A New Rhodium(I) Hexapentaene Complex Prepared from a Precursor Containing a RhC_5 Chain

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Summary: The metallacumulene $[RhCl(=C=C=C=C=CPh_2)(PiPr_3)_2]$ *(**6**) was prepared stepwise from* $[RhCl(PiPr_3)_2]_2$ *(**1**) and* $HC\equiv CC\equiv CCPh_2OSiMe_3$ *via the π-alkyne complex **2**, the diynylhydridorhodium(III) species **3**, and the vinylidenerhodium(I) compound **4** as intermediates. The reaction of **6** with* CH_2N_2 *affords two isomers (**A** and **B**) of the square-planar rhodium(I) complex **7**, in which the hitherto unknown hexapentaene* $H_2C=C=C=C=C=CPh_2$ *is π-coordinated to the* $RhCl(PiPr_3)_2$ *fragment.*

In contrast to the large number of vinylidene and allenylidene transition-metal complexes containing a linear M=C=C or M=C=C=C fragment,[1] related compounds with a MC_4 or MC_5 unit are still quite rare. Recently, Dixneuf et al. described the synthesis of a *cationic* ruthenium complex of composition $[RuCl(=C=C=C=C=CPh_2)(dppe)_2]^+$ (dppe = $Ph_2PCH_2CH_2PPh_2$),[2] and shortly thereafter we reported the isolation and structural characterization of the first *neutral* species *trans*-$[IrCl(=C=C=C=C=CPh_2)(PiPr_3)_2]$, having a linear MC_5 chain.[3] In the meantime, a paper describing the preparation of the corresponding octahedral derivatives $[M(=C=C=C=C=C(NMe_2)_2)(CO)_5]$ (M = Cr, W) has also appeared.[4]

The unexpected thermodynamic stability of the IrC_5 complex prompted us to prepare also the analogous RhC_5 compound *trans*-$[RhCl(=C=C=C=C=CPh_2)(PiPr_3)_2]$ (**6**) with the particular aim of comparing the reactivity of this metallacumulene with that of the structurally similar RhC_3 species *trans*-$[RhCl(=C=C=CPh_2)(PiPr_3)_2]$.[5] The methodology to obtain **6** is outlined in Scheme 1. Treatment of the labile dimer **1**[6] with the substituted pentadiyne $HC\equiv CC\equiv CCPh_2OSiMe_3$[7] in pentane at −78 °C afforded, after warming up to room temperature, the π-alkyne complex **2** as an orange solid in 63% yield.[8,9] The couplings of the C≡C*H* proton and of the respective alkyne carbon atoms to ^{103}Rh support the assumption that it is the *terminal* triple bond which is coordinated to the metal center.

Thermal rearrangement of **2** in toluene, which was carefully monitored by ^{31}P NMR spectroscopy, gave first the diynylhydridorhodium(III) intermediate **3** and then the isomeric vinylidenerhodium(I) complex **4**. While **3** could only be characterized by its ^1H and ^{31}P NMR data (for comparison with the related compound $[RhH(C\equiv CC\equiv CPh)Cl(PiPr_3)_2]$, see ref 10), **4** was isolated as a red-violet, almost air-stable solid.[11] The most typical spectroscopic features of **4** are the resonance of the Rh=C=C*H* proton at δ 0.83 and the low-field signals at δ 291.3 and 90.4 (both doublets of triplets) for the α-C and β-C vinylidene carbon atoms, respectively.

