Synthesis of a Square-Planar Rhodium Alkylidene *N*-Heterocyclic Carbene Complex and its Reactivity Towards Alkenes

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Dedicated to Professor Christian Bruneau on the occasion of his 60th birthday

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Summary: The first rhodium-alkylidene square-planar complex stabilized by a *N*-heterocyclic carbene ligand RhCl(=CHPh)(IPr)PPh$_3$ (**2**) {IPr = 1,3-bis-(2,6-diisopropylphenyl)imidazol-2-carbene} has been prepared by reaction of RhCl(IPr)(PPh$_3$)$_2$ (**1**) with phenyldiazomethane and its dynamic behavior in solution studied. Treatment of **2** with alkenes results in the formation of η^2-olefin complexes RhCl(η^2-CH$_2$=CHR)(IPr)PPh$_3$ (**3**, R = H; **4** R = Ph; **5** R = OEt) and new olefins arising from the coupling of the alkylidene with the alkenes, likely via a metallacyclobutane intermediate.

Transition-metal alkylidene species are catalytic initiators for a myriad of useful organic transformations including olefin metathesis,[1] cyclopropanation,[2] C-H insertion[3] or cycloadditions.[4] In sharp contrast with other transition metals, the number of isolated rhodium-alkylidene complexes remain scarce, apart from the seminal work developed by Werner and Milstein's groups with phosphane stabilized derivatives.[5] The commonly used method for the preparation of alkylidene complexes via diazoalkane precursors[6] failed for the direct synthesis of rhodium-carbene species bearing two electron-rich phosphanes of type $RhCl(=CRR')(PR_3'')_2$. This problem was elegantly circumvented by the initial treatment of less sterically demanding rhodium-stibanes with diazoalkanes and subsequent exchange reaction by phosphanes, although no benzylidene species could be obtained following this approach.[5f] Latter on, Milstein and coworkers showed that rhodium-benzylidene derivatives could be attained by reaction of phenyldiazomethane with more stable square-planar pincer precursors,[5i,k] and even the compound $RhCl(=CHPh)(P^iPr_3)_2$ was prepared by an alternative method employing a sulfur ylide as precursor for the alkylidene moiety.[5i]

The special stereoelectronic properties of N-heterocyclic carbenes[7] (NHCs) make them suitable ancillary ligands not only for stabilization of reactive intermediates, but also for the improvement of catalytic activity.[8] Specially prominent is the case of olefin metathesis, where the catalytic performances of commercially available second generation Grubb's catalyst surpass the phosphane counterparts.[9] This "NHC effect" has been also observed in osmium-alkylidene derivatives.[10] With the aim of studying the potential of NHCs ligands in rhodium-alkylidene chemistry, we have prepared a new rhodium-alkylidene complex stabilized by a NHC ligand using phenyldiazometane as alkylidene precursor and investigated its behavior towards olefins.

Reaction of the bis-phosphane-NHC rhodium complex $RhCl(IPr)(PPh_3)_2$[11] (**1**) [IPr = 1,3-bis-(2,6-diisopropylphenyl)imidazol-2-carbene] with a freshly prepared THF solution of phenyldiazomethane[12] at -20 ºC under argon atmosphere gave rise to a dark green solution with concomitant gas bubbling (N_2). Work up at low temperature led to the complex $RhCl(=CHPh)(IPr)PPh_3$ (**2**) as a green solid in 76 % yield (Equation 1). Related Rh-NHC-Fischer carbene complexes have been previously reported,[13] but **2**

