Easy and Reversible C−H Activation of a Substituted Benzene

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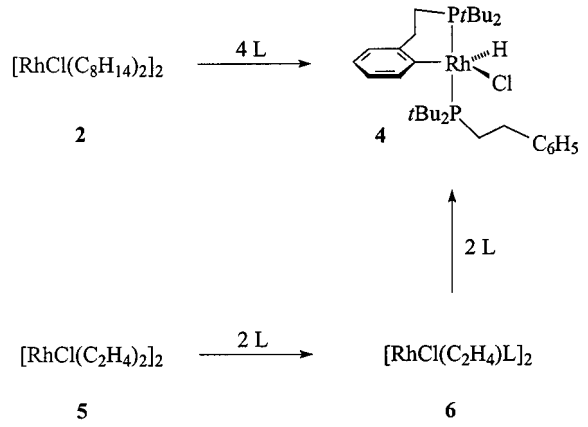
Summary: The reaction of either $[RhCl(C_8H_{14})_2]_2$ *or* $[RhCl(C_2H_4)_2]_2$ *with* $tBu_2PCH_2CH_2C_6H_5$ (***3***) *affords at room temperature the five-coordinate arylhydridorhodium(III) complex* ***4****, the molecular structure of which has been determined by X-ray crystallography. The C−H metalation is completely reversible, as is shown by the formation of trans-*$[RhCl(CO)(\mathbf{3})_2]$ *from* ***4*** *and CO. Compound* ***4*** *also reacts with* $PhC{\equiv}CH$, H_2, *and* $AgPF_6$ *to give products* ***7***−***9*** *containing the intact phosphine ligand* ***3****.*

The bis(triisopropylphosphine)rhodium(I) complex $[RhCl(P\mathit{i}Pr_3)_2]_2$ (**1**) is probably one of the most reactive rhodium(I) compounds known to date.[1] It reacts not only with H_2, O_2, N_2, CO, and C_2H_4 but also with terminal alkynes to give stepwise π-alkyne, alkynyl hydrido, and vinylidene rhodium derivatives.[2] While **1** is easily accessible from $[RhCl(C_8H_{14})_2]_2$ (**2**) and 4 equiv of $P\mathit{i}Pr_3$,[1b] the analogous complex $[RhCl(P\mathit{t}Bu_3)_2]_2$ cannot be obtained by a similar route.[3] Since we knew that even small differences in the size of the phosphine ligand can change the stability and reactivity of compounds of the general composition $[RhCl(PR_3)_2]_n$ significantly, we considered instead of $P\mathit{t}Bu_3$ the somewhat less bulky derivative $\mathit{t}Bu_2PCH_2CH_2C_6H_5$ (**3**), which was recently prepared in our laboratory,[4] as a candidate to isolate an analogue of **1**.

Under conditions similar to those used for the preparation of **1**, the reaction of **2** with a 4-fold excess of **3** in pentane at room temperature resulted in the formation of the yellow solid **4**, the analytical composition of which corresponds to that of $[RhCl(\mathbf{3})_2]$.[5] However, the ^1H and ^{31}P NMR spectra of **4** (see Scheme 1) reveal that the product is not a rhodium(I) complex containing two intact phosphine ligands but an arylhydridorhodium(III) species. The most typical features are the high-field resonance in the ^1H NMR spectrum at δ −18.11 for the RhH proton and the ^{13}C NMR signal at δ 146.9 for the metalated carbon atom of the six-membered ring.[6] Due to $^{103}Rh-^1H$ (or $^{103}Rh-^{13}C$) and 2-fold $^{31}P-^1H$ (or $^{31}P-^{13}C$) couplings, each of these signals is split into a doublet of doublets of doublets. Moreover, the two doublets of doublets at δ 65.7 and 43.0 in the ^{31}P NMR spectrum of **4** confirm that the two phosphorus atoms are chemically nonequivalent.

Scheme 1[a]



[a] L = $\mathit{t}Bu_2PCH_2CH_2C_6H_5$ (**3**).

