DOI: 10.1002/chem.200700320

Methylene Transfer from SnMe Groups Mediated by a Rhodium(I) Pincer Complex: Sn–C, C–C, and C–H Bond Activation

Christian M. Frech,*[a] Linda J. W. Shimon,[b] and David Milstein*[c]

Abstract: The PCP-Rh^{I} complex **1a** based on the [1,3-phenylenebis(methylene)]bis(diisopropylphosphine) ligand reacts with [diazo(phenyl)methyl]trimethylstannane (**2**) at room temperature to give novel pincer-type phenyl(dimethylstannyl)methylene]hydrazinato complex **3a**. The reaction sequence involves a unique combination of Sn–C bond cleavage, C–C bond formation, C–H activation and intramolecular deprotonation of a rhodium hydride intermediate, which results in methylene transfer from an SnMe group to the pincer system and PCP-chelate expansion. A methylene-transfer reaction was also demonstrated with tetramethyltin as the methylene source in the presence of $KOC(CH_3)_3$ at room temperature. The resulting unstable "chelate-expanded" Rh^{I} complex [$(C_{10}H_5$-$(CH_2P\mathit{i}Pr_2)_2)(CH_2)Rh(L)$] (L = N_2, THF; **4a**) was isolated as its carbonyl derivative **5a**. Heating **4a** in benzene yielded an equimolar amount of toluene and **1a**, which demonstrates the ability of the Rh^{I} pincer complex to extract a methylene group from an unactivated alkyl tin substrate and transfer it, via C–C followed by C–H activation, to an arene. Use of fluorobenzene resulted in formation of fluorotoluene. Catalytic methylene-group transfer mediated by **1a** was not possible, because of formation of *o*-xylylene complex **8** under the reaction conditions. Steric parameters play a decisive role in the reactivity with tin compounds; while *i*PrP derivative **1a** underwent facile reactions, *t*BuP complex **1b** was inert.

Keywords: C–C activation · C–H activation · pincer ligands · rhodium · tin

Introduction

We have reported a methylene-transfer reaction[1,2] involving C–C activation in "methylene-bridged" pincer-type complexes followed by selective transfer of methylene groups to organic compounds such as benzene, silanes, and disilanes,[1a] as well as to HCl[1b,c] and H_2.[1d] The reverse reaction, in which a methylene unit is abstracted from an organic substrate molecule and transferred to the bis-chelating ligand to regenerate the "methylene bridge" is known for methyl iodide as methylene source.[1] A related rare example of transfer of a benzyl group by using benzyl halides was also reported by us.[2a] We are interested in finding new sources of methylene groups for transfer to a bis-chelating pincer-type complex with chelate expansion, towards the development of catalytic methylene-transfer reactions based on C–C activation (Scheme 1).

We report here reactions of a naphthyl-based Rh^{I} pincer complex with methyltin compounds, which involve an unprecedented sequence of Sn–C bond cleavage, C–C bond formation, C–H activation, and transfer of a methylene group. Thus, a methylene group can be extruded from tetramethyltin and transferred to benzene to yield toluene in a unique transition metal promoted reaction.

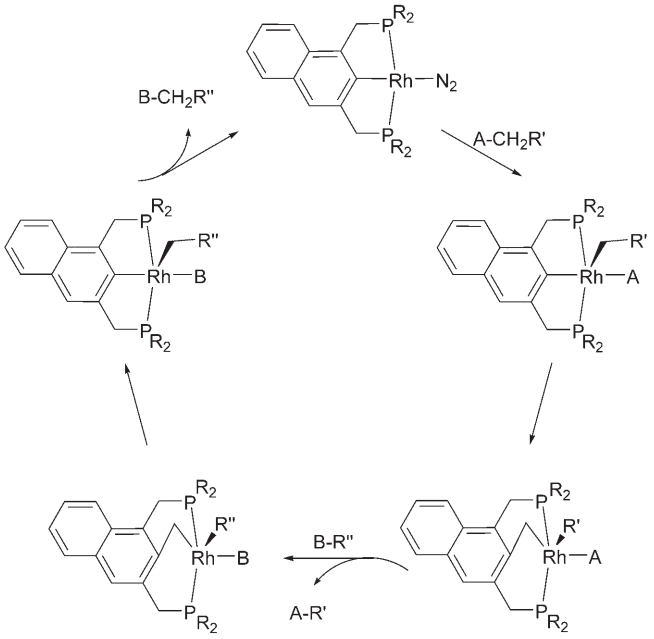
[a] Dr. C. M. Frech
Department of Inorganic Chemistry
University of Zürich
8057 Zürich (Switzerland)
Fax: (+41) 44-635-6802
E-mail: chfrech@aci.unizh.ch

[b] Dr. L. J. W. Shimon
Unit of Chemical Research Support
The Weizmann Institute of Science
Rehovot, 76100 (Israel)

[c] Prof. Dr. D. Milstein
Department of Organic Chemistry
The Weizmann Institute of Science
Rehovot, 76100 (Israel)
Fax: (+972) 8-934-4142
E-mail: david.milstein@weizmann.ac.il

Results and Discussion

When a solution of dinitrogen complex [{$C_{10}H_5$-$(CH_2P\mathit{i}Pr_2)_2$}Rh(η^1-N_2)][3] (**1a**) in THF was treated with a slight excess (ca. 1.2 equiv) of [diazo-



Scheme 1. Hypothetical catalytic cycle for the methylene-transfer reaction. A–CH_2R', B–R″ represent bonds capable of oxidative addition to Rh^I.

(phenyl)methyl]trimethylstannane (**2**) at room temperature, the novel pincer-type phenyl(dimethylstannyl)methylene]hydrazinato complex **3a**, which incorporates a five-membered heterocyclic ligand comprising four different elements (see X-ray structure of **3a** in Figure 1), was formed (Scheme 2). Complex **3a** was isolated as a dark green solid in 75% yield. Insertions of transition metals into unstrained and unactivated Sn–C bonds to yield stable products of oxidative addition are not common.[4,5] Moreover, relatively few examples of crystallographically characterized rhodium complexes with Rh–Sn bonds are known.[4f,6–8] In contrast to the reactivity of **1a**, no reaction was observed when P*t*Bu_2 analogue[9] **1b** was treated with **2**.

The $^{31}P\{^1H\}$ NMR spectrum of **3a** exhibits two resonances with a dd (AB) pattern centered at $\delta = 47.95$ and 42.44 ppm ($^2J_{P,P} = 334.1$, $^1J_{Rh,P} = 117.4$ Hz). In the ^1H NMR spectrum the $Sn(CH_3)_2$ groups give rise to a doublet with Sn satellites at $\delta = 0.65$ ppm ($^3J_{Rh,H} = 25.6$, $^2J_{Sn,H} = 21.4$ Hz), which indicates formation of a rhodium–tin bond. A broad singlet at $\delta =$ 5.69 ppm is assigned to the NH unit of the hydrazinato ligand. The CH_2Rh protons give rise to broad, unresolved signals centered at $\delta = 2.64$ and 2.52 ppm. The corresponding signal in the $^{13}C\{^1H\}$ NMR spectrum appears as a doublet at $\delta = 26.09$ ppm ($^1J_{Rh,C} = 19.5$ Hz). Besides the signals in the aromatic region, a singlet at $\delta = 161.75$ ppm and a doublet at $\delta = 26.09$ ppm ($J = 19.5$ Hz) are assigned to the methylene and methyl carbon atoms of the hydrazinato ligand. The identity of **3a** was confirmed by X-ray diffraction (Figure 1),

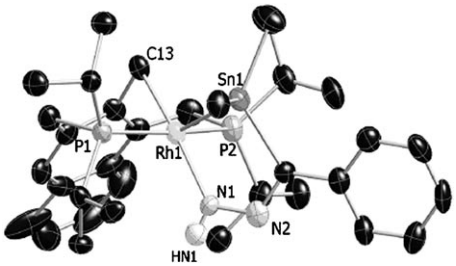
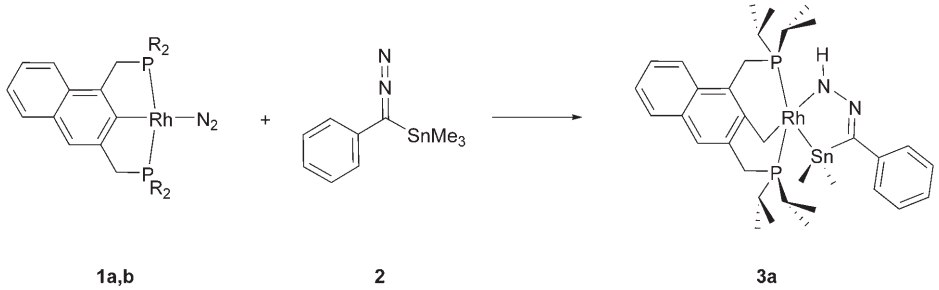


Figure 1. ORTEP diagram of a molecule of **3a** (50% probability). Hydrogen atoms (except HN1) are omitted for clarity. Selected bond lengths and angles are given in Table 1.

which revealed a five-coordinate Rh^{III} center with a distorted square-pyramidal environment. Selected bond lengths and angles are listed in Table 1. The dimethyltin unit is located in the apical position. The C13-Rh1-Sn1 (112.03(17)°) and N1-Rh1-Sn1 (76.03(16)°) angles significantly deviate from the 90° of an ideal square pyramid. The Rh1–N1 (2.120(5) Å) and N1–N2 (1.322(8) Å) bond lengths indicate single-bond character, while the N2–C26 distance of 1.304(8) Å corresponds to an elongated double bond. The Rh1–C13 distance (2.112(6) Å) compares well to those of similar pincer systems.[10] The Sn1–Rh1 bond length (2.545(1) Å) is one of the shortest reported for structurally characterized rhodium complexes with Rh–Sn bonds.[4d,f,6–8]

