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

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ABSTRACT: Complex [RhCl(κ^3-P,O,P-{xant(P^{i}Pr$_2$)$_2$}$_2$)] (**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$_2$)$_2$}$_2$)] (**2**) and cyclohexene and promotes the dehalogenation of the chlorocycloalkane to cyclohexane using 2-propanol solutions of sodium formate as 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$_2$)$_2$}$_2$)] (**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$_2$)$_2$}$_2$)] (**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$_2$)$_2$}$_2$)] (**6a**), which evolves into its isomer *trans*-dichloride **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.

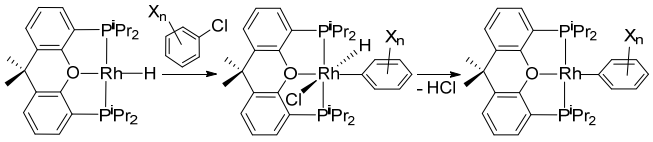
INTRODUCTION

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 their accumulation 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 bonds activations. However, chlorides are most interesting to working due to 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 of 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 ones have demonstrated their capacity for dehalogenation reactions.[9] In the same vein, the study of the 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 of adapting their coordination mode to the requirements of the each particular species.[11] As a consequence of this flexibility POP-rhodium derivatives are proving a 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$_2$)$_2$}$_2$)] (xant(P^{i}Pr$_2$)$_2$ = 9,9-dimethyl-4,5-bis(diisopropylphosphino)xanthene) undergoes the 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$_2$)$_2$}$_2$)] complexes (Scheme 1).[15]

Scheme 1. C-Cl Bond Activation of Halogenated Arenes

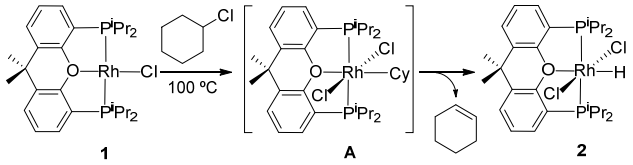


Our interest in dehalogenation and C-C coupling processes has prompted us to study now the activation of C(sp^3)-Cl bonds of mono- and dichloroalkanes, with and without β-hydrogens, promoted by [RhCl(κ^3-P,O,P-{xant(P^{i}Pr$_2$)$_2$}$_2$)] (**1**). In this paper, we report the oxidative addition of these classes of substrates to **1** and a first exploration of the behavior of this square-planar rhodium(I) complex in the dehalogenation of these organic compounds and towards 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 the rhodium(III) monohydride [$RhHCl_2(\kappa^3$-P,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 ºC. Attempts for detecting and characterizing 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.

Scheme 2. C-Cl Bond Activation of Chlorocyclohexane



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 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)º, 82.26(5)º, and 83.04(5)º, 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)º) and the chloride ligands laid mutually *trans* (Cl(1)-Rh-Cl(2) = 177.44(2)º. 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 (δ_{1H}, 1.49 and 1.45; δ_{13C}, 21.9 and 19.6) and a signal for the methyl substituents of the central heterocycle (δ_{1H},1.21; δ_{13C}, 30.9). In agreement with the presence of the hydride, the ^1H NMR spectrum contains at -19.79 ppm a doublet of triplets with $^1J_{H\text{-}Rh}$ and $^2J_{H\text{-}P}$ coupling constants of 13.6 and 11.5 Hz, respectively. As expected for equivalent P^{i}Pr$_2$ groups, the $^{31}P\{^1H\}$ NMR spectrum shows at 42.2 ppm a doublet, which display a typical $^1J_{P\text{-}Rh(III)}$ 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 [$RhH_2Cl(\kappa^3$-P,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, they are receiving noticeable attention as reducing agents in metal-mediated hydrodehalogenation reactions.[17]