The reaction of **2** with pyridine in benzene led, probably via **3** as an intermediate, to the formation of a stable off-white solid which according to elemental analysis and IR and NMR spectroscopy is the octahedral complex **5**. Treatment of **5** in toluene at −78 °C with 2 equiv of Tf_2O ($Tf = CF_3SO_2$), followed by addition of an excess of NEt_3 when the mixture reached room temperature, gave a deep violet solution. From this solution upon chromatography on Al_2O_3 (first with toluene at −50 °C and then with pentane at −20 °C) and removal of the solvent the deep violet viscous product **6** was obtained in ca. 60% yield. The preparation of **6** could also be achieved by treatment of the vinylidene compound **4** with an equimolar amount of Tf_2O in toluene at −78 °C, followed by addition of NEt_3 at room temperature. Although we failed to obtain **6** as a crystalline material, the IR and NMR spectroscopic data are in good agreement with the structure proposed in Scheme 1.[12] By analogy to the iridium counterpart *trans*-$[IrCl(=C=C=C=C=CPh_2)(PiPr_3)_2]$,[3] the IR spectrum of **6** displays two bands at 1962 and 1860 cm^{-1} which are assigned to the C−C−C stretching frequencies of the RhC_5 unit. In the ^{13}C NMR spectrum, the five carbon atoms of the metallacumulene chain give rise to five signals between δ 246 and 141, of which

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[6] (a) Isolation: Werner, H.; Wolf, J.; Höhn, A. *J. Organomet. Chem.* **1985**, *287*, 395−407. (b) X-ray crystal structure: Binger, P.; Haas, J.; Glaser, G.; Goddard, R.; Krüger, C. *Chem. Ber.* **1994**, *127*, 1927−1929.

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[8] Correct elemental analyses have been obtained for complexes **2**, **4**, **5** and **7.**

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[10] Selected spectroscopic data for **2**: IR (KBr) $\nu(C\equiv C)_{uncoord}$ 2210, $\nu(C\equiv C)_{coord}$ 1805 cm^{-1}; ^1H NMR (C_6D_6, 200 MHz) δ 4.12 (d, J_{H-Rh} = 2.2 Hz, 1H, ≡C*H*), 0.21 (s, 9H, $OSiMe_3$); ^{13}C NMR (toluene-d_8, 50.3 MHz, −20 °C) δ 92.9 (s, $\equiv CCPh_2OSiMe_3$), 85.6 (d, J_{C-Rh} = 15.3 Hz, C≡*C*H), 80.4 (s, $C\equiv CCPh_2OSiMe_3$), 77.6 (s, CPh_2OSiMe_3), 55.4 (d, J_{C-Rh} = 15.3 Hz, *C*≡CH), 1.7 (s, $OSiMe_3$); ^{31}P NMR (C_6D_6, 81.0 MHz) δ 34.8 (d, J_{P-Rh} = 114.8 Hz).

[11] Selected spectroscopic data for the isomers **3** and **4** are as follows: **3**: ^1H NMR (C_6D_6, 200 MHz) δ −16.42 (dt, J_{H-Rh} = 44, J_{H-P} = 13 Hz, 1H, Rh*H*); ^{31}P NMR (C_6D_6, 81.0 MHz) δ 50.2 (d, J_{P-Rh} = 97.4 Hz). **4**: IR (KBr) $\nu(C\equiv C)$ 2195, $\nu(C=C)$ 1606 cm^{-1}; ^1H NMR (C_6D_6, 200 MHz) δ 0.83 (dt, J_{H-Rh} = 0.6, J_{H-P} = 2.9 Hz, 1H, Rh=C=C*H*); ^{13}C NMR (C_6D_6, 100.6 MHz) δ 291.3 (dt, J_{C-Rh} = 62.3, J_{C-P} = 15.9 Hz, Rh=*C*), 101.5 (s, $C\equiv CCPh_2OSiMe_3$), 90.4 (dt, J_{C-Rh} = 17.8, J_{C-P} = 6.4 Hz, Rh=C=*C*), 77.0 (s, CPh_2OSiMe_3), 66.3 (t, J_{C-P} = 3.5 Hz, $C\equiv CCPh_2OSiMe_3$), 1.8 (s, $OSiMe_3$); ^{31}P NMR (C_6D_6, 162.0 MHz) δ 43.1 (d, J_{P-Rh} = 132.3 Hz).

