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C(sp^3)−Cl Bond Activation Promoted by a POP-Pincer Rhodium(I) Complex

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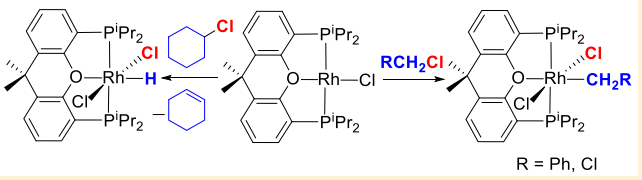
Supporting Information

ABSTRACT: The complex [RhCl(κ^3*P,O,P*-{xant(P^{i}Pr$_2$)$_2$})] (**1**; xant(P^{i}Pr$_2$)$_2$ = 9,9-dimethyl-4,5-bis-(diisopropylphosphino)xanthene) activates C(sp^3)−Cl bonds of mono- and dichloroalkanes and catalyzes the dehalogenation of chloroalkanes and the homocoupling of benzyl chloride. Complex **1** reacts with chlorocyclohexane to give [RhHCl$_2$(κ^3*P,O,P*-{xant(P^{i}Pr$_2$)$_2$})] (**2**) and cyclohexene and promotes the dehalogenation of the chlorocycloalkane to cyclohexane using 2-propanol solutions of sodium formate as the reducing agent. The oxidative addition of benzyl chloride to **1** leads to [Rh(CH$_2$Ph)Cl$_2$(κ^3*P,O,P*-{xant(P^{i}Pr$_2$)$_2$})] (**4**). The dehalogenation of this chloroalkane with 2-propanol solutions of sodium formate, in the presence of **1**, gives toluene and 1,2-diphenylethane. The latter is selectively formed with KOH instead of sodium formate. Complex **1** also reacts with *trans*-1,2-dichlorocyclohexane and dichloromethane. The reaction with the former gives [RhCl$_3$(κ^3*P,O,P*-{xant(P^{i}Pr$_2$)$_2$})] (**5**) and cyclohexene, whereas complex **1** undergoes oxidative addition of dichloromethane to afford *cis*-dichloride-[Rh(CH$_2$Cl)-Cl$_2$(κ^3*P,O,P*-{xant(P^{i}Pr$_2$)$_2$})] (**6a**), which evolves into its *trans*-dichloride isomer **6b**. The kinetic study of the overall process suggests that the oxidative addition is cis-concerted and the isomerization an intramolecular reaction which takes place through a σ-C−Cl intermediate with two conformations.



INTRODUCTION

Oxidative addition to transition-metal complexes is one of the most relevant procedures for the activation of σ bonds.[1] The oxidative addition of C−X bonds of organic halides to basic unsaturated metal centers has particular interest by its connection with the catalytic formation of C−C bonds[2] and with the metal-catalyzed degradation of these substrates.[3] The latter is a priority target from an environmental point of view, since the accumulation of these substrates is a serious health hazard.[4] The C−X bond enthalpy increases as we go down the group in the periodic table. Thus, the C−Cl rupture is more challenging than the C−Br and C−I bond activations. However, chlorides are the most interesting to work with due to their lower cost and wider diversity.

Most metal-promoted C−C coupling reactions involve aryl or alkenyl halides. Alkyl halides have been comparatively much less employed, particularly those bearing β-hydrogen atoms,[5] because the resulting alkyl intermediates decompose by means of a β-hydride elimination reaction. Palladium(0) compounds are the most used catalysts for these reactions.[6] According to this, there is a significant amount of work centered about the oxidative addition of C(sp^3)−X bonds to d^{10} metal centers.[7] In recent years, examples proving the rhodium efficiency for coupling of alkyl halides have been also reported,[8] whereas other examples have demonstrated their capacity for dehalogenation reactions.[9] In the same vein, the study of rhodium-mediated C(sp^3)−X bond activation reactions is awakening notable interest.[10]

Neutral POP diphosphines are hemilabile pincer ligands, which have the ability to adapt their coordination mode to the requirements of each particular species.[11] As a consequence of this flexibility, POP-rhodium derivatives are proving to have noticeable efficiency in reactions of σ-bond activation[12] with implication in a wide range of interesting organic reactions,[13] as well as in the dehydrocoupling and dehydropolymerization of amine−boranes.[14] In agreement with this, we have recently shown that the square-planar monohydride [RhH(κ^3*P,O,P*-{xant(P^{i}Pr$_2$)$_2$})] (xant(P^{i}Pr$_2$)$_2$ = 9,9-dimethyl-4,5-bis-(diisopropylphosphino)xanthene) undergoes a sterically governed C−Cl bond cis-oxidative addition of chlorobenzene, chlorotoluenes, chlorofluorobenzenes, and di- and trichlorobenzenes to afford rhodium(III) derivatives, which experience dehydrochlorination to give a wide range of [Rh(aryl)-(κ^3*P,O,P*-{xant(P^{i}Pr$_2$)$_2$})] complexes (Scheme 1).[15]

Our interest in dehalogenation and C−C coupling processes has prompted us to study now the activation of C(sp^3)−Cl bonds of mono- and dichloroalkanes, with and without β-hydrogens, promoted by [RhCl(κ^3*P,O,P*-{xant(P^{i}Pr$_2$)$_2$})] (**1**). In this paper, we report the oxidative addition of these classes of substrates to **1** and the first exploration of the behavior of

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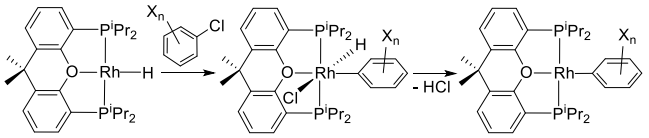
Scheme 1. C−Cl Bond Activation of Halogenated Arenes

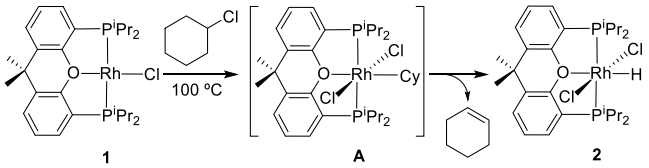


this square-planar rhodium(I) complex in the dehalogenation of these organic compounds and toward the use of some of them for C−C coupling reactions.

RESULTS AND DISCUSSION

Monochloroalkanes. Complex **1** activates the C−Cl bond of chlorocyclohexane. However, the presence of four *β*-hydrogen atoms in the substrate destabilizes the resulting alkyl intermediate, which undergoes a *β*-hydride elimination reaction (Scheme 2). Thus, complex **1** affords cyclohexene and

Scheme 2. C−Cl Bond Activation of Chlorocyclohexane



the rhodium(III) monohydride [$RhHCl_2(\kappa^3P,O,P$-{xant-(P^iPr_2)$_2$})] (**2**) in chlorocyclohexane as solvent. According to the $^{31}P\{^1H\}$NMR spectrum of the solution, the reaction is quantitative after 24 h, at 100 °C. Attempts to detect and characterize the alkyl intermediate **A** were unsuccessful, even at room temperature. Under these conditions, complex **2** was also the only detected species, although its formation is excessively slow.