is, as far as we know, the first Rh-NHC-alkylidene derivative. Complex **2** is an air-sensitive solid which smoothly decomposes in solution after 1 h at room temperature to give a mixture of unidentified hydrides. In addition to **2**, the formation of Wilkinson's catalyst $RhCl(PPh_3)_3$ was observed when the diazomethane solution was added at room temperature. Similar cleavage of a supposed robust Rh-NHC bond has been previously reported.[14] The preparation of related alkylidene derivatives by using diphenyldiazomethane or methylphenyldiazomethane, or starting from different free-phosphane Rh^I-NHC complexes were unsuccessful.
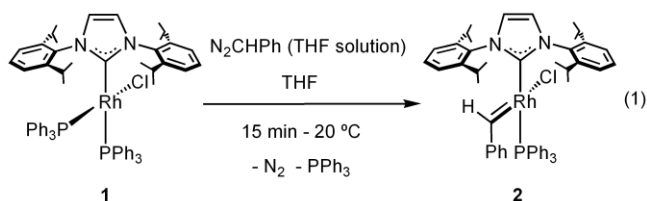
Green single crystals of **2** suitable for an X-ray analysis were obtained by diffusion of hexane into a concentrated THF solution of the complex. The molecular structure of **2** (Figure 1) displays a slightly distorted square-planar structure, with the IPr ligand disposed *trans* to PPh_3 [P-Rh-C(8) = 167.60(5)°]. The wingtip functionalities of the IPr are located out of the coordination plane, whereas the alkylidene is deviated from de coordination plane (54.61(12)°) with the phenyl substituent pointing to the less congested phosphane ligand. The rhodium-carbon separations [Rh-C(1) = 1.873(2) and Rh-C(8) = 2.044(2) Å] compare well with previously reported rhodium-alkylidene[5a-f,l] double bond or rhodium-NHC[15] single bond distances, respectively.
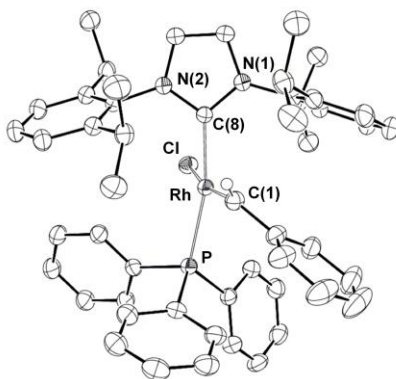
Figure 1. Molecular diagram of **2**. Selected bond lengths (Å) and angles (°): Rh-C(1) 1.873(2), Rh-C(8) 2.044(2), Rh-P 2.3293(5), Rh-Cl 2.4134(5); P-Rh-Cl 89.60(2), P-Rh-C(1) 96.36(7), Cl-Rh-C(1) 167.18(7), Cl-Rh-C(8) 87.46(6), C(1)-Rh-C(8) 88.99(8), Rh-C(1)-C(2) 129.16(17).

The most striking feature of this molecule involves the particular conformation of one of the phenyl rings {C(35)-C(40)} of the phosphane ligand. While the Rh-P-C_{ipso}-C torsional angles of two phenyl rings exhibit normal values for the typical propeller-like conformation of the phosphine (Rh-P-C(47)-C(49) -30.36°, and Rh-P-C(41)-C(42) -29.98°), the third phenyl shows for this analogous torsion an anomalous value of -84.93° {Rh-P-C(35)-C(40)}. A detailed analysis of the structural parameters makes evident the presence of a weak CH/π interaction between one of the hydrogen atoms of this phenyl ring {H(40)} and the aromatic ring of the alkylidene (H(40)…G 2.77 Å, H(40)…π-ring 2.71 Å, g 12.2°, C(2)…H(40) 2.87 Å, C(3)…H(40) 2.85 Å) that could be most likely responsible of this conformational modification.[16]

The ^{1}H NMR spectrum of **2** shows a characteristic low field singlet at δ 15.65 ppm corresponding to the alkylidene proton. The ^{13}C{^{1}H} NMR spectrum presents two doublets of doublets for the alkylidene (δ 256.2 ppm, J_{C-Rh} = 47.2 and J_{C-P} = 13.6 Hz) and IPr (187.6 ppm, J_{C-P} = 118.1 and J_{C-Rh} = 64.4 Hz) carbon atoms attached to rhodium. The large J_{C-P} observed for IPr is in accordance with the *trans* disposition of the phosphane and the NHC ligands. Compound **2** is fluxional as evidenced by the resonances for the isopropyl substituents of the IPr ligand in a ^{1}H VT-NMR study. Thus, the broad resonance at 3.60 ppm (CH) and the two doublets at 1.40 and 1.11 ppm (CH_3) observed at room temperature split at -30 °C into two septuplets at 3.95 and 3.13 ppm (CH), and four doublets at 1.62, 1.27, 1.22, and 1.11 ppm (CH_3). The presence of only one signal for the four CH protons of the isopropyl group at room temperature could be ascribed to two facts: the presence on the NMR time scale of a mirror plane and a rotational process that exchanges unsymmetrical isopropyl groups. The plane of symmetry matches the metal coordination plane and should bisect the imidazol ring of the IPr ligand. The substituents of the alkylidene moiety should be coplanar to this plane as no evidence of rotation of alkylidene is observed by broadening of the low field proton signal,[17] although the partial

