Two Alternative Routes for the Migratory Insertion of a Carbene Ligand into a C−H Bond

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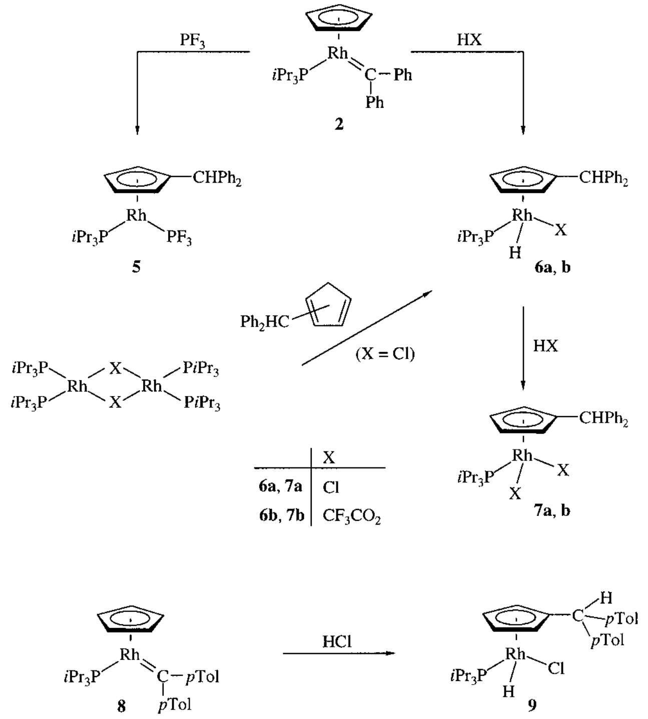
*Summary: Reaction of [(η^5-C_5H_5)Rh(=CPh_2)(PiPr$_3$)] (**2**) with either PF_3 or HX (X = Cl, CF_3CO_2) leads to a migratory insertion of the carbene ligand into one of the C−H bonds of the cyclopentadienyl ring. The X-ray crystal structures of [(η^5-$C_5H_4CHPh_2$)Rh(PF_3)(PiPr$_3$)] (**5**) and [(η^5-$C_5H_4CHPh_2$)RhCl_2(PiPr$_3$)] (**7a**) have been determined.*

It is well-known that transition-metal carbene complexes readily undergo C−C coupling reactions not only with alkenes (olefin metathesis) and alkynes (Dötz reaction) but also with CO and other C-nucleophiles.[1] During attempts to study the reactivity of the half-sandwich-type compounds [(η^5-C_5H_5)Rh(=CPh_2)(Sb*i*Pr$_3$)] (**1**) and the corresponding triisopropylphosphine derivative **2** (Scheme 1), which were prepared from the square-planar precursors *trans*-[RhCl(=CPh_2)L_2] and NaC_5H_5,[2] we observed that the course of the reaction of **1** and **2** with CO and isocyanides depends critically on the ligand L of the starting material. While the stibane complex **1** on treatment with CO or CN*t*Bu yields the mixed (carbene)(carbonyl) and (carbene)(isocyanide)rhodium compounds [(η^5-C_5H_5)Rh(=CPh_2)(CX)] (**3a**, X = O; **3b**, X = N*t*Bu), the phosphine derivative **2** affords the non-carbene-containing products [(η^5-C_5H_5)Rh(P*i*Pr$_3$)(CX)] (**4a**,**b**) together with diphenylketene or the corresponding ketenimine.[2,3] We have now found that PF_3, despite the similarity of its σ-donor/π-acceptor capabilities with those of CO, reacts with **2** in a completely different way, leading to an unprecedented migratory insertion of the CPh_2 unit into an sp^2 C−H bond.

Scheme 1



	X
6a, 7a	Cl
6b, 7b	CF$_3$CO$_2$

Treatment of compound **2** with PF_3 in benzene at room temperature leads to a smooth change of color from blue to orange and finally to the isolation of the orange air- and moisture-sensitive solid **5** in moderate yield.[4] The most characteristic spectroscopic features of **5** are the signals for the C*H*Ph$_2$ proton at δ 4.79 in the ^{1}H NMR and the two resonances for the phosphorus nuclei of the PF_3 and P*i*Pr$_3$ ligands at δ 119.4 and 79.0 in the ^{31}P NMR spectrum.[5] Both ^{31}P NMR signals show strong Rh−P couplings of 446 and 221 Hz, respectively. The X-ray crystal structure analysis of **5** (Figure 1)[6]

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[1] (a) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissl, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Weinheim, Germany, **1983**. (b) Dötz, K. H. *Angew. Chem.* **1984**, *96*, 573−594; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587−608. (c) Lappert, M. F. *J. Organomet. Chem.* **1988**, *358*, 185−214. (d) Erker, G. *Angew. Chem.* **1989**, *101*, 411−426; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 397−412. (e) Grubbs, R. H.; Tumas, W. *Science* **1989**, *243*, 907−915. (f) Feldmann, J.; Schrock, R. R. *Prog. Inorg. Chem.* **1991**, *39*, 1−74. (g) Hegedus, L. S. *Organische Synthese mit Übergangsmetallen*; VCH Verlag: Weinheim, Germany, 1995.

