General Method for Stereoselective Coupling of an Alkyl, Aryl, or Vinyl Group with a Vinylidene Unit at a Transition-Metal Center

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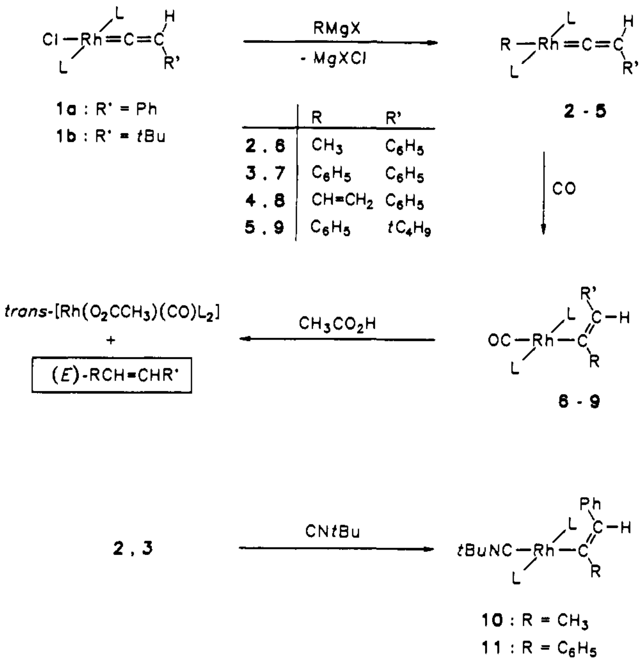
Although the formation of vinylidene transition-metal compounds as intermediates in various C–C coupling reactions has been postulated,[1] examples for an intramolecular migration of a metal-bound hydrocarbyl group to a vinylidene ligand are still very rare.[2,3] Following our recent work on the synthesis of *trans*-[Rh(C≡CR)(=C=CHR)(P-*i*-Pr$_3$)$_2$] from [(η^3-C$_3$H$_5$)Rh(P-*i*-Pr$_3$)$_2$] and 2 equiv of 1-alkynes HC≡CR,[4] we describe a general route to the corresponding alkyl-, aryl-, and vinyl(vinylidene)metal derivatives *trans*-[Rh(R)(=C=CHR′)(P-*i*-Pr$_3$)$_2$] and the CO- or isocyanide-initiated coupling of the ligands R and C=CHR′ to give substituted vinyl- and butadienylrhodium(I) complexes.

Compound **1a**, which was prepared from [RhCl(P-*i*-Pr$_3$)$_2$] and phenylacetylene,[5] reacted with an equimolar amount of CH$_3$MgI in ether–toluene at –30 °C to give *trans*-[Rh(CH$_3$)(=C=CHPh)(P-*i*-Pr$_3$)$_2$] (**2**) as light-violet crystals in 87% yield. In contrast to the starting material **1a**, the methyl derivative **2** is only stable as a solid and slowly decomposes in solution. The phenyl(vinylidene) and vinyl(vinylidene) complexes **3** and **4** (Scheme I) were obtained in the same way, using C$_6$H$_5$MgBr in ether and CH$_2$=CHMgBr in ether–THF as substrates.[6,7] In order to prove that even a very bulky and also electron-donating substituent R′ at the β-C atom of the vinylidene ligand can be tolerated, compound **5** was prepared from **1b**[8] and C$_6$H$_5$MgBr. It was also isolated in 87% yield. The most characteristic feature of the spectroscopic data of **2–5** is the low-field position of the vinylidene α-carbon signal in the ^{13}C NMR spectrum, which appears at δ 290–300 (in C$_6$D$_6$) and shows a strong Rh–C coupling (ca. 47 Hz).

Scheme I[a]



[a] L = P-*i*-Pr$_3$.

