%). Anal. Calcd for $C_{31}H_{43}N_6BrRh_2\cdot 2H_2O$: C, 45.33; H, 5.77; N, 10.23. Found: C, 45.24; H, 5.61; N, 10.17. IR (CH_2Cl_2, cm^{-1}): ν(CN) 2222 (s), 2202 (s). ^{1}H NMR (232 K, acetone-d_6): δ 7.88 (d, 2.0 Hz, 2H, H^{3}Pz), 7.46 (d, 2H, H^{5}Pz), 7.29 (m, 4H, H^{o,m}Ph), 7.16 (m, 1H, H^{p}Ph), 6.06 (t, 2H, H^{4}Pz), 5.85 (d, $^2J_{H-Rh}$ = 3.2 Hz, 2H, CH_2), 4.30 and 3.89 (m, 2H + 2H, =CH cod), 2.54 and 2.24 (m, 2H + 2H, H_2C^{exo} cod), 1.85 and 1.72 (m, 2H + 2H, H_2C^{endo} cod), 1.42 (s, 18H, CNBu^t). MS (FAB$^+$, CH_2Cl_2, *m/z*): 785, 7% (M^+); 705, 97% (M − Br$^+$); 614, 100% (M − CH_2Ph-Br$^+$). Λ_M (4.45 10^{-4} M in acetone): 3.5 S cm^2 mol^{-1}.

Reaction of 1 with PhCH(Me)Br. Neat PhCH(Me)Br (44 μL, 0.31 mmol) was added to a solution of **1** (100 mg, 0.15 mmol) in benzene (7 mL). Fine orange needles and a yellow solution were formed in the Schlenk tube after 15 min in the dark. Hexane (30 mL) was added to complete the precipitation of the solid characterized as [{Rh(μ-Pz)(Br)(CNBu^t)$_2$}$_2$] (**13**), which was filtered and washed with 5 × 5 mL portions of diethyl ether/hexane (1:1) and vacuum-dried. Yield: 123 mg (90%). Anal. Calcd for $C_{26}H_{42}N_8Br_2Rh_2$: C, 37.52; H, 5.09; N, 13.46. Found: C, 37.49; H, 5.02; N, 13.40. IR (CH_2Cl_2, cm^{-1}): ν(CN) 2204 (s), 2178 (s). ^{1}H NMR (293 K, $CDCl_3$): δ 7.61 (d, 1.8 Hz, 4H, H^{3,5}Pz), 5.98 (t, 2H, H^{4}Pz), 1.47 (s, 36H, CNBu^t). MS (FAB$^+$, CH_2Cl_2, *m/z*): 830, 7% (M^+); 751, 100% (M − Br$^+$). The mother liquors were concentrated to ca. 3 mL and filtered over Celite. Analysis of this solution by gas chromatography coupled with mass spectrometry allowed the identification of the following products (relative amounts): ethylbenzene (0.6%), styrene (8.7%), 2,3-diphenylbutane (85.1%), acetophenone (5.6%).

[(cod)(Br)Rh(μ-Pz)$_2$Rh(Br)(CNBu^t)$_2$] (14) was prepared as described above for complex **13** starting from **6** (100 mg, 0.16 mmol) and PhCH(Me)Br (48 μL, 0.34 mmol) to render red microcystals. Yield: 88 mg (70%). Anal. Calcd for $C_{24}H_{36}N_6Br_2Rh_2$: C, 37.23; H, 4.69; N, 10.85 Found: C, 37.15; H, 4.50; N, 10.73. IR (CH_2Cl_2, cm^{-1}): ν(CN) 2207 (s), 2190 (s). ^{1}H NMR (295 K, $CDCl_3$): δ 7.69 (d, 1.9 Hz, 2H, H^{3}Pz), 7.66 (d, 1.7 Hz, 2H, H^{5}Pz), 6.03 (t, 2H, H^{4}Pz), 5.07 and 4.33 (m, 2H+2H, = CH cod), 3.29 and 2.66 (m, 2H+2H, H_2C^{exo} cod), 2.33 and 2.25 (m, 2H + 2H, H_2C^{endo} cod), 1.48 (s, 18H, CNBu^t). ^{13}C{^{1}H} NMR (295 K $CDCl_3$): δ 138.7 (C^{3}Pz), 136.8 (C^{5}Pz), 106.1 (C^{4}Pz), 96.6 (d, $^1J_{C-Rh}$ = 7 Hz, =CH cod), 92.4 (d, $^1J_{C-Rh}$ = 8 Hz, =CH cod), 58.9 (*C*−(CH_3)$_3$), 32.7 and 30.5 (H_2C cod), 30.4 (C−(*C*H$_3$)$_3$).

