Favored C–H Activation in Comparison to Cyclopropyl C–C Activation using a Vaska-Analogous Complex

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Dedicated to Prof. R. R. Schrock on the occasion of his 60th birthday.

Supporting Information for this article is available on the WWW under http://asc.wiley-vch.de/home/.

Abstract: Through ligand exchange reaction of Vaska's complex with a chelating diphosphinite ligand containing a cyclopropyl group, C–H activation rather than C–C activation of the strained cyclopropyl ring is induced. The activation takes place as a second step preceded by the ligand exchange reaction. The fixation of the C–H bond near to the metal through the geometry of the diphosphinite ligand is essential for the activation process.

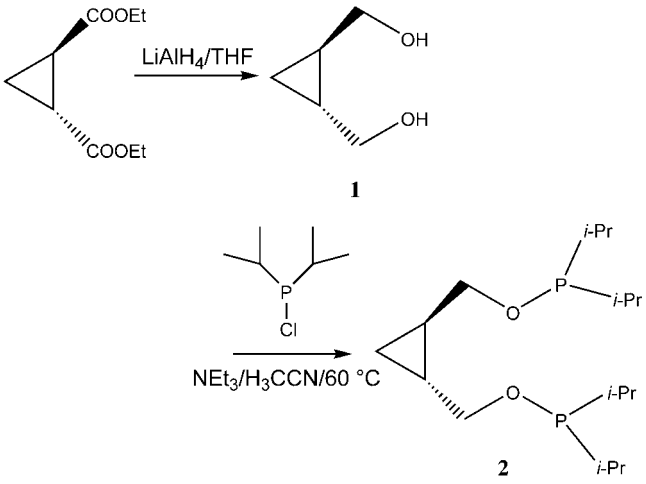
Keywords: C–C activation; C–H-activation; cyclopropane; iridium; P ligands; Vaska complex

Controlled C–H activation and C–C single bond activation, using transition metals, are still among the most challenging reactions in chemistry[1] and understanding as well as prediction of these reactions are still poorly developed. In general, C–H activation is thought to be easier than C–C activation both kinetically and thermodynamically. Two kinetic reasons are believed to be most responsible that C–C single bond activation is found so rarely:[2] steric protection of the C–C single bond through six substituents and the energy necessary to reorientate the bond orbitals during the activation process. Both barriers are less pronounced for C–H activation making this reaction more favorable than C–C activation.

A common strategy to decrease the second problem is to offer strained C–C-single bonds,[3] especially those in 3-membered rings, because in that case the reorientation of the C–C bond orbitals towards the metal is predefined in the substrate. To overcome the first problem we introduced a 3-membered ring in a chelating ligand in such a way that the strained C–C single bond of the cyclopropyl fragment is placed in a promising and defined position within the coordination sphere of the metal. The ligand was designed in such a manner that, once C–C single bond activation occurs, two five-membered rings are formed. A similar strategy was used earlier successfully for the activation of C–C single bonds.[4a–c] The ligand synthesis is shown in Scheme 1.

The distance of the central strained C–C single bond of the embedded cyclopropyl ring to the metal after complexation is mainly determined by the bite angle of the two phosphinite hands. Forcing the phosphinite hands to coordinate *trans* to each other would place the C–C single bond under focus most closely to the metal. In the few examples which exist for C–C single bond activation, group 9 metals (Rh, Ir) are among the most promising center metals.[4] Since the M–C bond strength should increase when going down a group, Ir seemed to be the best choice as center metal. We thus decided to use Vaska's complex as a precursor, performing a ligand exchange reaction in an apolar solvent, to achieve the favorable *trans* geometry, since the OC–Ir–Cl axis should remain untouched under these conditions (Scheme 2).

If the reaction is performed at concentrations higher than 5 mmol/L almost only coordination polymer **3** is isolated. It is most easily characterized by a singlet in



Scheme 1.

