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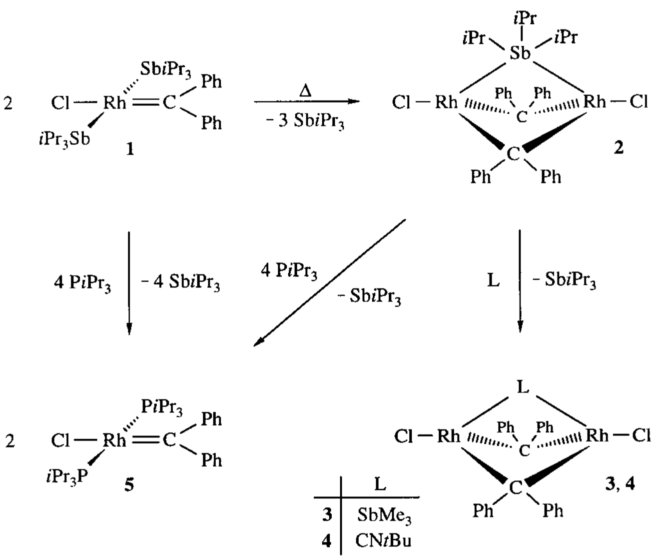
Breaking the Rule: Synthesis and Molecular Structure of Dinuclear Rhodium Complexes with Bridging and Semibridging Trialkylphosphane Ligands[**]

Thomas Pechmann, Carsten D. Brandt, and Helmut Werner[*]

In memory of John Osborn

Tertiary phosphanes PR_3 with R = alkyl or aryl belong like CO to the most well-known ligands in coordination chemistry.[1] While with regard to CO not only numerous metal complexes with *terminal* but also with *bridging* carbonyl ligands have been reported, the same is not true for tertiary phosphanes. Textbooks on Inorganic Chemistry[2] as well as corresponding monographs and reviews[3] mention without exception that tertiary phosphanes (and tertiary arsanes AsR_3 and stibanes SbR_3 as well) behave exclusively as terminal coordinated ligands.

Recently, we have begun to illustrate that this postulate may need to be modified by showing that the thermal reaction of the square-planar precursor **1** leads to the dinuclear complex **2** from which the related compounds **3** and **4** were obtained by exchange of the bridging Sb*i*Pr_3 ligand for $SbMe_3$ and CN*t*Bu (Scheme 1).[4] However, attempts to substitute the stibane by a tertiary phosphane failed. Treatment of **2** with P*i*Pr_3 did not afford $[Rh_2Cl_2(\mu\text{-P}i\text{Pr}_3)(\mu\text{-CPh}_2)_2]$ but gave the mononuclear complex **5** by displacement of the stibane *and* cleavage of the carbene bridges. Now we have found that replacing one of the chloro ligands in **2** by acetylacetonate (acac) changes the reactivity of the stibane-bridged dinuclear compound dramatically and turns the dream of the isolation of a transition metal complex with $M(\mu\text{-PR}_3)M$ as a molecular unit into reality.



Scheme 1.

The dinuclear compound **6**, obtained from **2** and an equimolar amount of [Tl(acac)] , reacts with PMe_3 in the molar ratio of 1:1 in pentane/diethyl ether to give the substitution product **7** (Scheme 2). After recrystallization from acetone, red-brown crystals of **7** were isolated in 82 % yield. The ^{31}P NMR spectrum of **7** (in C_6D_6) displays a doublet of doublets at $\delta = -36.4$ with $^{31}P-^{103}Rh$ coupling constants of 147.5 and 81.4 Hz, indicating that the PMe_3 ligand is not linked to one of the metal centers in a terminal fashion. For the dirhodium compound $[(acac)Rh(\mu\text{-CO})\{\mu\text{-C}(p\text{-Tol})_2\}_2Rh(acac)(PMe_3)]$, which is formed by stepwise reaction of $[(acac)Rh(\mu\text{-Sb}i\text{Pr}_3)\{\mu\text{-C}(p\text{-Tol})_2\}_2Rh(acac)]$ with PMe_3 and CO and which contains a *terminal* Rh–PMe_3 bond,[5] the $^{31}P-^{103}Rh$ coupling constants of the signal observed in the ^{31}P NMR spectrum at $\delta = -5.2$ are 129.7 and 7.6 Hz, respectively. The ^{31}P NMR resonance signals for the PMe_3 ligand of other