[2] (a) Schwab, P.; Mahr, N.; Wolf, J.; Werner, H. *Angew. Chem.* **1993**, *105*, 1498−1500; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1480−1482. (b) Schwab, P. Dissertation, Universität Würzburg, 1994.

[3] Review: Werner, H. *J. Organomet. Chem.* **1995**, *500*, 331−336.

[4] The preparation of **5** is as follows. A slow stream of PF_3 was passed through a solution of **2** (100 mg, 0.20 mmol) in 20 mL of benzene for 20 min at room temperature. After the solution was stirred for another 20 min, the solvent was removed and the oily residue dissolved in 3 mL of pentane. Column chromatography on Al_2O_3 (neutral, activity grade V) gave upon elution with pentane an orange fraction which was brought to dryness in vacuo. The solid was recrystallized from pentane (−78 °C) to afford orange crystals: yield 48 mg (41%).

[5] Selected spectroscopic data for **5**, **6a**, **6b**, and **7a** (omitting the ^{1}H and ^{13}C NMR data for isopropyl and phenyl groups) are as follows. **5**: ^{1}H NMR (200 MHz, C_6D_6) δ 5.1 (m, 4H, C_5H_4), 4.8 (m, 1H, C*H*Ph$_2$); ^{31}P NMR (81.0 MHz, C_6D_6) δ 119.4 (ddq, ^1J(PF) = 849.3, ^1J(RhP) = 446.3, ^2J(PP) = 77.6 Hz, PF_3), 79.0 (dd, ^1J(RhP) = 221.0, ^2J(PP) = 77.6 Hz, P*i*Pr$_3$). **6a**: ^{1}H NMR (400 MHz, C_6D_6) δ 5.72 (d, ^3J(RhH) = 2.9 Hz, 1H, C*H*Ph$_2$), 5.1, 4.4 (both m, 2H each, C_5H_4), −12.21 (dd, ^1J(RhH) = 35.1, ^2J(PH) = 13.8 Hz, 1H, RhH); ^{13}C NMR (100.6 MHz, C_6D_6) δ 124.5 (dd, ^1J(RhC) = 3.0, ^2J(PC) = 5.0 Hz, *C*CHPh$_2$), 92.7 (s, C_5H_4), 85.9 (dd, ^1J(RhC) = 3.6, ^2J(PC) = 8.9 Hz, C_5H_4), 81.0 (d, ^2J(PC) = 5.8 Hz, C_5H_4), 75.4 (d, ^2J(PC) = 6.4 Hz, C_5H_4), 48.9 (s, *C*HPh$_2$); ^{31}P NMR (162.0 MHz, C_6D_6) δ 81.7 (d, ^1J(RhP) = 145.0 Hz). **6b**: ^{1}H NMR (200 MHz, C_6D_6) δ 5.4 (s, br, 1H, C*H*Ph$_2$), 4.6 (m, 4H, C_5H_4), −11.04 (dd, ^1J(RhH) = 35.5, ^2J(PH) = 13.4 Hz, 1H, RhH); ^{31}P NMR (81.0 MHz, C_6D_6) δ 80.5 (d, ^1J(RhP) = 144.1 Hz). **7a**: ^{1}H NMR (400 MHz, C_6D_6) δ 6.03 (d, ^3J(RhH) = 6.6 Hz, 1H, C*H*Ph$_2$), 4.84, 4.65 (both d, ^2J(RhH) = 2.0 Hz, 2H each, C_5H_4); ^{13}C NMR (100.6 MHz, C_6D_6) δ 123.1 (s, br, *C*CHPh$_2$), 89.8, 79.7 (both s, br, C_5H_4), 47.7 (s, br, *C*HPh$_2$); ^{31}P NMR (162.0 MHz, C_6D_6) δ 59.4 (d, ^1J(RhP) = 135.1 Hz).