Complex **2** was isolated as pale yellow crystals and characterized by X-ray diffraction analysis. Figure 1 shows a view of the structure. As expected for a pincer coordination of the diphosphine, the (POP)Rh skeleton is T-shaped with the

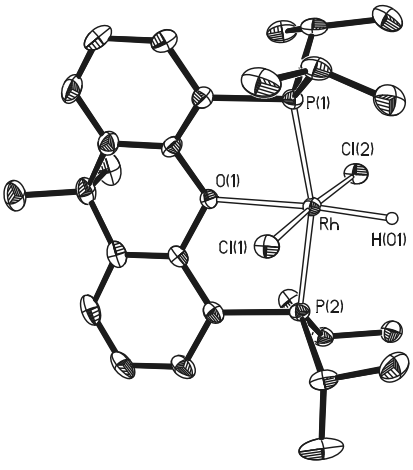
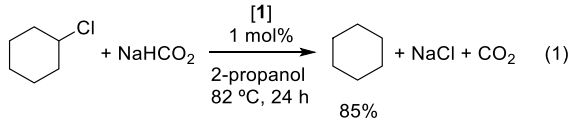


Figure 1. Molecular diagram of complex **2** (ellipsoids shown at 50% probability). All hydrogen atoms (except the hydride) are omitted for clarity. Selected bond distances (Å) and angles (deg): Rh−P(1) = 2.3054(7), Rh−P(2) = 2.3063(7), Rh−Cl(1) = 2.3438(6), Rh−Cl(2) = 2.3412(6), Rh−O(1) = 2.2591(16); P(1)−Rh−P(2) = 163.49(2), Cl(1)−Rh−Cl(2) = 177.44(2), P(1)−Rh−O(1) = 82.26(5), P(2)−Rh−O(1) = 83.04(5), O(1)−Rh−H(01) = 176.0(9).

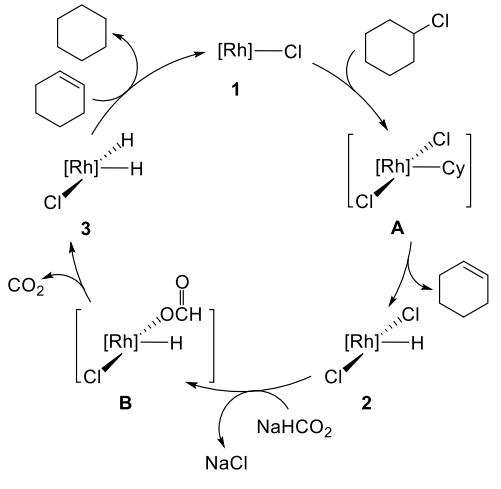
metal center situated in the common vertex and P(1)−Rh−P(2), P(1)−Rh−O(1), and P(2)−Rh−-O(1) angles of 163.49(2), 82.26(5), and 83.04(5)°, respectively. Thus, the coordination polyhedron around the rhodium atom can be described as an octahedron with the hydride disposed trans to the oxygen atom of the diphosphine (O(1)−Rh−H(01) = 176.0(9)°) and the chloride ligands disposed mutually trans (Cl(1)−Rh−Cl(2) = 177.44(2)°. This is also evident in the ^1H and $^{13}C\{^1H\}$ NMR spectra of the crystals, in benzene-d_6 at room temperature, which display two signals for the methyl groups of the phosphine isopropyl substituents ($\delta_{^1H}$, 1.49 and 1.45; $\delta_{^{13}C}$, 21.9 and 19.6) and a signal for the methyl substituents of the central heterocycle ($\delta_{^1H}$,1.21; $\delta_{^{13}C}$, 30.9). In agreement with the presence of the hydride, the ^1H NMR spectrum contains at −19.79 ppm a doublet of triplets with $^1J_{H-Rh}$ and $^2J_{H-P}$ coupling constants of 13.6 and 11.5 Hz, respectively. As expected for equivalent P^iPr_2 groups, the $^{31}P\{^1H\}$ NMR spectrum shows a doublet at 42.2 ppm, which displays a typical $^1J_{P-Rh(III)}$ coupling constant of 98.9 Hz.

Chlorocyclohexane reacts with sodium formate to give cyclohexane, NaCl, and CO_2, in the presence of **1** (eq 1). The



dehalogenation is catalytic. Using 1.0 mol % of complex **1** and 1.2 equiv of sodium formate in 2-propanol, the cycloalkane is formed in 85% yield, after 24 h, under reflux. Acetone is not observed during the reaction, indicating that the solvent does not participate in the dehalogenation. The formation of **2** and cyclohexene, according to Scheme 2, is consistent with this fact and should constitute the first part of the catalysis. Thus, the replacement of one of the chloride ligands by the formate anion could afford the intermediate **B**, which should release CO_2 to give the previously described dihydride [RhH_2Cl-(κ^3P,O,P-{xant(P^iPr_2)$_2$})] (**3**).[12a] The hydrogenation of cyclohexene by the latter would lead to the cycloalkane and to regenerate the catalyst (Scheme 3). Formate salts are promising chemical hydrogen carriers.[16] As a consequence,

Scheme 3. Dehalogenation of Chlorocyclohexane



[Rh] = Rh{κ^3-P,O,P-[xant(P^iPr_2)$_2$]}

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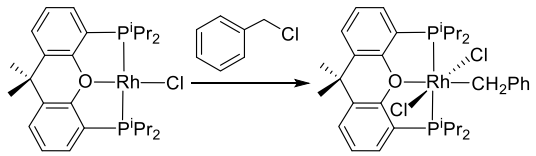
they are receiving noticeable attention as reducing agents in metal-mediated hydrodehalogenation reactions.[17]

Complex **1** also activates the C−Cl bond of benzyl chloride. Treatment of toluene solutions of this compound with 2.0 equiv of the chloroalkane, at room temperature, for 7 h quantitatively leads to the benzyl derivative [Rh(CH_2Ph)-Cl_2(κ^3*P,O,P*-{xant(P^iPr_2)$_2$})] (**4**), as a result of the oxidative addition of the C(sp^3)−Cl bond of the organic substrate to the metal center of **1** (Scheme 4). In contrast to **A**, complex **4** is

Scheme 4. C−Cl Bond Activation of Benzyl Chloride



1 **4**

stable and was isolated as a beige solid in 70% yield. The presence of a coordinated benzyl group in the new species is strongly supported by the ^{1}H and ^{13}C{^{1}H} NMR spectra of the obtained beige solid, in benzene-d_6, at room temperature, which display a doublet of triplets at 5.64 ($^2J_{H-Rh}$ = 3.4 Hz and $^3J_{H-P}$ = 4.1 Hz) and 17.3 ($^1J_{C-Rh}$ = 21.5 Hz and $^2J_{C-P}$ = 4.1 Hz) ppm, respectively. These spectra also reveal the mutually trans disposition of the chloride ligands. Thus, in agreement with the spectra of **2**, they contain two signals for the methyl groups of the phosphine isopropyl substituents ($\delta_{^1H}$, 1.35 and 1.22; $\delta_{^{13}C}$, 20.0 and 19.9) and a signal for the methyl substituents of the central heterocycle ($\delta_{^1H}$, 1.19; $\delta_{^{13}C}$, 29.7). The ^{31}P{^{1}H} NMR spectrum shows a doublet ($^1J_{P-Rh}$ = 105.2 Hz) at 19.1 ppm.