The result of the X-ray crystal structure analysis of **4** is shown in Figure 1.[7] It reveals that during the reaction of **2** and **3** a C−H metalation of one of the phenyl groups has indeed taken place. The coordination geometry around the rhodium center corresponds to a distorted trigonal bipyramid with the two phosphorus atoms in the apical positions. The Rh−P distances are slightly longer than in the related, more symmetrical chelate complex $[RhHCl\{\mathit{t}Bu_2PCH_2C_6H_3CH_2P\mathit{t}Bu_2\text{-}\kappa^3(P,C,P)\}]$ (**A**) obtained from $RhCl_3{\cdot}3H_2O$ and 1,3-bis[(*tert*-butylphosphino)methyl]benzene in $\mathit{i}PrOH/H_2O$ under reflux.[8] In contrast, the Rh−C31 bond length of **4** (1.967(5) Å) is slightly shorter than in **A** (1.999(7) Å) and in the Milstein compound $[Rh(CH_3)Cl\{\mathit{t}Bu_2PCH_2\text{-}C_6H\text{-}3,5\text{-}(CH_3)_2CH_2P\mathit{t}Bu_2\text{-}\kappa^3(P,C,P)\}]$ (2.02(2) Å).[9] The P−Rh−P axis of **4** is significantly bent (160.18(5)°), which could be due both to steric hindrance between the phosphine substituents and the strain of the six-

(1) (a) Preparation in situ: Busetto, C.; D'Alfonso, A.; Maspero, F.; Perego, G.; Zazzetta, A. *J. Chem. Soc., Dalton Trans.* **1977**, 1828−1834. (b) Isolation: Werner, H.; Wolf, J.; Höhn, A. *J. Organomet. Chem.* **1985**, *287*, 395−407. (c) X-ray crystal structure analysis: Binger, P.; Haas, J.; Glaser, G.; Goddard, R.; Krüger, C. *Chem. Ber.* **1994**, *127*, 1927−1929.

(2) Reviews: (a) Werner, H. *Nachr. Chem. Technol. Lab.* **1992**, *40*, 435−444. (b) Werner, H. *J. Organomet. Chem.* **1994**, *475*, 45−55.

(3) (a) Wolf, J. Unpublished results. (b) The preparation of "crude" $[RhCl(P\mathit{t}Bu_3)_2]$ has been reported,[3c] but the authors as well as we could not obtain a pure sample of the given composition. (c) Yoshida, T.; Otsuka, S.; Matsumoto, M.; Nakatsu, K. *Inorg. Chim. Acta* **1978**, *29*, L257-L259.

(4) Werner, H.; Canepa, G.; Ilg, K.; Wolf, J. *Organometallics* **2000**, *19*, 4756−4766.

(5) The preparation of **4** is as follows. A suspension of **2** (1.51 g, 2.11 mmol) in 10 mL of pentane was treated under continuous stirring with **3** (2.11 g, 8.43 mmol). A yellow solution was formed, which was evaporated to dryness in vacuo. After the oily residue was layered with 10 mL of pentane and stored for 8 h, a yellow solid was obtained. It was separated from the mother liquor, washed five times with 4 mL portions of pentane, and dried. The pentane washings were combined and then evaporated to ca. 3 mL in vacuo. The concentrated solution was stirred for 3 h at room temperature, which gave a second fraction of the product: yield 2.29 g (85%); mp 97 °C dec. Alternatively, compound **4** could also be prepared from **5** (303 mg, 0.78 mmol) and **3** (780 mg, 3.12 mmol): yield 808 mg (81%).

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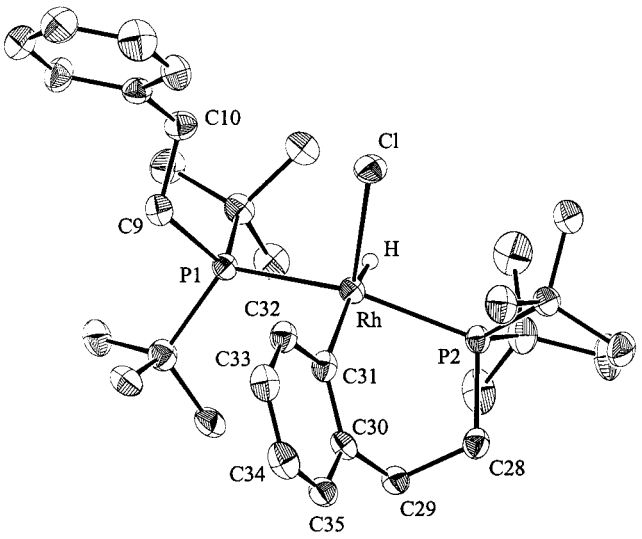
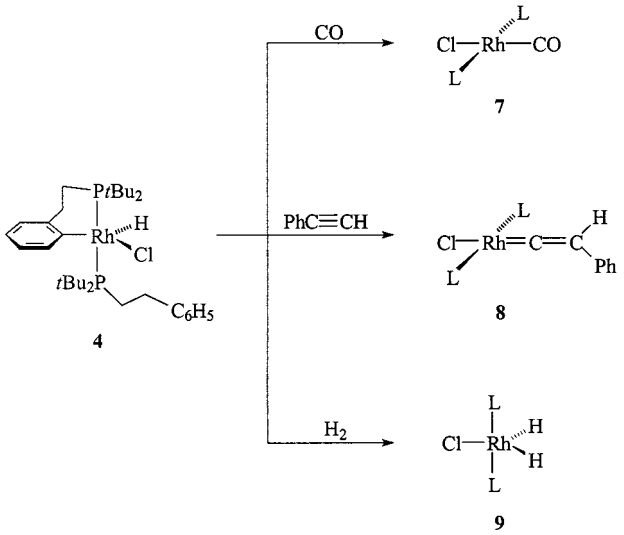