4

windshield-wiper motion of the alkylidene ligand cannot be ruled out on the light of the molecular structure. Moreover, the alkylidene proton displays NOE effect with the CH and CH_3 signals of the IPr and not with the PPh_3 resonances. On the other hand, with regard to the exchange process, rotation around the Rh-C_{IPr} axis seems more likely that the more hindered diisopropylphenyl rotation around the N-C axis.[18] The rate constants for the rotational process were obtained from a line shape analysis of the temperature dependent CH isopropyl resonances in the temperature range -30 ℃ to 30 ℃ (Figure 2). The activation parameters obtained from the corresponding Eyring analysis are $\Delta H^{\neq} = 13.4 \pm 0.8$ kcal mol^{-1} and $\Delta S^{\neq} = 2.5 \pm 1.3$ cal K^{-1} mol^{-1}.
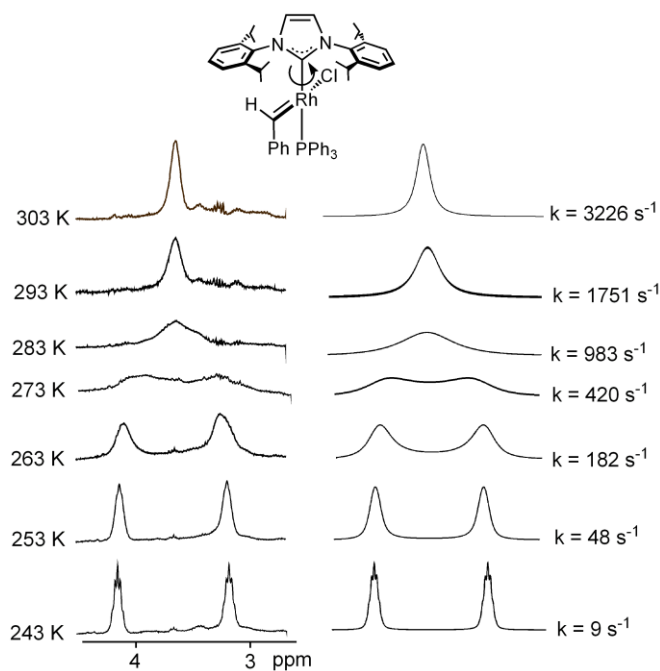

Figure 2. Variable-temperature ^{1}H NMR spectra in the CH isopropyl region of RhCl(=CHPh)(IPr)PPh$_3$ (**2**) in toluene-d_8: experimental (left) and calculated (right).

Complex **2** is the first isolated square-planar rhodium-alkylidene derivative stabilized by an NHC ligand. Dissociation of the phosphane ligand on this 16-electron derivative could generate 14-electron metal-alkylidene species which has been postulated as the active species in ruthenium-catalyzed olefin metathesis.[1] Complex **2** is not an active catalyst for this process. A polymerization test carried out in toluene at room temperature for 20 h with 1000/1 norbornene/catalyst loading gave, after precipitation in

methanol, only 5 % of polymeric material. In the same way, the ring closing metathesis of diethyldiallymalonate using 5 mol % of **2** in toluene was not observed after 20 h at 50 ºC.

In order to understand the poor catalytic activity of **2** for olefin metathesis, the reactivity of **2** towards olefins has been investigated. Bubbling of ethylene through a green solution of **2** for 15 min at room temperature resulted in the formation of the η^2-ethylene complex RhCl(η^2-CH$_2$=CH$_2$)(IPr)PPh$_3$ (**3**). The fate of the alkylidene ligand was determined by analysis of the mother liquor by NMR and GC methods that showed the presence of 3-phenylprop-1-ene, *cis/trans* 3-phenylprop-2-ene and phenylcyclopropane (Scheme 1).

R = H (**3**), Ph (**4**) OEt (**5**)
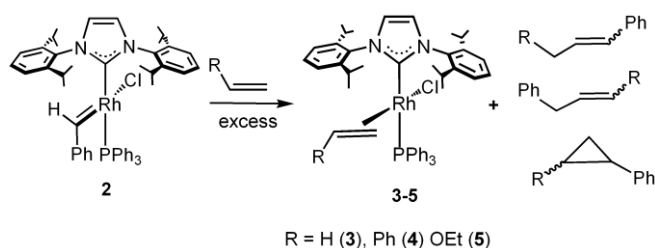
Scheme 1. Reactivity of **2** towards olefins.