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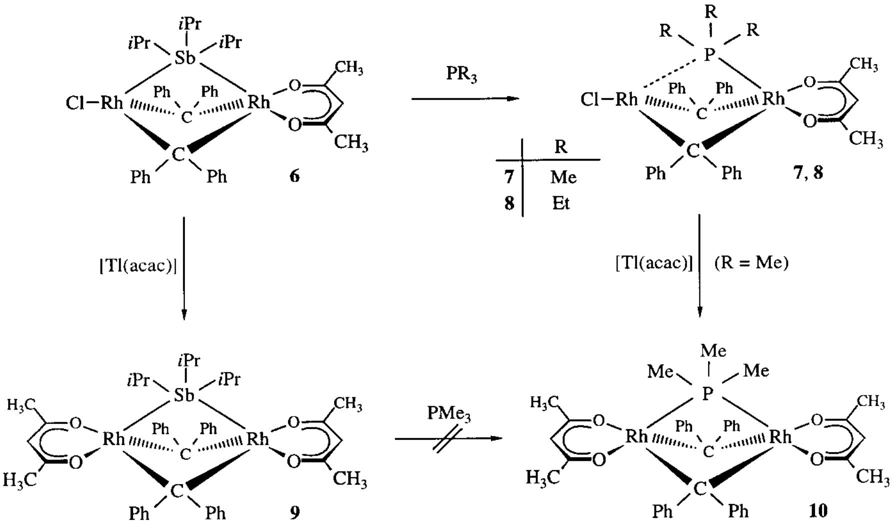
[**] This work was supported by the Deutsche Forschungsgemeinschaft (SFB 347) and the Fonds der Chemischen Industrie. We thank in particular Dr. J. Wolf and Dr. U. Herber, Universität Würzburg, for valuable advice and discussions.



Scheme 2.

dinuclear complexes of the general composition $[(L)_xRh(\mu\text{-}X)_nRh(PMe_3)(L')_y]$ show differences for $^1J(^{31}P,^{103}Rh)$ and $^3J(^{31}P,^{103}Rh)$ also of this magnitude.[6] The reaction of **6** with PEt_3 takes a similar course to that with PMe_3 and affords compound **8** in 81% yield.

The X-ray crystal structure analysis of **7** (Figure 1) confirms[7] that the phosphane ligand occupies a *semibridging* position rather than a terminal position.[8] Apart from the distances Rh1–P and Rh2–P, characteristic features are in particular the bond angles in the Rh_2P triangle, which are significantly smaller than 90°. In the case of a nonbridging arrangement, the angle Rh1-Rh2-P should be considerably larger than 90°.[9] Owing to the higher coordination number of Rh1 compared to Rh2, not only the phosphane but also the two diphenylcarbene ligands are linked to the metal centers in an unsymmetrical fashion. The distances Rh2–C1 and Rh2–C2 are about 0.11 Å shorter than those from Rh1 to C1 and C2, quite similar to the situation found for compound **6**.[10] The bond length Rh1–Rh2 (2.5318(8) Å) in **7** is rather short and comparable with that in the dinuclear complex **2** (2.5349(5) Å).[4a]

Compound **7** reacts with [Tl(acac)] in the molar ratio of 1:1.2 in acetone at room temperature by substitution of the chloro for the acetylacetonato ligand to give the dinuclear complex **10** (Scheme 2). The light-brown, only moderately air-sensitive solid is obtained in 98% yield. In contrast to **7**, the ^{31}P NMR spectrum of **10** does not display a doublet of doublets but a *triplet*, illustrating that the trimethylphosphane ligand is coordinated to both rhodium centers in a *bridging* (and not in a semibridging) mode. The X-ray crystal structure analysis confirms this proposal (Figure 2).[7] Although the two Rh–P bond lengths are not exactly the same, the difference of about 0.3 Å is only half of that in **7**. Since neither the ^{31}P nor the ^1H NMR spectrum of **10** is temperature-dependent, it is conceivable that the small deviation of the ideal symmetry for the sterically hindered molecule found in the crystal is due to packing effects. In our opinion the more important fact is that the bond angles Rh1-Rh2-P, Rh2-Rh1-P, and Rh1-P-Rh2 deviate only by a maximum of 7.1° from the value of 60° required for an isosceles triangle. It should be mentioned that we failed to prepare **10** from **9** by treatment with an equimolar amount of PMe_3. In this case a dinuclear compound of