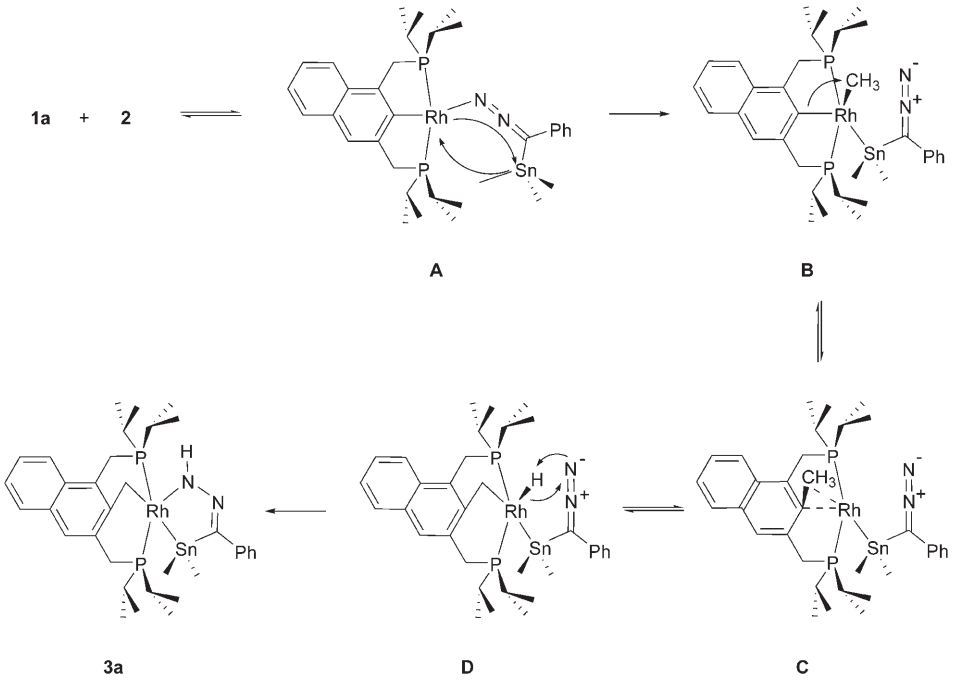
Table 1. Selected bond lengths [Å] and angles [°] for **3a**.

Rh1–N1	2.120(5)	N1–N2	1.322(8)
N2–C26	1.304(8)	C26–Sn1	2.165(7)
Sn1–Rh1	2.545(1)	Rh1–C13	2.112(6)
C13-Rh1-Sn1	111.89(17)	N1-Rh1-Sn1	76.07(16)
C13-Rh1-N1	171.3(2)	P1-Rh1-P2	163.09(7)



Scheme 2. Reaction of **1a** with **2**. R = *i*Pr (**a**), *t*Bu (**b**).

Although detailed mechanistic studies were not performed, a possible scenario for the formation of **3a** is outlined in Scheme 3. Following coordination of **2** to the metal center through the terminal nitrogen atom (**A**),[11] Sn–C bond activation can yield rhodium methyl stannyl intermediate **B**. This reaction step is apparently suppressed in the case of **1b**

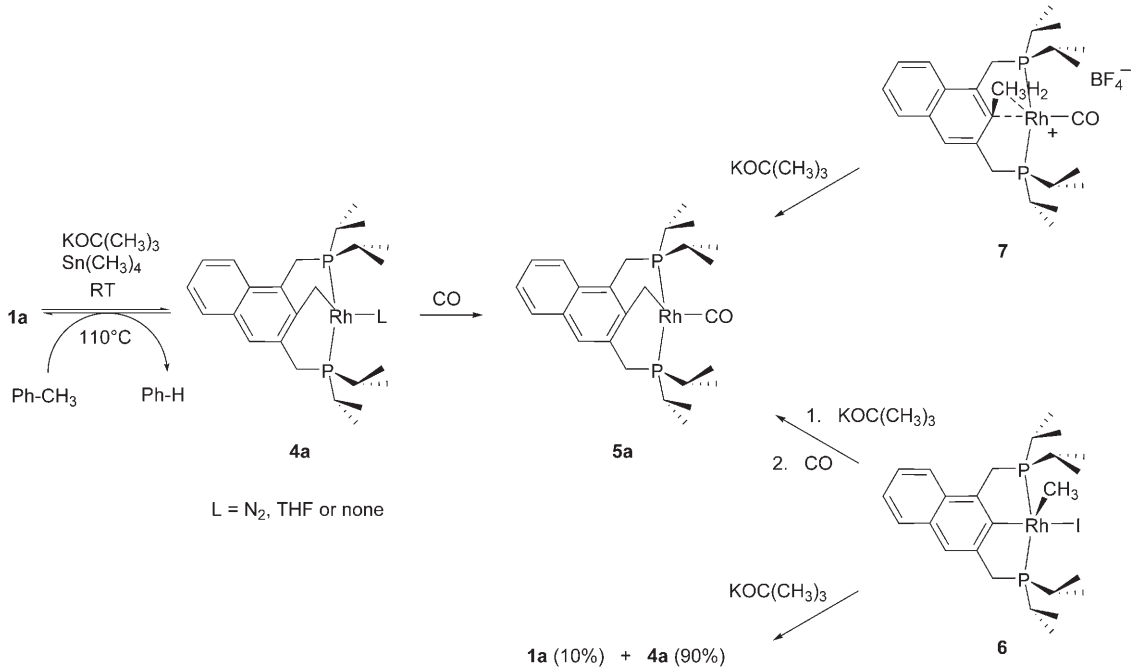


Scheme 3. Proposed mechanism for the transformation of **1a** into **3a**.

for steric reasons. Migration of the methyl group from the rhodium center of **B** to the aromatic unit (**C**) and subsequent C–H bond activation can result in formation of rhodium hydride intermediate **D**.[12] Complex **3a** is then formed by intramolecular deprotonation and cyclization.

Following the observation of facile Sn–C bond activation of **2** by **1a**, we were interested whether methylene-transfer reactions with $Sn(CH_3)_4$ as the methylene source might be possible. However, on addition of an excess (ca. 5 equiv) of $Sn(CH_3)_4$ to THF solutions of **1a** or **1b**, no noticeable changes were observed by $^{31}P\{^1H\}$ NMR spectroscopy. Next we examined the possibility of promoting the reaction by addition of a base. While no reaction was observed when an excess of $KOC(CH_3)_3$ was added to a solution containing the bulky complex **1b** and $Sn(CH_3)_4$, addition of an excess (ca. 5 equiv) of $KOC(CH_3)_3$ to a solution of **1a** and $Sn(CH_3)_4$ led to exclusive formation of $[\{C_{10}H_5(CH_2PiPr_2)_2(CH_2)\}Rh(L)]$ (**4a**; $L=N_2$, THF) over a few hours (Scheme 4). The $^{31}P\{^1H\}$ NMR spectrum of **4a** exhibits two signals with dd (AX) patterns centered at $\delta=79.02$ ($^2J_{P,P}=267.7$, $^1J_{Rh,P}=180.6$ Hz) and 59.33 ppm ($^2J_{P,P}=267.5$, $^1J_{Rh,P}=170.1$ Hz), indicative of an electron-rich Rh^I center. Unfortunately, attempts to isolate **4a** failed, since decomposition occurred on evaporation of the solvent.

First indications of the identity of **4a** were obtained by studying its reaction with CO. When an excess (ca. 50 equiv)



Scheme 4. Methylene transfer from $SnMe_4$ and related reactions.

of CO was added to a THF solution of **4a**, the stable Rh^I complex $[\{C_{10}H_5(CH_2PiPr_2)_2(CH_2)\}Rh(CO)]$ (**5a**) was exclusively obtained and isolated in high yield (Scheme 4). Furthermore, treatment of $[\{C_{10}H_5(CH_2PiPr_2)_2\}Rh(CH_3)(I)]$[9] (**6**) with an equimolar amount of $KOC(CH_3)_3$ yielded complexes **4a** (ca. 90%) and **1a** (ca. 10%). Deprotonation and methyl-group abstraction were confirmed by mass spectrometric detection of $HOC(CH_3)_3$ and $CH_3OC(CH_3)_3$, respectively. Treatment of this mixture with an excess (ca. 50 equiv) of CO resulted in formation of **5a** (ca. 90%) and $[\{C_{10}H_5(CH_2PiPr_2)_2\}Rh(CO)]$[9] (ca. 10%). In addition, **5a** was exclusively formed on treatment of THF solutions of the cationic C–C agostic complex $[\{C_{10}H_5(CH_2PiPr_2)_2(CH_3)\}Rh(CO)]BF_4$[13] (**7**) with an equimolar amount (or a slight excess) of $KOC(CH_3)_3$. Pincer-type complexes with an agostic C–C bond were reported.[9,14–16]

The $^{31}P\{^1H\}$ NMR spectrum of **5a** exhibits two signals with dd (AX) patterns centered at $\delta = 93.41$ ($^2J_{P,P} = 246.0$, $^1J_{Rh,P} = 170.2$ Hz) and 71.63 ppm ($^2J_{P,P} = 246.0$, $^1J_{Rh,P} = 160.9$ Hz). The ^1H NMR spectrum shows, in addition to signals due to the aromatic protons and the phosphines, two resonances with a dd pattern at $\delta = 2.61$ ($^2J_{Rh,H} = 19.1$, $^3J_{P,H} = 5.1$ Hz) and 2.46 ppm ($^2J_{Rh,H} = 17.0$, $^3J_{P,H} = 5.1$ Hz), which were assigned to the magnetically inequivalent hydrogen atoms of the rhodium coordinated methylene "bridge". The $^{13}C\{^1H\}$ NMR spectrum of **5a** exhibits a doublet resonance assigned to a methylene carbon atom at $\delta = 21.96$ ppm ($^1J_{Rh,C} = 19.7$ Hz), which correlates with the hydrogen atoms resonating at $\delta = 2.61$ and 2.46 ppm. In addition, a signal due to the carbonyl carbon atom at $\delta = 196.73$ ppm (dt, $^1J_{Rh,C} = 65.6$, $^2J_{P,C} = 13.4$ Hz) was detected.