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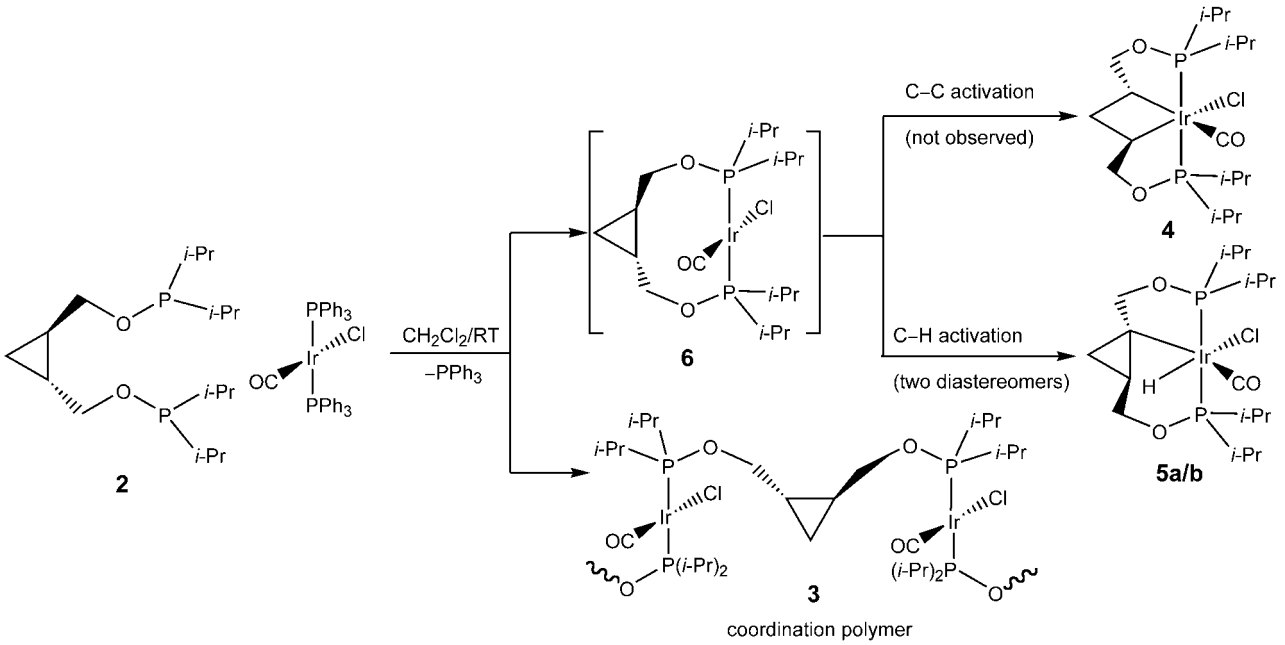


Scheme 2.

the ^{31}P NMR spectrum at 148.3 ppm. The C–H activated material **(5a/b)** is observed in very low yield, most easily recognized by the Ir–H triplet at about −19 ppm in the ^{1}H NMR spectrum. At concentrations lower than 5 mmol/L the C–H activated material more and more becomes the main product. No evidence for C–C activation (compound **4**) could be found. Despite the fact that Vaska-analogous complexes oxidatively add all sorts of molecules, to our knowledge this is the first example that oxidative addition of an alkyl–H bond was observed to this type of complexes.

The formation of the coordination polymer **3** seems to be irreversible. Once built, it cannot be transferred into the C–H activated product by dilution even at elevated temperature (toluene, reflux 12 h). Running the reaction at a concentration of 0.5 mmol/L by stirring at room temperature for 4 days, the C–H activated material was received quantitatively. It can be separated from the PPh_3 by column filtration with silica gel using hexane as eluent to wash out the PPh_3 and CH_2Cl_2 to re-isolate **5a/b** afterwards. The ^{1}H NMR spectrum of the yellow material indicates two slightly overlapping Ir–H triplets at −19.1 ppm and −19.3 ppm in the ratio 7:1 which we assign to the two possible diastereomers. This interpretation is in accordance with the ^{31}P NMR spectrum showing two pairs of doublets (153.2 ppm/119.3 ppm and 146.2 ppm/115.3 ppm) in approximately the same ratio (8:1). The main product of the two diastereomers (**5a**) could be isolated purely through recrystallization from hexane yielding in yellow crystals that were suitable for X-ray analysis.[9] A molecule in the solid state of the main C–H activated product **5a** is shown in Figure 1.