Complex **3** was isolated as an orange solid in 88% yield. Similarly to **2**, the ^{1}H NMR spectrum in toluene-d_8 evidenced a fluxional behavior associated to the isopropyl groups of the IPr ligand. In addition, rotation of the coordinated olefin was also observed. Thus, the broad signal at 2.01 ppm observed at room temperature corresponding to the η^2-ethylene ligand splits into two broad signals at low temperature at 2.20 and 1.82 ppm. The determined activation parameters were $\Delta H^{\neq} = 16.6 \pm 0.7$ kcal mol^{-1} and $\Delta S^{\neq} = 0.7 \pm 1.3$ cal K^{-1} mol^{-1} for the rotation of the IPr ligand, and $\Delta H^{\neq} = 13.4 \pm 0.9$ kcal mol^{-1} and $\Delta S^{\neq} = 1.1 \pm 1.2$ cal K^{-1} mol^{-1} for the rotation of the olefin.[19] The activation barrier for the rotation of the IPr in **3** is around 3 kcal mol^{-1} kcal higher than that in **2**, probably due to the additional steric hindrance introduced by a rotating coordinated olefin. The ^{13}C{^{1}H} NMR spectrum of **3** at 243K shows the η^2-ethylene moiety at 40.1 ppm as a doublet of doublets with J_{C-Rh} and J_{C-P} of 15.4 and 2.0 Hz, respectively. The presence of only one resonance indicates an out-of-plane coordination for the η^2-ethylene ligand in the frozen state, typical for this type of rhodium(I) square-planar complexes.[20]

6

In the same way, treatment of **2** with terminal olefins such as styrene or ethyl vinyl ether resulted in the formation of η^2-olefin complexes RhCl(η^2-CH$_2$=CHPh)(IPr)PPh$_3$ (**4**) and RhCl{η^2-CH$_2$=CH(OEt)}(IPr)PPh$_3$ (**5**), which were isolated in 84 and 87 % yield, respectively, and the corresponding cyclopropanes and phenylpropenes. Treatment of **2** with bulkier olefins such *cis*-stilbene, cyclooctene or α-methylstyrene gave a mixture of unidentified complexes that also contains RhCl(PPh$_3$)$_3$.

The ^{1}H NMR spectra of **4** and **5** display shifted resonances at 5.10 and 5.44 ppm, respectively, characteristic for the α-proton of the η^2-alkene ligand. The β-protons appear at 2.71 and 2.56 ppm for **4** and 1.66 and 1.40 ppm for **5**. The IPr-isopropyl resonances are observed as four septuplets for both complexes even at 80 ºC indicating a high rotation barrier for the IPr ligand. The ^{13}C{^{1}H} NMR spectra show the resonances corresponding to the IPr carbenic atoms at 186.6 (**4**) and 186.8 ppm (**5**) ppm as doublet of doublets with J_{C-P} of 138.7 (**4**) and 135.7 Hz (**5**) and J_{C-Rh} of 47.5 (**4**) and 49.0 Hz (**5**). The alkene carbon atoms are observed at 58.0 (d, J_{C-Rh} = 14.8 Hz, CH) and 34.0 ppm (dd, J_{C-Rh} = 14.8, J_{C-P} = 3.7 Hz, CH$_2$) for **4** and 103.6 (d, J_{C-Rh} = 16.1 Hz, CH) and 26.5 ppm (dd, J_{C-Rh} = 14.8, J_{C-P} = 2.2 Hz, CH$_2$) for **5**.[21]

The disposition of η^2-olefin ligands in Rh-NHC complexes is very important with regard to the reactivity, as has been recently shown for the selective deuteration of styrenes by Rh-NHC catalysts.[22] Then, the disposition of η^2-alkene in **4** was determined by selective 1D NOE experiments (Figure 3). The α- and β-*trans* protons display NOE effect with a CH {α (2.44 ppm) and β-*trans* (3.16 ppm)} and one of the CH$_3$, {α (1.04 ppm) and β-*trans* (1.56 ppm)}, of the IPr-isopropyl group, each of them located at different phenyl ring as determined by the ^{1}H-^{13}C HMBC experiment. This fact evidences an out-of-plane coordination of the alkene parallel to the IPr-imidazol ring (Figure 3). In addition, the β-*cis* proton shows a NOE effect with the *orto*-substituents of the phenyl group of the PPh$_3$ ligand (7.22 ppm) indicating that the phenyl group points towards the phosphane ligand.
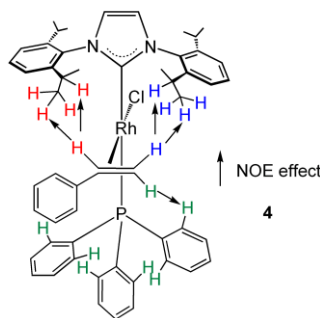
Figure 3. Coordination of the η^2-styrene ligand in **4** determined by selective 1D NOE experiments.