The new alkyl-, aryl- and vinyl(vinylidene) complexes are highly reactive toward carbon monoxide and *tert*-butyl isocyanide. When CO was passed for 10 s through a solution of **2–5** in toluene or pentane at –30 °C, a characteristic change of color from violet to yellow took place, and after recrystallization from acetone (–30 °C), yellow crystals of **6–9** were isolated in almost quantitative yield.[9] According to the NMR spectra, there is no doubt that the *Z* isomers having the substituents R and R′ in a *trans* orientation at the C=C double bond were formed exclusively.[10] The reactions of **2** and **3** with CN-*t*-Bu occurred selectively as well and gave compounds **10** and **11** as yellow crystalline solids in 70–80% yield. With regard to the mechanism of the migratory insertion process we assume that initially CO or CN-*t*-Bu adds to the rhodium atom, thus generating a five-coordinate intermediate, which after migration of the group R on the α-carbon of the vinylidene ligand transforms to the isolated product. The importance of steric factors probably explains why the attack of R occurs only at that side of the molecule which is opposite to R′ (Ph or *t*-Bu).

The stereochemical assignment shown in Scheme I was confirmed by the X-ray crystal structure analysis of **8**.[11] The results are summarized in Figure 1 along with the principal bond lengths and interbond angles. The Rh–C1 distance of 2.088(5) Å is significantly longer than in *trans*-[RhCl(=C=CHMe)(P-

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(2) (a) Beevor, R. G.; Freeman, M. J.; Green, M.; Morton, C. E.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1985**, 68–69. (b) Höhn, A.; Werner, H. *J. Organomet. Chem.* **1990**, *382*, 255–272. (c) Selnau, H. E.; Merola, J. S. *J. Am. Chem. Soc.* **1991**, *113*, 4008–4009.

(3) Fryzuk, M. D.; Huang, L.; McManus, N. T.; Paglia, P.; Rettig, S. J.; White, G. S. *Organometallics* **1992**, *11*, 2979–2990.

(4) Schäfer, M.; Wolf, J.; Werner, H. *J. Chem. Soc., Chem. Commun.* **1991**, 1341–1343.

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(6) A typical procedure is as follows: A solution of **1a** (180 mg, 0.32 mmol) in 3 mL of ether was treated at –30 °C with 0.33 mL of a 0.1 M solution of C$_6$H$_5$MgBr in ether. The solution was warmed to room temperature, and after it was stirred for 1 h, the solvent was removed in vacuo. The residue was extracted three times with 10 mL of pentane, and the extract was concentrated to 5 mL and cooled to –78 °C. After 12 h, light-violet crystals of **3** were formed, which were separated and repeatedly washed with 2 mL of acetone (–30 °C): yield 153 mg (79%); mp 110 °C dec. For **2** (mp 75 °C dec), **4** (mp 76 °C dec), and **5** (mp 73 °C dec), the yield was 87%, 81%, and 85%, respectively.

(7) A complete set of the analytical and spectroscopic data for the complexes **2–11** has been provided as supplementary material.

(8) Werner, H.; Brekau, U. *Z. Naturforsch., B* **1989**, *44*, 1438–1446.

(9) A typical procedure for the preparation of **6–9** is as follows: A slow stream of CO was passed for 10 s through a solution of **3** (115 mg, 0.19 mmol) in 3 mL of toluene at –30 °C. After the solution was stirred for 5 min, the solvent was removed in vacuo. The residue was dissolved in 2 mL of acetone, and the solution was cooled to –30 °C. After 24 h, yellow crystals of **7** precipitated, which were separated and repeatedly washed with 2 mL of acetone (–30 °C): yield 112 mg (93%); mp 106 °C. For **6** (mp 148 °C), **8** (mp 96 °C), and **9** (mp 89 °C), the yield was 87%, 92%, and 91%, respectively.