The S_N2 mechanism is the most common for the oxidative addition of alkyl halides to basic metal centers.[18] It leads to a mutually trans disposition of the added fragments. Nevertheless, the cis disposition of the benzyl group to both chloride ligands in **4** is not consistent with this reaction pathway. Because transitory intermediates were not spectroscopically detected during the reaction, even at low temperatures, we assume that the stereochemistry of **4** is the result of a concerted addition, which takes place along the O−Rh−Cl axis of **1** with the benzyl group above the chloride ligand.[19] The preference of this orientation is probably steric.

Complex **1** also catalyzes the dehalogenation of benzyl chloride with 2-propanol solutions of sodium formate, under reflux. However, there are significant differences from the dehalogenation of chlorocyclohexane. In contrast to the latter, the reaction gives acetone and two dehalogenated products, 1,2-diphenylethane and toluene. With 1.0 mol % of catalyst, after 6 h, 42% of the chloroalkane was transformed into 1,2-diphenylethane, whereas another 50% gave toluene. The formation of acetone suggests that in this case both sodium formate and sodium isopropoxide are the reducing agents: i.e. the formate anion acts as a hydrogen carrier and as a base to generate the isopropoxide. The hydrocarbons are the result of two competitive reactions, a dehalogenative homocoupling (eqs 2 and 3) and a simple dehalogenation (eqs 4 and 5), which have as a common intermediate in the benzyl derivative **4** and can be rationalized according to Scheme 5.

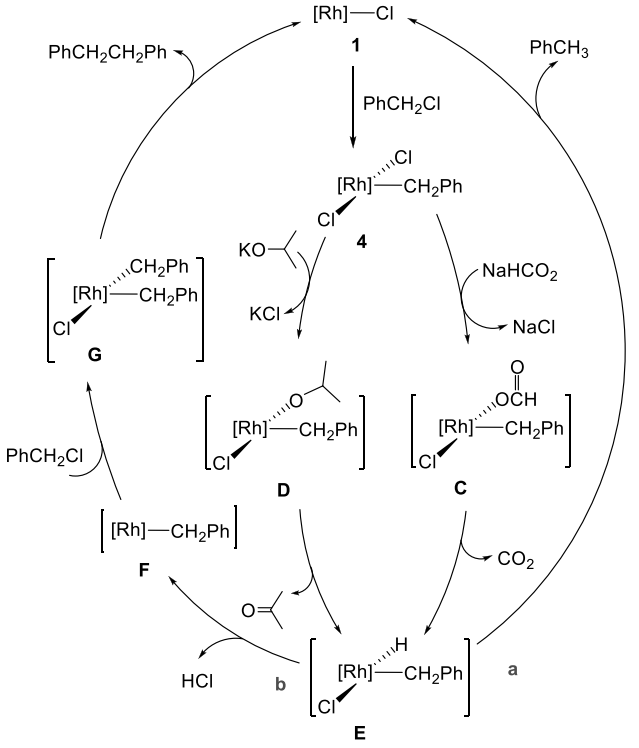
$$2PhCH_2Cl + 2NaHCO_2 + (CH_3)_2CHOH \rightarrow PhCH_2CH_2Ph + 2NaCl + 2HCO_2H + (CH_3)_2CO \quad (2)$$

$$2PhCH_2Cl + 2KOH + (CH_3)_2CHOH \rightarrow PhCH_2CH_2Ph + 2KCl + 2H_2O + (CH_3)_2CO \quad (3)$$

$$PhCH_2Cl + NaHCO_2 \rightarrow PhCH_3 + NaCl + CO_2 \quad (4)$$

$$PhCH_2Cl + KOH + (CH_3)_2CHOH \rightarrow PhCH_3 + KCl + (CH_3)_2CO + H_2O \quad (5)$$

Scheme 5. Proposed Mechanism for the Dehalogenative Homocoupling and Simple Dehalogenation of Benzyl Chloride



Once complex **4** is formed, one of its chloride ligands could be replaced by a formate anion or alternatively by an isopropoxide group, which should be generated in the basic reaction media. Both species, **C** and **D**, would afford the hydride−Rh(III)−benzyl intermediate **E** by release of CO_2 or acetone, respectively. Intermediate **E** could evolve in two different manners: reductive elimination of toluene (a) or reductive elimination of HCl (b). The first process, (a), closes the cycle for the simple dehalogenation of benzyl chloride to toluene. The reductive elimination of HCl (b) should lead to the square-planar intermediate **F**. This Rh(I)−-benzyl species could undergo the oxidative addition of a second molecule of benzyl chloride to give **G**. Thus, the reductive coupling of the benzyl groups would generate 1,2-diphenylethane, closing the cycle for the dehalogenative homocoupling of the chloroalkane. Strong bases should favor the dehalogenative homocou-

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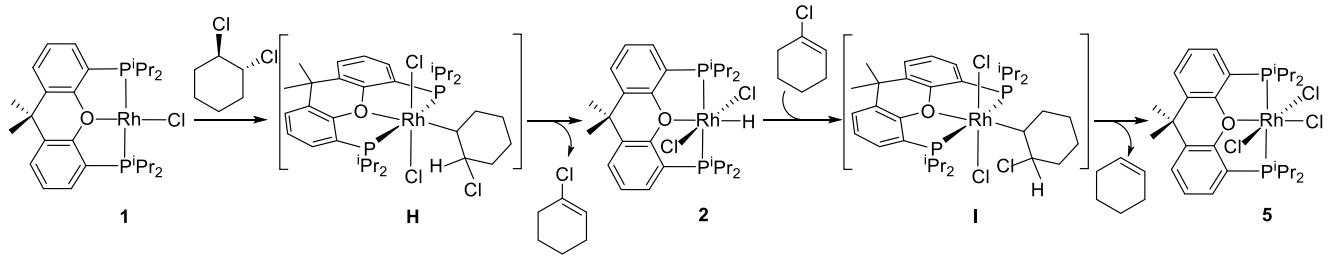
Scheme 6. Reaction of 1 with *trans*-1,2-Dichlorocyclohexane



pling (b) with regard to the simple dechlorination (a), given its higher ability to trap the HCl generated from **E**, whereas it should increase the isopropoxide concentration to facilitate the formation of **D**. In order to corroborate this, we replaced sodium formate by potassium hydroxide and, in effect, two significant increases take place: the dehalogenation rate and the amount of 1,2-diphenylethane. After 2 h, the chloroalkane disappeared; 93% of benzyl chloride was transformed into the homocoupling product and only 7% into toluene.