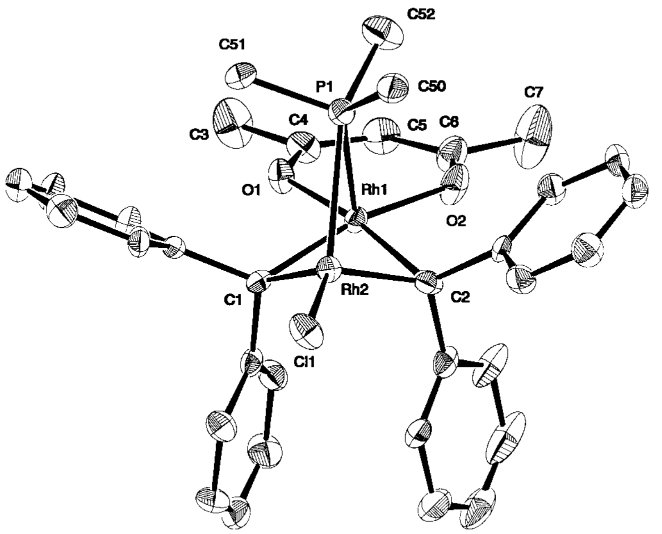


Figure 1. Molecular structure of **7** (ORTEP plot) in the crystal. Selected bond lengths [Å] and angles [°]: Rh1-Rh2 2.5318(8), Rh1-P1 2.2406(15), Rh2-P1 2.8410(14), Rh1-C1 2.060(5), Rh1-C2 2.057(5), Rh2-C1 1.939(5), Rh2-C2 1.949(5), Rh1-O1 2.115(3), Rh1-O2 2.116(4), Rh2-Cl 2.3072(15); Rh1-P1-Rh2 58.34(4), P1-Rh1-Rh2 72.78(4), P1-Rh2-Rh1 48.88(4), Rh1-Rh2-Cl 172.30(4), Rh1-C1-Rh2 78.49(16), Rh1-C2-Rh2 78.36(18), C1-Rh1-C2 86.77(19), C1-Rh2-C2 93.3(2), O1-Rh1-O2 85.42(13).

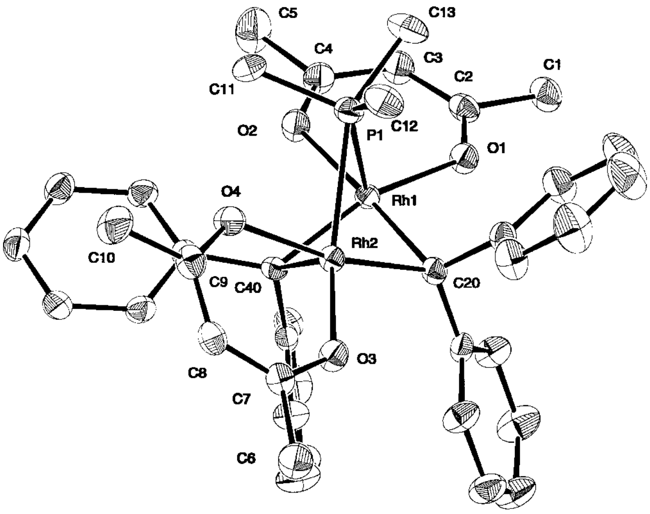


Figure 2. Molecular structure of **10** (ORTEP plot) in the crystal. Selected bond lengths [Å] and angles [°]: Rh1-Rh2 2.5281(5), Rh1-P1 2.2707(7), Rh2-P1 2.5700(8), Rh1-C20 2.069(3), Rh1-C40 2.038(2), Rh2-C20 1.995(2), Rh2-C40 1.974(3), Rh1-O1 2.1138(18), Rh1-O2 2.1596(19), Rh2-O3 2.0760(19), Rh2-O4 2.2097(19); Rh1-P1-Rh2 62.61(2), P1-Rh1-Rh2 64.50(2), P1-Rh2-Rh1 52.890(19), Rh1-C20-Rh2 76.90(9), Rh1-C40-Rh2 78.09(9), C20-Rh1-C40 84.55(10), C20-Rh2-C40 88.23(10), O1-Rh1-O2 84.11(7), O3-Rh2-O4 83.67(7).

unknown structure is formed which presumably contains a terminal phosphane ligand.