Figure 1. ORTEP diagram of **4**. The metal-bonded hydrogen is not exactly located; the other hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Rh−P1, 2.3746(14); Rh−P2, 2.3344(13); Rh−Cl, 2.4687(13); Rh−C31, 1.967(5); P1−Rh−P2, 160.18(5); P1−Rh−Cl, 98.01(5); P1−Rh−C31, 96.89(13); P2−Rh−Cl, 99.74-(5); P2−Rh−C31, 87.54(13); Cl−Rh−C31, 103.40(14); Rh−P2−C28, 110.62(15); P2−C28−C29, 113.8(3); C28−C29−C30, 109.0(4); C29−C30−C31, 121.1(4); C30−C31−Rh, 126.8(4).

membered chelate ring. We note that besides **2** also the dimeric bis(ethene)rhodium(I) derivative **5** can be used as starting material for the preparation of **4**. If **5** is treated with 2 instead of 4 equiv of **3**, the intermediate $[RhCl(C_2H_4)(\mathbf{3})]_2$ (**6**) is detected by ^{1}H and ^{31}P NMR spectroscopy,[6] which reacts with excess **3** to give **4**. Compound **6** is accessible in analytically pure form from **4** and **5** in the molar ratio of 2:1 in pentane and isolated as a yellow solid in 86% yield.

Scheme 2[a]



[a] L = tBu$_2$PCH$_2$CH$_2$C$_6$H$_5$ (**3**).

If a suspension of **4** in pentane is stirred at room temperature under an atmosphere of carbon monoxide, a gradual change of color occurs and after ca. 30 s a light yellow solid precipitates. The spectroscopic data of this compound indicate that instead of the anticipated six-coordinate 1:1 adduct of **4** and CO the square-planar carbonyl complex **7** is formed (Scheme 2). The practically quantitative yield of **7** from the rhodium(III) precursor **4** illustrates that the insertion of the metal into one of the ring C−H bonds of the phosphine **3** is completely reversible. With regard to the structure of **7**, the noteworthy aspect is that in solution at low temperature at least three rotamers can be observed, the existence of which is probably due to the steric bulk of the *tert*-butyl groups.[10]

The reaction of **4** with phenylacetylene proceeds similarly to that with CO. Treatment of a solution of **4** with PhC≡CH in toluene at room temperature affords, after chromatographic workup (Al_2O_3, neutral, activity grade III, hexane) and recrystallization of the oily residue from pentane, a blue-violet solid whose elemental analysis corresponds to **8** (Scheme 2). Typical spectroscopic data of **8** are the signal for the Rh=C=CH proton at δ 1.36 in the ^{1}H NMR and two low-field resonances for the vinylidene carbon atoms at δ 290.6 and 116.2 in the ^{13}C NMR spectrum.[6] Monitoring the reaction of **4** with PhC≡CH in toluene-d_8 in an NMR tube suggests that an alkynylhydridorhodium(III) species is formed as an intermediate, which rearranges smoothly to the final product.

The C−H metalation of **3** leading to **4** is also reversed upon stirring a suspension of **4** in pentane at room