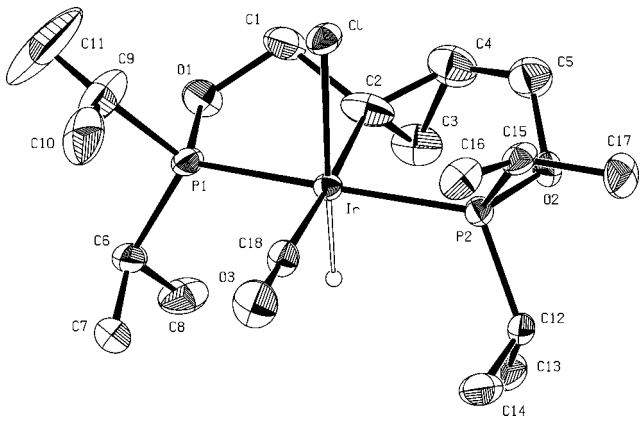
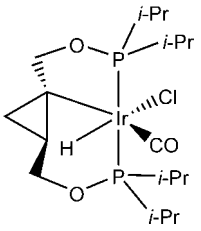
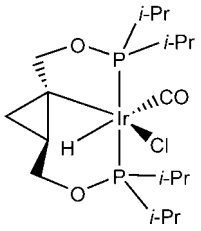
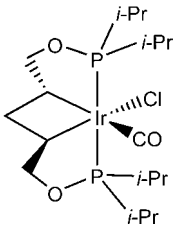


Figure 1. ORTEP style plot of the main C–H activated product **5a** in the solid. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

In the Supporting Information, a table can be found which contains selected bond lengths and angles for **5a** experimental and calculated, both on the B3LYP/LANL2DZ (Gaussian 03[5]) level and on the B3LYP/6-311 g(d, p) level for C, H, O, P, Cl with Stuttgart ECP60MDF[6] for Ir.

The hydrogen atom, bound to iridium, could unequivocally be localized. A complete activation of the C–H bond has occurred. The distance between the Ir-bound H and C2 in the cyclopropyl ring is 2.71 Å and the C2–Ir–H bond angle is even larger than 90°. This proves that the C–H bond was completely broken, thus ruling out any kind of σ-type C–H complex. The Ir–Cl bond is fairly long, most likely because of the strong *trans* influence of the hydride. The P1–Ir–P2 angle deviates decisively from 180° proving that there is ring strain in the

Table 1. Calculated thermodynamic data for the two C–H activated diastereomers **5a/b** and the hypothetical cyclopropyl-C–C activated product **4** using B3LYP/LANL2DZ[5] and B3LYP/6311 g(d, p) for C, H, O, P, Cl with Stuttgart ECP60MDF[6] for Ir.

Compound	 **5a**	 **5b**	 **4**
$G_{298} - G_{298}$(**5a**)			
B3LYP/LANL2DZ	0 kcal/mol	1.72 kcal/mol	–18.8 kcal/mol
B3LYP/6–311 g(d, p) for C, H, O, P, Cl and Stuttgart ECP60MFD[6] for Ir	0 kcal/mol	2.46 kcal/mol	–11.8 kcal/mol

chelating ligand after complexation. The ligand's bow length is too short to bind to the Ir center strain-free. We assume that this is most likely the main reason why only C–H activation and no C–C activation is observed. A comparison of the experimental and calculated structure parameters shows a fairly good agreement on the B3LYP/6-311 g(d, p) level with Stuttgart ECP60MDF for Ir. The results on the B3LYP/LANL2DZ level deviate decisively from the ones determined by X-ray structure, though. The calculated thermodynamic data for the two C–H activated diastereomers **5a/b** and the hypothetical cyclopropyl-C–C activated product **4** are listed in Table 1.

The free enthalpies at 298 K of the two diastereomers are predicted correctly relative to each other (**5a** is more stable than **5b**) but according to this calculation by far the most stable reaction should be the C–C activation of the cyclopropyl fragment (on both theoretical levels applied), which was not observed. Still more sophisticated basis sets might be tried to confirm the thermodynamic data, but even qualitatively the difference in thermodynamic stabilities of C–H and C–C activated products is remarkable, indicating that the activation reaction is most likely kinetically controlled.

