

Note

Preparation and molecular structure of a dinuclear rhodium complex having an unbalanced (15 + 17)-electron count

Ulrich Herber, Kerstin Ilg, Helmut Werner*

Institut für Anorganische Chemie, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

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Abstract

The reaction of $[\text{Rh}_2(\text{acac})_2\{\mu\text{-C}(p\text{-tol})_2\}_2(\mu\text{-SbiPr}_3)]$ (**1**) with PMe_3 led to the displacement of the stibine by phosphine and afforded the highly labile intermediate $[\text{Rh}_2(\text{acac})_2(\text{PMe}_3)\{\mu\text{-C}(p\text{-tol})_2\}_2]$ (**2**) in which the PMe_3 ligand possibly occupies a terminal position. Treatment of **2** with CO at low temperatures gave the unsymmetrical dinuclear complex $[\text{Rh}_2(\text{acac})_2(\text{PMe}_3)\{\mu\text{-C}(p\text{-tol})_2\}_2(\mu\text{-CO})]$ (**3**), the molecular structure of which was determined crystallographically.

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1. Introduction

Recently, we reported that the stibine-bridged compounds $[\text{Rh}_2(\text{acac})_2(\mu\text{-CR}_2)_2(\mu\text{-SbiPr}_3)]$ ($\text{R} = \text{Ph}, p\text{-tol}$) react with Lewis bases L such as CO, CNtBu and SbEt_3 by displacement of the triisopropylstibine ligand and formation of analogous dinuclear rhodium complexes, in which the ligand L like SbiPr_3 in the starting material occupies a bridging position [1,2]. In contrast, if the precursors $[\text{Rh}_2(\text{acac})_2(\mu\text{-CR}_2)_2(\mu\text{-SbiPr}_3)]$ were treated with $\text{P}i\text{Pr}_3$ or PPh_3 not only a substitution of SbiPr_3 for $\text{P}i\text{Pr}_3$ or PPh_3 occurred but also, most unusually, the migration of one acetylacetonato ligand from one metal center to the next. Following this route, a series of mixed-valence Rh(0)–Rh(II) complexes were generated for which there was no precedence [1,2].

After our attempts to prepare analogous mixed-valence compounds $[(\text{PR}'_3)\text{Rh}(\mu\text{-CR}_2)_2\text{Rh}(\text{acac})_2]$ with phosphines that are sterically less demanding than $\text{P}i\text{Pr}_3$

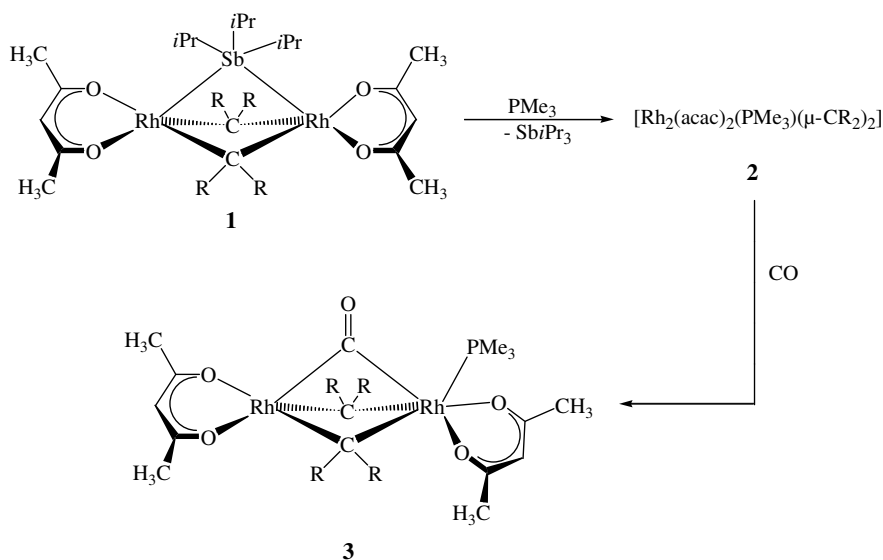
or PPh_3 failed [3], we found in the continuation of these studies that under strictly controlled conditions the stibine-containing precursor $[\text{Rh}_2(\text{acac})_2(\mu\text{-CPh}_2)_2(\mu\text{-SbiPr}_3)]$ reacts with PMe_3 by bridge-ligand exchange and formation of $[\text{Rh}_2(\text{acac})_2(\mu\text{-CPh}_2)_2(\mu\text{-PMe}_3)]$ [4]. This complex, which is also accessible on an alternative route [4,5], has been characterized crystallographically. In this communication, we illustrate that the reactivity of the related starting material $[\text{Rh}_2(\text{acac})_2\{\mu\text{-C}(p\text{-tol})_2\}_2(\mu\text{-SbiPr}_3)]$ (**1**) towards trimethylphosphine is somewhat different and that on stepwise treatment of **1** with PMe_3 and CO a dinuclear rhodium complex with an unbalanced (15 + 17)-electron count is accessible.