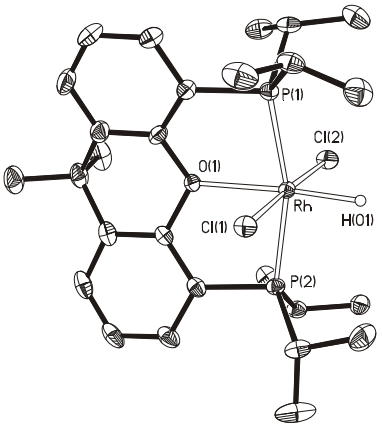
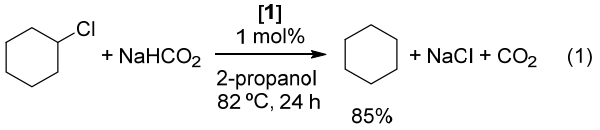
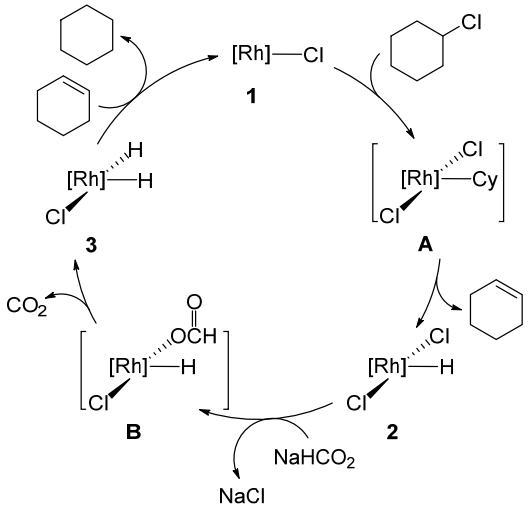


Figure 1. Molecular diagram of complex **2** (ellipsoids shown at 50% probability). All hydrogen atoms (except the hydride) are omitted for clarity. Selected bond distances (Å) and angles (deg): Rh-P(1) = 2.3054(7), Rh-P(2) = 2.3063(7), Rh-Cl(1) = 2.3438(6), Rh-Cl(2) = 2.3412(6), Rh-O(1) = 2.2591(16);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



Scheme 3. Dehalogenation of Chlorocyclohexane

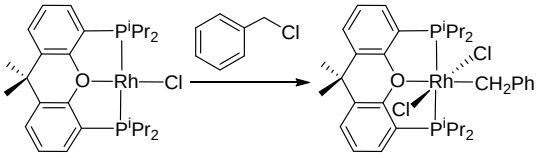


[Rh] = Rh{κ^3-P,O,P-[xant(P^iPr_2)$_2$]}

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 [$Rh(CH_2Ph)Cl_2(\kappa^3$-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 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 ($^{2}J_{H\text{-}Rh}$ = 3.4 Hz and $^{3}J_{H\text{-}P}$ = 4.1 Hz) and 17.3 ($^{1}J_{C\text{-}Rh}$ = 21.5 Hz and $^{2}J_{C\text{-}P}$ = 4.1 Hz) ppm, respectively. These spectra also reveal the disposition mutually *trans* 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 (δ_{1H}, 1.35 and 1.22; δ_{13C}, 20.0 and 19.9) and a signal for the methyl substituents of the central heterocycle (δ_{1H}, 1.19; δ_{13C}, 29.7). The $^{31}P\{^{1}H\}$ NMR spectrum shows a doublet ($^{1}J_{P\text{-}Rh}$ = 105.2 Hz) at 19.1 ppm.

Scheme 4. C-Cl Bond Activation of Benzyl Chloride



1 **4**

The S_N2 mechanism is the most common for the oxidative addition of alkyl halides to basic metal centers.[18] It leads to a disposition mutually *trans* of the added fragments. Nevertheless, the disposition *cis* 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 with 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, the 42% of the chloroalkane was transformed into 1,2-diphenylethane, whereas other 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 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 to the benzyl derivative **4** and can be rationalized according to Scheme 5.

