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Product Diversity in the Reaction of [(norbornadiene){CpP(*i*Pr)$_2$}Rh] with Alkyl Iodides

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The reagents [(CpPR$_2$)Li] [R = *i*Pr (**2b**), cyclohexyl (**2c**)] react with [(nbd)RhCl] (nbd = norbornadiene) dimer [(**1a**)$_2$] to yield the respective mononuclear complexes [(nbd)Rh(CpPR$_2$)] (**3b**,**c**). Subsequent treatment of **3b** with a large excess of MeI led to the formation of the stable organometallic phosphonium salt [(nbd)Rh{CpP(*i*Pr)$_2$Me}]I (**4b**). The analogous reaction of **3b** with the slightly more bulky EtI or *n*PrI resulted in the formation of the dinuclear [μ-CpP(*i*Pr)$_2$]-bridged dirhodium complex [(nbd)Rh{CpP(*i*Pr)$_2$}Rh(nbd)I] (**5b**) and the corresponding ylides C$_5$H$_4$P(*i*Pr)$_2$R^1 [R^1 = Et (**6b**), *n*Pr (**6c**)]. The rhodium complexes **3b**, **4a** and **5b** were characterised by X-ray crystal-structure analyses.

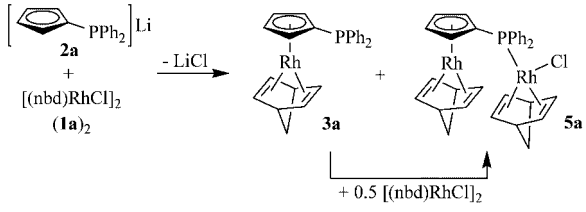
Introduction

[CpRh(L)$_n$] complexes have been of increasing interest lately due to some remarkable reactivities, for example their ability to catalyse selective C–H activation processes in conjunction with R$_2$B–BR$_2$ reagents.[1] It may be of interest to use Rh cyclopentadienides that bear functional groups at their Cp rings in order to potentially facilitate such currently high activation energy C–H cleavage reactions by precoordination of suitable substrates in a second coordination sphere around the catalytically active metal centre. For that reason, we have prepared a couple of (dialkylphosphanyl)-cyclopentadienyl-containing rhodium(I) complexes[2] and have encountered some unexpected features with regard to their reactions with alkyl iodides. This will be described and discussed in this article.

Results and Discussion

Synthetic Developments

The (diphenylphosphanyl)cyclopentadienide anion was prepared by treatment of CpLi with ClPPh$_2$ followed by deprotonation with *n*-butyllithium/hexane in toluene.[3] When we wanted to attach this simple functionalised ligand to an Rh(diene) framework, we encountered the same difficulties that had previously been observed by Poilblanc et al.[2] For example, treatment of the (nbd)RhCl (nbd = norbornadiene) dimer [(nbd)RhCl]$_2$ [(**1a**)$_2$][4] with [(CpPPh$_2$)Li] (**2a**) always resulted in the formation of a mixture of the desired mononuclear complex **3a** and its dinuclear adduct **5a** containing an unreacted monomeric (nbd)RhCl unit from the starting material (**1a**)$_2$. These two products could not be separated with sufficient ease, nor were we able to convert **5a** back to the desired **3a**, for example by treatment with additional **2a** (Scheme 1).



Scheme 1.

Therefore, we made a variety of changes in our synthetic scheme and slightly changed the substituents and reagents to eventually achieve a clean formation of mononuclear Rh^I complexes of the desired type. The reagents [{CpP(*i*Pr)$_2$}Li] (**2b**) and [(CpPCy$_2$)Li] (**2c**; Cy = cyclohexyl) were prepared as described in the literature.[5,6] The reaction of [(nbd)-RhCl]$_2$ [(**1a**)$_2$] with **2b** was carried out in THF at room temperature. Removal of the solvent and extraction of the residue with pentane cleanly gave the mononuclear complex [(nbd)Rh{CpP(*i*Pr)$_2$}] (**3b**; 85% isolated yield). Complex **3b** was characterised by X-ray diffraction. Single crystals were obtained from pentane. The structure shows a typical disturbed trigonally planar coordination geometry around the rhodium atom made up by the pair of norbornadiene C=C double bonds [C=C(centroid)–Rh–C=C(centroid) = 70.7°] and the substituted Cp ring [Cp(centroid)–Rh–C=C(centroid) = 144.4° and 144.9°]. The norbornadiene ligand is almost symmetrically bonded to the metal atom through its

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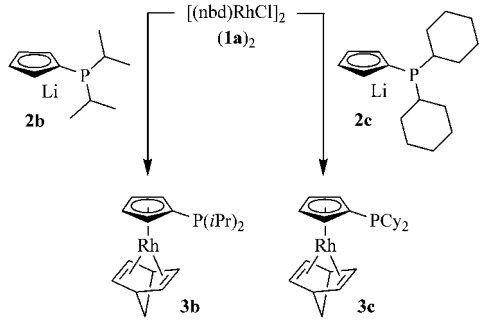
endo face [Rh–C14/C15 = 2.119(2), 2.127(2) Å; Rh–C18/C17 = 2.127(2), 2.135(2) Å]. The diisopropylphosphanyl-substituted Cp ring is rather uniformly η^5-coordinated to the rhodium atom, with Rh–C(Cp) distances being in a narrow range between 2.214(2) and 2.290(2) Å.[7] In the crystal, a metal complex conformation is found that has the bulky P(*i*Pr)$_2$ substituent rotated toward one side of the coordinated nbd ligand, with the C1–P vector almost bisecting the C15–Rh–C17 angle in the respective projection. The phosphorus centre in complex **3b** is three-coordinate and prochiral [C1–P–C7 = 103.1(1)°; C1–P–C6 = 99.7(1)°; C7–P–C6 = 101.9(1)°].