2. Results and discussion

Addition of excess trimethylphosphine to a solution of compound **1** in pentane at -50°C leads, after warming to room temperature, to the precipitation of a red solid which correctly analyzes as $[\text{Rh}_2(\text{acac})_2(\text{PMe}_3)\{\text{C}(p\text{-tol})_2\}_2]$ (**2**) (Scheme 1). While **2** is thermally quite stable and only moderately air-sensitive, it decomposes in solution almost instantaneously. Thus, no

* Corresponding author. Tel.: +49 931 888 5270; fax: +49 931 888 4623.

E-mail address: helmut.werner@mail.uni-wuerzburg.de (H. Werner).



Scheme 1.

reliable ^1H or ^{31}P NMR spectrum of **2** in C_6D_6 or acetone- d_6 could be obtained. The ^{31}P CP/MAS NMR spectrum displays a single resonance at $\delta = 5.7$ ppm, which is split into a doublet indicating that the phosphine ligand probably occupies a terminal and not a bridging position. The ^{13}C CP/MAS NMR spectrum of **2** shows two signals for the CO and equally two signals for the CH carbon atoms of the acetylacetonate units. This illustrates that the two acac ligands are spectroscopically and presumably also stereochemically different.

Taking into consideration that the CO-bridged complex $[\text{Rh}_2(\text{acac})_2\{\mu\text{-C}(p\text{-tol})_2\}_2(\mu\text{-CO})]$ was already known [2], we studied the reactivity of intermediate **2** towards carbon monoxide. When we passed a slow stream of CO through a solution of **2** in acetone, rapid decomposition occurred. To avoid this, we first prepared a saturated solution of CO in acetone, cooled the solution to -50°C and then added a sample of **2** to this solution. After warming to room temperature and evaporation of the solvent, a red microcrystalline solid of the analytical composition corresponding to **3** was isolated in 78% yield. In contrast to **2**, compound **3** is stable in solution and can be stored under argon for weeks without decomposition. The IR spectrum of **3** shows a strong absorption at 1822 cm^{-1} , i.e. in a region where the stretching modes for doubly bridging carbonyl ligands should appear. The ^{31}P NMR spectrum of **3** displays a doublet-of-doublet resonance at $\delta = -5.2$ ppm with a large (129.7 Hz) and a small (7.6 Hz) $^{31}\text{P}\text{--}^{103}\text{Rh}$ coupling.

The X-ray crystal structure analysis of **3** illustrates (see Fig. 1) that indeed the CO group occupies a bridging and the PMe_3 ligand a terminal position. The coordination geometry around Rh(1) is distorted octahedral while that around Rh(2) is best described as distorted

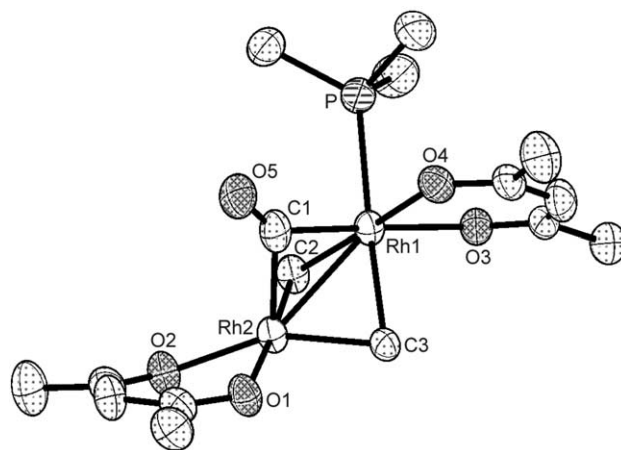


Fig. 1. Molecular structure of compound **3**; anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms and carbon atoms of the *p*-tolyl rings are omitted for clarity.

trigonal-bipyramidal with C(1), C(3) and O(2) in the equatorial and C(2) and O(1) in the axial positions. Despite the dissymmetry, the two bond lengths between the metal centers and the carbonyl carbon atom C(1) are nearly the same (Table 1). However, the distances between both Rh(1) and Rh(2) and the carbene carbon atoms C(2) and C(3) differ significantly as was also found in the unsymmetrical stibine-bridged compound $[\text{Rh}_2(\text{acac})\text{Cl}(\mu\text{-CPh}_2)_2(\mu\text{-Sb}i\text{Pr}_3)]$ [2]. The dissymmetry of the molecule **3** is also reflected in the unequal bond lengths between Rh(2) and the oxygen atoms O(1) and O(2) of the corresponding acetylacetonate unit. The distance Rh(1)–Rh(2) of 2.5163(6) Å differs only slightly to that of the symmetrical complex $[\text{Rh}_2(\text{acac})_2(\mu\text{-CPh}_2)_2(\mu\text{-CO})]$ (2.4933(9) Å) and lies in the range of other dinuclear rhodium(I) compounds with a metal–metal bond [6–9].