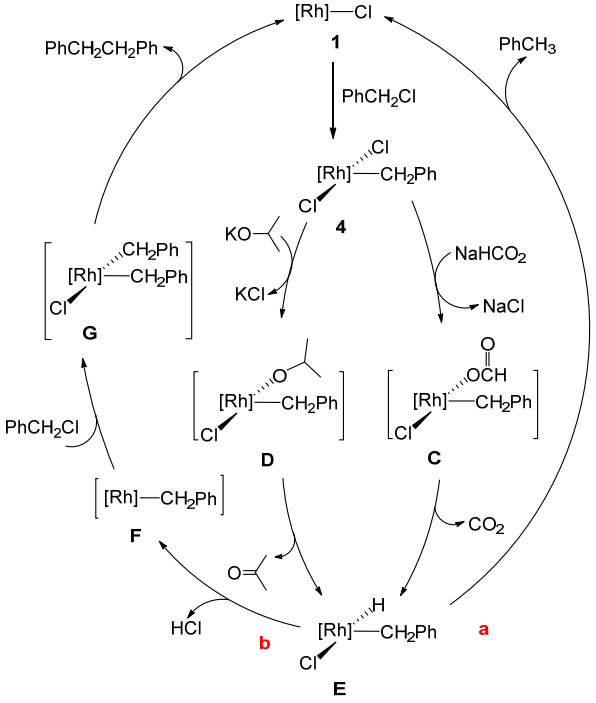
$$2\ PhCH_2Cl + 2\ NaHCO_2 + (CH_3)_2CHOH \longrightarrow PhCH_2CH_2Ph + 2\ NaCl + 2\ HCO_2H + (CH_3)_2CO \quad (2)$$

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

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

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

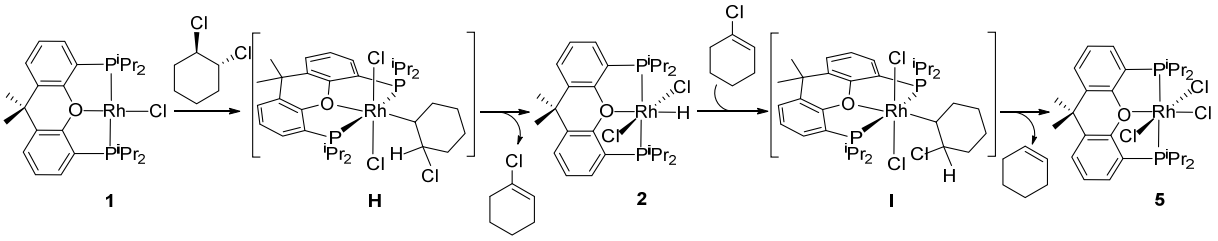
Scheme 5. Proposed Mechanism for the Dehalogenative Homocoupling and Simple Dehalogenation of Benzyl Chloride



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

Once formed complex **4**, 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 of them (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 homocoupling (b) with regard to the simple dechlorination (a), given its higher ability to trap the HCl generated from **E**, whereas should increase the isopropoxide concentration facilitating 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; the 93% of benzyl chloride was transformed into homocoupling product and only the 7% into toluene.

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



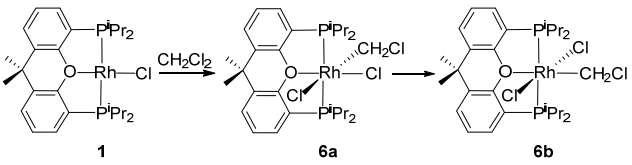
Ando and coworkers have performed the $[RhCl(PPh_3)_3]$-mediated homocoupling of benzyl bromides. There are however significant differences in the reaction conditions with regard to those previously mentioned, not only in the catalyst but also in the dehalogenation agent and therefore in the wastes. 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 second one is stable.