In solution, rotation around the Rh–Cp[P] vector is fast. Consequently, complex **3b** shows only one norbornene olefinic ^{1}H NMR multiplet (δ = 3.24 ppm) representing four protons plus a signal for the two bridgehead hydrogen atoms (δ = 3.22 ppm). The methyl groups of the isopropyl substituents at the prochiral phosphorus atom are pairwise diastereotopic, as expected (^{13}C: δ = 19.7/20.4 ppm). The ^{1}H NMR signals of the pairs of Cp hydrogen atoms are observed at δ = 4.93 (2 H) and 5.20 (2 H) ppm. The corresponding ^{31}P NMR resonance of **3b** occurs at δ = –3.2 ppm.

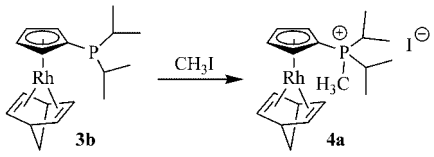
The reaction of dimer (**1a**)$_2$ with [(CpPCy$_2$)Li] (**2c**) took place analogously. The product [(nbd)Rh(CpPCy$_2$)] (**3c**) was isolated in 68% yield. It was characterised spectroscopically and by C,H elemental analysis (for details see the Experimental Section and Scheme 2).



Scheme 2.

Reactions with Alkyl Iodides

We expected that the CpPR$_2$ subunit in complex **3b**, for example, should show a typical reactivity pattern of a phosphorus nucleophile. Treatment with suitable alkyl electrophiles might, therefore, yield the respective quaternized phosphonium salts at the organometallic backbone. This was actually observed when we treated complex **3b** with methyl iodide. Treatment of **3b** with a large excess of MeI in pentane rapidly led to the formation of the organometallic phosphonium salt **4a** (Scheme 3), which precipitated from the solution and was obtained as a slightly beige-coloured solid in 92% yield.[8] Slow diffusion of pentane vapour into a solution of **3b** in dichloromethane gave single crystals that were suitable for an X-ray crystal structure analysis. The structure of phosphonium salt **4a** is very similar to that of phosphane complex **3b** as it features the same framework structure (see Figure 1 and Table 1). This similarity even extends to the overall characteristics of the favoured conformational orientation of the Cp[P] ring system. The C1–P bond in **4a** is shorter [1.767(5) Å] than in **3b** [1.822(2) Å] and the phosphorus centre is tetracoordinate (Figure 2).



Scheme 3.

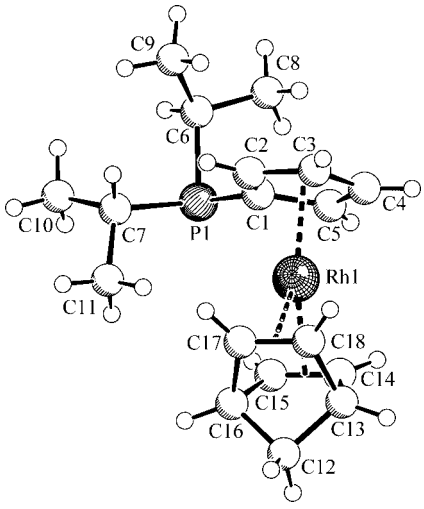


Figure 1. View of the molecular structure of [(nbd)Rh{CpP(*i*Pr)$_2$}] (**3b**).

Table 1. Comparison of selected structural parameters of complexes **3b**, **4a** and **5b**.[a]

	3b	**4a**	**5b** (Rh1)		**5b** (Rh2)
Rh–C1	2.290(2)	2.276(5)	2.291(3)		
Rh–C2	2.281(2)	2.256(5)	2.216(3)		
Rh–C3	2.252(2)	2.268(6)	2.256(3)		
Rh–C4	2.261(2)	2.249(6)	2.256(3)		
Rh–C5	2.214(2)	2.291(5)	2.248(3)	Rh2–I1	2.6624(4)
C1–P	1.822(2)	1.767(5)	1.811(3)	Rh2–P1	2.2992(7)
Rh1–C14	2.119(2)	2.129(6)	2.118(3)	Rh2–C14b	2.218(3)
Rh1–C15	2.127(2)	2.122(5)	2.126(3)	Rh2–C15b	2.223(3)
Rh1–C17	2.135(2)	2.122(5)	2.125(3)	Rh2–C17b	2.096(3)
Rh1–C18	2.127(2)	2.133(5)	2.105(3)	Rh2–C18b	2.105(3)
C14–C15	1.409(4)	1.396(9)	1.404(4)	C14b-C15b	1.361(4)
C17–C18	1.404(4)	1.401(8)	1.403(4)	C17b-C18b	1.391(4)

[a] Bond lengths [Å].