Scheme 2 shows a mechanistic proposal for the formation of the η^2-alkene complexes **3-5** and the coupled products. Initial dissociation of PPh$_3$ in **2** should allow for the coordination of the olefin that reacts with the alkylidene moiety to form a metallacyclobutane. This intermediate could evolve via different pathways. The retro-[2+2] cycloaddition reaction leads to the olefin metathesis cycle. However, it could alternatively evolve to a hydride-allyl species via β-hydride elimination.[23] Subsequent reductive elimination should give rise to an η^2-olefinic complex that generates **3-5** and the corresponding phenylpropene derivatives by phosphane and alkene exchange. The formation of cyclopropanes could be rationalized by the reductive elimination in the metallacycle intermediate.[2]
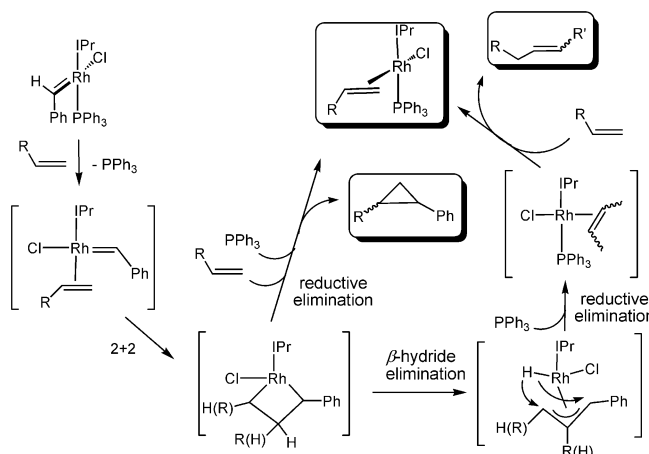
Scheme 2. Proposed mechanism for the formation of the η^2-alkene complexes (**3-5**) and the coupled products.

In conclusion, we have described the preparation of the first rhodium-alkylidene square-planar complex stabilized by a NHC ligand. It is noteworthy that IPr ligand rotates around Rh-C bond, whereas no rotation is observed for the alkylidene moiety as shown by NOE NMR experiments. This compound

exhibited a limited catalytic activity for olefin metathesis, probably due to alternative reaction pathways of the crucial metallacyclobutane intermediate. It gives rise to η^2-alkene complexes, cyclopropanes and a new olefin arising from the coupling of the alkylidene ligand with the alkene, via reductive or β-hydride eliminations within the metallacyclobutane.

Supporting Information Available. Crystal data and processing parameters for compound **2** and NOE NMR experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

Experimental Section

All reactions were carried out with rigorous exclusion of air using Schlenk-tube techniques. The solvents were distilled immediately prior to use from the appropriate drying agents or obtained from a Solvent Purification System (Innovative Technologies). The starting material **1**[11] and N_2CHPh[12] were prepared as previously described in the literature. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (^{1}H, ^{13}C) or external H_3PO_4 (^{31}P). Coupling constants, *J* and *N*, are given in hertz. Spectral assignments were achieved by combination of ^{1}H-^{1}H COSY, ^{13}C APT and ^{1}H-^{13}C HSQC/HMBC experiments. C, H, and N analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer. GC experiments were run on either an Agilent 5973 mass selective detector interfaced to an Agilent 6890 series gas chromatograph system, using a HP-5MS 5% phenyl methyl siloxane column (30 m x 250 μm with a 0.25 μm film thickness).