(10) Selected spectroscopic data are as follows. **6**: IR (KBr) ν(CO) 1925 cm^{-1}; ^{1}H NMR (C$_6$D$_6$, 200 MHz) δ 7.22 (m, =C*H*R′), 2.40 (s, RhCC*H*$_3$); ^{13}C{^{1}H} NMR (C$_6$D$_6$, 50.3 MHz) δ 195.85 (dt, $J_{\text{Rh-C}} = 53.2$, $J_{\text{P-C}} = 15.3$ Hz, *C*O), 182.28 (dt, $J_{\text{Rh-C}} = 28.7$, $J_{\text{P-C}} = 14.3$ Hz, Rh*C*CH$_3$), 135.62 (t, $J_{\text{P-C}} = 3.7$ Hz, RhC(R)=*C*HR′), 33.37 (dt, $J_{\text{Rh-C}} = 2.4$, $J_{\text{P-C}} = 2.4$ Hz, RhC*C*H$_3$). **7**: IR (KBr) ν(CO) 1930 cm^{-1}; ^{1}H NMR (C$_6$D$_6$, 200 MHz) δ 7.64 (dt, $J_{\text{Rh-H}} = 2.0$, $J_{\text{P-H}} = 2.0$ Hz, =C*H*R′); ^{13}C{^{1}H} NMR (C$_6$D$_6$, 50.3 MHz) δ 195.48 (dt, $J_{\text{Rh-C}} = 54.7$, $J_{\text{P-C}} = 15.9$ Hz, *C*O), 181.40 (dt, $J_{\text{Rh-C}} = 29.4$, $J_{\text{P-C}} = 14.0$ Hz, Rh*C*R), 137.32 (t, $J_{\text{P-C}} = 4.5$ Hz, RhC(R)=*C*HR′). **8**: IR (KBr) ν(CO) 1930 cm^{-1}; ^{1}H NMR (C$_6$D$_6$, 200 MHz) δ 7.49 (m, =C*H*R′), 5.39 (dd, $J_{\text{H1-H2}} = 16.7$, $J_{\text{H2-H3}} = 3.1$ Hz, CH^1=C*H*^{2}H^3), 4.88 (dd, $J_{\text{H1-H3}} = 10.0$, $J_{\text{H2-H3}} = 3.1$ Hz, CH^1=CH^2*H*^{3}), signal of H^1 covered by the multiplet of the C$_6$H$_5$ protons; ^{13}C{^{1}H} NMR (C$_6$D$_6$, 50.3 MHz) δ 195.66 (dt, $J_{\text{Rh-C}} = 54.0$, $J_{\text{P-C}} = 15.2$ Hz, *C*O), 181.62 (dt, $J_{\text{Rh-C}} = 28.2$, $J_{\text{P-C}} = 13.9$ Hz, Rh*C*R), 152.72 (s, RhC(*C*H=CH$_2$)), 136.53 (t, $J_{\text{P-C}} = 3.7$ Hz, RhC(R)=*C*HR′), 108.60 (s, RhC(CH=*C*H$_2$)). **9**: IR (KBr) ν(CO) 1930 cm^{-1}; ^{1}H NMR (C$_6$D$_6$, 200 MHz) δ 6.63 (dt, $J_{\text{Rh-H}} = 1.8$, $J_{\text{P-H}} = 2.0$ Hz, =C*H*R′), 1.51 (s, CC*H*$_3$); ^{13}C{^{1}H} NMR (C$_6$D$_6$, 50.3 MHz) δ 195.56 (dt, $J_{\text{Rh-C}} = 54.3$, $J_{\text{P-C}} = 16.9$ Hz, *C*O), 162.57 (dt, $J_{\text{Rh-C}} = 30.3$, $J_{\text{P-C}} = 13.4$ Hz, Rh*C*R), 147.41 (t, $J_{\text{P-C}} = 3.9$ Hz, RhC(R)=*C*HR′), 35.12 (dt, $J_{\text{Rh-C}} = 1.2$, $J_{\text{P-C}} = 1.2$ Hz, *C*CH$_3$), 31.80 (t, $J_{\text{P-C}} = 1.6$ Hz, C*C*H$_3$).

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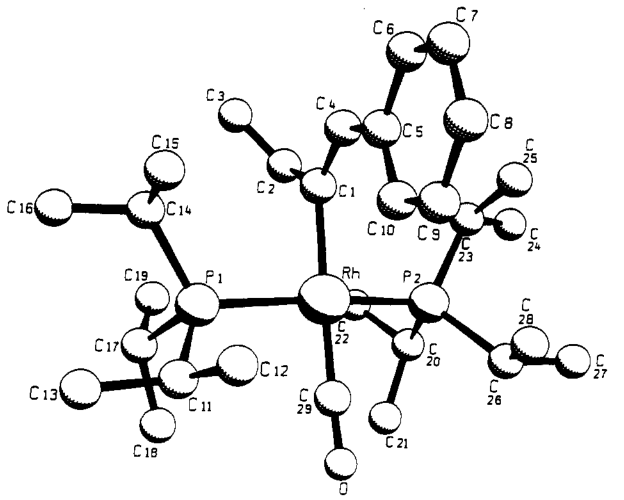