[12] Selected spectroscopic data for **6**: IR (hexane) $\nu(C=C=C)$ 1962, 1860 cm^{-1}; ^{13}C NMR (C_6D_6, 100.6 MHz) δ 246.1 (dt, J_{C-Rh} = 16.5, J_{C-P} = 6.4 Hz, Rh=C=*C*), 205.3 (dt, J_{C-Rh} = 67.4, J_{C-P} = 17.8 Hz, Rh=*C*), 197.8 (dt, J_{C-Rh} = 1.3, J_{C-P} = 3.8 Hz, Rh=C=C=*C*), 156.1 (t, J_{C-P} = 1.9 Hz, CPh_2), 141.4 (t, J_{C-P} = 3.5 Hz, $C=CPh_2$); ^{31}P NMR (C_6D_6, 162.0 MHz) δ 34.5 (d, J_{P-Rh} = 128.8 Hz).

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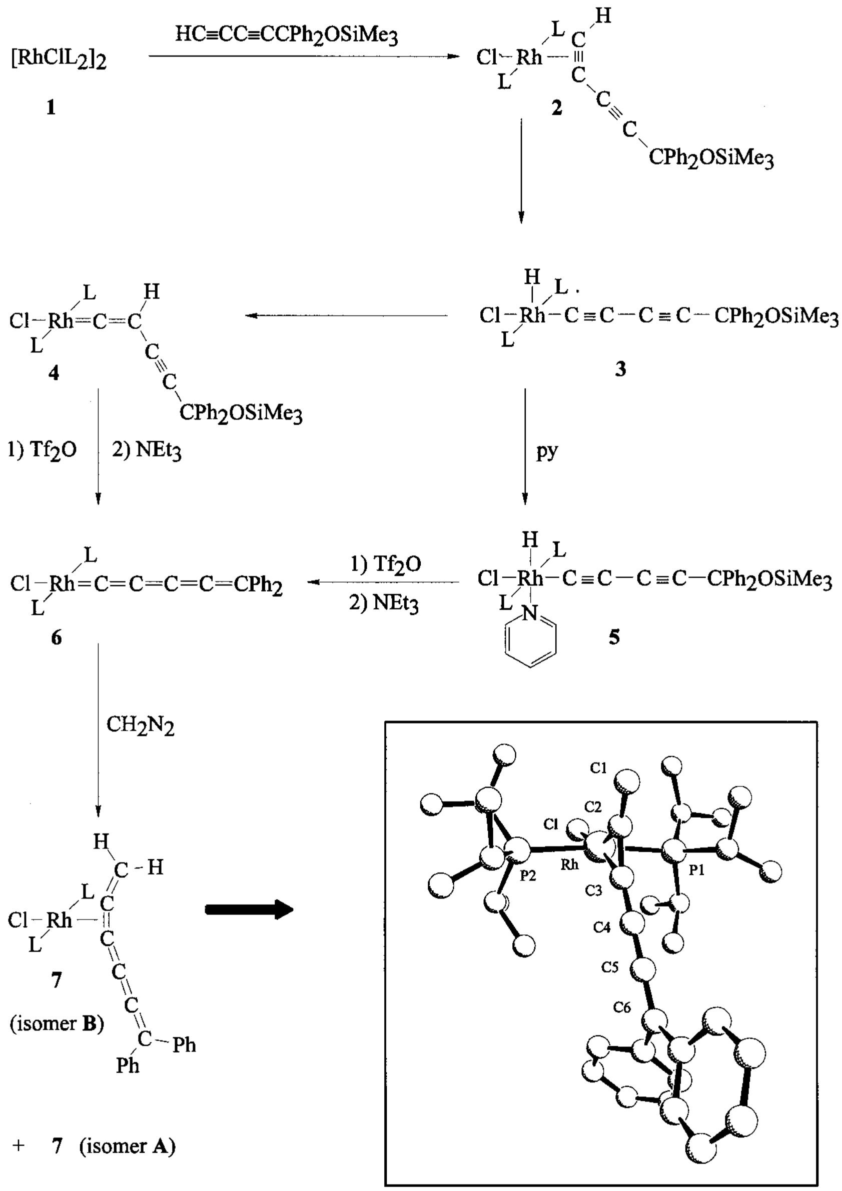
Scheme 1[a]