Complex **1** reacts with *trans*-1,2-dichlorocyclohexane to give $[RhCl_3(\kappa^3\text{-}P,O,P\text{-}\{xant(P^iPr_2)_2\})]$ (**5**) and cyclohexene, as a result of a chloride transfer from the organic substrate to the metal center of **1**. At 100 ºC, using the dichloroalkane as 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 ($^1J_{P\text{-}Rh}$ = 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 disposition *trans* of the rhodium and chloride atoms. However, when in equivalent β-positions there are atoms of hydrogen and chloride, as in **I**, the chloride abstraction is favored with regard to the hydride. In addition, it should be mentioned that, in contrast to the previously 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 the dihaloalkane as solvent, complex **1** initially gives the *cis*-dichloride-$[Rh(CH_2Cl)Cl_2(\kappa^3\text{-}P,O,P\text{-}\{xant(P^iPr_2)_2\})]$ (**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 a 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 ($^1J_{P\text{-}Rh}$ = 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 (δ_{1H}, 1.43 and 1.38; δ_{13C}, 21.6 and 20.6), whereas the methyl substituents of the heterocyclic linker give rise to a signal (δ_{1H}, 1.19; δ_{13C}, 32.5). In both spectra, the resonance corresponding to the chloromethyl group is observed as a doublet of triplets at 6.30 ($^2J_{H\text{-}Rh}$ = 3.4 Hz and $^3J_{H\text{-}P}$ = 4.1 Hz) ppm in the ^1H NMR spectrum and at 34.3 ($^1J_{C\text{-}Rh}$ = 28.6 Hz and $^2J_{C\text{-}P}$ = 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 ($^1J_{P\text{-}Rh}$ = 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)º, P(1)-Rh-O = 81.69(14)º and P(2)-Rh-O = 81.84(14)º), the chloride ligands disposed mutually *trans* (Cl(1)-Rh-Cl(2) = 177.28(7)º) and the chloromethyl group situated *trans* to the oxygen atom of the diphosphine (C(28)-Rh-O = 177.4(3)º). The rhodium-alkyl distance of 2.018(8) (Rh-C(28)) Å compares well with the expected one for a Rh(III)-C(sp^3) bond.[20]

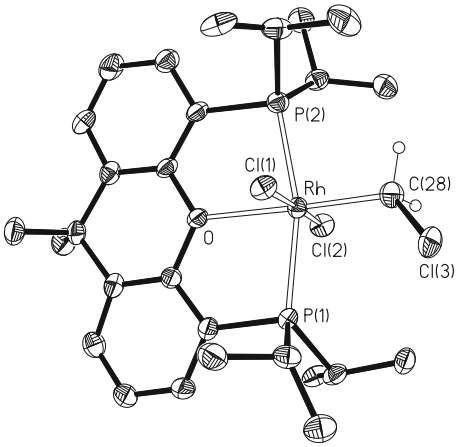


Figure 2. Molecular diagram of complex **6b** (ellipsoids shown at 50% probability). All hydrogen atoms (except those of the CH_2Cl moiety) are omitted for clarity. Selected bond distances (Å) and angles (deg): Rh-P(1) = 2.3334(19), Rh-P(2) = 2.354(2), Rh-Cl(1) = 2.341(2), Rh-Cl(2) = 2.362(2), Rh-O = 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).

The disposition *trans* of the chloromethyl group to a chloride ligand in **6a** is consistent with a 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 addition *trans*-S_N2 and *cis*-concerted 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 second one.[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 and fit to eqs 6-8, respectively. Table 1 collects the rate constants k_1 and k_2 obtained from these expressions.

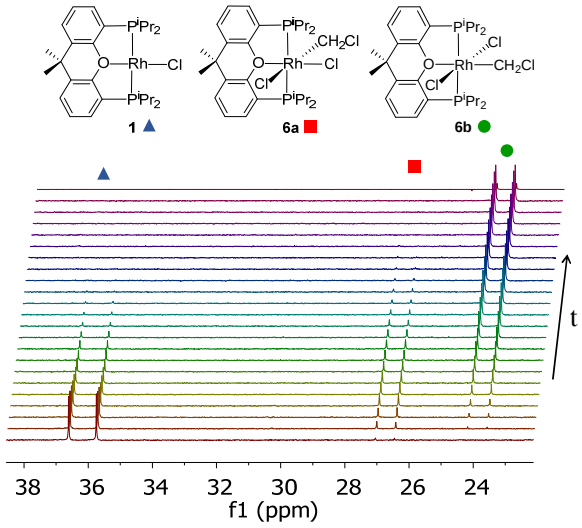


Figure 3. Stacked $^{31}P\{^1H\}$ NMR spectra (161.98 MHz, CD_2Cl_2, 303 K) showing the evolution of **1** in dichloromethane as a function of time.