(6) Selected spectroscopic data for **4** and **6**−**10** are as follows. **4**: ^{1}H NMR (C_6D_6, 600 MHz) δ −18.11 (ddd, J(RhH) = 22.9, J(PH) = 15.9 and 9.5 Hz, 1H, RhH); ^{13}C NMR (C_6D_6, 150.9 MHz) δ 146.9 (ddd, J(RhC) = 34.2, J(PC) = 12.0 and 5.8 Hz, RhC), 144.3 (d, J(PC) = 8.6 Hz, RhC*C*CH$_2$), 42.2 (dd, J(RhC) = 5.7, J(PC) = 5.2 Hz, RhCC*C*H$_2$), 19.1 (d, J(PC) = 29.3 Hz, PCH$_2$); ^{31}P NMR (C_6D_6, 162.0 MHz) δ 65.7 (dd, J(RhP) = 120.4, J(PP) = 366.2 Hz, tBu$_2$P of chelate ring), 43.0 (dd, J(RhP) = 110.2, J(PP) = 366.2 Hz, tBu$_2$P of monodentate ligand). **6**: ^{1}H NMR (C_6D_6, 200 MHz) δ 3.56, 3.06 (both m, 4H each, C$_2$H$_4$), 2.84 (m, 4H, PCH$_2$C*H*$_2$), 1.56 (m, 4H, PCH$_2$); ^{13}C NMR (C_6D_6, 50.3 MHz) δ 44.7 (d, J(RhC) = 14.9 Hz, C$_2$H$_4$), 32.9 (s, PCH$_2$*C*H$_2$), 22.4 (d, J(PC) = 15.6 Hz, PCH$_2$); ^{31}P NMR (C_6D_6, 81.0 MHz) δ 65.8 (d, J(RhP) = 185.7 Hz). **7**: IR (KBr) ν(CO) 1937 cm^{-1}; ^{31}P NMR (toluene-d_8, 162.0 MHz, 223 K) δ 58.9 (dd, J(RhP) = 118.7, J(PP) = 312.0 Hz, tBu$_2$P of rotamer I), 58.1 (d, J(RhP) = 120.4 Hz, tBu$_2$P of rotamer II), 47.4 (dd, J(RhP) = 123.8, J(PP) = 312.0 Hz, tBu$_2$P of rotamer I), 46.6 (d, J(RhP) = 120.4 Hz, tBu$_2$P of rotamer III). **8**: ^{1}H NMR (C_6D_6, 300 MHz, 313 K) δ 3.23 (m, 4H, PCH$_2$C*H*$_2$), 2.53 (m, 4H, PCH$_2$), 1.36 (dt, J(PH) = 3.2, J(RhH) = 1.1 Hz, Rh=C=CH); ^{13}C NMR (C_6D_6, 75.4 MHz, 313 K) δ 290.6 (m, Rh=C), 116.2 (m, Rh=C=*C*), 33.3 (s, PCH$_2$*C*H$_2$), 23.1 (vt, N = 15.3 Hz, PCH$_2$); ^{31}P NMR (C_6D_6, 81.0 MHz, 308 K) δ 52.5 (d, J(RhP) = 137.3 Hz). **9**: IR (KBr) ν(RhH) 2138 cm^{-1}; ^{1}H NMR (C_6D_6, 400 MHz) δ 3.25 (m, 4H, PCH$_2$C*H*$_2$), 2.31 (m, 4H, PCH$_2$), −22.63 (dt, J(RhH) = 26.3, J(PH) = 14.7 Hz, 2H, RhH$_2$); ^{13}C NMR (C_6D_6, 100.6 MHz) δ 34.4 (s, PCH$_2$*C*H$_2$), 26.2 (vt, N = 15.3 Hz, PCH$_2$); ^{31}P NMR (C_6D_6, 162.0 MHz) δ 65.6 (d, J(RhP) = 115.3 Hz). **10**: ^{1}H NMR (acetone-d_6, 200 MHz) δ 3.20, 2.71, 2.53, 2.33 (all m, 2H each, PCH$_2$ and PCH$_2$C*H*$_2$); ^{13}C NMR (acetone-d_6, 50.3 MHz) δ 142.5 (d, J(PC) = 9.3 Hz, *ipso*-C of C$_6$H$_5$ uncoord), 111.5 (ddd, J(RhC) = 3.7, J(PC) = 9.2 and 4.7 Hz, *ipso*-C of C$_6$H$_5$ coord), 40.8 (dd, J(PC) = 25.0 and 2.0 Hz, PC*H*$_2$CH$_2$-η^6-C$_6$H$_5$), 30.6 (s, PCH$_2$*C*H$_2$-η^6-C$_6$H$_5$); ^{31}P NMR (acetone-d_6, 81.0 MHz) δ 81.5 (dd, J(RhP) = 211.1, J(PP) = 15.3 Hz, tBu$_2$P of chelate ligand), 68.6 (dd, J(RhP) = 203.4, J(PP) = 15.3 Hz, tBu$_2$P of monodentate ligand), −142.7 (sept, J(PF) = 707.0 Hz, PF$_6^-$).