An X-ray diffraction study of **5a** (Figure 2) revealed a distorted square-planar geometry around the Rh^I center (P2-Rh1-P3 158.83(3), C1-Rh1-C2 177.84(12)°). Selected bond lengths and angles are listed in Table 2. The Rh1–C1 (1.837(3) Å) and C1–O1 (1.161(3) Å) distances indicate considerable backbonding to the carbonyl ligand and high electron density at the metal center. The Rh–CH_2 distance (Rh1–C2 2.156(3) Å) is longer than the corresponding bond of **3a** (Rh1–C13 2.112(6) Å). This elongation can be attributed to the stronger *trans* influence of the carbonyl as compared with the hydrazinato ligand.

A possible mechanism for methylene-group transfer from tetramethyltin to **1a** is outlined in Scheme 5. Formation of

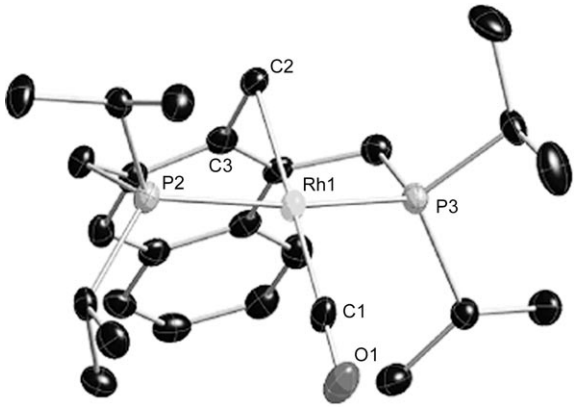
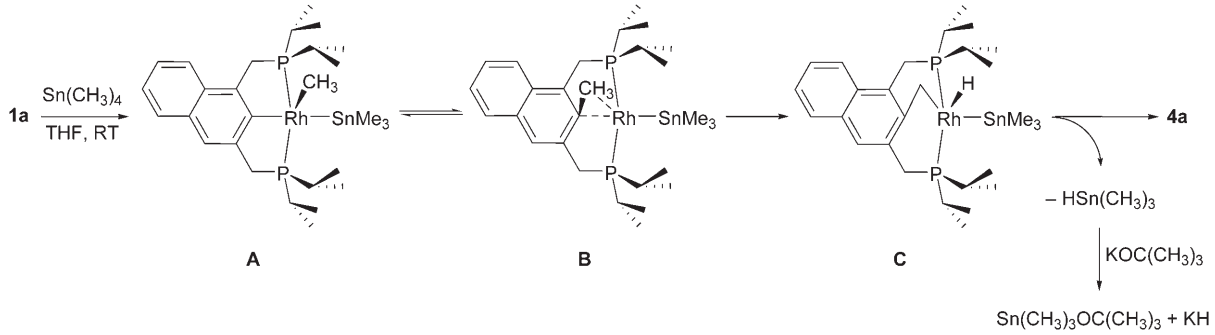


Figure 2. ORTEP diagram of a molecule of **5a** (50% probability). Hydrogen atoms are omitted for clarity. Selected bond lengths and angles are given in Table 2.

Table 2. Selected bond lengths [Å] and angles [°] for **5a**.

Rh1–P2	2.301(1)	Rh1–P3	2.309(1)
Rh1–C1	1.837(3)	Rh1–C2	2.156(3)
C1–O1	1.161(3)	C2–C3	1.463(4)
P2-Rh1-P3	158.83(3)	C1-Rh1-C2	177.84(12)
P2-Rh1-C2	81.11(8)	P2-Rh1-C1	98.43(9)
P3-Rh1-C1	97.46(9)	P3-Rh1-C2	82.49(8)
C1-Rh1-C3	143.85(11)	C2-Rh1-C3	34.01(9)
P2-Rh1-C3	80.19(7)	P3-Rh1-C3	78.72(7)

4a may be initiated by Sn–Me oxidative addition of tetramethyltin to **1a** (**A**), followed by methyl migration to the *ipso* carbon atom to form η^2 C–C agostic intermediate **B**, which could undergo C–H activation to give intermediate **C**. Reductive elimination of trimethylstannane would yield Rh^I complex **4a**. The driving force of this reaction sequence could be nucleophilic attack of the butoxide on the oxophilic tin atom of trimethylstannane, which would lead to *tert*-butoxytrimethylstannane and potassium hydride. The importance of the nucleophilic nature of the butoxide base in this transformation was indicated by the observed lack of reactivity of an excess (ca. 5 equiv) of the non-nucleophilic bases K_3PO_4, K_2CO_3, and 2,6-di-*tert*-butylpyridine. No spectroscopic evidence for the formation of **4a** was obtained in these cases after stirring overnight.



Scheme 5. Proposed mechanism for the transformation of **1a** into **4a**.

Treatment of solutions of **4a** in THF with benzene or fluorobenzene led to formation of "methylene-depleted" complex **1a**, as indicated by $^{31}P\{^1H\}$ NMR spectroscopy, accompanied by a corresponding amount of toluene (detected by GC/MS) and 2-fluorotoluene (detected by GC/MS and $^{19}F\{^1H\}$ NMR spectroscopy), respectively, over 36 h at 110 °C. Similar reactivity was observed with the analogous complex $[\{(C_6H(CH_3)_2)(CH_2P\textit{i}Pr_2)_2(CH_2)\}Rh(PPh_3)]$.[1] Overall, a methylene group was transferred from a methyl group of Me_4Sn and inserted into the C–H bond of benzene and into the *ortho* C–H bond of fluorobenzene. This is an extremely rare example of a "methylene-transfer" process,[1,2] in which a transition metal mediates extrusion of a methylene group from an alkyl group and its insertion into a bond of another molecule. The only other example involves methyl iodide as methylene source.[1]

Catalytic production of toluene or 2-fluorotoluene, respectively, would require reaction of regenerated **1a** with Me_4Sn and a base to give "methylene-bridged" Rh^I complex **4a** under the reaction conditions.[17] However, in contrast to the formation of **4a** on treatment of **1a** with Me_4Sn in the presence of $KOC(CH_3)_3$ at room temperature described above, heating at 110 °C overnight resulted in exclusive formation of the *o*-xylylene rhodium(I) methyl complex $[\{C_{10}H_5(CHP\textit{i}Pr_2)(CH_2P\textit{i}Pr_2)(CH_2)\}Rh(CH_3)]$ (**8**; Scheme 6).

Complex **8** is a rare example of a thermally stable *o*-xylylene complex in which a metal center is coordinated in an η^1 fashion to only one of the exocyclic double bonds.[15] Free *p*- and *o*-xylylenes are highly reactive species which undergo spontaneous polymerization even at very low temperatures.[18] Transition metal complexes of *o*-xylylenes in which the metal center is coordinated to both exocyclic double bonds were reported.[19] Stabilization of the *o*-xylylene unit in **8** can be attributed to the effect of phosphine chelation and distortion of the xylylene moiety from planarity. The $^{31}P\{^1H\}$ NMR spectrum of **8** exhibits two doublets (AB) centered at $\delta = 42.89$ and 42.77 ppm with coupling constants of $^1J_{Rh,P} = 145.8$ and $^1J_{Rh,P} = 144.2$ Hz, respectively. The ^1H NMR spectrum exhibits broad singlets at $\delta = 5.95$ and at 6.11 ppm corresponding to the only proton on the double bond of the "side arm" and the olefinic proton in the pincer core. The hydrogen atoms of the coordinated double bond give rise to a signal at $\delta = 3.21$ ppm with a dt pattern ($^1J_{Rh,H} = 39.1$, $^2J_{P,H} = 3.2$ Hz). A doublet of triplets at $\delta = 0.84$ ppm ($^2J_{Rh,H} = 6.3$, $^3J_{P,H} = 2.1$ Hz) was assigned to the methyl ligand. The $^{13}C\{^1H\}$ NMR spectrum exhibits a signal with a dd pattern at $\delta = 110.85$ ppm ($^1J_{P,C} = 24.1$, $^2J_{Rh,C} = 7.8$ Hz) due to the "side-arm" olefinic carbon atom, and resonances at $\delta = 56.43$ (dt, $^2J_{Rh,C} = 11.7$, $^3J_{P,C} = 2.6$ Hz) and 83.72 ppm (dt, $J_{Rh,C} = 22.8$ Hz, $J_{Rh,C} = 7.8$ Hz) assigned to the carbon atoms of the coordinated exocyclic methylene group. The methyl ligand gives rise to a doublet of triplets at -8.34 ppm ($^1J_{Rh,H} = 25.4$, $^2J_{P,H} = 11.1$ Hz).