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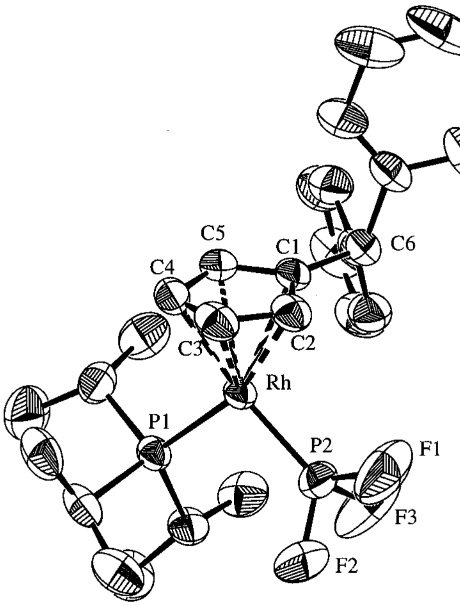

Figure 1. ORTEP diagram of compound **5**. Selected bond distances (Å) and angles (deg): Rh−P1, 2.275(3); Rh−P2, 2.082(4); Rh−C1, 2.307(5); Rh−C2, 2.220(5); Rh−C3, 2.294(6); Rh−C4, 2.258(5); Rh−C5, 2.304(6); C1−C6, 1.518(5); P1−Rh−P2, 97.0(1); F1−P2−Rh, 117.6(2); F2−P2−Rh, 125.6(2); F3−P2−Rh, 125.1(2); C1−C6−C20, 112.3(3); C1−C6−C30, 112.3(4); C20−C6−C30, 112.3(3).

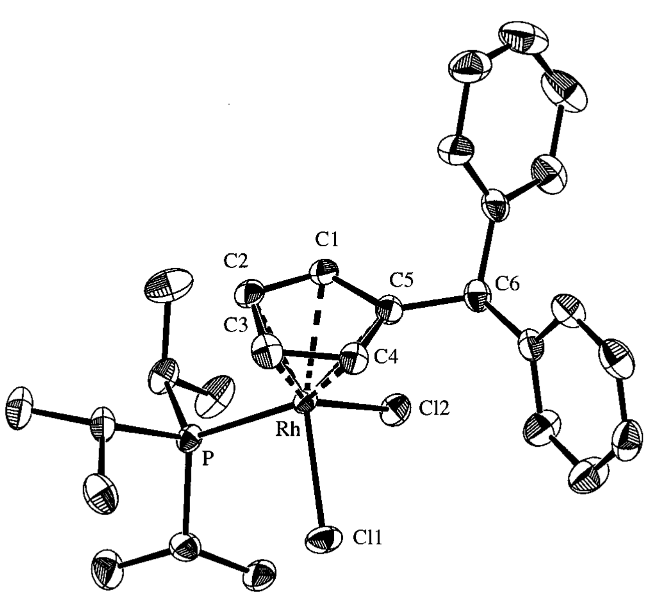

Figure 2. ORTEP diagram of compound **7a**. Selected bond distances (Å) and angles (deg): Rh−P, 2.328(1); Rh−Cl1, 2.382(1); Rh−Cl2, 2.400(1); Rh−C1, 2.155(4); Rh−C2, 2.167(4); Rh−C3, 2.135(4); Rh−C4, 2.237(4); Rh−C5, 2.226(4); P−Rh−Cl1, 89.79(4); P−Rh−Cl2, 95.72(4); Cl1−Rh−Cl2, 94.30(4); C5−C6−C20, 111.1(4); C5−C6−C30, 110.2(4); C20−C6−C30, 115.9(4).

reveals that the rhodium has a somewhat distorted trigonal coordination sphere if the midpoint of the cyclopentadienyl ring is taken as one coordination site. The Rh-PF_3 bond is significantly shorter than the Rh-P*i*Pr_3 distance, which illustrates the distinct difference in the π-acceptor strength of the two phosphine ligands.

Most unexpectedly, the migratory insertion of the CPh_2 moiety of **2** into a C-H bond of the five-membered ring can also be initiated by HCl or CF_3CO_2H. If a solution of **2** in acetone is treated with a solution of HCl in benzene or with an equimolar amount of CF_3CO_2H at room temperature, a spontaneous change of color from blue to orange occurs and, upon addition of pentane, orange crystals of **6a** or **6b** are isolated in virtually quantitative yield.[7] An alternative preparative procedure for **6a** consists of the reaction of the labile dimer [RhCl(P*i*Pr_3)$_2$]$_2$[8] with $C_5H_5CHPh_2$, which also affords the chloro hydrido complex almost quantitatively. In agreement with the structural proposal, the ^1H NMR spectra of both **6a** and **6b** display a hydride resonance at high field (δ −12.21 and −11.04), which due to Rh−H and P−H coupling is split into a doublet of doublets.[5] The (di-*p*-tolylcarbene)rhodium compound **8** behaves similarly to **2** and on treatment with HCl gives the corresponding ring-substituted product **9** in good yield.