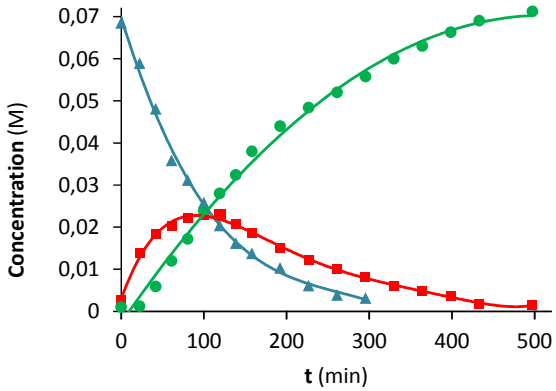


Figure 4. Composition of the mixture as a function of the time for the reaction at 303 K (**1** blue ▲ ; **6a** red ■; **6b** green ●).

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

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

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

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

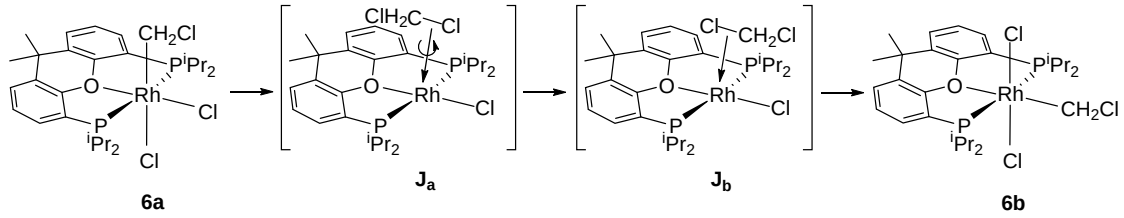


Table 1. Rate Constants for the Formation of 6a (k_1, s^{-1}) and for the Isomerization of 6a into 6b (k_2, s^{-1}) Calculated According to eqs 6-8, as a Function of Temperature (K)

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 the 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.

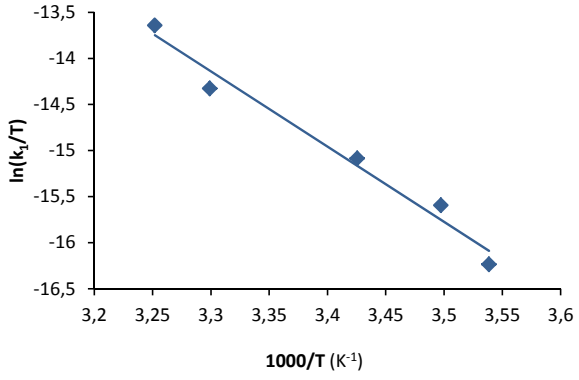


Figure 5. Eyring plot for the formation of **6a**.

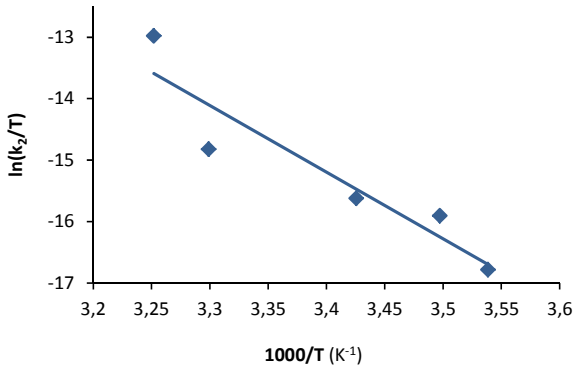


Figure 6. Eyring plot for the isomerization of **6a** to **6b**.

CONCLUDING REMARKS

This study has revealed that the rhodium(I) complex [RhCl(κ^3-P,O,P-{xant(P^{i}Pr$_2$)$_2$})] 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 β position with regard to the metal center. Species bearing β-hydrogen atoms release the olefin resulting of 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 to promote 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 2-propanol solutions 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^{i}Pr$_2$)$_2$})] (**1**)[12a] was prepared by the published methods.

