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The truly symmetrical doubly-bridging mode of trimethylphosphine in a dinuclear rhodium complex†

Thomas Pechmann, Carsten D. Brandt and Helmut Werner*
Institut für Anorganische Chemie der Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany.
E-mail: helmut.werner@mail.uni-wuerzburg.de; Fax: ++49-931-888-4623

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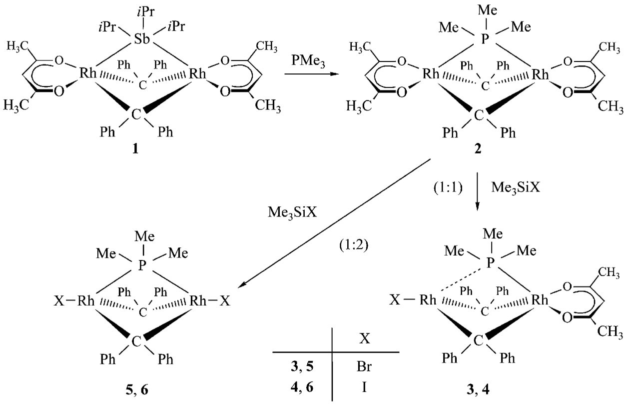
The dinuclear complex [$Rh_2I_2(\mu\text{-}CPh_2)_2(\mu\text{-}PMe_3)$] was prepared from the $Rh_2(acac)_2$ counterpart and Me_3SiI and shown crystallographically to contain the PMe_3 ligand in a truly symmetrical bridging position; a new synthetic route to migrate more bulky phosphines such as PPh_3 and P^iPr_3 from a terminal into a bridging site is also described.

In contrast to CO and isocyanides, tertiary phosphines such as PMe_3 or PPh_3 are assumed to coordinate to transition-metal centres in a terminal but not in a doubly-bridging mode.[1] In attempting to obtain a dinuclear palladium compound with Pd(μ_2-PF_3)Pd as the core unit, Balch and coworkers reported in 1990 the preparation and structural characterization of a cationic Pd_3 complex consisting of a nearly equilateral triangle of palladium atoms capped by the triply bridging phosphorus atom of PF_3.[2] More recently, we found in the context of our work on mono- and di-nuclear carbenerhodium(I) complexes,[3] that the bis(acac) compound **1** reacts with trimethylphosphine by ligand exchange and formation of **2**. While according to the NMR data there was no doubt, that the PMe_3 ligand should occupy a symmetrical bridging position, the X-ray crystal structure analysis of **2** revealed that in the solid the distances between phosphorus and the two rhodium centres differ by 0.30 Å.[4]

To explore whether by replacing the bidentate acac ligands for monodentate chloro ligands the situation would change and a complex with a truly symmetrical Rh(μ-PMe_3)Rh bridge would be formed, we treated compound **2** with Me_3SiCl and isolated a product which gave a correct elemental analysis for [$Rh_2Cl_2(\mu\text{-}CPh_2)_2(\mu\text{-}PMe_3)$]. While we anticipated, owing to the ^1H and ^{13}C NMR spectra, that the required complex had been obtained, a crystallographic study confirmed that in the solid two dinuclear moieties are connected through two bridging chlorides to afford a Rh_4 species with a chain-like [$ClRh_2(\mu\text{-}Cl)_2Rh_2Cl$] core.[5] Although cryoscopic measurements indicated that at low concentrations a cleavage of the Rh_4 into two Rh_2 units probably occurs, the problem of whether a discrete compound of the composition [$Rh_2X_2(\mu\text{-}CPh_2)_2(\mu\text{-}PMe_3)$] (where X is a monodentate ligand) with a truly symmetrical Rh(μ-PMe_3)Rh bridge exists remained unresolved.

We have now found that, by using Me_3SiBr or Me_3SiI instead of Me_3SiCl, the final goal can be achieved. Treatment of **2** with an equimolar amount of Me_3SiBr or Me_3SiI in toluene at room temperature leads to the replacement of one acac ligand for one bromide or iodide and gives compounds **3** and **4** as deeply coloured solids in nearly quantitative yields (Scheme 1). Similarly to the corresponding acac(chloro) derivative [$ClRh(\mu\text{-}CPh_2)_2(\mu\text{-}PMe_3)Rh(\kappa^2\text{-}acac)$],[4] the NMR spectroscopic data of **3** and **4** reveal that the trimethylphosphine ligand occupies a semi-bridging position. The most typical feature is the doublet of doublet resonance in the ^{31}P NMR spectra which appears at δ −27.3 (**3**) and −22.3 (**4**) with ^{31}P–^{103}Rh coupling constants of 157.7 and 64.4 (**3**) and 165.2 and 53.5 Hz (**4**), respectively.