The IR spectrum of **5a** shows a ν(CO) at 2007 cm^{-1} and a ν(Ir–H) at 2210 cm^{-1}. The larger ν(CO) value of the activated product in comparison to the coordination polymer **3**, which shows the ν(CO) at 1955 cm^{-1}, can be explained by the stronger *trans* influence of an alkyl group in comparison to Cl.

C–H activation as the first kinetically favored step does not seem to be uncommon for group 9 metal centers even in the presence of cyclopropyl fragments.[7] Bergman found a C–H activation of cyclopropane at low temperatures with $Cp^*RhH_2PMe_3$ on irradiation, which at 0–10 °C was at least partly converted into a C–C activation, leading to a metallacyclobutane.

In contrast, **5a** is very stable or at least kinetically inert, most likely because of the chelating effect of the ligand arms. Even refluxing the compound in toluene for 2 days resulted only in complete re-isolation of the starting material.

The fact that at high concentration almost no C–H activated product is found can be taken as a hint that direct attack of the C–H bond without pre-coordination does not play an important role. Another mechanistic possibility is that the activation only requires the coordination of one of the two phosphinite hands but not the strict fixation within the coordination sphere (Scheme 3).

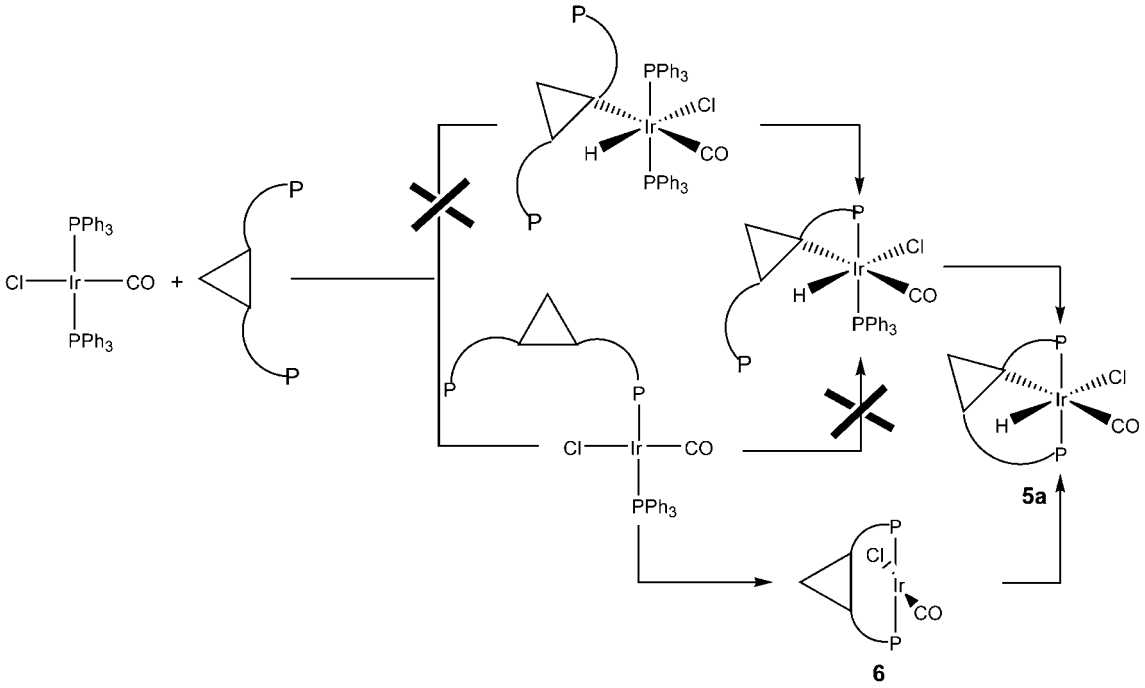
To prove that the mechanism shown in Scheme 3 is the correct one, namely that the fixation of the C–H bond near to the metal is essential for the activation, the following control experiments have been performed (Scheme 4):

If Vaska's complex is stirred at room temperature with one equivalent of cyclopropylmethanol (**10**) in CH_2Cl_2 at 5 mmol/L for 48 h no reaction is observed. This rules out the direct C–H activation without any pre-coordination.