Preparation of RhCl(=CHPh)(IPr)PPh₃ (2). A THF solution of N_2CHPh (10 mL, 0.09 M, 0.9 mmol) was slowly added to an orange solution of **1** (300 mg, 0.285 mmol) in 10 mL of THF at -20 ºC. Immediate formation of gas was observed. The solution was keep stirring for 20 min at -20 ºC allowing gas to escape of the reaction vessel via a bubbler. After filtration through celite, the resulting brown solution was evaporated to dryness at low temperature. Addition of *n*-hexane caused the precipitation of a green solid which was washed (3 x 3 mL) and dried under vacuum. Yield: 177 mg (76%). Anal. Calcd. for $C_{52}H_{57}N_2ClPRh$: C, 71.02; H, 6.53; N, 3.19. Found: C, 70.78; H, 6.24; N, 3.22. ^{1}H NMR (300 MHz, toluene-d_8, 243 K): δ 15.65 (s, 1H, Rh=CH), 7.3-6.7 (23H, H_{Ph}, =CHN), 7.25 (d, J_{H-H} = 7.7, 2H, Ph_{o-Alk}), 7.01 (t, J_{H-H} = 7.7, 1H, Ph_{p-Alk}), 6.37 (vt, N = 15.4., 2H, Ph_{m-Alk}), 3.95 and 3.13 (both sept, J_{H-H} = 6.4, 4H, C*H*Me), 1.62, 1.27, 1.22, and 1.11 (all d, J_{H-H} = 6.4, 24H, CH*Me*) ^{13}C{^{1}H} NMR (75.4 MHz, toluene-d_8, 243 K) δ 256.2 (dd, J_{C-Rh} = 47.2, J_{C-P} = 13.6, Rh=C), 187.6 (dd, J_{C-P} = 118.1, J_{C-Rh} = 64.4, Rh-C_{IPr}), 160.5 (d, J_{C-Rh} = 9.1, $C_{ipso-Alk}$), 147.3 and 145.2 (both s, C_{q-IPr}), 137.3 (s, C_qN), 135.3 (d, J_{C-P} = 35.7, C_qP), 135.0, 134.9, 132.2, 132.0, 131.4, 129.3, 127.2, 127.0, 123.7, 123.0, and 122.8 (all s, CH), 28.7 and 28.5 (both s, *C*HMe), 26.5, 26.3, 23.2, and 22.1 (all s, CH*Me*). ^{31}P{^{1}H} NMR (121.5 MHz, toluene-d_8, 243 K): δ 21.4 (d, J_{P-Rh} = 147.6).

Preparation of RhCl(η^2-CH₂=CH₂)(IPr)PPh₃ (3). Ethylene was bubbled through a green solution of **2** (100 mg, 0.113 mmol) in 10 mL of toluene at room temperature for 15 min to give an orange solution that was stirred for 1 h. Then, the solution was concentrated to ca. 1 mL and *n*-hexane added to induce the precipitation of a yellow solid, which was washed with *n*-hexane (5 x 3 mL) and dried under vacuum. Yield: 81 mg (88%). Anal. Calcd. for $C_{47}H_{55}N_2ClPRh$: C, 69.07; H, 6.78; N, 3.43. Found: C, 68.41; H, 6.35; N, 3.49. ^{1}H NMR (300 MHz, toluene-d_8, 243 K): δ 7.6-6.0 (21H, H_{Ph}), 6.52 (s, 2H, =CHN), 3.99 and 3.14 (both sept, J_{H-H} = 6.4, 4H, C*H*Me), 2.20 and 1.82 (both br, 4H, η^2-CH₂=CH₂), 1.76, 1.36, 1.18, and 1.07 (all d, J_{H-H} = 6.4, 24H, CH*Me*) ^{13}C{^{1}H} NMR (75.4 MHz, toluene-d_8, 243 K) δ 188.5 (dd, J_{C-P} = 141.8, J_{C-Rh} = 47.8, Rh-C_{IPr}), 148.0 and 145.6 (both s, C_{q-IPr}), 136.9 (s, C_qN), 135.4 (d, J_{C-P} = 10.8, CH_{o-PPh}), 133.7 (d, J_{C-P} = 35.4, C_qP), 129.5, 124.9, and 122.8 (all s, CH_{ph-Ipr}), 127.2 (s,

CH$_{p\text{-PPh}}$), 126.6 (d, $J_{\text{C-P}}$ = 8.6, CH$_{m\text{-PPh}}$), 124.3 (s, =CHN), 40.1 (dd, $J_{\text{C-Rh}}$ = 15.4, $J_{\text{C-P}}$ = 2.0, η^2-CH$_2$=CH$_2$), 29.0 and 28.7 (both s, CHMe), 26.3, 26.1, 23.2, and 22.7 (all s, CHMe). ^{31}P{^{1}H} NMR (121.5 MHz, toluene-d_8, 243 K): δ 39.1 (d, $J_{\text{P-Rh}}$ = 117.7).