In solution, complex **4a** features a typical phosphonium-type ^{31}P NMR chemical shift (δ = +35.1 ppm).[9,10] Again, the system is conformationally equilibrated in solution. The isopropyl methyl groups at the prochiral phosphorus atom are pairwise diastereotopic [^{13}C NMR: δ = 16.6/16.7 (CH_3), 22.8 (d, $^1J_{P,C}$ = 49.7 Hz, CH) ppm] and there is an additional CH_3 group bonded to the phosphorus centre [^{1}H NMR: δ = 2.24 ($^2J_{P,H}$ = 12.5 Hz) ppm; ^{13}C NMR: δ = 4.3 ($^1J_{P,C}$ = 54.4 Hz) ppm].

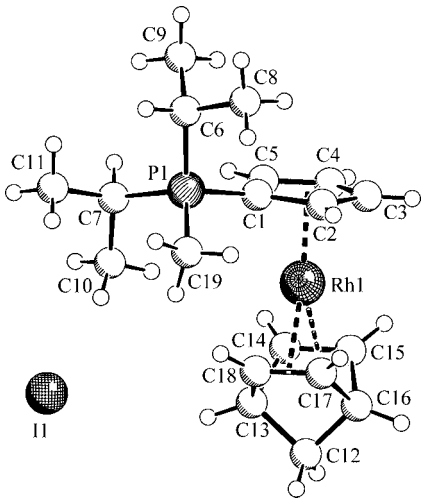
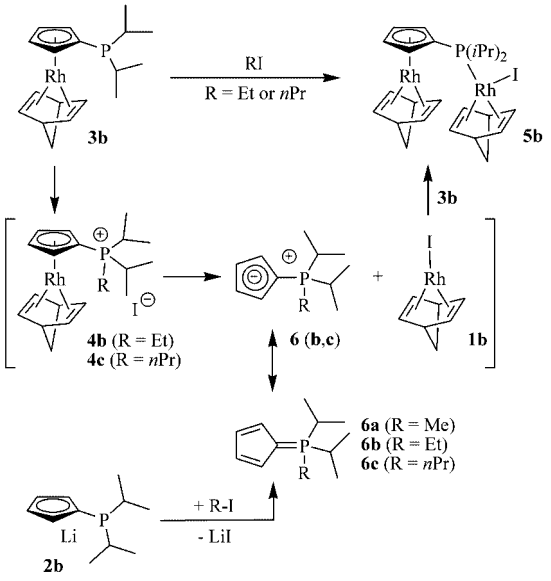


Figure 2. Molecular structure of [(nbd)Rh{CpP(*i*Pr)$_2$Me}]I (**4a**).

The reaction of complex **3b** with excess ethyl iodide under similar conditions gave a different reaction product. After removal of the volatiles in vacuo, we isolated the dinuclear [μ-CpP(*i*Pr)$_2$]-bridged dirhodium complex **5b** in good yield (86%; Scheme 4). This product was characterised spectroscopically, by C,H elemental analysis and by X-ray diffraction (single crystals were obtained from a pentane solution at –30 °C).



Scheme 4.

The X-ray crystal structure analysis of **5b** shows the presence of an [(nbd)Rh{CpP(*i*Pr)$_2$}] subunit that is structurally very similar to that found in **3b** or **4a** (see above and Table 1). The phosphorus atom of this unit coordinates to the Rh centre of an (nbd)RhI subunit. The norbornadiene ligand is again *endo*-coordinated through both its C=C double bonds. The rhodium centre Rh2 is distorted square-planar coordinated by this pair of C=C double bonds and P1 and I1 are *cis* to each other [Rh2–I1 = 2.6624(4), Rh2–P1 = 2.2992(7) Å; I1–Rh2–P1 = 95.76(2)°]. The resulting bond angle at the phosphorus atom (Rh2–P1–C1) is 119.24(9)° (Figure 3).

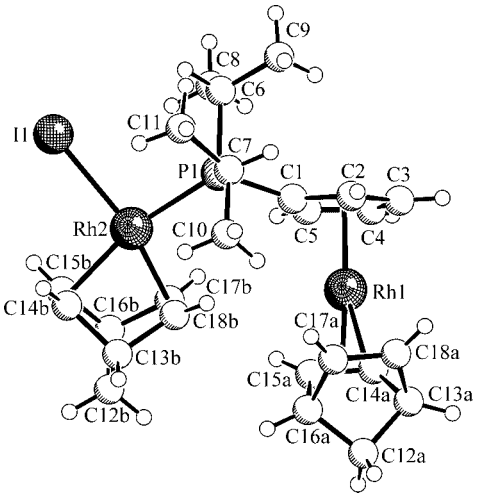


Figure 3. Molecular structure of complex **5b**.

In solution, there is again a rapid rotation around the Rh1–Cp[P] vector, resulting in the observation of a single ^{1}H NMR =CH resonance [δ = 3.09 (4 H) ppm] for the nbd-1 ligand. In contrast, nbd-2, which is bonded to the distorted square planar Rh2 centre, exhibits a clearly differentiated pair of HC=CH ^{1}H/^{13}C NMR features of the double bonds *cis* to I and *cis* to P1 [^{1}H NMR: δ = 3.83/5.36 (each 2 H) ppm; ^{13}C NMR: δ = 51.0/78.4 ppm], respectively. Again, the isopropyl groups at the prochiral phosphorus atom are pairwise diastereotopic, as expected (^{1}H NMR: δ = 1.12/1.36 ppm; ^{13}C NMR: δ = 19.7/20.1 ppm). The ^{31}P NMR resonance of complex **5b** is located at δ = +40.1 ppm.