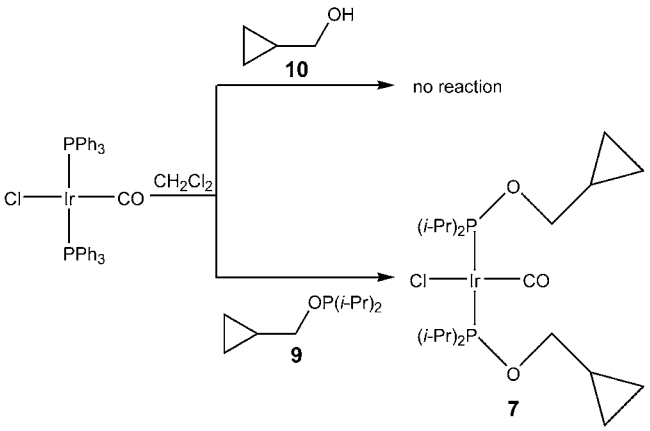
If Vaska's complex is stirred at room temperature with two equivalents of (cyclopropyl)-$CH_2OP(i\text{-}Pr)_2$ (**9**) in CH_2Cl_2 at 8 mmol/L for 48 h only complete ligand exchange is observed (compound **7**) without any hint for C–H activation using the ^1H NMR spectrum area around –19 ppm and the IR spectrum (no Ir–H band) as diagnostic criteria.

The main C–H activated product **5a** is the one with H and CO *cis* to each other. A kinetic explanation for this can be given using steric reasons as shown in Scheme 5.

The chlorine has a larger van der Waals volume than a CO group. Thus, H_b in Scheme 5 is forced away from the metal center in the non-activated complex **6**. As a consequence, H_a moves towards the metal center and is more



Scheme 3.



Scheme 4.

likely to be activated. This leads to the observed main product (**5a**). Thermodynamics also predict the observed main product to be more stable, since in that case the two ligands with the strongest *trans* influence (CO and H) are *cis* to each other and, thus, do not compete.

If the analogous Rh complex is employed in the reaction with the chelating diphosphinite ligand containing the cyclopropyl fragment, only coordination polymer **8** could be isolated. No other products, in particular no C–H activated material could be observed, even at concentrations lower than 5 mmol/L.

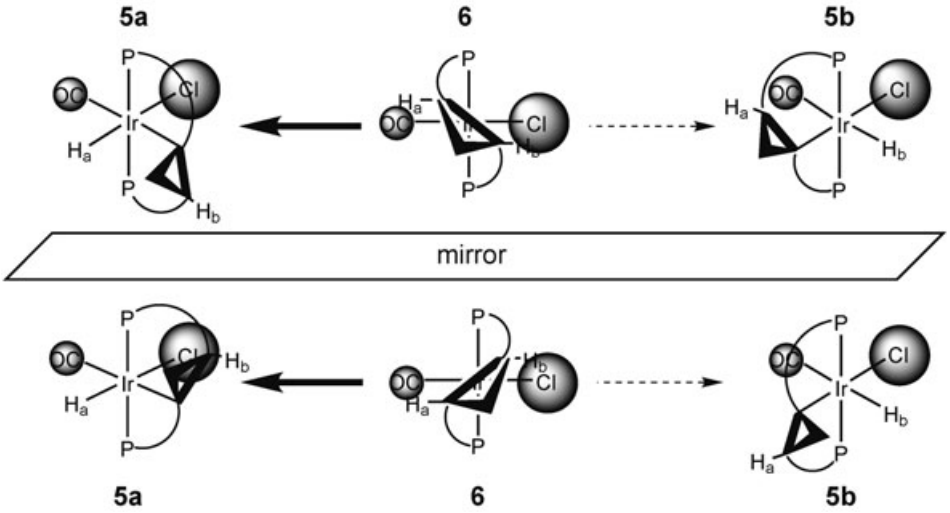
As a conclusion we propose a mechanism for the complete reaction in Scheme 6 with Ir.