Dark red single crystals were obtained by slow evaporation of a concentrated diethyl ether solution of **8** at −30 °C. An X-ray diffraction study confirmed the identity of **8** (Figure 3). Selected bond lengths and angles are presented in Table 3. The carbon–carbon distances of the pseudo-aromatic ring system in **8** are significantly different to those in complex **5a**, as expected for an *o*-xylylene structure.

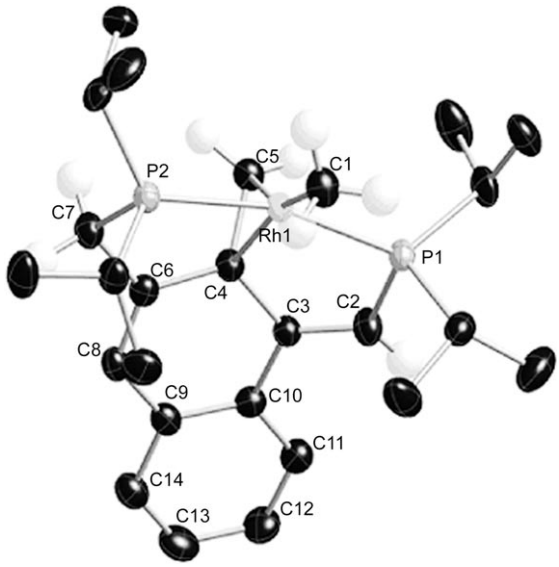
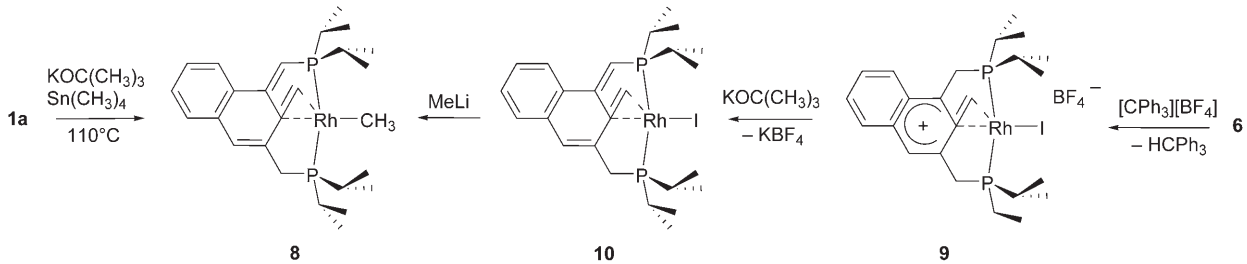


Figure 3. ORTEP diagram of a molecule of **8** (30% probability). The hydrogen atoms (except those of the xylylene moiety and RhMe) are omitted for clarity. Selected bond lengths and angles are given in Table 3.

Xylylene complex **8** was independently prepared as follows (Scheme 6). Hydride abstraction from complex **6** with trityl cation resulted in methylene arenium complex **9**. Pincer-type methylene arenium complexes are known.[16b,20] Treatment of **9** with $KOC(CH_3)_3$ resulted in immediate deprotonation of a benzylic proton to quantitatively form *o*-xy-



Scheme 6. Syntheses of xylylene complex **8**.

Table 3. Selected bond lengths [Å] and angles [°] for **8**.

Rh1–P1	2.2815(9)	Rh1–P2	2.2885(9)
Rh1–C1	2.114(4)	Rh1–C5	2.109(3)
C4–C5	1.440(5)	C4–C6	1.473(5)
C6–C7	1.521(5)	C6–C8	1.351(5)
C8–C9	1.444(5)	C9–C10	1.422(5)
C10–C3	1.481(5)	C3–C2	1.350(5)
C3–C4	1.492(5)	C10–C11	1.404(5)
C11–C12	1.381(6)	C12–C13	1.395(6)
C13–C14	1.379(6)	C14–C9	1.406(5)
P1-Rh1-P2	163.95(4)	C1-Rh1-C4	163.36(15)
C1-Rh1-C5	157.61(14)	C4-Rh1-C5	39.03(13)

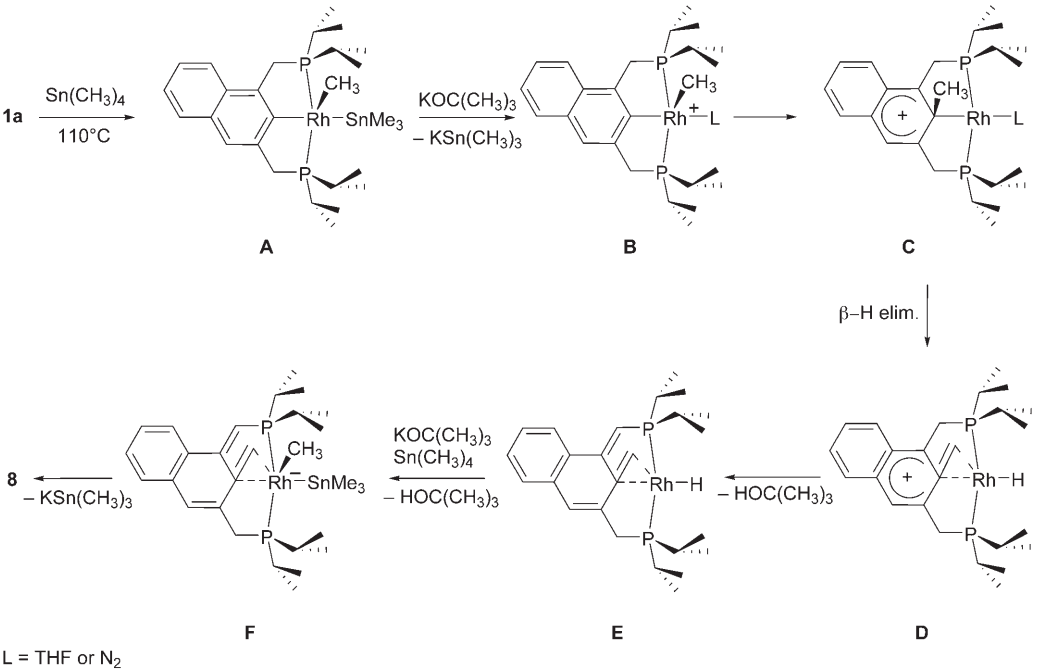
lylene complex [{$C_{10}H_5$(CHP*i*Pr$_2$)(CH_2P*i*Pr$_2$)(CH_2)}Rh(I)] (**10**). Reaction of this complex with an equimolar amount of methyllithium gave complex **8**, as indicated by $^{31}P\{^1H\}$ NMR spectroscopy.

Although detailed mechanistic studies were not performed, a mechanism that might account for formation of **8** is presented in Scheme 7. Oxidative addition of tetramethyltin to **1a** to yield intermediate **A** is expected to initiate the reaction sequence. Thermally induced dissociation of the sterically demanding trimethylstannyl group may lead to a cationic intermediate of type **B**. Subsequent migration of the methyl group to the *ipso*-carbon atom may yield σ-arenium intermediate **C**, which could undergo β-H elimination to give intermediate **D**. The involvement of intermediates of type **C** seems plausible, since σ-arenium complexes have already been proposed as intermediates in the formation of methylene arenium complexes.[15] Moreover, carbonyl derivatives of σ-arenium complexes are stable and were isolated.[9,15] However, in contrast to the reaction of dinitrogen complex **1a** with $KOC(CH_3)_3$ and tetramethyltin at room temperature, in which C–H activation and formation of neutral "methylene-bridged" complex **4a** were observed, β-H elimination may be favored at 110 °C to give a methylene arenium intermediate of type **D**. Formation of intermediate **D** is likely,[10a] since methylene arenium complexes easily undergo deprotonation of the "side arm" on treatment with bases to give *o*-xylylene complexes of type **E**.[16b,20] Indeed, deprotonation of **9** resulted in quantitative formation of *o*-xylylene complex **10**, as described above (Scheme 6). Deprotonation of the hydride ligand of **E** by $KOC(CH_3)_3$ and subsequent oxidative addition of tetramethyltin (**F**) followed by elimination of $KSn(CH_3)_3$ might give neutral *o*-xylylene complex **8**. On the other hand, C–H activation and formation of **4a** as an intermediate in this reaction sequence cannot be excluded, since thermal treatment of mixtures of **4a**, tetramethyltin, and $KOC(CH_3)_3$ overnight also led to exclusive conversion to complex **8**. Deprotonation of the "side arm" of **4a** could yield an anionic *o*-xylylene complex, which subsequently could undergo oxidative addition of tetramethyltin (**F**) followed by elimination of $KSn(CH_3)_3$.

Further evidence for the involvement of rhodium methyl and σ-arenium intermediates of types **B** and **C**, respectively, was obtained by treatment of a dichloromethane solution of methyl iodide adduct **6** with one equivalent of CPh_3BF_4 at room temperature, which almost quantitatively yielded methylene arenium complex [{$C_{10}H_5$(CH_2P*i*Pr$_2$)$_2$-(CH_2)}Rh(I)][BF_4][14] (**9**; see Scheme 6).