Although the complete mechanistic elucidation of the unexpected formation of the dinuclear product **5b** must await further detailed studies, we would like to propose a tentative scheme for the possible formation of this product. It may be assumed that the formation of the unexpected product **5b** might also be initiated by phosphonium salt formation. The resulting intermediates (**4b**, **4c**) seem not to be stable under the applied reaction conditions but rather undergo a nucleophilic displacement of the respective (C$_5$H$_4$)P(*i*Pr)$_2$R moiety (**6b**, **6c**) by iodide. Substitution of the Cp-phosphonium ylides **6b**, **6c** might be facilitated by their higher steric bulk as compared to the [P]-CH$_3$ derivative **6a** in **4a**. In the case of **4b** and **4c** the nucleophilic substitution reaction probably leads to the formation of the ethyl- or *n*-propyl-substituted phosphonium salts **6b** or **6c**, respectively, which must be assumed to be slightly more bulky than their methylphosphonium analogue **6a**. Apparently, the reaction in the cases **4b** and **4c**, in contrast to the more persistent **4a**, proceeds with cleavage of the Cp ligand bearing the bulky phosphonium substituent from the rhodium atom, with the possible formation of (nbd)RhI (**1b**). Under the applied reaction conditions, this monomeric species seems never to reach a high enough concentration to give rise to observable dimer formation, but is apparently

efficiently trapped by the neutral starting material **3b** to yield the $CpPR_2$-bridged dinuclear product **5b**.[5,11] We have only observed this unexpected reaction pathway in the case of treatment of **3b** with ethyl iodide or *n*-propyl iodide but so far not with methyl iodide, which only gave the organometallic phosphonium salt **4a** that is stable under the applied reaction conditions.

In order to further support the proposed reaction course, we treated **2b** with methyl iodide, ethyl iodide and *n*-propyl iodide. The corresponding trialkyl(Cp)phosphonium ylide products (**6a**–**c**) were isolated as pale-yellow solids and characterised spectroscopically. The resulting ylide **6a** features a ^{31}P NMR signal at δ = 24.7 ppm and a ^{13}C NMR resonance for the adjacent C1 ring carbon atom at δ = 74.0 ppm with a very characteristic $^1J_{P,C}$ coupling constant of 104 Hz [C=P(*i*Pr)$_2$Me].[12,13] The ethyl-substituted CpP(*i*Pr)$_2$Et ylide **6b** shows an analogous ^{13}C NMR feature at δ = 74.3 ppm ($^1J_{P,C}$ = 101 Hz). This signal was detected in the crude reaction mixture obtained by treatment of complex **2b** with ethyl iodide to eventually yield **5b**.

Conclusions

The reaction of [(nbd){CpP(*i*Pr)$_2$}Rh] (**3b**) with simple alkyl iodides shows some remarkably different outcomes depending on the bulk of the alkyl group of the RI reagent used. The reaction with methyl iodide leads to the formation of a stable phosphonium salt **4a**, whereas the analogous reaction of **3b** with either EtI or *n*PrI rapidly results in the formation of the dinuclear product **5b**. The experimental characteristics of these reactions led us to assume that in the latter cases the corresponding phosphonium salts might also have been formed initially. However, these slightly more bulky systems seem to be unstable with regard to CpP(*i*Pr)$_2$R ylide dissociation,[14] a pathway that eventually leads to the formation of **5b**. For the less bulky [(nbd){CpP(*i*Pr)$_2$Me}Rh]I system this pathway seems not to be readily available under our typical reaction conditions. This specific alkyl group dependent behaviour makes the **3b** + RI reaction system a remarkable example of an observed borderline behaviour along a threshold determined by rather subtle differences in steric bulk.

Experimental Section

General: All reactions involving air- or moisture-sensitive compounds were carried out under an inert gas using Schlenk-type glassware or in a glove box. Solvents were dried and distilled prior to use. The following instruments were used for physical characterisation of the compounds: Melting points: DSC 2010 TA-instruments; elemental analyses: Foss-Heraeus CHNO-Rapid; MS: Micromass Quattro LC-Z electrospray mass spectrometer; NMR: Bruker AC 200 P (^1H: 200 MHz; ^{13}C: 50 MHz), ARX 400 (^1H: 400 MHz; ^{13}C: 100 MHz), Varian 500 INOVA (^1H: 500 MHz; ^{13}C: 125 MHz) or Varian UNITY plus 600 (^1H: 600 MHz; ^{13}C: 151 MHz). The complex [(nbd)RhCl]$_2$ (**1a**)[4] and the reagents [{CpP(*i*Pr)$_2$}Li] (**2b**)[5] and [{CpPCy$_2$}Li] (**2c**)[5] were prepared according to literature procedures.