Scheme 1

The reactions of **2** with Me_3SiBr and Me_3SiI in the molar ratio of 1 : 2 proceed more slowly and afford in toluene after 24 h (X = Br) or 2 h (X = I) at room temperature the dibromo and diiodo complexes **5** and **6** in 90–92% isolated yield. In contrast to [{$Rh_2Cl_2(\mu\text{-}CPh_2)_2(\mu\text{-}PMe_3)$}$_2$], the ^{31}P NMR spectra of **5** and **6** (in CD_2Cl_2) are independent on the concentration of the solution and display in each case a sharp triplet at δ −18.3 (**5**) and −20.8 (**6**), respectively. Moreover, cryoscopic measurements indicate that no dimerisation (as it happens in the case of the dichloro compound) takes place.

The hope that the PMe_3 ligand occupies even in the solid a truly symmetrical bridging position was confirmed by an X-ray crystal structure analysis of **6**.†‡ As shown in Fig. 1, the molecule contains a C_2 axis passing through the phosphorus atom and the midpoint of the Rh–Rh distance. The I–Rh–Rh–I

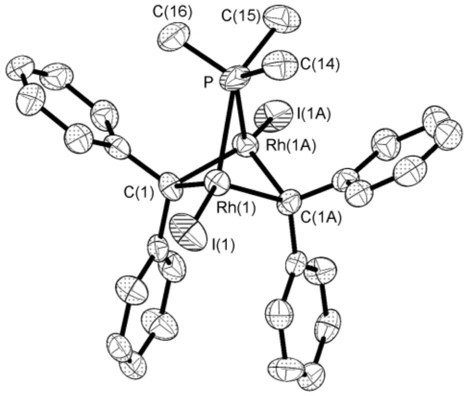


Fig. 1 Molecular structure of compound **6**. Selected bond lengths (Å) and angles (°): Rh(1)–C(1) 1.999(9), Rh(1)–C(1A) 2.004(9), Rh(1A)–C(1) 2.004(9), Rh(1)–Rh(1A) 2.5040(14), Rh(1)–P 2.412(3), Rh(1A)–P 2.412(3), Rh(1)–I(1) 2.5983(10); Rh(1)–C(1)–Rh(1A) 77.4(3), C(1)–Rh(1)–C(1A) 86.7(4), I(1)–Rh(1)–Rh(1A) 174.37(2), Rh(1)–P–Rh(1A) 62.54(10), C(1)–Rh(1)–P 89.6(3), C(1A)–Rh(1)–P 89.5(3), I(1)–Rh(1)–P 126.89(6), I(1)–Rh(1)–C(1) 126.1(3), I(1)–Rh(1)–C(1A) 125.7(3), C(1)–Rh(1)–Rh(1A) 51.4(2), C(1A)–Rh(1)–Rh(1A) 51.2(3), P–Rh(1)–Rh(1A) 58.73(5).

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† Electronic supplementary information (ESI) available: experimental details. See http://www.rsc.org/suppdata/cc/b3/b301251d/

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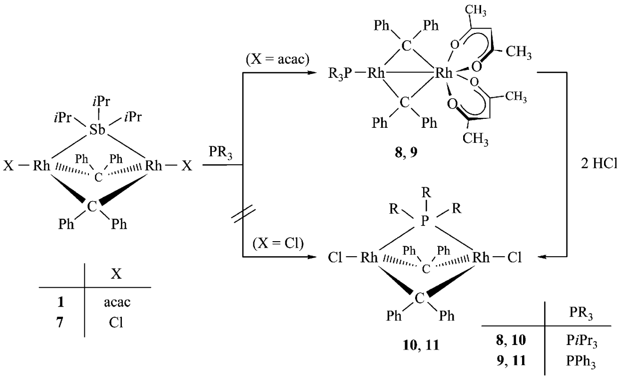
axis is nearly linear with bond angles Rh(1)–Rh(1A)–I(1A) = Rh(1A)–Rh(1)–I(1) = 174.37(2)°. The Rh–P bond lengths in **6** are 2.412(3) and thus in between those of **2** (2.2707(7) and 2.5700(8) Å).[4]