Attack of HX at the Rh−H bond of **6a** and **6b** leads to the displacement of the hydride ligand and to the formation of the dichloro and bis(trifluoracetato) complexes **7a** and **7b**, respectively. In contrast to **6a** and **6b**, both substitution products are significantly more stable and for a short period of time can even be handled in air. The ORTEP plot (Figure 2)[9] showing the molecular structure of **7a** illustrates the piano-stool configuration of the molecule. While the Rh−C(ring) distances in **7a** are somewhat shorter than in **5**, in agreement with the oxidation state +III of the metal in **7a** compared with +I in **5**, the Rh-P*i*Pr_3 bond length in **7a** is slightly longer than in **5**. The P-Rh-Cl and Cl-Rh-Cl bond angles in **7a** are near to 90°, thus reflecting the pseudooctahedral geometry.

In order to elucidate the mechanism of the migratory insertion process leading to **6a**, a labeling experiment was carried out. Treatment of **2**-d_5, which was prepared from *trans*-[RhCl(=CPh_2)(P*i*Pr_3)$_2$] and TlC_5D_5 in THF, with an equimolar amount of HCl in benzene affords exclusively the compound **6a**-d_5 (Scheme 2). We assume that in the initial step addition of HCl to the Rh=CPh_2

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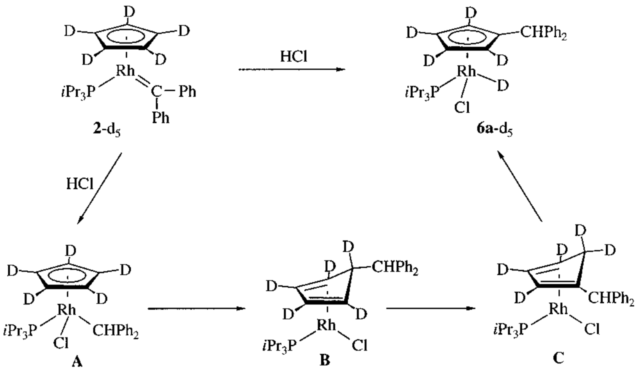
(6) Crystal data for **5**: crystals from pentane (5 °C); crystal size 0.55 × 0.30 × 0.25 mm; monoclinic, space group *C*2/*c* (No. 15), *Z* = 8; *a* = 34.48(9) Å, *b* = 8.96(2) Å, *c* = 17.67(3) Å, β = 96.82(9)°, *V* = 5427(3) Å^3, d_{calcd} = 1.426 g cm^{-3}; 2θ(max) = 48° (Mo Kα, λ = 0.709 30 Å, graphite monochromator, ω/θ scan, Zr filter with factor 16.4, T = 293(2) K); 4548 reflections scanned, 4162 unique (*R*(int) = 0.0136), 3736 observed ($I > 2\ \sigma(I)$), Lorentz−polarization and empirical absorption corrections (ψ scans, minimum transmission 80.0%); Patterson method (SHELXS-86), 408 parameters, reflex/parameter ratio 10.2; R1 = 0.0364, wR2 = 0.0922; residual electron density 1.058/−0.425 eÅ^{-3}.

(7) The preparation of **6a** is as follows. A solution of **2** (119 mg, 0.24 mmol) in 5 mL of acetone was treated dropwise with 482 μL of a 0.5 M solution of HCl in benzene at room temperature. After the solution was stirred for 5 min and then concentrated to ca. 0.5 mL in vacuo, pentane was added, which led to the precipitation of an orange solid. This was washed twice with 5 mL portions of pentane and dried: yield 116 mg (91%). Compound **6b** was prepared analogously, using **2** (54 mg, 0.11 mmol) and CF_3CO_2H (8.35 μL, 0.11 mmol) as starting materials: orange solid, yield 62 mg (93%).

(8) Werner, H.; Wolf, J.; Höhn, A. *J. Organomet. Chem.* **1985**, *287*, 395−407.