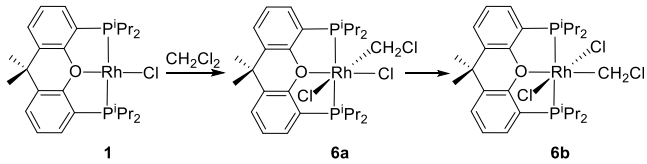
Ando and co-workers have performed the $[RhCl(PPh_3)_3]$-mediated homocoupling of benzyl bromides. There are, however, significant differences in the reaction conditions with regard to those previously mentioned, not only in the catalyst but also in the dehalogenation agent and therefore in the wastes. In contrast to 2-propanol solutions of KOH, they used Me_2Zn in tetrahydrofuran, which generates ethane and $ZnBr_2$ instead of NaCl, water, and acetone. Furthermore, their catalytic system is much less efficient than **1**/KOH/2-propanol, since it only affords 58% yield after 24 h for the homocoupling of benzyl chloride.[8d]

Dichloroalkanes. The reactions of **1** with dichloroalkanes also show a marked dependence upon the presence of β-hydrogen atoms in the chloroalkyl fragment, which is evident in the reactions with *trans*-1,2-dichlorocyclohexane and dichloromethane. Thus, while the former undergoes double C−Cl rupture, the product of the oxidative addition of the latter is stable.

Complex **1** reacts with *trans*-1,2-dichlorocyclohexane to give $[RhCl_3(\kappa^3P,O,P\text{-}\{xant(P^iPr_2)_2\})]$ (**5**) and cyclohexene, as a result of a chloride transfer from the organic substrate to the metal center of **1**. At 100 °C, using this dichloroalkane as the solvent, the reaction is quantitative after 4 h. This is strongly supported by the $^{31}P\{^1H\}$ NMR spectrum of the resulting solution, which only displays a doublet ($^1J_{P-Rh}$ = 86.1 Hz) at 24.9 ppm. The formation of **5** and the olefin can be rationalized according to Scheme 6. The oxidative addition of one of the C−Cl bonds of *trans*-1,2-dichlorocyclohexane to **1** should afford intermediate **H**, which could evolve to **2**, releasing 1-chlorocyclohexene. Thus, the insertion of the chloroolefin into the Rh−H bond of the latter, followed by the β-chloride elimination on the chloroalkyl ligand of the resulting intermediate **I**, would give **5** and the cycloolefin. In this context, it should be noted that a hydride abstraction in **H** is favored with regard to the chloride abstraction due to the trans disposition of the rhodium and chloride atoms. However, when there are atoms of hydrogen and chloride in equivalent β positions, as in **I**, the chloride abstraction is favored with regard to the hydride. In addition, it should be mentioned that, in contrast to the previous monochloroalkanes, *trans*-1,2-dichlorocyclohexane does not undergo dehalogenation under the conditions of eqs 1−5.

The reaction of **1** with dichloromethane affords two products, one of them of kinetic control and the other of thermodynamic control. In dihaloalkane as the solvent, complex **1** initially gives the *cis*-dichloride-$[Rh(CH_2Cl)Cl_2(\kappa^3P,O,P\text{-}\{xant(P^iPr_2)_2\})]$ (**6a**), which evolves to its *trans*-dichloride isomer **6b** (Scheme 7).

Scheme 7. C−Cl Bond Activation of Dichloromethane



The disposition of the chloromethyl group in **6a**, cis to one chloride and trans to the other, is revealed by the $^{13}C\{^1H\}$ NMR spectrum of the new species, which shows four resonances between 24 and 19 ppm for the diasterotopic methyls of the equivalent P^iPr_2 groups and two resonances at 36.9 and 30.7 ppm corresponding to the inequivalent methyl substituents of the heterocyclic link of the diphosphine. The signal due to the chloromethyl ligand appears at 36.9 ppm, as a doublet of triplets, with C−Rh and C−P coupling constants of 28.6 and 5.5 Hz, respectively. In agreement with the $^{13}C\{^1H\}$ NMR spectrum, the ^1H NMR spectrum shows the choromethyl resonance as an ABX_2Y spin system, at 5.17 ppm. The $^{31}P\{^1H\}$ NMR spectrum contains a doublet ($^1J_{P-Rh}$ = 96.9 Hz) at 26.4 ppm, proving the equivalence of the P^iPr_2 groups.

The *trans*-dichloride isomer **6b** was isolated as a brown solid in 83% yield. In agreement with the benzyl complex **4**, which bears the same stereochemistry, its ^1H and $^{13}C\{^1H\}$ NMR spectra contain two signals for the methyl groups of the phosphine isopropyl substituents ($\delta_{^1H}$, 1.43 and 1.38; $\delta_{^{13}C}$, 21.6 and 20.6), whereas the methyl substituents of the heterocyclic linker give rise to a signal ($\delta_{^1H}$, 1.19; $\delta_{^{13}C}$, 32.5). In both spectra, the resonance corresponding to the chloromethyl group is observed as a doublet of triplets at 6.30 ($^2J_{H-Rh}$ = 3.4 Hz and $^3J_{H-P}$ = 4.1 Hz) ppm in the ^1H NMR spectrum and at 34.3 ($^1J_{C-Rh}$ = 28.6 Hz and $^2J_{C-P}$ = 5.5 Hz) ppm in the $^{13}C\{^1H\}$ NMR spectrum. As expected for equivalent P^iPr_2 groups, the $^{31}P\{^1H\}$ NMR spectrum shows a doublet ($^1J_{P-Rh}$ = 100.1 Hz) at 23.6 ppm. The stereochemistry inferred from the NMR spectra was confirmed by X-ray diffraction analysis. Figure 2 shows a view of the structure. In agreement with the spectroscopic data, the coordination polyhedron around the rhodium atom can be described as a distorted octahedron, with the diphosphine *mer* coordinated (P(1)−Rh−P(2) = 163.45(7)°, P(1)−Rh−O = 81.69(14)°, and P(2)−Rh−O = 81.84(14)°), the chloride ligands disposed mutually trans

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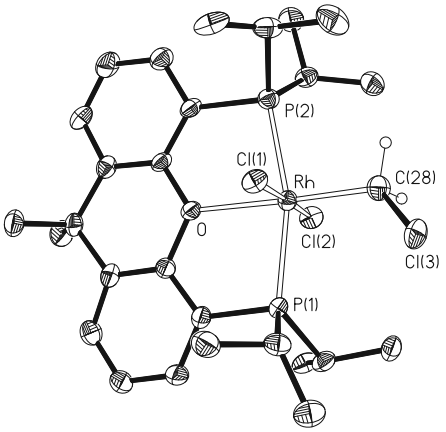

Figure 2. Molecular diagram of complex **6b** (ellipsoids shown at 50% probability). All hydrogen atoms (except those of the CH_2Cl moiety) are omitted for clarity. Selected bond distances (Å) and angles (deg): Rh−P(1) = 2.3334(19), Rh−P(2) = 2.354(2), Rh−Cl(1) = 2.341(2), Rh−Cl(2) = 2.362(2), Rh−O = 2.252(5), Rh−C(28) = 2.018(8); P(1)−Rh−P(2) = 163.45(7), Cl(1)−Rh−Cl(2) = 177.28(7), P(1)−Rh−O = 81.69(14), P(2)−Rh−O = 81.84(14), O−Rh−C(28) = 177.4(3).