X-ray Crystal-Structure Determinations: Data sets were collected with a Nonius KappaCCD diffractometer equipped with a rotating anode generator. Programs used: data collection COLLECT (Nonius B.V., **1998**), data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods in Enzymology* **1997**, *276*, 307–326), absorption correction SORTAV (R. H. Blessing, *Acta Crystallogr., Sect. A* **1995**, *51*, 33–37; R. H. Blessing, *J. Appl. Crystallogr.* **1997**, *30*, 421–426) and Denzo (Z. Otwinowski, D. Borek, W. Majewski, W. Minor, *Acta Crystallogr., Sect. A* **2003**, *59*, 228–234), structure solution SHELXS-97 (G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467–473), structure refinement SHELXL-97 (G. M. Sheldrick, University of Göttingen, **1997**), graphics SCHAKAL (E. Keller, University of Freiburg, **1997**). CCDC-600987 to -600989 (for **3b**, **4a** and **5b**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Reaction of [{CpP(*i*Pr)$_2$}Li] (2b) With [(nbd)RhCl]$_2$ [(1a)$_2$]. Formation of Complex 3b: A solution of **2b** (94 mg, 0.50 mmol) in THF (3 mL) was added to a solution of (**1a**)$_2$ (115 mg, 0.25 mmol) in THF (3 mL) at ambient temperature and the suspension was stirred at room temperature overnight. Subsequently, the solvent was removed in vacuo and the crude product was extracted through Celite with pentane (4 mL) five times. Evaporation of the solvent yielded the rhodium complex **3b** as a yellow powder (160 mg, 0.43 mmol, 85%). Crystals suitable for X-ray crystal structure analysis were obtained by slow evaporation of the solvent from a concentrated pentane solution at ambient temperature. ^1H NMR (500 MHz, C_6D_6, 298 K): δ = 0.95 (t, J = 1.5 Hz, 2 H, CH_2^{nbd}), 1.13 (dd, J = 14.6, 7.1 Hz, 6 H, Me^{iPr}), 1.25 (dd, J = 10.8, 6.8 Hz, 6 H, Me^{iPr}), 1.90 (dsept, J = 7.0, 0.9 Hz, 2 H, CH^{iPr}), 3.22 (m, 2 H, CH^{nbd}), 3.24 (m, 4 H, =CH^{nbd}), 4.93 (m, 2 H, Cp), 5.20 (m, 2 H, Cp) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6, 298 K): δ = 19.7 (d, J = 9.3 Hz, Me^{iPr}), 20.4 (d, J = 17.5 Hz, Me^{iPr}), 23.8 (d, J = 12.8 Hz, CH^{iPr}), 30.5 (d, J = 10.5 Hz, =CH^{nbd}), 47.0 (d, J = 2.8 Hz, CH^{nbd}), 57.4 (d, J = 7.0 Hz, CH_2^{nbd}), 86.3 (m, Cp), 89.0 (m, Cp), 94.7 (Cp; detected by $^1H/^{13}C$ ghmbc experiment) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6, 81 MHz, 298 K): δ = –3.2 (s, P*i*Pr$_2$) ppm. $C_{18}H_{26}PRh$ (376.27): calcd. C 57.45, H 6.96; found C 57.49, H 6.92.

X-ray Crystal Structure Analysis of 3b: $C_{18}H_{26}PRh$, M = 376.27, colourless crystal 0.30 × 0.30 × 0.05 mm, a = 5.875(1), b = 10.749(1), c = 13.870(1) Å, α = 104.53(1), β = 90.22(1), γ = 93.37(1)°, V = 846.3(2) Å^3, $\rho_{calcd.}$ = 1.477 g cm^{-3}, μ = 1.093 mm^{-1}, empirical absorption correction ($0.735 \leq T \leq 0.947$), Z = 2, triclinic, space group $P\bar{1}$ (no. 2), λ = 0.71073 Å, T = 198 K, ω- and φ-scans, 8037 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.67 Å^{-1}, 4102 independent (R_{int} = 0.034) and 3745 observed reflections [$I \geq 2\sigma(I)$], 185 refined parameters, R = 0.027, wR_2 = 0.070, max. (min.) residual electron density 0.41 (–1.06) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Reaction of [(CpPCy$_2$)Li] (2c) with [(nbd)Rhcl]$_2$ [(1a)$_2$]. Formation of Complex 3c: According to the procedure described for the formation of **3b**, **3c** was obtained as a yellow powder (54 mg, 0.118 mmol, 68%) from **2c** (46 mg, 0.173 mmol) in THF (2 mL) and (**1a**)$_2$ (40 mg, 0.087 mmol) in THF (1 mL). The crude product was extracted three times through Celite with pentane (2 mL). ^1H NMR (400 MHz, C_6D_6, 298 K): δ = 0.97 (m, 2 H, CH_2^{nbd}), 1.11–1.47 (m, 12 H, Cy), 1.65 (dm, J = 11.9 Hz, 2 H, Cy), 1.78 (dm, J = 11.2 Hz, 2 H, Cy), 1.85 (m, 2 H, Cy), 1.93 (dm, J = 11.7 Hz, 2 H, Cy), 2.31 (dm, J = 11.7 Hz, 2 H, Cy), 3.25 (m, 4 H, =CH^{nbd}), 3.24 (m, 2 H, CH^{nbd}), 4.95 (m, 2 H, Cp), 5.18 (m, 2 H, Cp) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, 298 K): δ = 27.0 (s, Cy), 27.6

(d, J = 7.8 Hz, Cy), 27.8 (d, J = 11.5 Hz, Cy), 30.4 (broad d, J = 10.6 Hz, Cy), 30.4 (d, J = 8.7 Hz, Cy), 30.6 (d, J = 15.2 Hz, =CH^{nbd}), 34.1 (d, J = 12.8 Hz, Cy), 47.1 (d, J = 2.1 Hz, CH^{nbd}), 57.4 (d, J = 6.8 Hz, CH$_2^{nbd}$), 86.5 (m, Cp), 89.3 (dd, J = 14.6, J = 3.3 Hz, Cp), 95.1 (dd, J = 23.5, J = 4.6 Hz, Cp) ppm. ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6, 298 K): δ = –11.2 (s, PCy$_2$) ppm. $C_{24}H_{34}$PRh (456.39): calcd. C 63.16, H 7.51; found C 63.55, H 7.62.

