Formation and Structure of a New Dinuclear Rhodium Complex $[(i\mathrm{Pr}_3\mathrm{P})\mathrm{RhCl}]_2[\mathrm{P}_3\mathrm{C}_3t\mathrm{Bu}_3]$

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Received March 3, 1995

Key Words: Rhodium complex, dinuclear / Phosphaalkyne / Trimerization

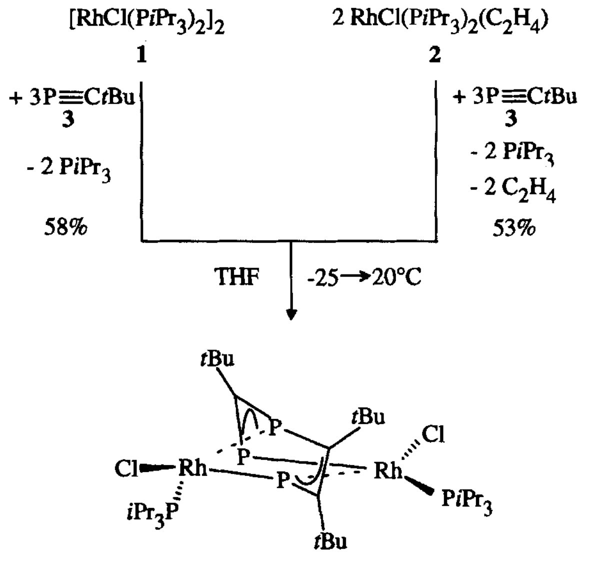
The new dinuclear rhodium complex **4** was synthesized by reaction of $[(i\mathrm{Pr}_3\mathrm{P})_2\mathrm{RhCl}]_2$ (**1**) or $[(i\mathrm{Pr}_3\mathrm{P})_2(\mathrm{CH}_2{=}\mathrm{CH}_2)\mathrm{RhCl}]$ (**2**) with 2-*tert*-butyl-1-phosphaacetylene (**3**) in 58% yield. An X-ray analysis reveals that in **4** a 1,3,6-triphosphahexadiene-1,6-diyl chain is bound to each of the two rhodium atoms in an η^1,η^3 manner.

Whereas cyclodimerizations of 2-*tert*-butyl-1-phosphaacetylene (**3**) in the coordination sphere of transition metal complexes leading to η^4-1,3-diphosphacyclobutadiene metal complexes (M = Co, Rh, Fe)[1,2] or 1,3-diphosphabicyclo[1.1.0]butanediyl metal compounds (M = Zr, Hf)[2,3] are well-known reactions, only one example of a successful cyclotrimerization of **3** is known. Compound **3** reacts with (η^6-naphthalene)(η^5-pentamethylcyclopentadiene)vanadium to give a (1,3,5-triphospha Dewar benzene)vanadium complex[4a]. A reported synthesis of an (η^6-1,3,5-triphosphabenzene)molybdenum complex[4b] could not be confirmed by independent investigation[5] and therefore remains tentative.

In this paper we describe the preparation and characterization of the new dinuclear rhodium(I) complex **4** which contains a 1,3,6-triphosphahexadiene-1,6-diyl chain bound to each of the two rhodium atoms in an η^1,η^3 manner. It is noteworthy that this trimerization of **1** is achieved by simply exchanging the trimethylphosphane ligands attached to the rhodium for triisopropylphosphane, since reaction of **3** with a trimethylphosphane-modified rhodium chloride leads to the formation of an (η^4-1,3-diphosphacyclobutadiene)bis(trimethylphosphane)rhodium chloride via the corresponding 2-rhodia-1,4-diphosphacyclopentadiene complex[2f].

Complex **4** was obtained as the only isolable product in 53–58% yield when one of the two rhodium complexes **1**[6] or **2**[6c] was treated with three equivalents of the phosphaalkyne **3** in THF at room temperature. From the brownish black precipitate black crystals suitable for an X-ray structure analysis were obtained by controlled cooling (0.02 °C/min) to −60 °C of a solution of **4** in hexane/$\mathrm{Et_2O}$/THF (2:4:1).