(Cl(1)−Rh-Cl(2) = 177.28(7)°), and the chloromethyl group situated trans to the oxygen atom of the diphosphine (C(28)−Rh−O = 177.4(3)°). The rhodium−alkyl distance of 2.018(8) Å (Rh−C(28)) compares well with the expected value for a Rh^{III}−C(sp^3) bond.[20]

The trans disposition of the chloromethyl group to a chloride ligand in **6a** is consistent with an S_N2 oxidative addition. Nevertheless, this stereochemistry could be also the result of a cis concerted addition along the O−Rh−Cl axis with a chloride of the dichloroalkane above the chloride ligand of **1**. The isomerization of **6a** into **6b** should involve the reductive elimination of the dichloroalkane followed by a new concerted oxidative addition along the O−Rh−Cl axis: now, with the chloride of the substrate above the oxygen atom. A noticeable difference between the trans-S_N2 and cis-concerted additions is the value of the negative activation entropy of the process: lower than −40 eu for the former and higher than −25 eu for the latter.[21] To gain insight about what is going on, we followed the evolution of **1** in dichloromethane as a function of the time by $^{31}P\{^1H\}$ NMR spectroscopy, in the temperature range 307−282 K. Figure 3 shows the spectra at 303 K. The dependence of the amounts of **1**, **6a**, and **6b** with time (Figure 4) is in accordance with two consecutive irreversible reactions

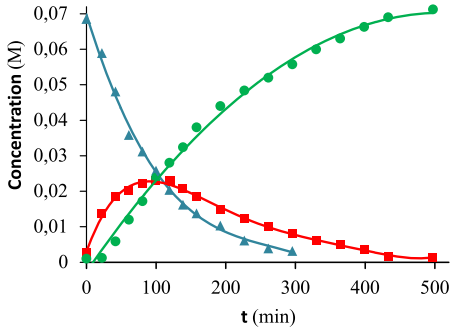

Figure 4. Composition of the mixture as a function of time for the reaction at 303 K (**1**, blue ▲; **6a**, red ■; **6b**, green ●).

and fits to eqs 6−8, respectively. Table 1 collects the rate constants k_1 and k_2 obtained from these expressions.

$$[\mathbf{1}] = [\mathbf{1}]_0 e^{-k_1 t} \quad (6)$$

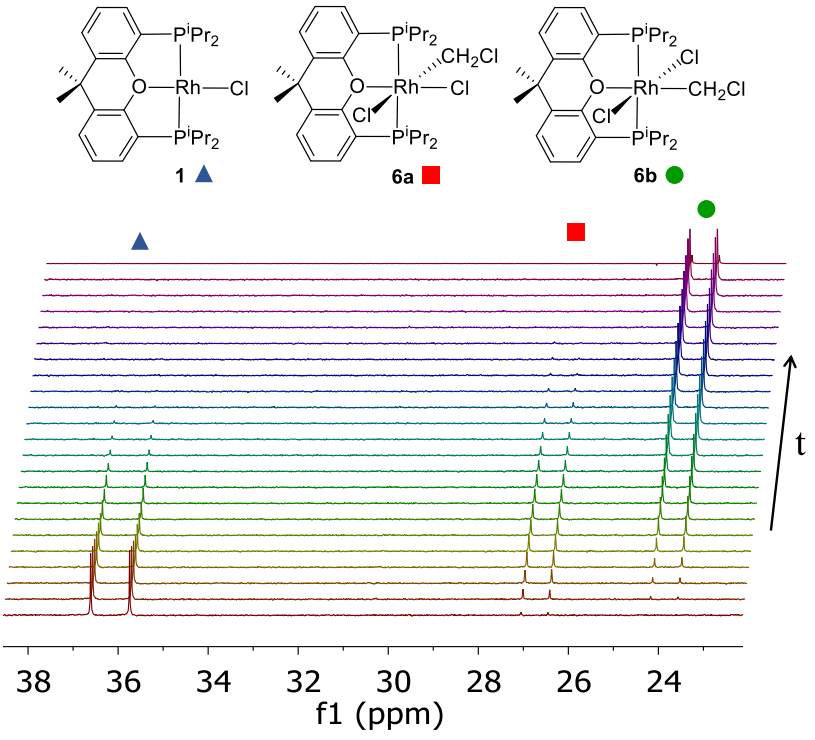

Figure 3. Stacked $^{31}P\{^1H\}$ NMR spectra (161.98 MHz, CD_2Cl_2, 303 K) showing the evolution of **1** in dichloromethane as a function of time.

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$$[\mathbf{6a}] = \frac{[\mathbf{1}]_0 k_1}{k_2 - k_1}[e^{-k_1 t} - e^{-k_2 t}] \quad (7)$$

$$[\mathbf{6b}] = [\mathbf{1}]_0 + \frac{[\mathbf{1}]_0}{k_1 - k_2}[k_2 e^{-k_1 t} - k_1 e^{-k_2 t}] \quad (8)$$

Table 1. Rate Constants for the Formation of 6a (k_1, s^{-1}) and for the Isomerization of 6a into 6b (k_2, s^{-1}) Calculated According to eqs 6–8, as a Function of Temperature (K)

temp	k_1	k_2
282	$(2.51 \pm 0.07) \times 10^{-5}$	$(1.47 \pm 0.07) \times 10^{-5}$
286	$(4.8 \pm 0.2) \times 10^{-5}$	$(3.5 \pm 0.2) \times 10^{-5}$
292	$(8.2 \pm 0.3) \times 10^{-5}$	$(4.8 \pm 0.2) \times 10^{-5}$
303	$(1.82 \pm 0.09) \times 10^{-4}$	$(1.11 \pm 0.06) \times 10^{-4}$
307	$(3.7 \pm 0.3) \times 10^{-4}$	$(7.1 \pm 0.3) \times 10^{-4}$

The activation parameters calculated from the corresponding Eyring analysis (Figures 5 and 6) are $\Delta H_a^{\ddagger} = 16.2 \pm 1.8$ kcal mol^{-1} and $\Delta S_a^{\ddagger} = -21.8 \pm 6.2$ eu for the formation of **6a** and $\Delta H_b^{\ddagger} = 21.5 \pm 2.5$ kcal mol^{-1} and $\Delta S_b^{\ddagger} = -4.2 \pm 8.5$ eu for the isomerization from **6a** to **6b**. The value of $\Delta S_a^{\ddagger}$, significantly far away from that expected for a S_N2 mechanism, is consistent with a cis-concerted addition, whereas the value of $\Delta S_b^{\ddagger}$, close to zero, supports an intramolecular isomerization. The latter could take place via the σ-C–Cl intermediate **J**, which would exist in the conformations $\mathbf{J_a}$ and $\mathbf{J_b}$ shown in Scheme 8.

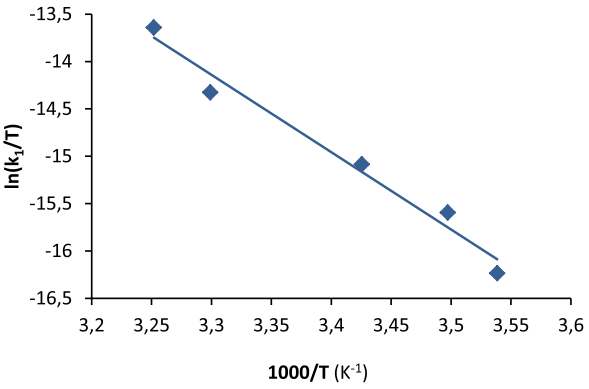


Figure 5. Eyring plot for the formation of **6a**.

