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Communications to the Editor

Novel C−C and C−C−P Coupling Reactions Using an Allenylidenerhodium Complex as a Precursor

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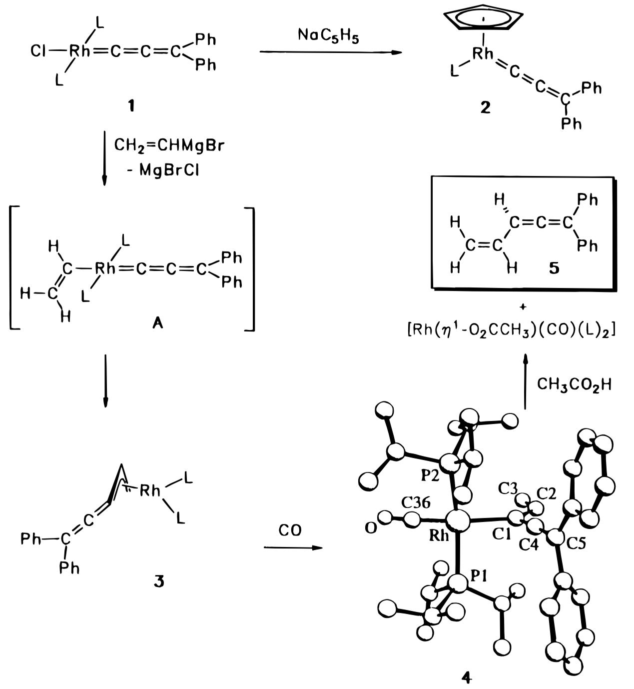
After we had recently shown that the Selegue method for the preparation of transition-metal allenylidenes[1] can also be applied to the synthesis of the square-planar rhodium complexes *trans*-$[\mathrm{RhCl}(=\mathrm{C}=\mathrm{C}=\mathrm{CRR'})(\mathrm{P}i\mathrm{Pr}_3)_2]$,[2] we started to investigate the reactivity of these molecules. In this paper we describe two types of C−C and C−C−P coupling reactions involving the rhodium-bonded allenylidene unit which finally lead to vinylallenes and a highly unsaturated Wittig-type ylide.

Compound **1**, which was prepared from $[\mathrm{RhCl}(\mathrm{P}i\mathrm{Pr}_3)_2]_2$ and $\mathrm{HC}\equiv\mathrm{CCPh}_2\mathrm{OH}$,[2a] reacted with $\mathrm{NaC}_5\mathrm{H}_5$ in THF at room temperature to give the half-sandwich type complex **2** as a dark-green solid in 62% yield. If, however, instead of sodium cyclopentadienide the vinyl Grignard reagent $\mathrm{CH}_2=\mathrm{CHMgBr}$ (in toluene/THF) was used as the substrate, not only the substitution of chloride by the C-nucleophile but also coupling of the vinyl and the allenylidene ligand occurred. The π-allylic complex **3** (Scheme 1), which forms red air-sensitive crystals, was isolated in 61% yield.[3] With regard to the mechanism of this reaction, we assume that initially a four-coordinate intermediate **A** is generated which rearranges by migratory insertion to give **3**. In this context it should be mentioned that the vinylidene compounds *trans*-$[\mathrm{RhCl}(=\mathrm{C}=\mathrm{CHR})(\mathrm{P}i\mathrm{Pr}_3)_2]$ (R = H, *t*Bu, Ph) react with $\mathrm{CH}_2=\mathrm{CHMgBr}$ to yield the *isolable* products *trans*-$[\mathrm{Rh}(\mathrm{CH}=\mathrm{CH}_2)(=\mathrm{C}=\mathrm{CHR})(\mathrm{P}i\mathrm{Pr}_3)_2]$, which upon heating (45−50 °C, benzene) slowly isomerize to give the π-butadienyl complexes $[\mathrm{Rh}(\eta^3\text{-}C\mathrm{H}_2\mathrm{CH}C=\mathrm{CHR})(\mathrm{P}i\mathrm{Pr}_3)_2]$.[4]

Treatment of a solution of **3** at 10 °C in benzene with CO led to a rapid change of color from red to light-yellow and finally to the isolation of yellow crystals of *trans*-$[\mathrm{Rh}\{\eta^1\text{-}\mathrm{C}(\mathrm{CH}=\mathrm{CH}_2)=\mathrm{C}=\mathrm{CPh}_2\}(\mathrm{CO})(\mathrm{P}i\mathrm{Pr}_3)_2]$ **4** in 65% yield.[5] The addition of CO to the metal center is accompanied by a $\pi-\sigma$ conversion of the C_5 ligand, possibly via an 18-electron intermediate $[\mathrm{Rh}(\eta^3\text{-}C\mathrm{H}_2\mathrm{CH}C=\mathrm{C}=\mathrm{CPh}_2)(\mathrm{CO})(\mathrm{P}i\mathrm{Pr}_3)_2]$. The X-ray crystal structure analysis of **4** reveals a square-planar coordination sphere around rhodium with the two phosphines in a trans disposition.[6] The C1−C4−C5 chain is almost linear (177.5(5)°) with the vinyl carbon atoms C2 and C3 lying in the same plane as Rh, C1, C4, and C5.