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

three (α-C, β-C, γ-C) are split into doublets of triplets and two into triplets. The ^{31}P NMR spectrum of **6** displays one doublet resonance at δ 34.5, indicating that the phosphine ligands are equivalent and are in a *trans* arrangement.

Like the allenylidene complex *trans*-[RhCl(=C=C=CPh$_2$)(P*i*Pr$_3$)$_2$],[13] compound **6** reacted with excess diazomethane at 25 °C within a few minutes. The reaction was accompanied by an evolution of gas (N$_2$) and a change of color from violet to orange. After removal of the solvent and addition of 1 mL of pentane to the viscous residue, orange-yellow, slightly air-sensitive crystals of **7** were isolated in 63% yield. While the elemental analysis and the mass spectra (EI, 170 °C) confirmed the composition of a four-coordinated rhodium(I) complex with π-bonded H$_2$C=C=C=C=C=CPh$_2$, the ^{1}H, ^{13}C, and ^{31}P NMR spectra of **7** revealed the presence of two isomers **A** and **B** in a ratio of approximately 1:1.[14] When a solution of the isomeric mixture in toluene was stirred at 80 °C for 4 h, the ratio **A**:**B** changed from 1:1 to 2:3; however, continuous heating caused decomposition. Quite unexpectedly, a 1:4 mixture of **A** and **B** was obtained upon storing a solid sample of **7** for 2 weeks at −60 °C. The more abundant isomer **B**, which was the same as that isolated upon fractional crystallization of the 2:3 isomeric mixture from diethyl ether, was investigated by X-ray crystallography.[15] The structural analysis (see Scheme 1) reveals a square-planar coordination sphere around the metal center with the two phosphines in a *trans* disposi-

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(14) Selected spectroscopic data of isomers **A** and **B** of compound **7** are as follows: Isomer **A**: ^{1}H NMR (C$_6$D$_6$, 200 MHz) δ 2.75 (s, br, 2H, $=CH_2$); ^{13}C NMR (C$_6$D$_6$, 100.6 MHz) δ 199.4 (s, $=C=$), 158.2 (dt, $J_{C-Rh} = 24.1$, $J_{C-P} = 5.1$ Hz, $C=CH_2$), 121.4, 117.4 (both s, $=C=$), 113.0 (s, CPh_2), 15.5 (d, $J_{C-Rh} = 12.7$ Hz, $=CH_2$); ^{31}P NMR (C$_6$D$_6$, 81.0 MHz) δ 35.5 (d, $J_{P-Rh} = 117$ Hz). Isomer **B**: ^{1}H NMR (C$_6$D$_6$, 200 MHz) δ 5.57 (t, $J_{H-P} = 2.6$ Hz, 1H of $=CH_2$), 5.33 (s, br, 1H of $=CH_2$); ^{13}C NMR (C$_6$D$_6$, 100.6 MHz) δ 167.5 (dt, $J_{C-Rh} = 1.9$, $J_{C-P} = 3.8$ Hz, $C=CPh_2$), 138.2 (dt, $J_{C-Rh} = 18.4$, $J_{C-P} = 4.5$ Hz, Rh-C), 135.4 (dt, $J_{C-Rh} = 3.2$, $J_{C-P} = 5.7$ Hz, $C=C=CPh_2$), 120.2 (dt, $J_{C-Rh} = 15.9$, $J_{C-P} = 5.1$ Hz, Rh-C), 117.5 (s, br, CPh_2), 101.4 (d, $J_{C-Rh} = 1.9$ Hz, $=CH_2$); ^{31}P NMR (C$_6$D$_6$, 81.0 MHz) δ 33.1 (d, $J_{P-Rh} = 117$ Hz); MS (70 eV) *m/z* 687 (M$^+$).