Figure 1. SCHAKAL diagram for the molecular structure of complex **8**. Principal bond lengths (Å) and interbond angles (deg): Rh–C1 2.088(5), Rh–P1 2.338(1), Rh–P2 2.340(1), Rh–C29 1.815(6), C29–O 1.171(6), C1–C2 1.470(6), C2–C3 1.299(7), C1–C4 1.356(6), P1–Rh–P2 167.73(4), P1–Rh–C1 91.4(1), P2–Rh–C1 91.5(1), P1–Rh–C29 88.8(2), P2–Rh–C29 89.1(2), C1–Rh–C29 175.7(2), Rh–C29–O 175.2(5), Rh–C1–C2 116.5(4), Rh–C1–C4 128.1(4), C1–C2–C3 127.0(6), C1–C4–C5 129.7(5), C2–C1–C4 115.4(5).

i-$Pr_3)_2]$ (1.775 Å)[5] and corresponds to that found for Rh–C(C_6H_5) in $[(C_5Me_5)Rh(C_6H_5)(PPh_3)Br]$ (2.08(1) Å).[12] The C4–C1–C2–C3 torsional angle is 46.95° and quite similar to that determined recently for the cobalt-substituted 1,3-butadiene $[Co\{C(CH{=}CH_2){=}CH_2\}(NC_5H_4\text{-}4\text{-}t\text{-}Bu)(DMG)_2]$ (54.5°).[13]

The cleavage of the vinyl– or dienyl–rhodium bond in **6**–**9** by acetic acid in benzene proceeded slowly at room temperature and gave, besides *trans*-$[Rh(O_2CCH_3)(CO)(P\text{-}i\text{-}Pr_3)_2]$,[14] exclusively the *E* olefins RCH=CHR′ and PhCH=CHCH=CH_2, respectively. With complex **9** as a substrate, preliminary experiments (performed in an NMR tube) indicate that with stronger acids the Rh–C cleavage reaction takes a different course and possibly leads to the 1,3-disubstituted allene PhCH=C=$CHCH_3$.

In conclusion, the results described in this paper illustrate that a stereoselective coupling of an alkyl, aryl, or vinyl group with a vinylidene unit can occur in the coordination sphere of rhodium(I). This migratory insertion process can be considered as a counterpart to the coupling of a hydrocarbyl moiety with a carbene ligand, for which several examples are known.[15] The closest analogy to the synthesis of **6**–**11** we are aware of consists of the reaction of the iridium(III) vinylidene $[IrCH_3({=}C{=}CH_2)I\{\eta^3\text{-}N(SiMe_2CH_2PPh_2)_2\}]$ with acetonitrile, which gave the vinyl complex $[Ir\{C(CH_3){=}CH_2\}(NCMe)I\{\eta^3\text{-}N(SiMe_2CH_2PPh_2)_2\}]$ in 33% isolated yield.[3]

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Supplementary Material Available: Analytical and spectroscopic data for complexes **2**–**11** and details of the X-ray analysis, tables of bond lengths and bond angles, and atomic positional and anisotropic thermal parameters for **8** (15 pages); observed and calculated structure factors for **8** (19 pages). Ordering information is given on any current masthead page.

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(11) Crystal data for **8**: monoclinic, $P2_1/n$, a = 10.640(3) Å, b = 20.070(3) Å, c = 15.476(5) Å, β = 108.05(1)°, V = 3142.3 Å^3, Z = 4, D_{calc} = 1.23 g cm^{-3}, T = 293 K, μ(Mo Kα) = 6.5 cm^{-1}. Data were collected on an Enraf-Nonius CAD4 diffractometer using $\omega/2\theta$-scan mode ($2\theta_{max}$ = 48°); of the 4157 reflections measured, 3563 were unique and 2569 had $F_o > 3\sigma(F_o)$; 298 variables were refined to give R = 3.4% and R_w = 3.5% with a reflex-parameter ratio of 8.62 and a residual electron density of +0.37/–0.24 e Å^{-3}.

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