Conclusion

We have demonstrated the ability of a Rh^I pincer complex to extract methylene groups from nonactivated methyltin substrates, with chelate expansion from five- to six-mem-



Scheme 7. Proposed mechanism for the transformation of **1a** into **8**.

bered, and then transfer the methylene group to another substrate via C–H activation. Thus, reaction of Rh^I complex **1a** with [diazo(phenyl)methyl]trimethylstannane (**2**) formed [phenyl(dimethylstannyl)methylene]hydrazinato complex **3a** in high yield. The reaction sequence involves a unique combination of a Sn–C bond cleavage, C–C bond formation, C–H activation, and intramolecular deprotonation of a rhodium hydride intermediate. Based on these observations, methylene transfer from tetramethyltin as methylene source to benzene and to fluorobenzene to yield equimolar amounts of toluene and 2-fluorotoluene, respectively, mediated by a rhodium(I) pincer complex in the presence of $KOC(CH_3)_3$, was discovered. The unstable "methylene-bridged" Rh^I complex $[\{C_{10}H_5(CH_2P\textit{i}Pr_2)_2(CH_2)\}Rh(L)]$ (L = N_2, THF; **4a**) reacted with CO to give stable carbonyl derivative **5a** in high yield. Catalytic methylene transfer was not possible, because of formation of a rare example of a thermally stable *o*-xylylene complex, namely, **8**, in which the metal center is coordinated to only one of the double bonds. Steric parameters play a decisive role in the reactivity of the tin compounds; while *i*PrP derivative **1a** underwent facile reactions, analogous *t*BuP complex **1b** was inert. A plausible mechanism is proposed.

Experimental Section

General procedures: All synthetic operations were carried out in oven-dried glassware under an atmosphere of purified nitrogen in a Vacuum Atmospheres glove box equipped with an MO 40-2 inert-gas purifier. Solvents were of reagent grade or better, dried, distilled, and degassed before introduction into the glove box, where they were stored over activated 4 Å molecular sieves. Deuterated solvents were purchased from Aldrich or Armar and were degassed and stored over activated 4 Å molecular sieves in the glove box. Commercial chemicals were used as received.

Analysis: ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, and ^{19}F NMR data were recorded at 500.13, 125.76, 202.46, and 235.40 MHz, respectively, on Bruker AMX-500 and DPX-250 spectrometers. The ^1H and $^{13}C\{^1H\}$ NMR chemical shifts are relative to tetramethylsilane; peaks of the residual protons of the solvents were used as internal standards for ^1H ($\delta = 7.15$ (benzene); 5.32 (CH_2Cl_2); 3.58 and 1.73 (THF)) and all-D solvent peaks for ^{13}C ($\delta =$ 128.0 (benzene); 53.8 (CH_2Cl_2); 68.00 and 25.77 ppm (THF)). $^{31}P\{^1H\}$ NMR chemical shifts are reported downfield relative to external 85% H_3PO_4 in D_2O at $\delta = 0.0$ ppm. All measurements were carried out at 298 K. IR spectra were measured with a Nicolet-510 FT-IR spectrometer. Elemental analyses were performed by H. Kolbe, Mikroanalytisches Laboratorium, Germany and at the Inorganic Chemistry Department at the University of Zurich.

Preparation of $[\{C_{10}H_5(CH_2P\textit{i}Pr_2)_2\}Rh\{NHN{=}C(Ph)SnMe_2\}]$ (3a): A slight excess (1.1 equiv) of $N_2C(Ph)SnMe_3$ was added to a THF solution (5 mL) of $[\{C_{10}H_5(CH_2P\textit{i}Pr_2)_2\}Rh(\eta^1\text{-}N_2)]_2$ (40 mg, 0.039 mmol) and the solution was stirred for 5 min, whereby the color changed from brown to green. The solvent was removed under reduced pressure and the residue extracted with pentane. The pentane extract was discarded, and the residue was vaccum-dried to give 47.0 mg (0.061 mmol, 77% yield) of **3a** as a green solid

^1H NMR (CD_2Cl_2): $\delta = 7.86$ (d, $J = 8.5$ Hz, 1H, Ar), 7.66 (d, $J = 7.9$ Hz, 1H, Ar), 7.43 (t, $J = 7.9$ Hz, 1H, Ar), 7.35 (m, 2H, Ar), 7.25 (d, $J =$ 7.9 Hz, 2H, Ar), 7.15 (t, $J = 7.9$ Hz, 2H, Ar), 6.89 (t, $J = 6.7$ Hz, 1H, Ar), 5.69 (s, 1H, RhNHN=C), 3.51 (m, 1H, CH_2P), 3.28 (m, 1H, CH_2P), 3.19 (m, 1H, CH_2P), 2.64 (m, 2H, CH_2P and $ArCH_2$), 2.52 (m, 1H, $ArCH_2$), 2.25 (m, 2H, $PCH(CH_3)_2$), 2.17 (m, 2H, $PCH(CH_3)_2$), 1.43 (m, 6H, $PCH(CH_3)_2$), 1.32 (m, 6H, $PCH(CH_3)_2$), 1.26 (m, 6H, $PCH(CH_3)_2$), 0.99 (m, 6H, $PCH(CH_3)_2$), 0.65 ppm (d, $J = 25.6$ Hz, 6H, $RhSn(CH_3)_2$); $^{13}C\{^1H\}$ NMR (CD_2Cl_2): $\delta = 161.75$ (s, $Sn(CH_3)_2C(Ph){=}N$), 143.70 (s, Ar), 136.85 (br d, $J = 3.8$ Hz, C_{ipso}), 134.78 (s, Ar), 130.54 (s, Ar), 130.41 (d, $J = 5.1$ Hz, Ar), 129.84 (s, Ar), 128.30 (s, Ar), 127.81 (s, Ar), 125.84 (s, Ar), 124.83 (d, $J = 8.4$ Hz, Ar), 123.63 (s, Ar), 123.54 (s, Ar), 122.39 (s, Ar), 121.28 (s, Ar), 27.38 (dd, $J = 16.1$, 5.7 Hz, CH_2P), 27.57 (dt, $J = 12.6$, 3.4 Hz, $PCH(CH_3)_2$), 26.92 (dd, $J = 16.1$, 4.6 Hz, CH_2P), 26.17 (dt, $J = 13.8$, 3.4 Hz, $PCH(CH_3)_2$), 26.09 (d, $J = 19.5$ Hz, $ArCH_2$), 19.51 (s, $PCH(CH_3)_2$), 19.03 (s, $PCH(CH_3)_2$), 19.01 (s, $PCH(CH_3)_2$), 18.45 (s, $PCH(CH_3)_2$), 17.03 (s, $PCH(CH_3)_2$), 17.02 (s, $PCH(CH_3)_2$), 17.00 (s, $PCH(CH_3)_2$), 16.66 (s, $PCH(CH_3)_2$), 2.68 ppm (ddd, $J = 40.0$, 7.9, 3.4 Hz, $Sn(CH_3)_2$); $^{31}P\{^1H\}$ NMR (CD_2Cl_2): $\delta = 47.95$ (dd (AB), $^2J_{P,P} = 334.1$, $^1J_{Rh,P} = 117.4$ Hz), 42.44 ppm (dd (AB), $^2J_{P,P} = 334.1$, $^1J_{Rh,P} = 117.4$ Hz); elemental analysis calcd (%) for $C_{34}H_{51}N_2P_2SnRh$: C 52.94, H 6.66; found: C 53.06, H 6.61.

Preparation of $[\{C_{10}H_5(CH_2P\textit{i}Pr_2)_2(CH_2)\}Rh(CO)]$ (5a): An excess (ca. 5 equiv) of $Sn(CH_3)_4$ and $KOC(CH_3)_3$ (ca. 5 equiv) was added to a THF solution (5 mL) of $[\{C_{10}H_5(CH_2P\textit{i}Pr_2)_2\}Rh(\eta^1\text{-}N_2)]$ (40 mg, 0.039 mmol). The reaction mixture was stirred at room temperature for about 4 h. After completion of the reaction (monitored by $^{31}P\{^1H\}$ NMR spectroscopy), an excess (ca. 50 equiv) of CO gas was added and the solution was stirred for 1 min. The solvent was removed under reduced pressure and **5a** extracted with pentane, filtered through a cotton pad, and dried under vacuum. 36.6 mg (0.034 mmol, 86% yield) of **5a** was obtained as a yellow solid.

^1H NMR (C_6D_6): $\delta = 7.90$ (d, $J = 8.0$ Hz, 1H, Ar), 7.80 (d, $J = 8.1$ Hz, 1H, Ar), 7.49 (t, 1H, $J = 8.0$ Hz, Ar), 7.35 (s, 1H, Ar), 7.30 (t, 1H, $J = 8.0$ Hz, Ar), 3.60 (vt, 1H, $J = 12.5$ Hz, CH_2P), 3.27 (dd, 1H, $J = 14.0$, 7.5 Hz, CH_2P), 2.96 (dd, 1H, $J = 14.0$, 5.1 Hz, CH_2P), 3.60 (vt, 1H, $J = 12.5$ Hz, CH_2P), 2.61 (dd, 1H, $J = 19.1$, 5.1 Hz, $ArCH_2$), 2.46 (dd, 1H, $J = 17.0$, 5.1 Hz, $ArCH_2$), 2.05 (m, 4H, $PCH(CH_3)_2$), 1.38 (dist q, $J = 7.0$ Hz, 3H, $PCH(CH_3)_2$), 1.27 (m, 9H, $PCH(CH_3)_2$), 1.24 (dist q, $J = 7.1$ Hz, 3H, $PCH(CH_3)_2$), 0.89 (m, 6H, $PCH(CH_3)_2$), 0.86 ppm (dist q, $J = 7.2$ Hz, 3H, $PCH(CH_3)_2$); $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = 196.73$ (dt, $J = 65.6$, 13.4 Hz, CO), 140.33 (dd, $J = 6.7$, 4.2 Hz, C_{ipso}), 134.14 (br s, Ar), 131.60 (d, $J = 3.7$ Hz, Ar), 129.05 (s, Ar), 128.64 (s, Ar), 126.67 (s, Ar), 125.29 (s, Ar), 124.05 (d, $J = 6.3$ Hz, Ar), 121.14 (s, Ar), 120.61 (s, Ar), 28.63 (d, $J = 20.1$ Hz, CH_2P), 27.85 (d, $J = 20.1$ Hz, $PCH(CH_3)_2$), 27.67 (d, $J = 20.3$ Hz, CH_2P), 27.13 (d, $J = 19.5$ Hz, $PCH(CH_3)_2$), 21.96 (d, $J = 19.7$ Hz, $ArCH_2$), 18.92 (d, $J = 5.0$ Hz, $PCH(CH_3)_2$), 18.81 (d, $J = 5.0$ Hz, $PCH(CH_3)_2$), 18.75 (s, $PCH(CH_3)_2$), 18.67 (d, $J = 4.9$ Hz, $PCH(CH_3)_2$), 18.63 (s, $PCH(CH_3)_2$), 18.52 (d, $J = 3.8$ Hz, $PCH(CH_3)_2$), 18.21 (s, $PCH(CH_3)_2$), 17.92 ppm (s, $PCH(CH_3)_2$); $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta = 93.41$ (dd, left part of an AX system (AX), $^2J_{P,P} = 246.0$, $^1J_{Rh,P} = 170.2$ Hz), 71.63 ppm (dd, right part of an AX system (AX), $^2J_{P,P} = 246.0$, $^1J_{Rh,P} = 160.9$ Hz); IR (film): $\tilde{\nu} =$ 1929 cm^{-1} (C=O); elemental analysis calcd (%) for $C_{26}H_{39}OP_2Rh$: C 58.65, H 7.38; found: C 58.73, H 7.32.