After we confirmed that PMe_3 can behave as a bridging ligand, we also succeeded with transferring the more bulky P^iPr_3 from a terminal into a bridging position. In our previous studies on the reactivity of **7** (the precursor of compound **1**) toward Lewis bases, we discovered that this complex reacts with P^iPr_3 to give *trans*-$[RhCl(=CPh_2)(P^iPr_3)_2]$.[3] In contrast, treatment of **1** with P^iPr_3 does not lead to cleavage of the Rh(μ-CPh_2)Rh bridges and affords by migration of one acac ligand from one metal center to the next the interesting mixed-valence compound **8** in excellent yield Scheme 2.[6] Since it could be conceivable that this reaction proceeds via the phosphine-bridged species $[Rh_2(\kappa^2\text{-acac})_2(\mu\text{-}CPh_2)_2(\mu\text{-}P^iPr_3)]$, we attempted to trap this intermediate by replacing the acac ligands for chloride. A clean reaction occurred, indeed, if a solution of HCl in benzene was dropped under vigorous stirring to a solution of **8** in the same solvent at room temperature. After removal of the volatile materials, the required complex **10** was isolated as a red, moderately air-stable solid in 91% yield. In the same way, the PPh_3 counterpart **11** could be generated from **9**; it was characterized by spectroscopic techniques. The ^{13}C NMR spectra of **10** and **11** display a triplet for the CPh_2 carbon atoms at δ 180.7 (**10**) and 191.2 (**11**) with a ^{13}C–^{103}Rh coupling constant of 28.6 Hz. Since the ^{31}P NMR spectra of **10** and **11** also show a sharp triplet at, respectively, δ 14.9 (**10**) and 9.8 (**11**), there is no doubt that the more bulky phosphines P^iPr_3 and PPh_3 can equally be linked to two metal centres in a bridging position. That this mode of coordination might be realized also in other di-nuclear complexes was recently pointed out by Braunstein and Boag,[7] who took the isolobal analogy of SiR_3^- and PR_3 into consideration. Moreover, the discovery by Reau *et al.*[8] that the phosphorus atom of substituted phospholes can bridge two palladium centres strongly supports this prediction.



Scheme 2

Notes and references

‡ Selected characterization data: **3**: Yield: 92%, mp 144 °C dec. NMR (CD_2Cl_2): δ_C (100.6 MHz) 174.1 (ddd, J(Rh,C) = 30.5, J(Rh′,C) = 21.0, J(P,C) = 4.8 Hz, CPh_2); δ_P (162.0 MHz) −27.3 (dd, J(Rh,P) = 157.7, J(Rh′,P) = 64.4 Hz). **4**: Yield 94%, mp 116 °C dec. NMR (CD_2Cl_2): δ_C (100.6 MHz) 171.5 (ddd, J(Rh,C) = 31.5, J(Rh′,C) = 20.0, J(P,C) = 4.3 Hz, CPh_2); δ_P (162.0 MHz) −22.3 (dd, J(Rh,P) = 165.2, J(Rh′,P) = 53.5 Hz). **5**: Yield 92%, mp 63 °C dec. NMR (CD_2Cl_2): δ_C (100.6 MHz) 188.6 (m, CPh_2); δ_P (162.0 MHz) −18.3 (t, J(Rh,P) = 108.5 Hz). **6**: Yield 90%, mp 80 °C dec. NMR (CD_2Cl_2): δ_C (100.6 MHz) 184.9 (m, CPh_2); δ_P (121.5 MHz) −20.8 (t, J(Rh,P) = 105.2 Hz). **10**: Yield 91%, mp 119 °C dec. NMR (CD_2Cl_2): δ_C (100.6 MHz) 180.7 (t, J(Rh,C) = 28.6 Hz, CPh_2); δ_P (162.0 MHz, 263 K) 14.9 (t, J(Rh,P) = 92.6 Hz). **11**: NMR (CD_2Cl_2): δ_C (100.6 MHz) 191.2 (t, J(Rh,C) = 28.6 Hz, CPh_2); δ_P (162.0 MHz) 9.8 (t, J(Rh,P) = 103.6 Hz).

Crystal data for **6**: $C_{29}H_{29}I_2PRh_2\cdot 2/3\ OC(CH_3)_2$, crystal size 0.30 × 0.17 × 0.16 mm, trigonal, space group $R\text{-}3c$ (no. 167), a = 22.9416(17), b = 22.9416(17), c = 31.230(3) Å, V = 14235(2) Å^3, Z = 18, D_c = 1.904 g cm^{-3}, μ = 3.066 mm^{-1}, λ = 0.71073 Å, T = 173(2) K, F(000) = 7836, for 2817 independent reflections, R_1 = 0.0658 [$I > 2\sigma(I)$], wR_2 = 0.1372, GOF on F^2 = 1.303, diff. peak/hole (e Å^{-3}) = 1.389/−1.044. Data were collected on a Bruker Smart Apex diffractometer and the structure was solved using the program SHELXL-97. CCDC 202931. See http://www.rsc.org/suppdata/cc/b3/b301251d/ for crystallographic files in CIF or other electronic format.

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