Preparation of RhCl(η^2-CH$_2$=CHPh)(IPr)PPh$_3$ (4). A green solution of **2** (175 mg, 0.21 mmol) in 10 mL of toluene was treated with styrene (250 μL, 2.06 mmol) and stirred for 1h at room temperature. Then, the solution was concentrated to ca. 1 mL and *n*-hexane added to induce the precipitation of a pale yellow solid, which was washed with *n*-hexane (3 x 3 mL) and dried under vacuum. Yield: 158 mg (84%). ^{1}H NMR (500 MHz, C$_6$D$_6$, 293 K): δ 7.7-7.2 (6H, H$_{\text{Ph-IPr}}$), 7.22 (dd, $J_{\text{H-P}}$ = 8.6, $J_{\text{H-H}}$ = 8.0, 6H, Ph$_{o\text{-PPh}}$), 6.97 (t, $J_{\text{H-H}}$ = 7.2, 3H, Ph$_{p\text{-PPh}}$), 6.90 (ddd, $J_{\text{H-H}}$ = 8.0, $J_{\text{H-H}}$ = 7.2, $J_{\text{H-P}}$ = 2.0, 6H, Ph$_{m\text{-PPh}}$), 6.84 (t, $J_{\text{H-H}}$ = 7.6, 1H, Ph$_{p\text{-sty}}$), 6.67 (vt, N = 15.2, 2H, Ph$_{m\text{-sty}}$), 6.66 and 6.56 (both d, $J_{\text{H-H}}$ = 2.0, 2H, =CHN), 6.21 (d, $J_{\text{H-H}}$ = 7.6, 2H, Ph$_{o\text{-sty}}$), 5.10 (ddd, $J_{\text{H-H}}$ = 9.8, $J_{\text{H-H}}$ = 7.6, $J_{\text{H-Rh}}$ = 2.1, 1H, η^2-CH$_2$=CHPh), 4.48, 3.60, 3.16 and 2.44 (all sept, $J_{\text{H-H}}$ = 6.4, 4H, CHMe), 2.71 (ddd, $J_{\text{H-H}}$ = 7.6, $J_{\text{H-P}}$ = 2.5, $J_{\text{H-Rh}}$ = 2.1, 1H, η^2-CH$_2$=CHPh), 2.56 (ddd, $J_{\text{H-H}}$ = 9.8, $J_{\text{H-P}}$ = 9.8, $J_{\text{H-Rh}}$ = 2.1, 1H, η^2- CH$_2$=CHPh), 1.56, 1.50, 1.42, 1.39, 1.12, 1.10, 1.04 and 1.01 (all d, $J_{\text{H-H}}$ = 6.4, 24H, CHMe). ^{13}C{^{1}H} NMR (100.2 MHz, C$_6$D$_6$, 293 K) δ 186.6, (dd, $J_{\text{C-P}}$ = 138.7, $J_{\text{C-Rh}}$ = 47.5, Rh-C$_{\text{IPr}}$), 148.6, 148.3, 146.9 and 146.7 (all s, C$_{\text{q-IPr}}$), 144.9 (dd, $J_{\text{C-P}}$ = 2.4, $J_{\text{C-Rh}}$ = 2.4, C$_{\text{ipso-sty}}$), 137.4 and 137.2 (both s, C$_q$N), 135.4 (d, $J_{\text{C-P}}$ = 11.0, CH$_{o\text{-PPh}}$), 135.3 (d, $J_{\text{C-P}}$ = 36.4, C$_q$P), 130.0, 129.6, 124.9, 124.2, 123.8, and 122.8 (all s, CH$_{\text{ph-Ipr}}$), 128.2 (s, CH$_{o\text{-sty}}$), 127.9 (s, CH$_{m\text{-sty}}$), 127.2 (s, CH$_{p\text{-PPh}}$), 126.8 (d, $J_{\text{C-P}}$ = 8.6, CH$_{m\text{-PPh}}$), 125,0 (s, CH$_{p\text{-sty}}$), 123.7 and 123.3 (both s, =CHN), 58.0 (d, $J_{\text{C-Rh}}$ = 14.8, η^2-CH$_2$=CHPh), 34.0 (dd, $J_{\text{C-Rh}}$ = 14.8, $J_{\text{C-P}}$ = 3.7, η^2-CH$_2$=CHPh), 29.2, 29.0, 28.8 and 28.3 (both s, CHMe), 27.1, 26.5, 26.3, 25.8, 23.0, 22.7, 22.1 and 21.9 (all s, CHMe). ^{31}P{^{1}H} NMR (121.5 MHz, C$_6$D$_6$, 293 K): δ 32.3 (d, $J_{\text{P-Rh}}$ = 122.9).