Preparation of $[\{C_{10}H_5(CH_2P\textit{i}Pr_2)_2\}(CH_3)Rh(CO)]BF_4$ (7): An equimolar amount of $AgBF_4$ (4.3 mg, 0.022 mmol) was added to a methylene chloride solution (5 mL) of $[\{C_{10}H_5(CH_2P\textit{i}Pr_2)_2\}Rh(CH_3)(CO)(I)]$[8] (15 mg, 0.022 mmol). On stirring the reaction mixture for 30 min, precipitation of AgI took place, accompanied by a color change from yellow brown to orange. The precipitate was removed by filtration over a cotton pad, followed by solvent removal under reduced pressure. The product was washed with pentane (2×10 mL) and vacuum-dried to yield 12.7 mg (0.020 mmol; 93%) of pure **7**.

^1H NMR (CD_2Cl_2): $\delta = 8.14$ (d, $J_{H,H} = 8.1$ Hz, 1H, Ar), 7.83 (d, $J_{H,H} =$ 6.8 Hz, 1H, Ar), 7.66 (t, $J_{H,H} = 6.7$ Hz, 1H, Ar), 7.62 (t, $J_{H,H} = 6.8$ Hz, 1H, Ar), 7.53 (s, 1H, Ar), 4.25 (dt, $J = 13.5$, 4.2 Hz, 1H, CH_2P), 3.69 (dd, $J =$ 14.8, 9.5 Hz, 1H, CH_2P), 3.60 (dd, $J = 14.8$, 9.5 Hz, 1H, CH_2P), 3.36 (dt, $J = 14.8$, 4.2 Hz, 1H, CH_2P), 2.40 (s, 3H, $ArCH_3$), 2.28 (m, 2H, $PCH(CH_3)_2$), 2.16 (m, 2H, $PCH(CH_3)_2$), 1.39 (m, 6H, $PCH(CH_3)_2$), 1.30 (m, 6H, $PCH(CH_3)_2$), 1.04 ppm (m, 12H, $PCH(CH_3)_2$); $^{13}C\{^1H\}$ NMR (CD_2Cl_2): $\delta = 187.08$ (dvt, $J = 97.7$, 12.5 Hz, CO), 140.3 (s, Ar), 137.28 (s, Ar), 134.83 (s, Ar), 129.50 (d, $J = 6.7$ Hz, Ar), 128.89 (s, Ar), 128.31 (s, Ar), 127.24 (d, $J = 9.4$ Hz, Ar), 126.47 (s, Ar), 124.90 (s, Ar), 103.48 (s, $ArCH_3$), 26.12 (d, $J_{P,C} = 18.7$ Hz, CH_2P), 25.84 (d, $J_{P,C} = 22.7$ Hz, $PCH(CH_3)_2$),

$(CH_3)_2$), 25.59 (d, $J=24.1$ Hz, P*C*H$(CH_3)_2$), 24.51 (d, $J=18.7$ Hz, P*C*H-$(CH_3)_2$), 23.90 (d, $J=18.7$ Hz, P*C*H$(CH_3)_2$), 20.29 (d, $J_{P,C}=20.1$ Hz, CH_2P), 19.28 (s, PCH$(CH_3)_2$), 19.02 (s, PCH$(CH_3)_2$), 18.74 (s, PCH-$(CH_3)_2$), 18.63 (s, PCH$(CH_3)_2$), 18.60 (s, PCH$(CH_3)_2$), 18.58 (s, PCH-$(CH_3)_2$), 18.52 (s, PCH$(CH_3)_2$), 18.13 (s, PCH$(CH_3)_2$), 5.98 ppm (s, Ar*C*H$_3$); ^{31}P{^{1}H} NMR (C_6D_6): $\delta=23.72$ (dd left part of an AX system, $^2J_{P,P}=261.7$, $^1J_{Rh,P}=101.2$ Hz), −4.97 ppm (dd, right part of an AX system, $^2J_{P,P}=261.7$, $^1J_{Rh,P}=101.2$ Hz); ^{19}F NMR (CD_2Cl_2): $\delta=-152.60$ ppm (s, BF_4); IR (film): $\tilde{\nu}=1974$ cm^{-1} (C=O); elemental analysis calcd (%) for $C_{26}H_{40}BF_4OP_2Rh$: C 50.35, H 6.50; found: C 50.13, H 6.42.

Preparation of [{C$_{10}$H$_5$(CHP*i*Pr$_2$)(CH$_2$P*i*Pr$_2$)(CH$_2$)}Rh(CH$_3$)] (8): A suspension containing **1a** (40 mg, 0.039 mmol), $KOC(CH_3)_3$ (22.4 mg; 0.20 mmol), and $Sn(CH_3)_4$ (35.8 mg; 0.20 mmol) in THF (5 mL) was stirred at 110 °C overnight. The color of the reaction mixture turned from brown to dark red. The solvent was removed under reduced pressure and complex **8** was extracted from the residue with pentane and crystallized at −30 °C from pentane. 28.0 mg (0.027 mmol, 68 % yield) of **8** was obtained as a dark red crystalline solid.

^{1}H NMR ([D$_8$]THF): $\delta=7.53$ (d, $J=7.8$ Hz, 1H, Ar), 7.31 (d, $J=7.6$ Hz, 1H, Ar), 7.06 (m, 2H, Ar), 6.11 (brs, 1H, Ar), 5.96 (brs, C=CHP), 3.21 (dt, $^1J_{Rh,H}=39.1$, $^2J_{P,H}=3.2$ Hz, ArC=C*H*$_2$), 2.49 (dd, $^1J_{P,H}=13.6$, $^2J_{Rh,H}=6.4$ Hz, 1H, CH_2P), 2.16 (m, 2H, CH_2P and PC*H*$(CH_3)_2$), 2.11 (m, 2H, PC*H*$(CH_3)_2$), 1.78 (m, 1H, PC*H*$(CH_3)_2$), 1.28 (m, 9H, PCH$(CH_3)_2$), 1.13 (m, 9H, PCH$(CH_3)_2$), 0.96 (m, 6H, PCH$(CH_3)_2$), 0.84 ppm (dt, $^2J_{Rh,H}=6.3$, $^3J_{P,H}=2.1$ Hz, 3H, Rh(*CH*$_3$)); ^{13}C{^{1}H} NMR ([D$_8$]THF): $\delta=168.20$ (dd, $J=13.7$, $J=8.9$ Hz, *C*=CHP), 146.95 (dd, $J=4.6$, $J=2.6$ Hz, C=*C*CH$_2$P), 135.81 (s, Ar), 129.42 (s, Ar), 128.81 (s, Ar), 127.82 (s, Ar), 126.68 (s, Ar), 123.97 (s, Ar), 116.94 (dd, $J=8.5$, 2.6 Hz, C=*C*H), 110.85 ($^1J_{P,C}=24.1$, $^2J_{Rh,C}=7.8$ Hz, C=*C*HP), 83.72 (dt, $J_{Rh,C}=22.8$, $J_{Rh,C}=7.8$ Hz, *C*=CH$_2$), 56.43 (dt, $^2J_{Rh,C}=11.7$ Hz, $^3J_{P,C}=2.6$ Hz, C=*C*H$_2$), 27.02 (dd, $J=12.4$, 3.9 Hz, CH_2P), 26.05 (2 overlapping dd, P*C*H$(CH_3)_2$), 24.25 (dd, $J=9.8$, 5.9 Hz, P*C*H$(CH_3)_2$), 23.85 (dd, $J=17.0$, 6.5 Hz, P*C*H$(CH_3)_2$), 21.00 (s, PCH$(CH_3)_2$), 20.63 (s, PCH$(CH_3)_2$), 19.76 (s, PCH$(CH_3)_2$), 19.42 (s, PCH$(CH_3)_2$), 18.84 (s, PCH$(CH_3)_2$), 18.34 (s, PCH$(CH_3)_2$), 18.01 (s, PCH-$(CH_3)_2$), 17.69 (s, PCH$(CH_3)_2$), 8.34 ppm (dt, $^1J_{Rh,H}=25.4$, $^2J_{P,H}=11.1$ Hz, Rh*C*H$_3$); ^{31}P{^{1}H} NMR (C_6D_6): $\delta=42.89$ (d (AB), $^1J_{Rh,P}=145.8$ Hz), 42.77 ppm (d (AB), $^1J_{Rh,P}=144.2$ Hz); elemental analysis calcd (%) for $C_{26}H_{41}P_2Rh$: C 60.23, H 7.97; found: C 60.55, H 8.33.