Scheme 1[a]



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

The cleavage of the Rh−C σ-bond in **4** by an equimolar amount of acetic acid in benzene at 10 °C proceeded smoothly and gave, besides *trans*-$[\mathrm{Rh}(\eta^1\text{-}\mathrm{O}_2\mathrm{CCH}_3)(\mathrm{CO})(\mathrm{P}i\mathrm{Pr}_3)_2]$,[7] quantitatively the new vinylallene **5**. One characteristic feature of the ^{13}C NMR spectrum of **5**[8] is the low-field signal at δ 210.20 for the central $\mathrm{C}=C=\mathrm{C}$ carbon atom, the position of which is typical for organic allenes.[9]

A second $\mathrm{C}_3 + \mathrm{C}_2 + \mathrm{P}$ coupling reaction with complex **1** is even more exceptional. If a solution of **1** and phenylacetylene in benzene was stirred for 20 h at 10 °C, a gradual change of color from red to bright-red occurred, and, after removal of the solvent, light-red crystals of **6** (Scheme 2) were isolated from $\mathrm{CH}_2\mathrm{Cl}_2$/pentane in practically quantitative yield. Both the elemental analysis and the mass spectrum of **6** indicated that a 1:1 adduct of **1** and the alkyne was formed which according to the ^{31}P NMR spectrum contained two distinctly different P*i*Pr$_3$ groups.[10] As the X-ray structural analysis confirmed,[11] one of

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(1) Selegue, J. P. *Organometallics* **1982**, *1*, 217−218.

(2) (a) Werner, H.; Rappert, T. *Chem. Ber.* **1993**, *126*, 669−678. (b) Werner, H.; Rappert, T.; Wiedemann, R.; Wolf, J.; Mahr, N. *Organometallics* **1994**, *13*, 2721−2727.

(3) Selected spectroscopic data of **3**: ^{1}H NMR ($\mathrm{C}_6\mathrm{D}_6$, 400 MHz) δ 4.79 (dd, $J_{\mathrm{H}^1-\mathrm{H}^3} = 12.1$, $J_{\mathrm{H}^1-\mathrm{H}^2} = 6.8$ Hz, $\mathrm{H}_2\mathrm{CC}H^1\mathrm{C}$), 3.01 (d, $J_{\mathrm{H}^1-\mathrm{H}^2} = 6.8$ Hz, H^2 (syn) of $\mathrm{C}H_2$), 2.45 (dd, $J_{\mathrm{P}^2\text{-}\mathrm{H}^3} = 5.8$, $J_{\mathrm{H}^1-\mathrm{H}^3} = 12.1$ Hz, H^3 (anti) of $\mathrm{C}H_2$); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{C}_6\mathrm{D}_6$, 100.6 MHz) δ 183.11 (s, $\mathrm{C}=C=\mathrm{CPh}_2$), 113.19 (ddd, $J_{\mathrm{Rh-C}} = 54.0$, $J_{\mathrm{P-C}} = 17.1$ and 16.7 Hz, $C=\mathrm{C}=\mathrm{CPh}_2$), 106.89 (m, $\mathrm{H}_2\mathrm{C}C\mathrm{HC}$), 79.74 (s, $C\mathrm{Ph}_2$), 50.32 (m, $C\mathrm{H}_2$).

(4) Wiedemann, R.; Wolf, J.; Werner, H. *Angew. Chem.* **1995**, *107*, 1359−1361. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1244−1246.