The fact that, in the case of Rh, no activation could be observed might be explained either by assuming that the C–H activation step is very slow for Rh in comparison to Ir, so it cannot compete with the irreversible polymerization even at low concentrations (kinetic reason), or that the activation is reversible in the case of Rh (both the M–C and the M–H bond should be less stable for Rh than for Ir) shifting the complete equilibrium to the coordination polymer at the end, since the intramolecular cyclization is disfavored through ring strain without a preceding irreversible C–H-activation step (thermodynamic reason).

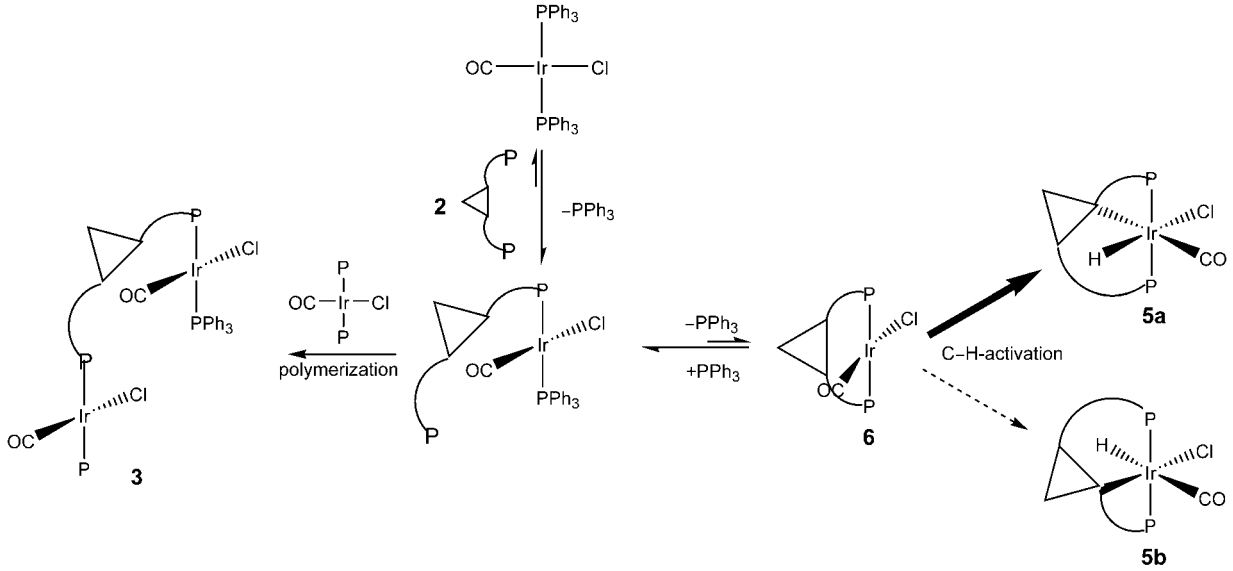
Experimental Section

Materials and Instrumentation

Vaska's complex was synthesized according to the literature method.[8] Chlorodiisopropylphosphine and diethyl *trans*-1,2-cyclopropanedicarboxylate were purchased from Aldrich and used as received. The Rh-analogous Vaska complex was purchased from Strem chemicals. Cyclopropylmethanol was purchased from Lancaster and used without further purification. The solvents acetonitrile, pentane, dichloromethane and $CDCl_3$ were degassed by bubbling N_2 through them for 30 min and stored under argon over molecular sieves. NMR measurements were performed on an AMX400 Bruker machine at room temperature. Peaks are referred to solvent peaks for ^1H NMR (400 MHz, $CHCl_3 = 7.24$ ppm) and ^{13}C NMR (100 MHz, $CDCl_3 = 77.0$ ppm) and to 85% H_3PO_4 as external standard for ^{31}P NMR (162 MHz) spectroscopy. IR spectroscopy was done on a JASCO FI7IR-460plus machine.



Scheme 5.



Scheme 6.