The presented compounds **7**, **8**, and **10** are the first dinuclear complexes with bridging or semibridging trialkylphosphane ligands. As far as we know, the capability of phosphanes (in particular of Ph_2PH) to possibly behave as bridging units was first discussed in a speculative way by Braunstein et al.[11] Shortly thereafter, van Leeuwen and co-workers described a dinuclear palladium(I) dication containing two chelated 1.3-bis(diphenylphosphanyl)propane ligands, in which two of the four PPh_2 groups occupy an unsymmetrical bridging position with respect to the palladium atoms.[12] A nearly symmetrical triply bridging position of PF_3 has been found in a Pd_3 complex,[13] which appears not so unusual regarding the analogy in the bonding mode of CO and PF_3 in coordination compounds.[14]

Experimental Section

7: A solution of **6** (77 mg, 0.08 mmol) in pentane/diethyl ether (30 mL, 2/1) was treated at −78 °C with PMe_3 (8.6 μL, 0.08 mmol) and, after warming, stirred for 30 min at room temperature. A change of color from dark red to yellow accompanied by the formation of a red-brown solid occurred. The mother liquor was decanted and the remaining residue washed three times with 5 mL portions of pentane/diethyl ether (2/1). After recrystallization from acetone (15 mL) at 5 °C red-brown crystals were isolated and dried in vacuo; yield 51 mg (82 %); m.p. 204 °C (decomp); ^1H NMR (200 MHz, C_6D_6):[15] $\delta = 5.45$ (s, 1H; CH of acac), 1.89 (s, 6H; CH_3 of acac), 0.74 (d, $^2J(P,H) = 10.6$ Hz, 9H, PCH_3); $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2): $\delta =$ 189.3 (s; CO of acac), 174.8 (ddd, $^1J(Rh,C) = 30.5$, $^1J(Rh',C) = 20.7$, $^2J(P,C) = 3.6$ Hz; CPh_2), 100.9 (d, $^3J(Rh,C) = 1.5$ Hz; CH of acac), 28.2 (s; CH_3 of acac), 22.4 (d, $^1J(P,C) = 40.7$ Hz, PCH_3); ^{31}P NMR (81.0 MHz, C_6D_6): $\delta = -36.4$ (dd, $^1J(Rh,P) = 147.5$, $^1J(Rh',P) = 81.4$ Hz); ^{31}P NMR (162.0 MHz, CD_2Cl_2): $\delta = -29.0$ (dd, $^1J(Rh,P) = 154.6$, $^1J(Rh',P) =$ 70.3 Hz).

8: Preparation analogous to that for **7**. Dark brown crystals; yield 81 %; m.p. 146 °C (decomp); ^1H NMR (200 MHz, C_6D_6): $\delta = 5.54$ (s, 1H; CH of acac), 1.94 (s, 6H; CH_3 of acac), 1.13 (m, 6H; PCH_2), 0.69 (m, 9H; PCH_2CH_3); $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2): $\delta = 189.4$ (s; CO of acac), 171.7 (ddd, $^1J(Rh,C) = 31.6$, $^1J(Rh',C) = 21.5$, $^2J(P,C) = 4.0$ Hz; CPh_2), 101.2 (d, $^3J(Rh,C) = 1.8$ Hz; CH of acac), 28.6 (d, $^3J(Rh,C) = 1.1$ Hz; CH_3 of acac), 21.6 (d, $^1J(P,C) = 34.5$ Hz; PCH_2), 8.5 (d, $^2J(P,C) = 5.1$ Hz; PCH_2CH_3); ^{31}P NMR (81.0 MHz, C_6D_6): $\delta = -2.7$ (dd, $^1J(Rh,P) = 144.9$, $^1J(Rh',P) =$ 68.7 Hz).