(5) Selected spectroscopic data of **4**: IR ($\mathrm{C}_6\mathrm{H}_6$) $\nu(\mathrm{C}\equiv\mathrm{O}) = 1930\ \mathrm{cm}^{-1}$; ^{1}H NMR ($\mathrm{C}_6\mathrm{D}_6$, 200 MHz) δ 6.84 (dd, $J_{\mathrm{H}^1-\mathrm{H}^2} = 17.0$, $J_{\mathrm{H}^1-\mathrm{H}^3} = 9.5$ Hz, $\mathrm{C}H^1=\mathrm{CH}_2$), 5.97 (dd, $J_{\mathrm{H}^1-\mathrm{H}^2} = 17.0$, $J_{\mathrm{H}^2-\mathrm{H}^3} = 3.1$ Hz, H^2 (trans to H^1) of $\mathrm{C}H_2$), 5.11 (dd, $J_{\mathrm{H}^1-\mathrm{H}^3} = 9.5$, $J_{\mathrm{H}^2-\mathrm{H}^3} = 3.1$ Hz, H^3 (cis to H^1) of $\mathrm{C}H_2$); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{C}_6\mathrm{D}_6$, 50.3 MHz) δ 209.92 (t, $J_{\mathrm{P-C}} = 3.2$ Hz, $\mathrm{C}=C=\mathrm{CPh}_2$), 195.12 (dt, $J_{\mathrm{Rh-C}} = 55.8$, $J_{\mathrm{P-C}} = 22.3$ Hz, $\mathrm{Rh}C\mathrm{O}$), 144.45 (s, br, $C\mathrm{H}=\mathrm{CH}_2$), 118.76 (dt, $J_{\mathrm{Rh-C}} = 27.0$, $J_{\mathrm{P-C}} = 11.4$ Hz, $\mathrm{Rh}C$), 117.80 (s, $C\mathrm{H}_2$), 98.37 (s, $C\mathrm{Ph}_2$); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{C}_6\mathrm{D}_6$, 81.0 MHz) δ 47.33 (d, $J_{\mathrm{Rh-P}} = 135.1$ Hz).

(6) Molecular structure of complex **4**. Principal bond lengths (Å) and interbond angles (deg): Rh−C1 2.143(5), Rh−C36 1.814(6), Rh−P1 2.359(1), Rh−P2 2.340(1), C1−C2 1.481(6), C1−C4 1.308(6), C2−C3 1.311(7), C4−C5 1.332(6), C36−O 1.166(8), P1−Rh−P2 164.92(4), C1−Rh−C36 165.8(2), C1−Rh−P1 91.8(1), C1−Rh−P2 93.0(1), P1−Rh−C36 89.1(2), P2−Rh−C36 89.7(2), Rh−C1−C2 116.9(3), Rh−C1−C4 127.0(3), Rh−C36−O 172.6(5), C1−C2−C3 126.2(5), C2−C1−C4 116.0(4), C1−C4−C5 177.5(5).

(7) (a) Ohgomori, Y.; Yoshida, S.; Watanabe, Y. *J. Chem. Soc., Dalton Trans.* **1987**, 2969−2974. (b) Schäfer, M.; Wolf, J.; Werner, H. *J. Organomet. Chem.* **1995**, *476*, 85−91.

(8) Selected spectroscopic data of **5**: $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{C}_6\mathrm{D}_6$, 100.6 MHz) δ 210.2 (s, $\mathrm{C}=C=\mathrm{C}$), 132.54 (s, $C\mathrm{H}=\mathrm{CH}_2$), 117.02 (s, $\mathrm{CH}=C\mathrm{H}_2$), 111.97 (s, $=C\mathrm{Ph}_2$), 97.94 (s, $=C\mathrm{HCH}=\mathrm{CH}_2$).

(9) Munson, J. W. *The Chemistry of Ketenes, Allenes and Related Compounds*; Patai, S., Ed.; Wiley: New York, 1980; Vol. 1, Chapter 5.

(10) Selected spectroscopic data of **6**: ^{1}H NMR ($\mathrm{C}_6\mathrm{D}_6$, 400 MHz) δ 2.36 (dd, $J_{\mathrm{P}^2-\mathrm{H}^1} = 9.6$, $J_{\mathrm{P}^1-\mathrm{H}^1} = 5.6$ Hz, $\mathrm{C}H\mathrm{P}i\mathrm{Pr}_3$); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (CDCl_3, 100.6 MHz) δ 187.49 (s, $\mathrm{C}=C=\mathrm{CPh}_2$), 108.87 (s, $C\mathrm{Ph}_2$), 106.69 (m, $C=\mathrm{C}=\mathrm{CPh}_2$), 71.80 (d, $J_{\mathrm{P-C}} = 6.8$ Hz, $\mathrm{CH}C\mathrm{PhC}$), 20.94 (ddd, $J_{\mathrm{Rh-C}} = 65.8$, $J_{\mathrm{P-C}} = 25.8$ and 10.6 Hz, $C\mathrm{HP}i\mathrm{Pr}_3$); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (CDCl_3, 162.0