Reaction of [RhCl(κ^3-P,O,P-{xant(P^{i}Pr$_2$)$_2$})] (1) with Chlorocyclohexane: Preparation of [RhHCl$_2$(κ^3-P,O,P-{xant(P^{i}Pr$_2$)$_2$})] (2). A solution of **1** (100 mg, 0.16 mmol) in chlorocyclohexane (5 mL) was heated at 100 ºC for 24 h. After this time, an analysis of the resulting solution by gas chromatography shows 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 x 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, $^4J_{H-H}$ = 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(C*H*$_3$)$_2$), 1.45 (dvt, $^3J_{H-H}$ = 5.7, *N* = 16.2, 12H, PCH(C*H*$_3$)$_2$), 1.21 (s, 6H, CH$_3$), -19.79 (dt, $^1J_{H-Rh}$ = 13.6, $^2J_{H-P}$ = 11.5, 1H, Rh-H). ^{13}C{^{1}H}-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(*C*H$_3$)$_2$), 25.3 (vt, *N* = 24.5, P*C*H(CH$_3$)$_2$), 21.9, 19.6 (both s, PCH(*C*H$_3$)$_2$). ^{31}P{^{1}H} 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^{i}Pr$_2$)$_2$})] (1) with Benzyl Chloride: Preparation of [Rh(CH$_2$Ph)Cl$_2$(κ^3-P,O,P-{xant(P^{i}Pr$_2$)$_2$})] (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). ^{1}H 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(C*H*$_3$)$_2$), 1.22 (dvt, $^3J_{H-H}$ = 7.12, *N* = 12.7, 12H, PCH(C*H*$_3$)$_2$), 1.19 (s, 6H, CH$_3$). ^{13}C{^{1}H}-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(*C*H$_3$)$_2$), 26.5 (vt, *N* = 10.1, P*C*H(CH$_3$)$_2$), 20.0, 19.9 (both s, PCH(*C*H$_3$)$_2$), 17.3 (dt, $^1J_{C-Rh}$ = 21.5, $^2J_{C-P}$ = 4.1, RhCH$_2$Ph). ^{31}P{^{1}H} 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^{i}Pr$_2$)$_2$})] (1) with *trans*-1,2-dichlorocyclohexane: Preparation of [RhCl$_3$(κ^3-P,O,P-{xant(P^{i}Pr$_2$)$_2$})] (5). A solution of **1** (100 mg, 0.17 mmol) in *trans*-1,2-dichlorocyclohexane (3 mL) was heated at 100 ºC 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, that was washed with further portions of pentane (5 x 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). ^{1}H 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(C*H*$_3$)$_2$), 1.61 (dvt, $^3J_{H-H}$ = 7.3, *N* = 14.9, 12H, PCH(C*H*$_3$)$_2$), 1.05 (s, 6H, CH$_3$). ^{13}C{^{1}H}-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(*C*H$_3$)$_2$), 26.6 (vt, *N* = 24.4, P*C*H(CH$_3$)$_2$), 21.7, 19.7 (both s, PCH(*C*H$_3$)$_2$). ^{31}P{^{1}H} 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^{i}Pr$_2$)$_2$})] (1) with CH$_2$Cl$_2$: Preparation of *trans*-[Rh(CH$_2$Cl)Cl$_2$(κ^3-P,O,P-{xant(P^{i}Pr$_2$)$_2$})] (6b). Complex **1** (100 mg, 0.17 mmol) was dissolved in dichloromethane (3 mL) and it was stirred for 16 hours 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). ^{1}H 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(C*H*$_3$)$_2$), 1.38 (dvt, $^3J_{H-H}$ = 7.2, *N* = 14.6, 12H, PCH(C*H*$_3$)$_2$), 1.19 (s, 6H, CH$_3$). ^{13}C{^{1}H}-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(*C*H$_3$)$_2$), 27.3 (vt, *N* = 22.3, P*C*H(CH$_3$)$_2$), 21.6, 20.6 (both s, PCH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (121.49 MHz, toluene-d_8, 298 K): δ 23.6 (d, $^1J_{Rh-P}$ = 100.1).