Preparation of [{C$_{10}$H$_5$(CH$_2$P*i*Pr$_2$)$_2$(CH$_2$)}RhI]BF$_4$ (9): One equivalent of Ph_3CBF_4 was added to a diethyl ether/dichloromethane (1/1) solution (10 mL) of [{$C_{10}H_5$(CH$_2$P*i*Pr$_2$)$_2$}Rh(CH$_3$)(I)] (25 mg, 0.045 mmol) and the solution was stirred for 1 h. The solvent was removed under reduced pressure and the residue was washed with pentane (3×10 mL) and vacuum-dried to give complex **9** (36.7 mg; 93 %) as a light brown solid.

^{1}H NMR (CD_2Cl_2): $\delta=8.39$ (d, $J=8.5$ Hz, 1H, Ar), 8.19 (t, $J=8.5$ Hz, 1H, Ar), 7.58 (d, $J=8.4$ Hz, 1H, Ar), 7.56 (t, $J=8.4$ Hz, 1H, Ar), 7.38 (s, 1H, Ar), 4.52 (dd, $J=10.0$, 4.0 Hz, 1H, Ar=C*H*$_2$), 4.18 (dd, $J=10.1$, 4.0 Hz, 1H, Ar=C*H*$_2$), 3.63 (ddd, $J=19.2$, 12.2, 3.4 Hz, 1H, CH_2P), 3.50 (dd, $J=15.3$, 8.2 Hz, 1H, CH_2P), 2.93 (ddd, $J=19.2$, 12.2, 3.3 Hz, 1H, CH_2P), 2.79 (m, 1H, PC*H*$(CH_3)_2$), 2.63 (dd, $J=15.3$, 8.3 Hz, 1H, CH_2P), 2.74 (m, 3H, PC*H*$(CH_3)_2$), 1.64 (dd, $J=24.5$, 12.2 Hz, 3H, PCH$(CH_3)_2$), 1.55 (dd, $J=24.5$, 12.1 Hz, 3H, PCH$(CH_3)_2$), 1.36 (dd, $J=42.9$, 12.1 Hz, 3H, PCH$(CH_3)_2$), 1.33 (dd, $J=42.8$, 12.1 Hz, 3H, PCH$(CH_3)_2$), 1.29 (dd, $J=42.7$, 12.0 Hz, 3H, PCH$(CH_3)_2$), 1.23 (dd, $J=42.9$, 12.0 Hz, 3H, PCH-$(CH_3)_2$), 0.96 (dd, $J=42.8$, 12.1 Hz, 3H, PCH$(CH_3)_2$), 0.88 ppm (dd, $J=42.8$, 12.1 Hz, 3H, PCH$(CH_3)_2$); ^{13}C{^{1}H} NMR (CD_2Cl_2): $\delta=154.69$ (s, Ar), 140.21 (s, Ar), 139.08 (s, Ar), 131.98 (d, $J=6.2$ Hz, Ar), 130.28 (s, Ar), 129.80 (s, Ar), 125.77 (s, Ar), 124.45 (s, Ar), 123.48 (s, Ar), 95.50 (d, $J=4.1$ Hz, Ar*C*=CH$_2$), 28.73 (d, $J=22.5$ Hz, ArC=*C*H$_2$), 26.87 (d, $J=20.0$ Hz, P*C*H$(CH_3)_2$), 24.54 (d, $J=17.5$ Hz, CH_2P), 23.78 (d, $J=17.6$ Hz, P*C*H$(CH_3)_2$), 20.49 (d, $J=17.5$ Hz, CH_2P), 19.14 (s, PCH$(CH_3)_2$), 18.78 (s, PCH$(CH_3)_2$), 18.43 (s, PCH$(CH_3)_2$), 18.32 (s, PCH$(CH_3)_2$), 16.44 (brs, PCH$(CH_3)_2$), 16.42 ppm (broad s, PCH$(CH_3)_2$). The assignment of the ^{13}C{^{1}H} NMR signals was confirmed by ^{13}C DEPT, HMQC, HSQC, and COSY experiments. ^{31}P{^{1}H} NMR ([D$_8$]THF): $\delta=21.76$ (dd, left part of an AX system, $^2J_{P,P}=412.1$, $^1J_{Rh,P}=96.1$ Hz), −13.96 ppm (dd, right part of an AX system, $^2J_{P,P}=499.5$, $^1J_{Rh,P}=110.8$ Hz); elemental analysis calcd (%) for $C_{25}H_{39}BF_4IP_2Rh$: C 41.81, H 5.47; found: C 41.93, H 5.58.

Preparation of [{C$_{10}$H$_5$(CHP*i*Pr$_2$)(CH$_2$P*i*Pr$_2$)(CH$_2$)}RhI] (10): An equimolar amount of $KOC(CH_3)_3$ (4.7 mg; 0.042 mmol) was added to a THF solution (8 mL) of **9** (30 mg, 0.042 mmol) and the solution was stirred for 15 min. The sparingly soluble complex **9** dissolved immediately after addition of the base. The solvent was removed under reduced pressure and complex **10** was extracted with benzene. 25.2 mg (0.040 mmol, 95 % yield) of **10** was obtained as a yellow-brown crystalline solid.

^{1}H NMR (C_6D_6): $\delta=7.46$ (d, $J=7.7$ Hz, 1H, Ar), 7.11 (m, 2H, Ar), 7.06 (d, $J=7.7$ Hz, 1H, Ar), 6.09 (brs, 1H, Ar), 5.99 (brs, C=CHP), 3.11 (dt, $^1J_{Rh,H}=60.2$, $^2J_{P,H}=4.1$ Hz, ArC=C*H*$_2$), 2.62 (m, 1H, PC*H*$(CH_3)_2$), 2.53 (m, 1H, PC*H*$(CH_3)_2$), 2.28 (brd, 1H, $^2J_{P,H}=16.5$ Hz, CH_2P), 2.03 (m, 1H, PC*H*$(CH_3)_2$), 1.98 (brd, 1H, $^2J_{P,H}=16.6$ Hz, CH_2P), 1.43 (m, 3H, P*CH*-$(CH_3)_2$), 1.41 (m, 3H, PCH$(CH_3)_2$), 1.29 (m, 3H, PCH$(CH_3)_2$), 1.21 (m, 6H, PCH$(CH_3)_2$), 1.02 (m, 3H, PCH$(CH_3)_2$)), 0.94 ppm (m, 6H, PCH-$(CH_3)_2$)); ^{13}C{^{1}H} NMR (C_6D_6): $\delta=167.76$ (dd, $J=9.3$, $J=8.0$ Hz, *C*=CHP), 145.80 (dd, $J=4.2$, $J=2.3$ Hz, C=*C*CH$_2$P), 135.12 (s, Ar), 131.60 (s, Ar), 128.86 (s, Ar), 127.00 (s, Ar), 126.75 (s, Ar), 124.35 (s, Ar), 116.94 (dd, $J=6.5$, 5.7 Hz, C=*C*H), 110.68 ($^1J_{P,C}=20.6$, $^2J_{Rh,C}=12.6$ Hz, C=*C*HP), 79.76 (dt, $J_{Rh,C}=13.2$, $J_{Rh,C}=5.6$ Hz, *C*=CH$_2$), 50.14 (dt, $^2J_{Rh,C}=16.1$ Hz, $^3J_{P,C}=2.2$ Hz, C=*C*H$_2$), 27.10 (2 overlapping dd, P*C*H$(CH_3)_2$), 26.34 (dd, $J=10.3$, 3.2 Hz, CH_2P), 25.21 (dd, $J=10.4$, 6.6 Hz, P*C*H$(CH_3)_2$), 24.38 (vt, $J=9.6$ Hz, P*C*H$(CH_3)_2$), 20.80 (s, PCH$(CH_3)_2$), 20.13 (s, PCH$(CH_3)_2$), 19.65 (s, PCH$(CH_3)_2$), 19.33 (s, PCH$(CH_3)_2$), 17.96 (s, PCH$(CH_3)_2$), 17.93 (s, PCH$(CH_3)_2$), 17.60 ppm (s, PCH$(CH_3)_2$). The assignment of the ^{13}C{^{1}H} NMR signals was confirmed by ^{13}C DEPT, HMQC, HSQC, and COSY experiments. ^{31}P{^{1}H} NMR (C_6D_6): $\delta=40.91$ (d (AB), $^1J_{Rh,P}=118.2$ Hz), 40.78 ppm (d (AB), $^1J_{Rh,P}=116.5$ Hz); elemental analysis calcd (%) for $C_{25}H_{38}IP_2Rh$: C 47.64, H 6.08; found: C 47.86, H 6.23.

CCDC-637691, CCDC-637692, and CCDC-637693 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.

Acknowledgements

This work was supported by the Swiss National Science Foundation (SNSF), the University of Zurich, the Israel Science Foundation (ISF), the Minerva Foundation and the Helen and Martin Kimmel Center for Molecular Design. D.M. is the holder of the Israel Matz Professorial Chair.