10: A solution of **7** (119 mg, 0.13 mmol) in acetone (20 mL) was treated with [Tl(acac)] (47 mg, 0.15 mmol) and stirred for 1 h at room temperature. The solvent was removed in vacuo and the remaining residue was extracted three times with pentane/diethyl ether (2/1; 30 mL each). The combined extracts were brought to dryness in vacuo and the residue was washed three times with 3 mL portions of pentane (−30 °C). After recrystallization from acetone (10 mL) at 5 °C light-brown crystals were isolated and dried in vacuo; yield 103 mg (98 %); m.p. 62 °C (decomp); ^1H NMR (300 MHz, C_6D_6): $\delta = 5.54$ (s, 2H; CH of acac), 1.96 (s, 12H; CH_3 of acac), 1.06 (d, $^2J(P,H) = 11.0$ Hz, 9H; PCH_3); $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6): $\delta = 188.7$ (s; CO of acac), 170.7 (dt, $^1J(Rh,C) = 24.7$, $^2J(P,C) = 4.4$ Hz; CPh_2), 100.8 (s; CH of acac), 28.4 (s; CH_3 of acac), 22.1 (d, $^1J(P,C) = 39.6$ Hz; PCH_3); ^{31}P NMR (81.0 MHz, C_6D_6): $\delta = -30.4$ (t, $^1J(Rh,P) = 110.6$ Hz).

Received: June 23, 2000 [Z15316]

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[7] Data for the X-ray structure analyses: **7**: Crystals from acetone, $C_{34}H_{36}ClO_2PRh_2$ ($M_r = 748.90$); crystal size $0.20 \times 0.20 \times 0.30$ mm^3; monoclinic, space group $C2/c$ (no. 15), $a = 33.925(7)$, $b = 10.279(2)$, $c = 18.109(4)$ Å, $\beta = 98.15(3)^\circ$, $Z = 8$, $V = 6251(2)$ Å^3, $\rho_{calcd} =$ 1.591 g cm^{-3}; $T = 173(2)$ K; $2\Theta = 50.00^\circ$; 12940 reflections measured, 5450 were unique ($R_{int} = 0.0663$), and 3183 observed ($I > 2\sigma(I)$); IPDS (Stoe), $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), graphite-monochromated; Lp correction. The structure was solved by direct methods and refined with the full-matrix, least-squares method; $R_1 = 0.0354$, $wR_2 = 0.0575$ (for 3183 reflections with $I > 2\sigma(I)$), $R_1 = 0.0814$, $wR_2 = 0.0632$ (for all 5450 data); data-to-parameter ratio 14.93; residual electron density +0.537/−1.091 e Å^{-3}. **10**: Crystals from acetone, $C_{39}H_{43}O_4PRh_2$ ($M_r = 812.52$); crystal size $0.40 \times 0.40 \times 0.40$ mm^3; monoclinic, space group $P2_1/c$ (no. 14), $a = 10.436(2)$, $b = 21.5125(10)$, $c = 16.678(4)$ Å, $\beta = 107.843(10)^\circ$, $Z = 4$, $V = 3564.2(11)$ Å^3, $\rho_{calcd} = 1.514$ g cm^{-3}; $T =$ 193(2) K; $2\Theta = 53.92^\circ$; 9426 reflections measured, 7753 were unique ($R_{int} = 0.0216$) and 6642 observed ($I > 2\sigma(I)$); CAD4 (Enraf-Nonius), $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), graphite-monochromated, Zr filter (faktor 15.20); Lp correction. The structure was solved by direct methods and refined with the full-matrix, least-squares method; $R_1 =$ 0.0292, $wR_2 = 0.0662$ (for 6642 reflections with $I > 2\sigma(I)$), $R_1 = 0.0375$, $wR_2 = 0.0713$ (for all 7753 data); data-to-parameter ratio 18.37; residual electron density +0.355/−0.856 e Å^{-3}. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-146302 (**7**) and CCDC-146303 (**10**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[9] In the dinuclear compound $[(acac)Rh(\mu\text{-}CO)\{\mu\text{-}C(p\text{-}Tol)_2\}_2Rh(acac)(PMe_3)]$ the bond angle Rh-Rh-P is 132.89(4)°.[5]

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[15] The ^1H and ^{13}C NMR data of the phenyl groups were omitted for simplicity.