Reaction of 3b with Methyl Iodide. Formation of the Organometallic Phosphonium Salt 4a: A large excess of methyl iodide (0.25 mL, 4.00 mmol) was added to a solution of **3b** (35 mg; 0.09 mmol) in pentane (5 mL). Precipitation occurred immediately and the tawny suspension was stirred at ambient temperature for 2 h. The supernatant was removed by filtration in air and the resulting beige filter cake was washed carefully with pentane (1 mL). Subsequently, the residue was dried in vacuo and **4a** was obtained as a brown powder (44 mg, 0.085 mmol, 92%). Crystals suitable for X-ray crystal structure analysis were obtained by slow diffusion of pentane into a concentrated solution of **4a** in dichloromethane. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 1.06 (t, J = 1.6 Hz, 2 H, CH$_2^{nbd}$), 1.43 (dd, J = 9.7, 7.1 Hz, 6 H, Me$^{i\mathrm{Pr}}$), 1.47 (dd, J = 9.5, 7.1 Hz, 6 H, Me$^{i\mathrm{Pr}}$), 2.24 (d, J = 12.5 Hz, 3 H, Me), 3.03 (m, 2 H, CH$^{i\mathrm{Pr}}$), 3.36 (broad s, 2 H, CH^{nbd}), 3.53 (m, 4 H, =CH^{nbd}), 5.19 (m, 2 H, Cp), 5.79 (m, 2 H, Cp) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 298 K): δ = 4.3 (d, J = 54.4 Hz, Me), 16.6 (d, J = 2.5 Hz, Me$^{i\mathrm{Pr}}$), 16.7 (d, J = 2.9 Hz, Me$^{i\mathrm{Pr}}$), 22.8 (d, J = 49.7 Hz, CH$^{i\mathrm{Pr}}$), 35.2 (d, J = 10.1 Hz, =CH^{nbd}), 46.7 (d, J = 2.6 Hz, CH^{nbd}), 58.4 (d, J = 6.9 Hz, CH$_2^{nbd}$), 72.8 (dd, J = 90.6, 6.0 Hz, Cp) 87.7 (dd, J = 11.6, 4.2 Hz, Cp), 92.4 (dd, J = 10.1, 3.7 Hz, Cp) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$, 121.5 MHz, 298 K): δ = 35.1 (s, PiPr$_2$) ppm. MS (ESI): m/z calcd. 391.105 [M–I]$^+$; found 391.00. $C_{19}H_{29}$IPRh (518.20): calcd. C 44.03, H 5.64; found C 43.94, H 5.50.

X-ray Crystal-Structure Analysis of 4a: $C_{19}H_{29}$IPRh·CH_2Cl_2, M = 603.13, yellow crystal 0.30×0.10×0.03 mm, a = 15.973(1), b = 10.887(1), c = 26.453(1) Å, V = 4600.1(5) Å^3, $\rho_{calcd.}$ = 1.742 g cm^{-3}, μ = 2.389 mm^{-1}, empirical absorption correction (0.534 ≤ T ≤ 0.932), Z = 8, orthorhombic, space group $Pbca$ (no. 61), λ = 0.71073 Å, T = 198 K, ω- and φ-scans, 22987 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.66 Å^{-1}, 5470 independent (R_{int} = 0.060) and 4556 observed reflections [$I \geq 2\sigma(I)$], 231 refined parameters, R = 0.045, wR_2 = 0.146, max. (min.) residual electron density 1.75 (–0.82) e Å^{-3} close to iodine, hydrogen atoms calculated and refined as riding atoms.