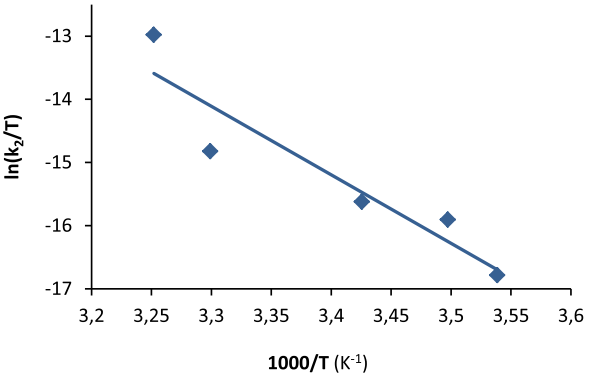


Figure 6. Eyring plot for the isomerization of **6a** to **6b**.

CONCLUDING REMARKS

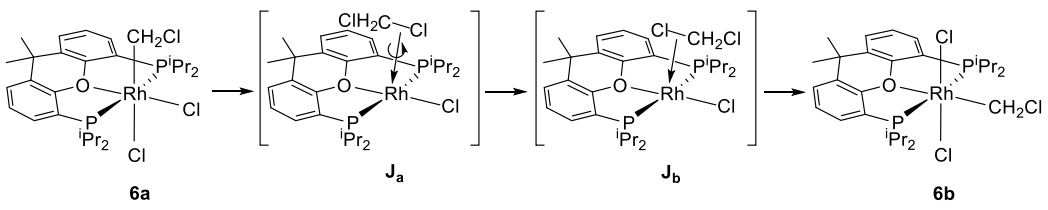
This study has revealed that the rhodium(I) complex [RhCl(κ^3*P,O,P*-{xant(P^iPr_2)$_2$})] activates C(sp^3)–Cl bonds of mono- and dichloroalkanes to give *trans*-dichloride–rhodium(III)–alkyl derivatives, which are stable when the alkyl group does not contain hydrogen atoms in a β position with regard to the metal center. Species bearing β-hydrogen atoms release the olefin, resulting in a β-hydride elimination reaction on the alkyl group. The activation by means of oxidative addition is a cis-concerted process, which takes place along the O–Rh–Cl axis. In agreement with its ability to activate C(sp^3)–Cl bonds, this rhodium(I) complex is also an efficient catalyst for the promotion of the simple dehalogenation of chloroalkanes to the corresponding alkanes, using sodium formate as reducing agent, and for the dehalogenative homocoupling of benzyl chloride to 1,2-diphenylethane, with a 2-propanol solution of KOH as a dehalogenating agent. For the homocoupling, the new system is more efficient than those previously reported and generates fewer wastes.

EXPERIMENTAL SECTION

General Information. All reactions were carried out with exclusion of air using Schlenk-tube techniques or in a drybox. Instrumental methods and X-ray details are given in the Supporting Information. In the NMR spectra the chemical shifts (in ppm) are referenced to residual solvent peaks (^{1}H, ^{13}C{^{1}H}) or external 85% H_3PO_4 (^{31}P{^{1}H}). Coupling constants J and N are given in hertz. [RhCl(κ^3*P,O,P*-{xant(P^iPr_2)$_2$})] (**1**)[12a] was prepared by the published methods.

Reaction of [RhCl(κ^3*P,O,P*-{xant(P^iPr_2)$_2$})] (1) with Chlorocyclohexane: Preparation of [$RhHCl_2$(κ^3*P,O,P*-{xant(P^iPr_2)$_2$})] (2). A solution of **1** (100 mg, 0.16 mmol) in chlorocyclohexane (5 mL) was heated at 100 °C for 24 h. After this time, an analysis of the resulting solution by gas chromatography showed a peak assigned to cyclohexene by comparison with the retention time of a pure sample of this olefin. The solution was cooled at room temperature, filtered through Celite, and evaporated to dryness, affording a pale yellow residue. Addition of pentane (4 mL) afforded a pale yellow solid that was washed with pentane (2 × 2 mL) and dried in vacuo. Yield: 44 mg (30%). The isolated yield is low due to the high solubility of the complex in pentane. Anal. Calcd for $C_{27}H_{41}Cl_2OP_2Rh$: C, 52.53; H, 6.69. Found: C, 52.24; H, 6.83. HRMS (electrospray, m/z): calcd for $C_{27}H_{41}OP_2Rh$ $[M - 2\ Cl]^+$, 547.1760; found, 547.1778. IR (cm^{-1}): ν(Rh–H) 2151 (w), ν(C–O–C) 1099 (m). ^{1}H NMR (300.13 MHz, C_6D_6, 298 K): δ 7.28 (m, 2H, CH-arom), 7.10 (dd, $^3J_{H-H} = 7.6$, $^4J_{H-H}$

Scheme 8. Mechanism for the Isomerization of 6a into 6b



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= 1.3, 2H, CH-arom), 6.91 (t, $^3J_{H-H}$ = 7.6, 2H, CH-arom), 2.90 (m, 4H, PC*H*$(CH_3)_2$), 1.49 (dvt, $^3J_{H-H}$ = 5.7, *N* = 15.6, 12H, PCH$(CH_3)_2$), 1.45 (dvt, $^3J_{H-H}$ = 5.7, *N* = 16.2, 12H, PCH$(CH_3)_2$), 1.21 (s, 6H, CH_3), −19.79 (dt, $^1J_{H-Rh}$ = 13.6, $^2J_{H-P}$ = 11.5, 1H, Rh−H). $^{13}C\{^1H\}$-apt NMR (75.47 MHz, C_6D_6, 298 K): δ 155.5 (vt, *N* = 11.5, C-arom POP), 133.1 (vt, *N* = 5.1, C-arom POP), 132.4 (s, CH-arom POP), 128.1 (s, CH-arom POP), 125.5 (vt, *N* = 24.6, C-arom POP), 124.3 (s, CH-arom POP), 35.1 (s, *C*$(CH_3)_2$), 30.9 (s, C$(CH_3)_2$), 25.3 (vt, *N* = 24.5, P*C*H$(CH_3)_2$), 21.9, 19.6 (both s, PCH$(CH_3)_2$). $^{31}P\{^1H\}$ NMR (121.49 MHz, C_6D_6, 298 K): δ 42.2 (d, $^1J_{Rh-P}$ = 98.9).