(7) Crystal data for **4**: crystals from acetone at room temperature; crystal size 0.20 × 0.20 × 0.10 mm; monoclinic, space group $P2_1/n$ (No. 14), Z = 4; a = 8.8783(18) Å, b = 17.190(3) Å, c = 21.126(4) Å, β = 98.92(3)°, V = 3185.2(11) Å^3, d_{calcd} = 1.333 g cm^{-3}; 2θ(max) = 52.74° (Mo Kα, λ = 0.710 73 Å, graphite monochromator, ψ scan, T = 173(2) K; 32 867 reflections scanned, 6512 unique, 4075 observed ($I > 2\sigma(I)$), direct methods (SHELXS-97), 340 parameters, reflex/parameter ratio 19.15; R1 = 0.0450, wR2 = 0.1026; residual electron density +0.897/−1.259 e Å^{-3}.

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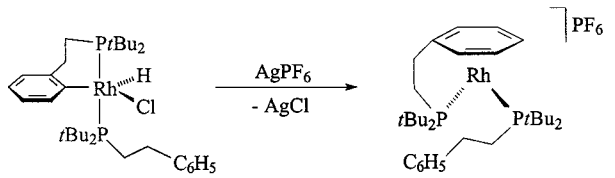
Scheme 3



4 **10**

temperature in the presence of hydrogen. Under these conditions, the dihydrido complex **9** (pale yellow solid) is formed, the ^{1}H NMR spectrum of which displays a hydride signal at δ −22.63. It is somewhat shifted upfield compared with that in **4**. From the appearance of a single resonance in the high-field region and the splitting of this signal into a doublet of triplets, we conclude that both the hydrido and the phosphine ligands are stereochemically equivalent. Since it is known that the related compound $[RhH_2Cl(PiPr_3)_2]$ has a trigonal-bipyramidal structure,[11] a similar coordination geometry of **9** is most likely.

An attempt to abstract the chloro ligand of **4** with $AgPF_6$ and generate the cationic 14-electron rhodium(III) species $[RhH\{C_6H_4$-2-$CH_2CH_2PtBu_2$-$\kappa^2(C,P)\}(\mathbf{3})]^+$ led instead to the isolation of the half-sandwich-type compound **10** (Scheme 3).[12] The inequivalence of the two $PtBu_2$ units is confirmed by the appearance of two signals in the ^{31}P NMR spectrum at δ 81.5 and 68.6, which due to ^{31}P−^{103}Rh and ^{31}P−^{31}P couplings are split into doublets of doublets. A related complex with *i*Pr instead of *t*Bu substituents at the phosphorus atoms has recently been prepared from the labile bis(acetone)-rhodium(I) precursor $[Rh(C_8H_{14})_2(acetone)_2]PF_6$ and 2 equiv of $C_6H_5CH_2CH_2PiPr_2$.[4]

In conclusion, we have shown that the reaction of **2**, frequently used as a starting material for the preparation of rhodium(I) complexes $[RhCl(PR_3)_2]_n$ (n = 1, 2),[1b,13] with the sterically demanding phosphine **3** leads to the arylhydridorhodium(III) compound **4** by C−H activation of one of the six-membered rings. The most noteworthy features are (i) that the insertion of the metal into the C−H bond proceeds under unusually mild conditions, as in the reaction of the cationic species $[Rh(C_8H_{14})_2(solv)_n]^+$ with the benzylic phosphine $tBu_2PCH_2C_6H_2Me_3$,[14] and (ii) that in the presence of CO, phenylacetylene, or H_2 this insertion process is completely reversible. The five-coordinate rhodium(III) complex **4** also provides access to the cationic half-sandwich-type compound **10**, which could not be obtained by established routes.[4,15]

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Supporting Information Available: A table giving the elemental analysis data for compounds **4** and **6**−**10** as well as tables of crystallographic data, data collection, and solution and refinement details, positional and thermal parameters, and bond distances and angles for **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0010159

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(12) The preparation of **10** is as follows. A solution of **4** (136 mg, 0.21 mmol) in 6 mL of toluene was treated at −60 °C with a solution of $AgPF_6$ (54 mg, 0.21 mmol) in 2 mL of ether. When the solution was warmed to room temperature, a change of color from yellow to brown occurred and a white solid precipitated. The solution was filtered, the filtrate was evaporated in vacuo, and the residue was extracted twice with 4 mL of CH_2Cl_2. The combined extracts were brought to dryness in vacuo, the residue was dissolved in 1 mL of acetone, and 6 mL of ether was added with stirring. A pale brown solid was obtained, which was separated from the mother liquor, washed twice with 5 mL each of ether and pentane, and dried: yield 138 mg (88%); mp 107 °C dec.

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