Reaction of 3b with Ethyl Iodide. Formation of Complex 5b: A large excess of ethyl iodide (0.25 mL, 3.10 mmol) was added to a solution of **3b** (30 mg; 0.08 mmol) in toluene (3 mL) at room temperature. After the reaction mixture had been stirred at ambient temperature overnight, all volatiles were removed in vacuo. The obtained yellow oil was washed twice with pentane (1 mL) and dried in vacuo. The pure product was obtained as a yellow solid (48 mg, 0.07 mmol, 86%). Crystals suitable for X-ray crystal structure analysis were obtained from a pentane solution at –30 °C. ^{1}H NMR (600 MHz, C_7D_8, 298 K): δ = 0.90 (br., 2 H, CH$_2^{nbd1}$), 1.10/1.14 (each dm, J = 8.5 Hz, each 1 H, CH$_2^{nbd2}$), 1.12 (dd, J = 14.5, 7.1 Hz, 6 H, Me$^{i\mathrm{Pr}}$), 1.36 (dd, J = 15.8, 7.0 Hz, 6 H, Me$^{i\mathrm{Pr}}$), 2.46 (dsept, J = 7.9, 7.1 Hz, 2 H, CH$^{i\mathrm{Pr}}$), 3.09 (m, 4 H, =CH^{nbd1}), 3.08 (m, 2 H, CH^{nbd1}), 3.36 (br., 2 H, CH^{nbd2}), 3.83 (m, 2 H, =CH^{nbd2}), 4.41 (m, 2 H, Cp), 5.07 (m, 2 H, Cp), 5.36 (m, 2 H, =CH^{nbd2}) ppm. ^{13}C{^{1}H} NMR (150 MHz, C_7D_8, 298 K): δ = 19.7 (Me$^{i\mathrm{Pr}}$), 20.1 (d, J = 4.7 Hz, Me$^{i\mathrm{Pr}}$), 27.9 (d, J = 24.1 Hz, CH$^{i\mathrm{Pr}}$), 31.9 (d, J = 10.2 Hz, =CH^{nbd1}), 47.1 (d, J = 2.4 Hz, CH^{nbd1}), 51.0 (dd, J = 2.3, 1.6 Hz, CH^{nbd2}), 52.2 (d, J = 11.7 Hz, =CH^{nbd2}), 57.7 (d, J = 6.7 Hz, CH$_2^{nbd1}$), 65.1 (dd, J = 4.9, 2.1 Hz, CH$_2^{nbd2}$), 78.4 (dd, J = 11.4, 5.5 Hz, =CH^{nbd2}), 87.2 (dd, J = 6.1, 4.2 Hz, Cp), 88.0 (dd, J = 7.6, 3.9 Hz, Cp). 89.1 (Cp, detected by ^{1}H/^{13}C ghmbc experiment) ppm. ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6, 298 K): δ = 40.1 (d, J = 163.4 Hz, PiPr$_2$) ppm. $C_{25}H_{34}$IPRh$_2$ (698.23): calcd. C 43.00, H 4.91; found C 43.03, H 5.26.

X-ray Crystal-Structure Analysis of 5b: $C_{25}H_{34}$IPRh$_2$, M = 698.21, red crystal 0.20×0.20×0.10 mm, a = 10.097(1), b = 17.498(1), c = 13.770(1) Å, β = 92.85(1)°, V = 2429.8(2) Å^3, $\rho_{calcd.}$ = 1.909 g cm^{-3}, μ = 2.704 mm^{-1}, empirical absorption correction (0.614 ≤ T ≤ 0.774), Z = 4, monoclinic, space group $P2_1/n$ (no. 14), λ = 0.71073 Å, T = 198 K, ω- and φ-scans, 16579 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.67 Å^{-1}, 5968 independent (R_{int} = 0.030) and 5230 observed reflections [$I \geq 2\sigma(I)$], 267 refined parameters, R = 0.026, wR_2 = 0.059, max. residual electron density 1.47 (–1.62) e Å^{-3} close to iodine, hydrogen atoms calculated and refined as riding atoms.

Reaction of 3b with *n*-Propyl Iodide. Formation of Complexes 5b and 6c: *n*-Propyl iodide (7.8 μL, 13.5 mg, 0.08 mmol) was added to a solution of **3b** (30 mg, 0.08 mmol) in C_6D_6 (1 mL) at room temperature. The reaction mixture was transferred into an NMR tube and the reaction was monitored by NMR spectroscopy.

Reaction of [{CpP(*i*Pr)$_2$}Li] (2a) with Methyl Iodide. Generation of 6a: Methyl iodide (99.30 μL, 227 mg, 1.60 mmol) was added to a solution of **2a** (300 mg, 1.60 mmol) in toluene (40 mL) at room temperature. After the reaction mixture had been stirred at ambient temperature overnight, all volatiles were removed in vacuo. The product was obtained as a bright yellow solid (310 mg, 0.94 mmol, 59%). M.p. 96 °C (DSC). ^{1}H NMR [400 MHz, C_6D_6/TDF (4:1), 298 K]: δ = 6.66, 6.31 (each m, each 2 H, C_5H_4), 1.83 (dsept, $J_{H,H}$ = 6.8, $J_{P,H}$ = 10.0 Hz, 2 H, CH$^{i\mathrm{Pr}}$), 1.08 (d, $J_{P,H}$ = 12.0 Hz, 3 H, Me), 0.82 (dd, $J_{P,H}$ = 16.2, $J_{H,H}$ = 6.8 Hz, 6 H, Me$^{i\mathrm{Pr}}$), 0.70 (dd, $J_{P,H}$ = 15.8, $J_{H,H}$ = 6.8 Hz, 6 H, Me$^{i\mathrm{Pr}}$) ppm. ^{13}C{^{1}H} NMR [100 MHz, C_6D_6/TDF (4:1), 298 K]: δ = 113.9 (d, J = 16.3 Hz, C_5H_4), 113.3 (d, J = 13.8 Hz, C_5H_4), 74.0 (d, J = 104.2 Hz, C=P), 22.7 (d, J = 52.9 Hz, CH$^{i\mathrm{Pr}}$), 15.6 (d, J = 1.8 Hz, Me$^{i\mathrm{Pr}}$), 15.4 (d, J = 2.1 Hz, Me$^{i\mathrm{Pr}}$), 0.6 (d, J = 56.9 Hz, Me–P) ppm. ^{31}P{^{1}H} NMR (81 MHz, C_6D_6, 298 K): δ = 24.7 (s, PiPr$_2$) ppm. MS (ESI): m/z calcd. 197.1459 [M + H]$^+$; found 197.1446. $C_{12}H_{21}$P·LiI (330.12): calcd. C 43.66, H 6.41; found C 42.61, H 6.52.