The crystal structure analysis reveals the dinuclear character of the new complex **4**. The characteristic feature of the molecule is the chair-like configuration of the 1,3,6-triphosphahexadiene-1,6-diyl chain which is fixed by two single bonds of P3 and P1 to Rh1 and Rh2 [Rh1–P3 2.256(1), Rh2–P1 2.277(1) Å], respectively, and two unsymmetrically bound η^3-allylic substructures between Rh1 and P1–C1–C6 and between Rh2 and P2–C11–P3 (for atom numbering see Figure 1). These η^3-allyl structures are documented by the bond lengths Rh1–C6 2.468(5), Rh1–C1 2.303(5), Rh1–P1 2.305(1), Rh2–P2 2.279(2), Rh2–P3 2.453(1), Rh2–C11 2.235(5) Å and by the distances P1–C1 1.837(6), C1–C6 1.379(7) Å for the monophosphaallyl unit and P2–C11 1.801(5), P3–C11 1.733(5) Å for the diphosphaallyl unit. These P–C- and C–C bond lengths are in the range of those of known η^3-phosphaallyl[7] and η^3-diphosphaallyl metal complexes[8] of iron, molybdenum, cobalt, and nickel.



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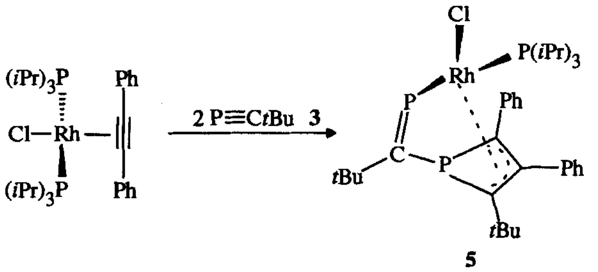
(1)



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(2)

The NMR-spectroscopic data of complex **4** are in agreement with the crystallographic data, but they do not allow a structure determination of **4** to be postulated unambiguously. Due to σ bonds to one of the two rhodium atoms, the signals of P1 and P3 of the triphosphahexatrienyl chain are shifted to δ = 201.6 and 206.7 in the ^{31}P-NMR spectrum, whereas the signal for P2 is lo-

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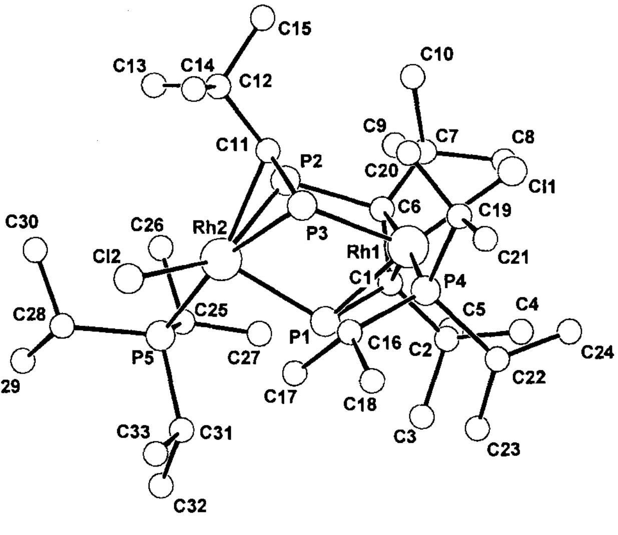
cated at δ = 24.9. In the ^{13}C-NMR spectrum the allylic carbon atoms are found at relatively low field (154-134) compared to the chemical shift of other known η^3-P−C−C or η^3-P−C−P metal complexes[7,8] (for a complete description of the ^{1}H-, ^{13}C- and ^{31}P-NMR spectra, see Experimental).