[1] a) M. Gozin, M. Aizenberg, S.-Y. Liou, A. Weisman, Y. Ben-David, D. Milstein, *Nature* **1994**, *370*, 42; b) M. E. van der Boom, H.-B. Kraatz, Y. Ben-David, D. Milstein, *Chem. Commun.* **1996**, 2167; c) M. E. van der Boom, H.-B. Kraatz, L. Hassner, Y. Ben-David, D. Milstein, *Organometallics* **1999**, *18*, 3873; d) S.-Y. Liou, M. E. van der Boom, D. Milstein, *Chem. Commun.* **1998**, 687. Reviews including C–C activation and methylene transfer: e) B. Rybtchinski, D. Milstein, *Angew. Chem. Angew Chem.* **1999**, *111*, 918; *Angew. Chem. Int. Ed.* **1999**, *38*, 871; f) M. E. van der Boom, D. Milstein, *Chem. Rev.* **2003**, *103*, 1759; g) B. Rybtchinski, D. Milstein in *ACS Symposium Series, Vol. 885* (Eds.: K. I. Goldberg, A. S. Goldman), **2004**, pp. 70–85.

[2] a) R. Cohen, M. E. van der Boom, L. J. W. Shimon, H. Rozenberg, D. Milstein, *J. Am. Chem. Soc.* **2000**, *122*, 7723; b) R. Cohen, J. M. L. Martin, D. Milstein, *Organometallics* **2004**, *23*, 2336.

[3] C. M. Frech, Y. Ben-David, L. Weiner, D. Milstein, *J. Am. Chem. Soc.* **2006**, *128*, 7128.

[4] a) T. A. K. Al-Allaf, *J. Organomet. Chem.* **1999**, *590*, 25; b) C. Müller, U. Schubert, *Chem. Ber.* **1991**, *124*, 2181; c) C. Stader, B. Wrackmeyer, *J. Organomet. Chem.* **1985**, *295*, C11; d) R. D. Adams, B. Captain, L. Zhu, *Organometallics* **2006**, *25*, 2049; e) T. Matsubara, *Organometallics* **2003**, *22*, 4286; f) D. Kruber, K. Merzweiler, C. Wagner, H. Weichmann, *J. Organomet. Chem.* **1999**, *572*, 117; g) U. Schubert, S. Grubert, U. Schulz, S. Mock, *Organometallics* **1992**, *11*,

3163; h) C. Muller, U. Schubert, *Chem. Ber.* **1991**, *124*, 2181; i) G. Butler, C. Eaborn, A. Pidcock, *J. Organomet. Chem.* **1978**, *144*, C23.

[5] For examples of methyl-transfer reactions with $Sn(CH_3)_4$ as methyl source, see: a) R. F. Heck, *J. Am. Chem. Soc.* **1968**, *90*, 1133; b) X. C. J.-J. Li, X.-S. Hao, C. E. Goodhue, J.-Q. Yu, *J. Am. Chem. Soc.* **2006**, *128*, 78.

[6] a) S. M. Hawkins, P. B. Hitchcock, M. F. Lappert, *J. Chem. Soc. Chem. Commun.* **1985**, 1592; b) D. M.-T. Chan, T. B. Marder, *Angew. Chem.* **1988**, *100*, 436; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 442; ; c) S. G. Bott, J. C. Machell, D. M. P. Mingos, M. J. Watson, *J. Chem. Soc. Dalton Trans.* **1991**, 859; d) M. Veith, L. Stahl, V. Hoch, *Inorg. Chem.* **1989**, *28*, 3278; e) V. Garcia, M. A. Garralda, E. Pinilla, *J. Organomet. Chem.* **1997**, *545*, 93; f) V. Garcia, M. A. Garralda, R. Hernandez, M. A. Monge, E. Pinilla, *J. Organomet. Chem.* **1994**, *476*, 41; g) V. Circu, M. A. Fernandes, L. Carlton, *Inorg. Chem.* **2002**, *41*, 3859; h) V. Garcia, M. A. Garralda, R. Hernandez, M. A. Monge, E. Pinilla, *J. Organomet. Chem.* **1994**, *476*, 41; i) M. A. Esteruelas, F. J. Lahoz, E. Onate, L. A. Oro, L. Rodriguez, *Organometallics* **1996**, *15*, 3670; j) H. Werner, O. Gevert, P. Haquette, *Organometallics* **1997**, *16*, 803; k) L. Carlton, R. Weber, D. C. Levendis, *Inorg. Chem.* **1998**, *37*, 1264; l) N. Mezailles, P. Rosa, L. Ricard, F. Mathey, P. Le Floch, *Organometallics* **2000**, *19*, 2941; m) M. A. Garralda, E. Pinilla, M. A. Monge, *J. Organomet. Chem.* **1992**, *427*, 193; n) M. Bikarani, M. A. Garralda, L. Ibarlucea, E. Pinilla, *J. Organomet. Chem.* **1995**, *489*, 93.

[7] a) D. Canseco-Gonzalez, V. Gomez-Benitez, O. Baldovino-Pantaleon, S. Hernandez-Ortega, D. Morales-Morales, *J. Organomet. Chem.* **2004**, *689*, 174; b) A. L. Balch, H. Hope, F. E. Wood, *J. Am. Chem. Soc.* **1985**, *107*, 6936; c) R. D. Adams, B. Captain, J. L. Smith, Jr., M. B. Hall, C. L. Beddie, C. Webster, *Eur. J. Inorg. Chem.* **2004**, *43*, 7576; d) M. Lutz, C. Galka, M. Haukka, T. A. Pakkanen, L. H. Gade, *Eur. J. Inorg. Chem.* **2002**, 1968; e) T. Marx, L. Wesemann, S. Dehnen, *Z. Anorg. Allg. Chem.* **2001**, *627*, 1146; f) M. A. Garralda, E. Pinilla, M. A. Monge, *J. Organomet. Chem.* **1992**, *427*, 193; g) M. Bikarani, M. A. Garralda, L. Ibarlucea, E. Pinilla, *J. Organomet. Chem.* **1995**, *489*, 93.

[8] a) S. Licoccia, R. Paolesse, T. Boschi, G. Bandoli, A. Dolmella, *Acta Crystallogr. Sect. B Acta Crystallogr. Sect. A* **1995**, *51*, 833; b) J.-M. Barbe, G. Morata, E. Espinosa, R. Guilard, *J. Porphyrins Phthalocyanines* **2003**, *7*, 120.

[9] C. M. Frech, D. Milstein, *J. Am. Chem. Soc.* **2006**, *128*, 12434.

[10] a) M. Gandelman, L. J. W. Shimon, D. Milstein, *Chem. Eur. J.* **2003**, *9*, 4295; b) R. Cohen, M. E. van der Boom, L. J. W. Shimon, H. Rozenberg, D. Milstein, *J. Am. Chem. Soc.* **2000**, *122*, 7725.

[11] R. Cohen, B. Rybtchinski, M. Gandelman, H. Rozenberg, J. M. L. Martin, D. Milstein, *J. Am. Chem. Soc.* **2003**, *125*, 6532.

[12] Treatment of **4a** with [diazo(phenyl)methyl]trimethylstannane did not lead to further transformations, and this supports the involvement of a methyl-migration step to the aromatic unit in the transformation of **1a** into **3a**.

[13] Complex **7** was obtained by reaction of complex **6** with $AgBF_4$. See Experimental Section for details.

[14] A. Vigalok, B. Rybtchinski, L. J. W. Shimon, Y. Ben-David, D. Milstein, *Organometallics* **1999**, *18*, 895.

[15] Pincer-type C–C agostic complexes: a) A. Vigalok, L. J. W. Shimon, D. Milstein, *J. Am. Chem. Soc.* **1998**, *120*, 477; b) M. E. van der Boom, Y. Ben-David, D. Milstein, *J. Am. Chem. Soc.* **1999**, *121*, 6652; c) A. Vigalok, D. Milstein, *Organometallics* **2000**, *19*, 2341; d) R. M. Gauvin, H. Rozenberg, L. J. W. Shimon, Y. Ben-David, D. Milstein, *Chem. Eur. J.* **2007**, *13*, 1382; e) A. Vigalok, D. Milstein, *Acc. Chem. Res.* **2001**, *34*, 798.

[16] Arenium NCN-type pincer complexes: a) D. M. Grove, G. van Koten, J. N. Louwen, J. G. Noltes, A. L. Spek, H. J. C. Ubbels, *J. Am. Chem. Soc.* **1982**, *104*, 6609; b) J. Terheijden, G. van Koten, I. C. Vinke, A. L. Spek, *J. Am. Chem. Soc.* **1985**, *107*, 2891.

[17] For catalytic transformation of benzene into toluene by methanol over zeolites, see: a) W. Hölderich, M. Hesse, F. Näumann, *Angew. Chem.* **1988**, *100*, 232; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 226; ; b) A. Corma, *Chem. Rev.* **1997**, *97*, 2373.

[18] L. A. Errede, J. H. Hoyt, *J. Am. Chem. Soc.* **1960**, *82*, 436.

[19] a) W. H. Hersh, R. G. Bergman, *J. Am. Chem. Soc.* **1981**, *103*, 6992; b) B. F. G. Johnson, J. Lewis, D. J. Thompson, *Tetrahedron Lett.* **1974**, *43*, 3789; c) W. R. Roth, J. D. Meier, *Tetrahedron Lett.* **1967**, *22*, 2053.

[20] M. Gandelman, L. Konstantinovski, H. Rozenberg, D. Milstein, *Chem. Eur. J.* **2003**, *9*, 2595.

Received: February 26, 2007
Published online: July 3, 2007