tion. The rhodium is bound to the double bond between C2 and C3, in close analogy to the situation found in *trans*-$[RhCl(\eta^2\text{-}Ph_2C{=}C{=}C{=}C{=}C{=}CPh_2)L_2]$ (L = PPh_3,[16] P*i*Pr_3[17]). While the Rh−P bond lengths are almost identical, the Rh−C2 and Rh−C3 distances differ by about 0.05 Å. The P−Rh−P axis is not exactly linear, possibly due to the unsymmetric bonding situation of the cumulene unit. The C_6 chain is bent, in agreement with previous findings, possessing C−C−C angles that are similar to those in related rhodium hexapentaene and butatriene complexes.[16−18] It is important to note, however, that in contrast to stable $Ph_2C{=}C{=}C{=}C{=}C{=}CPh_2$ (which is the ligand in the above-mentioned Rh(I) compounds[16,17]), the 1,1-disubstituted hexapentaene $H_2C{=}C{=}C{=}C{=}C{=}CPh_2$, generated during the formation of **7**, is an *unknown species* like other hexapentaenes with CH_2 as the terminal unit.[19] With regard to isomer **A** of complex **7**, we assume that in this molecule the C_6 ligand is coordinated via the terminal $C{=}CH_2$ bond. Some of the spectroscopic data (e.g. the position of the signal of the $=CH_2$ protons in the ^1H NMR and that of the phosphine resonance in the ^{31}P NMR spectrum)[14] are quite similar to those of *trans*-$[RhCl(\eta^2\text{-}H_2C{=}C{=}C{=}CPh_2)(PiPr_3)_2]$, the structure of which was determined by X-ray crystal structure analysis.[13]

In conclusion, the results reported here illustrate that derivatives of the readily accessible diynol $HC{\equiv}CC{\equiv}CCPh_2OH$[20] can be converted stepwise, in the coordination sphere of rhodium, to the highly unsaturated carbene $:C{=}C{=}C{=}C{=}CPh_2$. The corresponding metallacumulene **6** is an appropriate starting material for the generation of the coordinated hexapentaene $H_2C{=}C{=}C{=}C{=}C{=}CPh_2$, which due to its high lability has not been generated up to now in the free state.

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Supporting Information Available: Text giving synthetic details and characterization data for **2** and **5**−**7** and tables giving experimental details and data of the X-ray crystal structure analysis, bond lengths and bond angles, and atomic positional and anisotropic thermal parameters and an ORTEP drawing for **7** (isomer **B**) (12 pages). Ordering information is given on any current masthead page.

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(15) Principal bond lengths (Å) and interbond angles (deg) for isomer **B** of **7**: Rh−Cl 2.348(1); Rh−P1, 2.367(1); Rh−P2, 2.369(1); Rh−C2, 1.992(5); Rh−C3, 2.040(4); C1−C2, 1.321(8); C2−C3, 1.357(6); C3−C4, 1.302(6); C4−C5, 1.261(6); C5−C6, 1.337(7); P1−Rh−P2, 171.25(5); P1−Rh−Cl, 87.75(5); P2−Rh−Cl, 87.09(5); Cl−Rh−C2, 151.0(2); Cl−Rh−C3, 169.6(1); C1−C2−C3, 149.2(6); C2−C3−C4, 152.6(5); C3−C4−C5, 177.1(5); C4−C5−C6, 175.3(5); C2−Rh−C3, 39.3(2); Rh−C2−C1, 138.5(5); Rh−C3−C4, 138.9(4).

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