Reaction of [RhCl(κ^3*P,O,P*-{xant(P^iPr_2)$_2$})] (1) with Benzyl Chloride: Preparation of [Rh(CH_2Ph)Cl_2(κ^3*P,O,P*-{xant(P^iPr_2)$_2$})] (4). A solution of **1** (100 mg, 0.17 mmol) in toluene (3 mL) was treated with benzyl chloride (42 μL, 0.34 mmol), and the resulting solution was stirred at room temperature for 7 h. After this time, the solution was filtered through Celite and evaporated to dryness to afford a beige solid. Yield: 92 mg (70%). Anal. Calcd for $C_{34}H_{47}Cl_2OP_2Rh$: C, 57.72; H, 6.97. Found: C, 57.31; H, 6.59. HRMS (electrospray, *m*/*z*): calcd for $C_{34}H_{47}ClOP_2Rh$ $[M - Cl]^+$, 671.1808; found, 671.1840. IR (cm^{-1}): ν(C−O−C) 1195 (s). ^1H NMR (300.13 MHz, C_6D_6, 298 K): δ 8.25 (dd, $^3J_{H-H}$ = 7.7, $^4J_{H-H}$ = 1.6, 2H, CH Ph), 7.11 (m, 7H, CH-arom POP and CH Ph), 6.88 (t, $^3J_{H-H}$ = 7.6, 2H, CH-arom POP), 5.64 (dt, $^2J_{H-Rh}$ = 3.4, $^3J_{H-P}$ = 4.1, 2H, RhC*H*$_2$Ph), 2.42 (m, 4H, PC*H*$(CH_3)_2$), 1.35 (dvt, $^3J_{H-H}$ = 7.3, *N* = 15.7, 12H, PCH$(CH_3)_2$), 1.22 (dvt, $^3J_{H-H}$ = 7.12, *N* = 12.7, 12H, PCH$(CH_3)_2$), 1.19 (s, 6H, CH_3). $^{13}C\{^1H\}$-apt (75.47 MHz, C_6D_6, 298 K): δ 155.5 (vt, *N* = 10.8, C-arom POP), 153.2 (vt, *N* = 4.9, C_{ipso} Ph), 133.3 (vt, *N* = 5.2, C-arom POP), 131.7 (s, CH Ph), 131.1 (s, CH-arom POP), 127.1 (s, CH-arom POP), 125.3 (s, CH Ph), 124.1 (s, CH-arom POP), 123.7 (vt, *N* = 5.1, C-arom POP), 34.8 (s, *C*$(CH_3)_2$), 29.7 (s, C$(CH_3)_2$), 26.5 (vt, *N* = 10.1, P*C*H$(CH_3)_2$), 20.0, 19.9 (both s, PCH$(CH_3)_2$), 17.3 (dt, $^1J_{C-Rh}$ = 21.5, $^2J_{C-P}$ = 4.1, RhCH$_2$Ph). $^{31}P\{^1H\}$ NMR (121.49 MHz, C_6D_6, 298 K): δ 19.1 (d, $^1J_{Rh-P}$ = 105.2).

Reaction of [RhCl(κ^3*P,O,P*-{xant(P^iPr_2)$_2$})] (1) with *trans*-1,2-Dichlorocyclohexane: Preparation of [$RhCl_3$(κ^3*P,O,P*-{xant(P^iPr_2)$_2$})] (5). A solution of **1** (100 mg, 0.17 mmol) in *trans*-1,2-dichlorocyclohexane (3 mL) was heated at 100 °C for 4 h. After this time, the resulting solution was evaporated to dryness to afford an orange residue. Addition of pentane (4 mL) afforded an orange solid, which was washed with further portions of pentane (5 × 4 mL) and dried in vacuo. Yield: 95 mg (79%). Anal. Calcd for $C_{27}H_{40}Cl_3OP_2Rh$: C, 49.75; H, 6.18. Found: C, 49.93; H, 5.86. HRMS (electrospray, *m*/*z*): calcd for $C_{27}H_{40}Cl_2OP_2Rh$ $[M - Cl]^+$, 615.0954; found, 615.0981. IR (cm^{-1}): ν(C−O−C) 1187 (s). ^1H NMR (300.13 MHz, C_6D_6, 298 K): δ 7.29 (m, 2H, CH-arom), 6.93 (dd, $^3J_{H-H}$ = 7.6, J_{H-H} = 1.6, 2H, CH-arom), 6.81 (t, $^3J_{H-H}$ = 7.6, 2H, CH-arom), 3.45 (m, 4H, PC*H*$(CH_3)_2$), 1.69 (dvt, $^3J_{H-H}$ = 7.5, *N* = 15.6, 12H, PCH$(CH_3)_2$), 1.61 (dvt, $^3J_{H-H}$ = 7.3, *N* = 14.9, 12H, PCH$(CH_3)_2$), 1.05 (s, 6H, CH_3). $^{13}C\{^1H\}$-apt (75.47 MHz, C_6D_6, 298 K): δ 155.2 (vt, *N* = 12.2, C-arom), 134.6 (s, CH-arom), 132.4 (vt, *N* = 5.9, C-arom), 129.9 (s, CH-arom), 124.6 (vt, *N* = 5.5, CH-arom), 123.4 (vt, *N* = 25.4, C-arom), 34.4 (s, C$(CH_3)_2$), 33.2 (s, C$(CH_3)_2$), 26.6 (vt, *N* = 24.4, PCH$(CH_3)_2$), 21.7, 19.7 (both s, PCH$(CH_3)_2$). $^{31}P\{^1H\}$ NMR (121.49 MHz, C_6D_6, 298 K): δ 24.9 (d, $^1J_{Rh-P}$ = 86.1).

Reaction of [RhCl(κ^3*P,O,P*-{xant(P^iPr_2)$_2$})] (1) with CH_2Cl_2: Preparation of *trans*-[Rh(CH_2Cl)Cl_2(κ^3*P,O,P*-{xant(P^iPr_2)$_2$})] (6b). Complex **1** (100 mg, 0.17 mmol) was dissolved in dichloromethane (3 mL), and this mixture was stirred for 16 h at room temperature. The resulting solution was filtered through Celite and was evaporated to dryness to afford a brown solid. Yield: 95 mg (83%). Anal. Calcd for $C_{28}H_{42}Cl_3OP_2Rh$: C, 50.51; H, 6.35. Found: C, 50.79; H, 6.09. HRMS (electrospray, *m*/*z*): calcd, for $C_{28}H_{42}Cl_2OP_2Rh$ $[M - Cl]^+$, 629.1137; found, 629.1137. IR (cm^{-1}): ν(C−O−C) 1086 (m). ^1H NMR (300.13 MHz, toluene-d_8, 298 K): δ 7.12−7.06 (m, 4H, CH-arom POP), 6.90 (t, $^3J_{H-H}$ = 7.6, 2H, CH-arom POP), 6.30 (dt, $^2J_{H-Rh}$ = 3.4, $^3J_{H-P}$ = 4.1, 2H, RhCH$_2$Cl), 3.00 (m, 4H, PC*H*$(CH_3)_2$), 1.43 (dvt, $^3J_{H-H}$ = 7.3, *N* = 15.5, 12H, PCH$(CH_3)_2$), 1.38 (dvt, $^3J_{H-H}$ = 7.2, *N* = 14.6, 12H, PCH$(CH_3)_2$), 1.19 (s, 6H, CH_3). $^{13}C\{^1H\}$-apt NMR (75.47 MHz, toluene-d_8, 298 K): δ 154.7 (vt, *N* = 12.7, C-arom POP), 133.3 (s, CH-arom POP), 132.5 (s, C-arom POP), 129.1 (s, CH-arom POP), 124.4 (s, CH-arom POP), 123.4 (vt, *N* = 27.8, C-arom POP), 34.8 (s, *C*$(CH_3)_2$), 34.3 (dt, $^1J_{C-Rh}$ = 28.6, $^2J_{C-P}$ = 5.5, RhCH$_2$Cl), 32.5 (s, C$(CH_3)_2$), 27.3 (vt, *N* = 22.3, PCH$(CH_3)_2$), 21.6, 20.6 (both s, PCH$(CH_3)_2$). $^{31}P\{^1H\}$ NMR (121.49 MHz, toluene-d_8, 298 K): δ 23.6 (d, $^1J_{Rh-P}$ = 100.1).