Spectroscopic Detection of *cis*-[Rh(CH$_2$Cl)Cl$_2$(κ^3-P,O,P-{xant(P^{i}Pr$_2$)$_2$})] (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{^{1}H} NMR spectroscopy. After 90 min, the resulting solution was evaporated to dryness, getting a yellow residue. Addition in toluene-d_8 and subsequent filtration, afforded a solution whose ^{31}P{^{1}H} NMR spectrum shows a mixture of **1**, **6a** and **6b** in a 4 : 33 : 63 ratio. The ^{1}H, ^{31}P{^{1}H} and ^{13}C{^{1}H} NMR spectra of were recorded at 273 K in order to avoid the progress of the isomerization. *Spectroscopic data for **6a**:* ^{1}H 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$_2$Y 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(C*H*$_3$)$_2$), 1.58 (dvt, $^3J_{H-H}$ = 7.4, *N* = 15.2, 6H, PCH(C*H*$_3$)$_2$), 1.41 (dvt, $^3J_{H-H}$ = 7.4, *N* = 15.1, 6H, PCH(C*H*$_3$)$_2$), 1.35 (dvt, $^3J_{H-H}$ = 7.1, *N* = 14.3, 6H, PCH(C*H*$_3$)$_2$), 1.15 (s, 6H, CH$_3$). ^{13}C{^{1}H}-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(*C*H$_3$)$_2$), 30.8 (s, *C*(CH$_3$)$_2$), 30.7 (s, C(*C*H$_3$)$_2$), 27.4 (vt, *N* = 26.8, P*C*H(CH$_3$)$_2$), 25.8 (vt, *N* = 20.8, P*C*H(CH$_3$)$_2$), 23.2, 20.5, 20.4, 19.3 (all s, PCH(*C*H$_3$)$_2$). ^{31}P{^{1}H} 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, using a 100% cross-linked methyl silicone gum column (30 m × 0.32 mm, with 0.25 μm film thickness) was 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 equipped with a bonded polyethylene glycol (PEG) phases column (30 m × 0.25 mm, with 0.25 μm film thickness) was employed (oven conditions: 30 °C (hold 5 min) to 100 °C at 5 °C/min (hold 5 min) and 100 ºC to 250 ºC/min (hold 1 min)).

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

Dehalogenation of Benzyl Chloride Catalyzed by [RhCl(κ^3-P,O,P-{xant(P^{i}Pr$_2$)$_2$})] (1). In the presence of 1.8 x 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 argon atmosphere leads 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, the >99% of benzyl chloride is transformed into a mixture of 1,2-diphenylethane (93%) and toluene (7%), after 2 h. The presence of 1,2-diphenylethane was confirmed by ^{1}H NMR spectroscopy. *Spectro-*

scopic Data of 1,2-Diphenylethane: ^{1}H 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]

NMR Spectroscopic Study of the Reaction of [RhCl(κ^3-P,O,P-{xant(P^{i}Pr$_2$)$_2$})] (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 can 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.

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

Accession codes

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

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

Financial support from the MINECO of Spain (Projects CTQ2017-82935-P and Red de Excelencia Consolider CTQ2016-81797-REDC), the Diputación General de Aragón (Group E06_17R and project LMP148_18), FEDER, and the European Social Fund is acknowledged. L. A. de las H. thanks the MECD for her FPU Contract (FPU17/04813).

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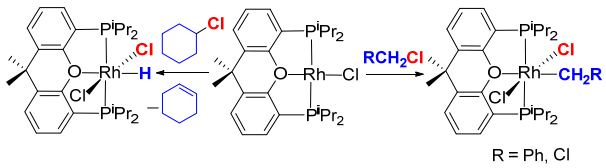
P^{i}Pr$_2$
Cl
O
Rh
H
Cl
P^{i}Pr$_2$
Cl
Cl
P^{i}Pr$_2$
O
Rh
Cl
P^{i}Pr$_2$
RCH$_2$Cl
P^{i}Pr$_2$
Cl
O
Rh
CH$_2$R
Cl
P^{i}Pr$_2$

R = Ph, Cl