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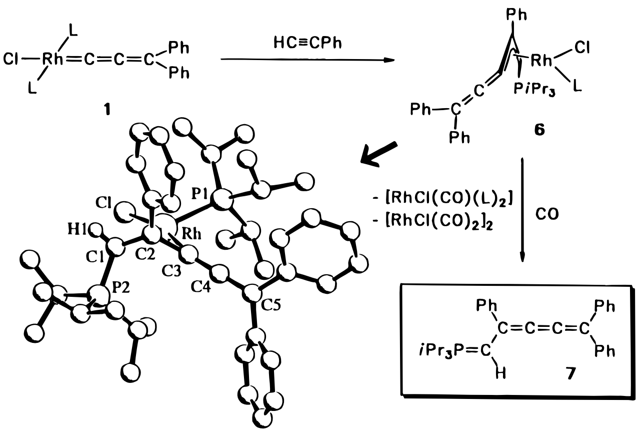
Scheme 2^a



^{a} L = P*i*Pr$_3$.

the phosphines is still coordinated to the metal center while the other is part of a π-bonded unsaturated ylide which is formed from the allenylidene, the alkyne, and the phosphine. The PC$_5$ ligand is coordinated like a π-allyl unit; however, the distances between the rhodium and the carbon atoms C1, C2, and C3 differ by ca. 0.15 Å. The bond length P2−C1 (1.752(3) Å) is significantly shorter than a P−C single bond but quite similar to that of [RhCl{η^3-*anti*-*C*H(P*i*Pr$_3$)*C*(Ph)=*O*}(P*i*Pr$_3$)] (1.799(4) Å)[12] and of metal-substituted ylides.[13] Although the carbon atoms of the =C=CPh$_2$ unit are not coplanar with the allylic fragment, the C3−C4−C5 chain is almost linear (177.3(4)°) with C3−C4 and C4−C5 distances that are comparable to those in the allenylidene complex *trans*-[RhCl{=C=C=C(Ph)Tol}(P*i*Pr$_3$)$_2$] (1.24(1) and 1.37(1) Å)[2b] and in **2** (1.29(2) and 1.39(2) Å).[14]

The free ylide **7**,[15] which to the best of our knowledge is unknown as yet, can be generated on treatment of complex **6** with CO (C$_6$H$_6$, 10 °C, 30 s). The rhodium containing products are *trans*-[RhCl(CO)(P*i*Pr$_3$)$_2$][16] and [RhCl(CO)$_2$]$_2$.[17] Ylide **7** was isolated upon extraction of the product mixture with pentane as a violet solid and characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopic data. The influence of the butatrienyl substituent on the electronic properties of the ylide carbon is reflected by the signal of the P=C*H* proton which appears at δ 3.05 and is shifted ca. 4 ppm downfield compared with the P=C*H*$_2$ resonance of *i*Pr$_3$P=CH$_2$.[18]

In conclusion, the results reported in this paper illustrate that not only carbene-[19] and vinylidenerhodium complexes[20] but also the related allenylidene compounds can be used as starting materials for C−C and even C−C−P coupling reactions. Experiments presently in progress are aimed to find out whether migratory insertion reactions, similar to the key step in the formation of **3**, can also occur with ligands other than vinyl groups.

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Supporting Information Available: Experimental procedures and analytical and spectroscopic data for compounds **2**−**7**, details of the X-ray analysis of **4** and **6**, tables of the bond lengths and bond angles, and atomic positional and anisotropic thermal parameters (26 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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MHz) δ 52.90 (dd, $J_{\text{Rh-P}}$ = 179.6, $J_{\text{P-P}}$ = 14.3 Hz, Rh−*P*^{1}), 39.29 (dd, $J_{\text{Rh-P}}$ = 4.2, $J_{\text{P-P}}$ = 14.3 Hz, C−*P*^{2}); MS (70 eV) *m/z* (%) = 750 (2) [M$^+$].

(11) Molecular structure of complex **6**. Principal bond lengths (Å) and interbond angles (deg): Rh−P1 2.295(1), Rh−C1 2.170(4), Rh−C2 2.046(3), Rh−C3 2.024(3), Rh−Cl 2.388(1), C1−P2 1.752(3), C1−C2 1.455(4), C2−C3 1.429(4), C3−C4 1.276(4), C4−C5 1.327(4), P1−Rh−Cl 94.93(4), P2−C1−C2 126.1(2), C1−C2−C3 116.7(3), C2−C3−C4 144.2(3), C3−C4−C5 177.3(4).

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(15) Selected spectroscopic data of **7**: ^{1}H NMR (C$_6$D$_6$, 400 MHz) δ 3.05 (d, $J_{\text{P-H}}$ = 15.2 Hz, C*H*P*i*Pr$_3$); ^{13}C{^{1}H} NMR (C$_6$D$_6$, 100.6 MHz) δ 45.88 (d, $J_{\text{P-C}}$ = 100.8 Hz, *i*Pr$_3$P=*C*HR); ^{31}P{^{1}H} NMR (C$_6$D$_6$, 162.0 MHz) δ 33.57 (s)

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