The reaction sequence which leads to complex **4** is not well understood at this time. Obviously besides a head-to-tail also a tail-to-tail connection of two phosphaalkynes takes place in the course of the formation of **4**. This have been observed only once[2g], the head-to-tail connection being by far the most common regiochemistry in the cyclodimerization and cyclotrimerization of phosphaalkynes. It is also remarkable that the recently published cotrimerization of **3** with tolan in the ratio 2:1 starting with the same rhodium complex **1** leads to rhodium complex **5** with a completely different structure[9]. A structurally closely related ruthenium complex to **5** has recently been prepared, in which three molecules of **3** were uniformly connected in a head-to-tail manner[10].

Figure 1. Molecular structure of **4**. Selected bond lengths [Å] and angles [°]: Rh1−Cl1 2.419(2), Rh1−P1 2.305(1), Rh1−P3 2.256(1), Rh1−P4 2.345(1), Rh1−C1 2.303(5), Rh1−C6 2.468(5), Rh2−Cl2 2.406(2), Rh2−P1 2.277(1), Rh2−P2 2.279(2), Rh2−P3 2.453(1), Rh2−P5 2.401(1), Rh2−C11 2.235(5), P1−C1 1.837(6), C1−C6 1.379(7), P2−C6 1.897(5), P2−C11 1.801(5), P3−C11 1.733(5), C1−C2 1.600(7), C6−C7 1.561(8), C11−C12 1.553(7); Cl1−Rh1−P4 89.3(1), Cl1−Rh1−C1 112.6(1), Cl1−Rh1−C6 95.5(1), Cl1−Rh1−P1 159.4(1), C6−Rh1−P4 175.1(1), C1−Rh1−P4 143.0(1), P1−Rh1−P4 107.0(1), C1−Rh1−C6 33.4(2), Cl2−Rh2−P5 90.8(1), Cl2−Rh2−P1 124.9(1), Cl2−Rh2−P3 93.1(1), P5−Rh2−P3 166.6(1), P5−Rh2−P2 105.0(1), P1−C1−C6 111.8(4), P2−C11−P3 114.6(3)