Preparation of RhCl{η^3-CH$_2$=CH(OEt)}(IPr)PPh$_3$ (5). This complex was prepared as described for **4** starting from **2** (100 mg, 0.12 mmol) and ethyl vinyl ether (115 μL, 2.06 mmol). Yield: 96 mg (93%). Anal. Calcd. for C$_{49}$H$_{59}$N$_2$ClOPRh: C, 68.32; H, 6.90; N, 3.24. Found: C, 67.99; H, 6.72; N, 2.98. ^{1}H NMR (300 MHz, C$_6$D$_6$, 293 K): δ 7.6-7.0 (24H, H$_{\text{Ph}}$), 6.47 and 6.45 (both d, $J_{\text{H-H}}$ = 2.0, 2H, =CHN),

5.44 {m, 1H, η^2-CH$_2$=C$\underline{H}$(OEt)}, 4.47, 3.44, 3.34, and 2.26 (all sept, J_{H-H} = 6.4, 4H, C$\underline{H}$Me), 3.56 and

2.72 (both m, CH$_3$C$\underline{H}_2$O), 1.84, 1.47, 1.39, 1.15, 1.13, 1.00, 0.96 and 0.92 (all d, J_{H-H} = 6.4, 24H,

CH$\underline{Me}$), 1.63 and 1.44 {both m, 2H, η^2-C$\underline{H}_2$=CH(OEt)}, 0.36 (t, J_{H-H} = 6.8, 3H, C$\underline{H}_3$CH$_2$O) ^{13}C{^{1}H}

NMR (75.4 MHz, C$_6$D$_6$, 293 K) δ 186.8, (dd, J_{C-P} = 135.7, J_{C-Rh} = 49.0, Rh-C$_{IPr}$), 148.5, 148.3, 145.5

and 145.1 (all s, C$_{q-IPr}$), 137.3 and 137.1 (both s, C$_q$N), 135.1 (d, J_{C-P} = 35.7, C$_q$P), 132.1 (d, J_{C-P} = 8.8,

CH$_{PPh}$), 129.9, 129.7, 128.4, 128.2, 127.2, 127.1, 124.9 and 123.4 (all s, CH$_{Ph}$), 124.7 and 123.2 (both s,

=CHN), 103.6 {d, J_{C-Rh} = 16.1, η^2-CH$_2$=$\underline{C}$H(OEt)}, 65.8 (s, CH$_3$$\underline{C}H_2$O), 29.3, 29.0, 28.4 and 28.4 (both

s, $\underline{C}$HMe),), 27.1, 26.2, 25.8, 25.6, 23.5, 23.0, 22.7 and 22.3 (all s, CH$\underline{Me}$), 26.5 {dd, J_{C-Rh} = 14.8, J_{C-P}

= 2.2, η^2-$\underline{C}$H$_2$=CH(OEt)}. ^{31}P{^{1}H} NMR (121.5 MHz, C$_6$D$_6$, 293 K): δ 34.8 (d, J_{P-Rh} = 131.6).

X-ray Structural Determination of RhCl(=CHPh)(IPr)PPh$_3$ (2). A green prismatic crystal of **2**

(0.07 x 0.12 x 0.14 mm) suitable for X-ray diffraction were obtained by slow diffusion of n-hexane into

a concentrated THF solution of the complex at 253 K. Intensity data was collected at low temperature

(100(2)K) on a single-axis HUBER diffractometer at the BM16 of the ESRF synchrotron, equipped with

a Si111 double-crystal monochromator (λ = 0.73780 Å) using wide frames (1˚ in ϕ). Two sets of data at

different orientations of the crystal (changing a pseudo-kappa angle by 40º approx.) were measured to

ensure data completeness. Cell parameters were refined from the observed setting angles and detector

positions of strong reflections (78866 refl., 2θ < 66.7º). Data were corrected for Lorentz and

polarisation, for absorption effects, scaled and merged using the SORTAV program.[24] The structure

were solved by Patterson method and completed by successive difference Fourier syntheses (SHELXS-

86).[25] Refinement, by full-matrix least-squares on F^2 with SHELXL97,[25] was carried out including

isotropic and subsequent anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen

atoms were included from observed positions and refined riding on their parent carbon atoms. Final

agreement factors were R_1 = 0.0542 (11427 refl., $I > 2\sigma(I)$) wR = 0.1543 (12781 unique refl.), *GoF* =

1.088. All the highest electronic residuals (smaller than 1.1 e/Å^3) were observed in close proximity of

the Rh metal and have no chemical sense. Atomic scattering factors, corrected for anomalous dispersion, were used as implemented in the refinement programs.[25]

Determination of rotational barriers. Full line-shape analysis of the dynamic ^{1}H NMR spectra of **2** and **3** were carried out using the program gNMR (Cherwell Scientific Publishing Limited). The transverse relaxation time, T_2, was estimated at the lowest temperature. Activation parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$ were obtained by linear least-squares fit of the Eyring plot. Errors were computed by published methods.[26]

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