1,2-Di(hydroxymethyl)cyclopropane (1)

1.69 g (44.5 mmol) $LiAlH_4$ were suspended in 100 mL of THF. At room temperature 4 mL (22.8 mmol) of diethyl *trans*-1,2-cyclopropanedicarboxylate were added dropwise. The mixture was refluxed for 12 h, then cooled with an ice bath and slowly first water and then 2 molar HCl were added until a clear solution was obtained. This solution was added into a continuous liquid/liquid extractor. Using 400 mL of diethyl ether the extraction was run for 24 h. 2.3 g of a light yellow viscous liquid were obtained after removing the diethyl ether in vacuum (61.2%). The liquid was distilled at 0.16 mbar and 85 °C to give a colorless viscous liquid.^{1}H NMR ($CDCl_3$): $\delta = 0.4293$ (2H, t, $^3J_{H,H} = 6.8$ Hz, cyclopropyl-CH_2), 1.0317 (2H, m, cyclopropyl-CH), 3.0540 (2H, dd, $^3J_{H,H} = 5.6$ Hz, $^1J_{H,H} = 11.2$ Hz, O-CH_2), 3.8182 (2H, dd, $^3J_{H,H} = 4.5$ Hz, $^1J_{H,H} = 11.3$ Hz O-CH_2), 4.0710 (2H, s, OH); ^{13}C NMR ($CDCl_3$): $\delta = 7.3763$ (s), 19.8962 (s), 66.1619 (s); anal. calcd. for $C_5H_{10}O_2$: C 58.8, H 9.9; found: C 58.9, H 9.8.

1,2-Bis(diisopropylphosphinyloxy)cyclopropane (2)

0.4 g (3.91 mmol) of **1** were dissolved with 1.65 mL (11.75 mmol) of triethylamine in 10 mL of acetonitrile. 1.31 mL (8.22 mmol) of chlorodiisopropylphosphine were added *via* syringe. Immediately, a white solid precipitated. The reaction mixture was stirred while heating to 60 °C for 12 h. After cooling to room temperature, 40 mL of pentane were added and the mixture was stirred for 1 h. Then the pentane phase was transferred into a new flask *via* syringe and the solvent was removed from this flask under vacuum to leave a colorless oil; yield: 1 g (76%). ^{1}H NMR ($CDCl_3$): $\delta = 0.4995$

(2H, t $^3J_{H,H}$ = 6.8 Hz, cyclopropyl-CH_2), 0.9722–1.0827 (28H, m, CHCH_3), 1.1563 (2H, m, cyclopropyl-CH), 1.6702 (4H, hept $^3J_{H,H}$ = 7.1 Hz, CHCH_3), 3.4474 (2H, m, O-CH_2), 3.6780 (2H, m, O-CH_2); ^{13}C NMR ($CDCl_3$): d = 8.9536 (s, cyclopropyl-CH_2), 16.939 (s, CHCH$_3$), 17.9281 (d, $^2J_{C,P}$ = 20.1 Hz, CHCH$_3$), 18.3640 (d, $^2J_{C,P}$ = 19.6 Hz), 28.0588 (d, $^3J_{C,P}$ = 15.7 Hz, cyclopropyl-CH), 75.8063 (d, $^2J_{C,P}$ = 19.1 Hz, O-CH$_2$); ^{31}P NMR ($CDCl_3$): δ = 152.66 (s); anal. calcd. for $C_{17}H_{36}O_2P_2$: C 61.1, H 10.9, P 18.5; found: C 60.4, H 10.3, P 17.7

General Procedure of the Ligand Exchange Reaction

A defined amount of Vaska's complex (or the Rh-analogue) was dissolved in a defined volume of CH_2Cl_2. To the yellow solution was added an equimolar amount of ligand (or two equivalents in the case of **7**), dissolved in 20 mL of CH_2Cl_2. The still yellow solution was stirred for a defined time period at room temperature. Then the solvent was removed under vacuum. A yellow solid remained which was dissolved (in some cases only suspended) in 20 mL of hexane and transferred onto a column with 4 cm of silica gel. The yellow solid remained on the top of the silica gel and was washed with 1000 mL of hexane in 5 portions of 200 mL. After that, the yellow solid is regained by flashing 60 mL of CH_2Cl_2 in three portions of 20 mL through the silica gel and removing the CH_2Cl_2 under vacuum. Yellow to pale yellow microcrystals were obtained.

Acknowledgements

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