Experimental

Synthesis of **4**: A solution of **3** (2.5 g, 25 mmol) in 10 ml of THF was added to a solution of **1** (3.2 g, 7 mmol) in 80 ml of THF at −25 °C, whereby the color of the reaction mixture changed immediately from violet to dark brown. The solution was warmed to room temp. and stirred for 12 h after which all volatile components were removed in vacuo. The brown-black residue was slurred in 40 ml of pentane, and **4** was isolated as a dark brown powder by filtration: yield 1.8 g (58%); mp 134 °C (dec.). Crystals suitable for an X-ray analysis were obtained by continued cooling (0.02 °C/min) to −60 °C of a concentrated solution of **4** in Et_2O/hexane/THF (4:2:1). − ^{1}H NMR (C_6D_6, 400 MHz): δ = 2.96 and 2.71 (m, both 3H), $P[CH(CH_3)_2]_3$, [1.59 (m, 9H), 1.45 (m, 9H), 1.32 (m, 9H), 1.31 (m, 9H) $P[CH(CH_3)_2]_3$], 1.84 (s, 9H, *t*Bu), 1.36 (s, 18H, *t*Bu). − ^{13}C NMR ([D_8]THF, −30 °C, 75.5 MHz): δ = 140.8 ($J_{C,P}$ = 84.0, 12.0, 5.0 Hz, C1), 134.5 ($J_{C,P}$ = 60.0, 24.0 Hz, C6); 154.2 ($J_{C,P}$ = 111.0, 90.0 Hz, C11); 42.1 ($J_{C,P}$ = 26.2 Hz, *t*Bu at C1); 32.4 ($^1J_{C,H}$ = 125, $J_{C,P}$ = 12.5 Hz, *t*Bu at C1); 39.5 ($J_{C,P}$ = 20.7 Hz, *t*Bu at C6); 33.7 ($^1J_{C,H}$ = 125, $J_{C,P}$ = 9.5 Hz, *t*Bu at C6); 42.8 ($J_{C,P}$ = 14.5 and 12.5 Hz, *t*Bu at C11); 33.2 ($^1J_{C,H}$ = 125, $J_{C,P}$ = 8.0 and 6.5 Hz, *t*Bu at C11); 26.9 ($^1J_{C,H}$ = 130, $J_{C,P}$ = 22.0 and 5.4 Hz, $P[CH(CH_3)_2]_3$ at Rh1); (20.8 ($^1J_{C,H}$ = 128 Hz), 20.5 ($^1J_{C,H}$ = 127 Hz) $P[CH(CH_3)_2]_3$ at Rh1]; 25.0 ($^1J_{C,H}$ = 128 Hz, $P[CH(CH_3)_2]_3$ at Rh2); 19.9 ($^1J_{C,H}$ = 127 Hz, $P[CH(CH_3)_2]_3$ at Rh2) (numbering of C atoms, see Figure 1). − ^{31}P NMR (C_6H_6, 27 °C, 81 MHz): δ = 206.7 ($J_{P3,P1}$ = 20.3, $J_{P3,P2}$ = 24.9, $J_{P3,P4}$ = 9.9, $J_{P3,P5}$ = 57.3, $J_{P3,Rh1}$ = 49.1, $J_{P3,Rh2}$ = 19.4 Hz, P3), 201.6 ($J_{P1,P2}$ = 17.8, $J_{P1,P3}$ = 20.3, $J_{P1,P4}$ = 35.9, $J_{P1,P5}$ = 0, $J_{P1,Rh1}$ = 8.5, $J_{P1,Rh2}$ = 43.2 Hz, P1), 57.3 ($J_{P5,P2}$ = 10.6, $J_{P5,P3}$ = 0.1, $J_{P5,P4}$ = 0 Hz, $J_{P5,Rh1}$ = 0.4, $J_{P5,Rh2}$ = 171.6 Hz, P5), 49.4 ($J_{P4,P2}$ = 7.4, $J_{P4,Rh1}$ = 143.9, $J_{P4,Rh2}$ = 0.1 Hz, P4), 24.9 ($J_{P2,Rh1}$ = 31.9, $J_{P2,Rh2}$ = 5.3 Hz, P2) (numbering of P and Rh atoms, see Figure 1). − $C_{33}H_{69}Cl_2P_5Rh_2$ (897.5): calcd. C 44.16, H 7.75, Cl 7.90, P 17.26, Rh 22.93; found C 44.55, H 7.98, Cl 7.16, P 17.16, Rh 22.65.

Complex **4** was obtained in 53% yield according to the above mentioned procedure starting with complex **2** at room temp.

X-ray Crystal Structural Analysis of **4**[11]: Single crystal from hexane/Et_2O/THF (2:4:1); 0.14 × 0.32 × 0.32 mm, Enraf-Nonius CAD4 diffractometer; Mo-K_α (graphite monochromator, λ = 0.71069), empirical formula $C_{33}H_{69}Rh_2P_5Cl_2$, space group $Pna2_1$; unit cell dimensions: a = 20.478(5), b = 16.061(2), c = 12.686(6) Å, $\alpha = \beta = \gamma$ = 90.0°; $d_{calc.}$ = 1.43 g·cm^{-3}, V = 4172(8) Å^3, Z = 4; μ(Mo-K_α) = 11.18 cm^{-1}, range for data collection $2\Theta_{max}$ = 30°; ω scan; index ranges: $-18 \le h \le 18$, $0 \le k \le 23$, $0 \le l \le 29$; reflections collected 11172; independent reflections 10339; parameters 379; no absorption correction. Structure solution: direct method, structure refinement: Full matrix least-squares on F, R = 0.047, R_w = 0.055 based on 8005 reflections with $I \ge 2\sigma(I)$.

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[11] Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen (FRG), on quoting the depository number CSD-58878, the names of the authors, and the journal citation.

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