Table 2. Crystal Data and Data Collection and Refinement for Complex 15

chem formula	$C_{36}H_{47}ClN_8Rh_2$
fw	833.09
cryst size, mm	0.49 × 0.36 × 0.39
cryst syst	monoclinic
space group	$P2_1/c$ (No. 14)
a, Å	19.403(2)
b, Å	9.1872(8)
c, Å	24.055(2)
β, deg	97.64(2)
V, Å^3	4250.0(7)
Z	4
D_{calcd}, g cm^{-3}	1.302
μ, mm^{-1}	0.871
no. of measd reflns	7859 ($2\theta \le 50°$)
no. of unique reflns	7516 (R_{int} = 0.0840)
min, max transm factor[a]	0.675, 0.727
no. data/restraints/params	7516/0/407
$R(F)$ ($F^2 \ge 2\sigma(F^2)$)[b]	0.0597
$wR(F^2)$ (all data)[c]	0.1666

[a] An semiempirical ψ-scan absorption correction was applied. [b] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$ for 5549 observed reflections. [c] $wR(F^2) = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (0.1064P)^2 + 2.999P]$, where $P = [\max(F_o^2, 0) + 2F_c^2)]/3$.

[(CNBu^t)$_2$(η^1-CH$_2$Ph)Rh(μ-Pz)$_2$(μ-Cl)Rh(η^1-CH$_2$Ph)(CN)-(CNBu^t)] (15). To a solution of **1** (100 mg, 0.15 mmol) in ethyl acetate (8 mL) was added neat $PhCH_2Cl$ (36 μL, 0.31 mmol) and the resulting solution carefully layered with diethyl ether (20 mL). White prismatic crystals of **2** were formed in 2 days, which redissolved to render white crystals of **15** in 2 weeks. The solid was filtered, washed with cold pentane, and dried under vacuum. Yield: 84 mg (60%). Anal. Calcd for $C_{36}H_{47}N_8ClRh_2\cdot H_2O$: C, 50.80; H, 5.80; N, 13.16. Found: C, 50.39; H, 5.28; N, 13.27. IR (CH_2Cl_2, cm^{-1}): ν(CNBu^t) 2222 (s), 2201 (vs); ν(CN) 2122 (w). ^{1}H NMR (293 K, $CDCl_3$): δ 8.01 (d, 2.1 Hz, 1H), 7.72 (d, 1.9 Hz, 1H), 7.68 (d, 2.0 Hz, 1H) and 7.63 (d, 2.0 Hz, 1H), (H^3 and H^5 Pz, Pz′), 7.81 (d, 7.1 Hz, 2H) and 7.49 (d, 7.0 Hz, 2H) (H^o Ph, Ph′), 7.27 (t, 7.0 Hz, 2H) and 7.21 (t, 7.1 Hz, 2H) (H^m Ph, Ph′), 7.14 (t, 7.19 Hz, 1H) and 7.11 (t, 7.3 Hz, 1H) (H^p Ph, Ph′), 6.30 (t, 1H) and 6.28 (t, 1H) (H^4 Pz, Pz′), 4.35 (δ_A, $^2J_{H-Rh}$ = 3.5 Hz, 1H) and 3.38 (δ_B, $^2J_{H-Rh}$ = 3.6 Hz, 1H, J_{A-B} = 8.2 Hz) (CH_2), 3.89 (δ_A, $^2J_{H-Rh}$ = 3.4 Hz, 1H) and 3.86 (δ_B, $^2J_{H-Rh}$ = 3.3 Hz, 1H, J_{A-B} = 9.1 Hz) (CH_2'), 1.35, 1.31 and 1.05 (s, 27H, CNBu^t). ^{13}C{^{1}H} NMR (293 K, $CDCl_3$): δ 151.9 and 150.7 (C^i Ph, Ph′), 140.8, 140.3, 138.8 and 138.7 (C^3 and C^5 Pz, Pz′), 131.8 (d, $^1J_{C-Rh}$ = 47 Hz, NC−Rh), 129.7, 128.9, 128.5 and 128.1 (C^o and C^m Ph, Ph′), 125.0 and 124.0 (C^p Ph, Ph′), 105.3 and 105.0 (C^4 Pz, Pz′), 59.7, 58.5 and 57.1 (*C*-(CH$_3$)$_3$), 30.0, 29.9, and 29.8 (C−(*C*H$_3$)$_3$), 27.7 (d, $^1J_{C-Rh}$ = 21 Hz) and 24.9 (d, $^1J_{C-Rh}$ = 23 Hz) (CH_2, CH_2'). MS (FAB$^+$, CH_2Cl_2, *m/z*): 833, 75% (M + H$^+$); 742, 100% (M − CH_2Ph^+).