Spectroscopic Detection of *cis*-[Rh(CH_2Cl)Cl_2(κ^3*P,O,P*-{xant-(P^iPr_2)$_2$})] (6a). A solution of **1** (15 mg, 0.03 mmol) in dichloromethane (1.5 mL) was placed in an NMR tube, and it was periodically checked by $^{31}P\{^1H\}$ NMR spectroscopy. After 90 min, the resulting solution was evaporated to dryness, giving a yellow residue. Addition of toluene-d_8 and subsequent filtration afforded a solution whose $^{31}P\{^1H\}$ NMR spectrum shows a mixture of **1**, **6a**, and **6b** in a 4:33:63 ratio. The ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were recorded at 273 K in order to avoid the progress of the isomerization. Spectroscopic data for **6a** are as follows. ^1H NMR (400.13 MHz, toluene-d_8, 273 K): δ 7.20 (m, 2H, CH-arom POP), 7.04 (d, $^3J_{H-H}$ = 7.4, 2H, CH-arom POP), 6.85 (t, $^3J_{H-H}$ = 7.7, 2H, CH-arom POP), 5.17 (ABX_2Y spin system, 2H, RhCH$_2$Cl), 3.61 (m, 2H, PC*H*$(CH_3)_2$), 2.83 (m, 2H, PC*H*$(CH_3)_2$), 1.85 (dvt, $^3J_{H-H}$ = 7.8, *N* = 15.7, 6H, PCH$(CH_3)_2$), 1.58 (dvt, $^3J_{H-H}$ = 7.4, *N* = 15.2, 6H, PCH$(CH_3)_2$), 1.41 (dvt, $^3J_{H-H}$ = 7.4, *N* = 15.1, 6H, PCH$(CH_3)_2$), 1.35 (dvt, $^3J_{H-H}$ = 7.1, *N* = 14.3, 6H, PCH$(CH_3)_2$), 1.15 (s, 6H, CH_3). $^{13}C\{^1H\}$-apt (100.61 MHz, toluene-d_8, 273 K): δ 155.5 (vt, *N* = 13.5, C-arom POP), 134.2 (s, CH-arom POP), 132.6 (vt, *N* = 6.1, C-arom POP), 129.6 (s, CH-arom POP), 124.7 (vt, *N* = 5.4, CH-arom POP), 123.6 (vt, *N* = 26.3, C-arom POP), 36.9 (dt, $^1J_{C-Rh}$ = 28.6, $^2J_{C-P}$ = 5.5, RhCH$_2$Cl), 36.9 (s, C$(CH_3)_2$), 30.8 (s, C$(CH_3)_2$), 30.7 (s, C$(CH_3)_2$), 27.4 (vt, *N* = 26.8, PCH$(CH_3)_2$), 25.8 (vt, *N* = 20.8, PCH$(CH_3)_2$), 23.2, 20.5, 20.4, 19.3 (all s, PCH$(CH_3)_2$). $^{31}P\{^1H\}$ NMR (161.95 MHz, toluene-d_8, 298 K): δ 26.4 (d, $^1J_{Rh-P}$ = 96.9, Rh−P).

Catalytic Dehalogenations. *General Procedure.* The dehalogenation reactions were carried out in a two-necked flask fitted with a condenser and containing a magnetic stirring bar. The second neck was capped with a Suba-Seal to allow samples to be removed by syringe without opening the system. Conversions were calculated from the relative peak area integrations of the reactants and products in the GC spectra using mesitylene as internal standard. For the reactions involving benzyl chloride a Hewlett-Packard 4890 gas chromatograph with a flame ionization detector and a 100% cross-linked methyl silicone gum column (30 m × 0.32 mm, with 0.25 μm film thickness) were used (oven conditions: 35 °C (hold 6 min) to 245 °C at 25 °C/min (hold 10 min)). For the reactions involving chlorocyclohexane as substrate, a Network GC System 6890N gas chromatograph with a flame ionization detector and a bonded polyethylene glycol (PEG) phase column (30 m × 0.25 mm, with 0.25 μm film thickness) were employed (oven conditions: 30 °C (hold 5 min) to 100 °C at 5 °C/min (hold 5 min) and 100 to 250 °C/min (hold 1 min)).

Dehalogenation of Chlorocyclohexane Catalyzed by [RhCl-(κ^3P,O,P-{xant(P^iPr_2)$_2$})] (1). In the presence of 1.8×10^{-3} M **1**, the treatment of 0.18 M chlorocyclohexane with 0.21 M sodium formate in 2-propanol at 100 °C under an argon atmosphere led after 24 h to the transformation of 85% of chlorocyclohexane into cyclohexane.

Dehalogenation of Benzyl Chloride Catalyzed by [RhCl(κ^3P,O,P-{xant(P^iPr_2)$_2$})] (1). In the presence of 1.8×10^{-3} M **1**, the treatment of 0.18 M benzyl chloride with 0.21 M sodium formate in 2-propanol (5 mL) at 100 °C under an argon atmosphere led after 6 h to the transformation of 92% of benzyl chloride into a mixture of 1,2-diphenylethane (42%) and toluene (50%). Under the same conditions, but using 0.21 M KOH instead of sodium formate, >99% of benzyl chloride was transformed into a mixture of 1,2-diphenylethane (93%) and toluene (7%), after 2 h. The presence of 1,2-diphenylethane was confirmed by ^1H NMR spectroscopy. Spectroscopic data of 1,2-diphenylethane are as follows. ^1H NMR (300.13 MHz, $CDCl_3$, 298 K): δ 7.30 (m, 4H, CH-arom), 7.22 (m, 6H, CH-arom), 2.95 (s, 4H, CH_2).[8d]

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NMR Spectroscopic Study of the Reaction of [RhCl(κ^3*P,O,P*-{xant(P^iPr_2)$_2$})] (1) with CH_2Cl_2. The experimental procedure is described for a particular case, but the same method was used in all experiments, which were run in duplicate. In the glovebox, an NMR tube was charged with a solution of **1** (20 mg, 0.03 mmol) in CD_2Cl_2 (0.5 mL), and a capillary tube filled with a solution of the internal standard (PCy_3) in toluene-d_8 was placed in the NMR tube. The tube was immediately introduced into an NMR probe at the desired temperature, and the reaction was monitored by $^{31}P\{^1H\}$ NMR at different intervals of time.

With these experiments we could calculate rate constants k_1 (from eq 6) and k_2 (from eq 8, by least-squares adjustment).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.9b00409.

General information, crystallographic data, and NMR spectra (PDF)

Accession Codes

CCDC 1925758−1925759 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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