Reaction of [{CpP(*i*Pr)$_2$}Li] (2a) with Ethyl Iodide. Generation of 6b: According to the procedure described for the generation of **6a**, **6b** was obtained as a colourless powder (435 mg, 1.26 mmol, 79%) from the reaction of **2a** (300 mg, 1.60 mmol) with ethyl iodide (129 μL, 249 mg, 1.60 mmol) in toluene (40 mL). M.p. 144 °C (DSC). ^{1}H NMR [600 MHz, C_6D_6/TDF (4:1), 298 K]: δ = 6.59, 6.28 (each m, each 2 H, C_5H_4), 1.99 (dsept, $J_{P,H}$ = 10.6, $J_{H,H}$ = 7.0 Hz, 2 H, CH$^{i\mathrm{Pr}}$), 1.77 (dq, $J_{P,H}$ = 12.7, $J_{H,H}$ = 7.7 Hz, 2 H, CH_2), 0.90 (dd, $J_{P,H}$ = 15.4, $J_{H,H}$ = 7.0 Hz, 6 H, Me$^{i\mathrm{Pr}}$), 0.86 (q, $J_{P,H}$ = $J_{H,H}$ = 7.7 Hz, 3 H, CH_3), 0.80 (dd, $J_{P,H}$ = 15.4, $J_{H,H}$ = 7.0 Hz, 6 H, Me$^{i\mathrm{Pr}}$) ppm. ^{13}C{^{1}H} NMR (125 MHz, C_6D_6/TDF, 4:1, 298 K): δ = 113.7 (d, J = 16.7 Hz, C_5H_4), 113.3 (d, J = 13.3 Hz, C_5H_4), 73.1 (d, J = 103.5 Hz, P=C), 22.0 (d, J = 51.8 Hz, CH$^{i\mathrm{Pr}}$), 16.2 (d, J = 1.8 Hz, Me$^{i\mathrm{Pr}}$), 16.0 (d, J = 1.9 Hz, Me$^{i\mathrm{Pr}}$), 11.7 (d, J = 52.9 Hz, CH_2), 7.5 (d, J = 4.8 Hz, CH_3) ppm. ^{31}P{^{1}H} NMR (81 MHz, C_6D_6, 298 K): δ = 24.7 (s, PiPr$_2$) ppm. MS (ESI): m/z calcd. 211.1616 [M + H]$^+$; found 211.1. $C_{13}H_{23}$P·LiI (344.15): calcd. C 45.37, H 6.74; found C 44.45, H 6.73.

Reaction of [{CpP(*i*Pr)$_2$}Li] (2a) with *n*-Propyl Iodide. Generation of 6c: According to the procedure described for the generation of **6a**, **6c** was obtained as a colourless powder (470 mg, 0.76 mmol, 82%) from the reaction of **2a** (300 mg, 1.60 mmol) with *n*-propyl

iodide (156.5 μL, 271 mg, 1.60 mmol) in toluene (40 mL). M.p. 101 °C (DSC). ^{1}H NMR (600 MHz, C_6D_6/TDF (4:1), 298 K): δ = 6.67, 6.33 (each m, each 2 H, C_5H_4), 1.96 (dsept, $J_{P,H}$ = 10.8, $J_{H,H}$ = 7.2 Hz, 2 H, CH^{iPr}), 1.76 (m, 2 H, PCH_2), 1.32 (m, 2 H, CH_2), 0.90 (dd, $J_{P,H}$ = 15.8, $J_{H,H}$ = 7.2 Hz, 6 H, Me^{iPr}), 0.79 (dd, $J_{P,H}$ = 15.6, $J_{H,H}$ = 7.2 Hz, 6 H, Me^{iPr}), 0.76 (td, $J_{H,H}$ = 7.1, $J_{H,H}$ = 1.5 Hz, 3 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR [125 MHz, C_6D_6/TDF (4:1), 298 K]: δ = 113.8 (d, J = 16.6 Hz, C_5H_4), 113.4 (d, J = 13.8 Hz, C_5H_4), 73.2 (d, J = 102.3 Hz, P=C), 22.3 (d, J = 52.3 Hz, CH^{iPr}), 20.9 (d, J = 51.8 Hz, PCH_2), 17.1 (d, J = 4.1 Hz, CH_2), 16.2 (d, J = 2.1 Hz, Me^{iPr}), 16.0 (d, J = 2.1 Hz, Me^{iPr}), 16.1 (d, J = 15.3 Hz, CH_3) ppm. $^{31}P\{^1H\}$ NMR [81 MHz, C_6D_6/TDF (4:1), 298 K]: δ = 26.1 (s, PiPr$_2$) ppm. MS (ESI): *m*/*z* calcd. 225.18 $[M + H]^+$; found 456.00 $[2M + H,Li]^+$. $C_{14}H_{25}P{\cdot}LiI$ (358.17): calcd. C 46.95, H 7.04; found C 47.24, H 7.34.

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