Crystal Structure Determination of Complex 15. A summary of crystal data, intensity collection, and refinement parameters is reported in Table 2. An irregular block white crystal used for the X-ray analysis was glued to a glass fiber and mounted on a Siemens-P4 diffractometer and irradiated with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Cell constants were obtained from the least-squares fit on the setting angles of 25 reflections ($20° \le 2\theta \le 41°$). A complete set of independent reflections with 2θ up to 50° ($-22 \le h \le 23$, $0 \le k \le 10$, and $-28 \le l \le 1$) was measured at room temperature, 293(1) K, using the $\omega/2\theta$ scan technique. Three standard reflections were monitored every 100 measurements throughout data collection as a check on crystal and instrument stability; no decay was observed. Data were corrected

for Lorentz and polarization effects. Reflections were also corrected for absorption by a semiempirical method (Ψ-scan).[36]

The structure was solved by Patterson and subsequent difference Fourier techniques (SHELXTL-PLUS)[37] and refined by full-matrix least-squares on F^2 (SHELXL-97).[38] Just at the isotropic model, the static disorder of all the terminal methyl groups of the isocyanide ligands was apparent. Each disordered *tert*-butyl group was modeled on the basis of two "Me_3" moieties related by a rotation around the N−C−Rh direction; complementary occupancy factors were assumed. Anisotropic thermal parameters were included for all remaining nonhydrogen and nondisordered atoms. At this step, both benzyl groups showed anomalous high anisotropic displacement parameters, with greater values for the atoms more distant from the metals. Eventually, a model of static disorder could be established for one phenyl group based on two geometrically constrained hexagonal rings (C(31a)−C(36a) and C(31b)−C(36b)) with complementary occupancies. Dynamic disorder was assumed for the second benzyl ligand (C(12), and C(41)−C(46)). All hydrogen atoms were included in calculated positions and were refined with positional and thermal riding parameters. The function minimized was $\sum[w(F_o^2 - F_c^2)^2]$. The calculated weighting scheme was $1/[\sigma^2(F_o^2) + (0.1064P)^2 + 2.999P]$, where $P = [\max(F_o^2,0) + 2F_c^2)]/3$. All the refinements converged to reasonable *R* factors (Table 2). The highest residual electron density peaks, weaker than 1.21 e/Å^3, were situated in close proximity to the metal atoms and have no chemical sense. Scattering factors were used as implemented in the refinement program.[38]

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Supporting Information Available: Full listings of crystallographic data, complete atomic coordinates, isotropic and anisotropic displacement parameters, and complete bond distances and angles for complex **15**. This material is available free of charge via the Internet at http://pubs.acs.org.

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