(9) Crystal data for **7a**: crystals from acetone (−20 °C); crystal size 0.40 × 0.25 × 0.08 mm; monoclinic, space group *Cc* (No. 9); *a* = 8.865(2) Å, *b* = 23.214(2) Å, *c* = 13.172(3) Å, β = 106.85(1)°, *V* = 2594(1) Å^3, d_{calcd} = 1.447 g cm^{-3}; 2θ(max) = 58° (Mo Kα, λ = 0.710 73 Å, graphite monochromator, ω/θ scan, Zr filter with factor 16.4, *T* = 173(2) K); 3624 reflections scanned, 3624 unique (*R*(int) = 0.0000), 3488 observed ($I > 2\sigma(I)$), Lorentz-polarization and empirical absorption corrections (ψ scans, minimum transmission 89.48%); direct methods (SHELXS-86), 290 parameters, reflex/parameter ratio 12.5; R1 = 0.0284, wR2 = 0.0675; residual electron density +0.673/−0.813 e Å^{-3}.

Scheme 2



bond takes place, similarly as in the reaction of **3a** with HCl.[2] The intermediate **A** then reacts by migration of the $CHPh_2$ fragment to the C_5D_5 ligand to afford the substituted cyclopentadienerhodium(I) species **B**. A subsequent 1,2-D-shift along the five-membered ring generates the intermediate **C**, which by deuterium transfer from the sp^3 carbon atom of the C_5 moiety to the metal would give the final product. An isotopomer of **C** of composition $[RhCl(\eta^4\text{-}C_5H_5CHPh_2)(P\textit{i}Pr_3)]$ is probably also involved in the reaction of $[RhCl(P\textit{i}Pr_3)_2]_2$ with $C_5H_5CHPh_2$ to yield **6a** (see Scheme 1). With regard to intermediate **B**, we note that quite recently Hughes et al. reported the isolation of coordinatively saturated $(\eta^4\text{-}C_5H_5R)Rh$ complexes (R = $CF_2CF_2CF_3$, $CF(CF_3)_2$), which were prepared from $[(\eta^5\text{-}C_5H_5)Rh(PMe_3)_2]$ and fluoroalkyl iodides.[10]

As far as the formation of **5** from **2** and PF_3 is concerned, a different mechanism probably operates. Since it is known that ligand displacement reactions of cyclopentadienylrhodium complexes $[(\eta^5\text{-}C_5H_5)RhL_2]$ with Lewis bases L′ follow second-order kinetics,[11] a reasonable assumption is that from **2** and PF_3 initially a labile 1:1 adduct is formed. A slippage of the carbene ligand to the temporarily generated $\eta^3\text{-}C_5H_5$ unit, followed by insertion into a C-H bond, could then afford the isolated compound **5**. It is conceivable that the repulsion between the sterically demanding P*i*Pr$_3$ ligand, the CPh_2 unit, and the incoming PF_3 donor in the postulated 1:1 adduct facilitates the migration of the carbene ligand to the five-membered ring.

Although various half-sandwich-type complexes $[(\eta^5\text{-}C_5H_5)M(=CRR')L_n]$, in particular those with $n = 2$ and M = Mn or Re, are known,[1,12] to the best of our knowledge it has never been observed that they react with either electrophilic or nucleophilic substrates by migratory insertion of the carbene ligand into a C−H bond of the ring. The closest analogy to the formation of $C_5H_4CHPh_2$ from C_5H_5 and CPh_2 we are aware of goes back to the work of Kirmse et al., which illustrates that arylcarbenes, generated from the corresponding diazo compounds, undergo an *intra*molecular insertion into the *ortho* C−H bond of a connected phenyl ring.[13] Currently we are trying to find out whether electrophiles other than HCl or CF_3CO_2H and nucleophiles other than PF_3 can also initiate an insertion of a carbene ligand into a C−H bond, possibly not only into that of C_5H_5 but also into that of other π-bonded ring systems.

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Supporting Information Available: Fully labeled diagrams and tables of crystallographic data, data collection, and solution and refinement details, positional and thermal parameters, and bond distances and angles for both **5** and **7a** (12 pages). Ordering information is given on any current masthead page.

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(10) Hughes, R. P.; Husebo, T. L.; Rheingold, A. L.; Liable-Sands, L. M.; Yap, G. P. A. *Organometallics* **1997**, *16*, 5−7.

(11) Basolo, F. *Inorg. Chim. Acta* **1985**, *100*, 33−39.

(12) (a) Herrmann, W. A. *Chem. Ber.* **1975**, *108*, 486−499. (b) Casey, C. P.; Vosejpka, P. C.; Askham, F. R. *J. Am. Chem. Soc.* **1990**, *112*, 3713−3715.

(13) Guth, M.; Kirmse, W. *Acta Chem. Scand.* **1992**, *46*, 606−613.