Table 1
Selected bond distances (Å) and bond angles (°) with estimated SD for compound **3**

Bond distances			
Rh(1)–Rh(2)	2.242(3)	Rh(2)–C(2)	2.074(5)
Rh(1)–P	2.4011(15)	Rh(2)–C(3)	2.018(4)
Rh(1)–C(1)	1.947(5)	Rh(1)–O(3)	2.147(3)
Rh(1)–C(2)	2.135(4)	Rh(1)–O(4)	2.169(3)
Rh(1)–C(3)	2.173(5)	Rh(2)–O(1)	2.156(3)
Rh(2)–C(1)	1.958(5)	Rh(2)–O(2)	2.098(3)
Bond angles			
Rh(1)–C(1)–Rh(2)	80.2(2)	C(2)–Rh(2)–O(1)	176.93(16)
Rh(1)–C(2)–Rh(2)	73.42(14)	P–Rh(1)–C(1)	96.40(16)
Rh(1)–C(3)–Rh(2)	73.70(16)	P–Rh(1)–C(2)	96.59(14)
C(1)–Rh(1)–C(2)	81.04(18)	P–Rh(1)–C(3)	175.01(11)
C(1)–Rh(2)–C(2)	82.3(2)	O(3)–Rh(1)–O(4)	85.44(12)
C(2)–Rh(1)–C(3)	88.34(17)	O(1)–Rh(2)–O(2)	84.16(13)
C(2)–Rh(2)–C(3)	94.37(13)	P–Rh(1)–Rh(2)	132.89(4)

In summarizing, the present investigations have shown that the size of the entering PR_3 ligand has a significant influence on the course of the reaction of the starting material **1** with trialkylphosphines. While upon treatment of **1** with the bulky $\text{P}i\text{Pr}_3$, apart from the displacement of the bridging stibine ligand, an unusual intramolecular rearrangement occurs, involving the migration of one acetylacetonato ligand from one rhodium center to the next, the reaction of **1** with the less bulky PMe_3 proceeds along a different route. Although the initially formed product **2** is rather labile, the ^{13}C CP/MAS NMR spectrum as well as the subsequent addition of CO confirms that also in the intermediate the two $\text{Rh}(\text{acac})$ fragments have been preserved. Despite the fact that the above-mentioned $\text{Rh}(\text{I})$ – $\text{Rh}(\text{II})$ complexes $[(\text{PR}'_3)\text{Rh}(\mu\text{-CR}_2)_2\text{Rh}(\text{acac})_2]$ are quite stable [2], attempts to transform **3** into the mixed-valence compound $[(\text{PMe}_3)\text{Rh}\{\mu\text{-C}(p\text{-tol})_2\}_2\text{Rh}(\text{acac})_2]$ failed.

3. Experimental section

The experiments were carried out under an atmosphere of argon by Schlenk techniques. The starting material **1** was prepared as described in the literature [2]. Melting points were measured by differential thermal analysis (DTA). Abbreviations used: s, singlet; d, doublet; m, multiplet.

2: A solution of 120 mg (0.12 mmol) of **1** in 15 ml of pentane was cooled at -50°C and treated dropwise with 60 μl (0.60 mmol) of trimethylphosphine. The solution was slowly warmed to r.t. and stirred for 30 min. A red solid precipitated, which was separated from the mother liquor, washed three times with 10 ml of pentane each and dried in vacuo; yield 96 mg (92%), m.p. (dec.) 102°C . Anal. Calc. for $\text{C}_{43}\text{H}_{51}\text{O}_4\text{PRh}_2$: C, 59.46; H, 5.92; Rh, 23.69. ^{13}C CP/MAS NMR (100.6 MHz): δ 186.7, 183.9 (both s, CO of acac), 151.3, 145.2 (both s,

ipso-C of *p*-tol), 137.4, 134.6 (both s, *para*-C of *p*-tol), 132.5, 128.6, 127.9, 122.7 (all s, *ortho*-C and *meta*-C of *p*-tol), 96.7, 95.7 (both s, CH of acac), 29.1 (s, CH_3 of acac), 24.7 (s, PCH_3), 21.2 (s, CH_3 of *p*-tol). ^{31}P CP/MAS NMR (162.0 MHz): δ 5.7 [d, $J(\text{Rh},\text{P}) = 119.6$ Hz]. Found: C, 58.98; H, 5.54; Rh, 22.87%.

3: A solid sample of 90 mg (0.10 mmol) of **2** was added to 20 ml of acetone, which was cooled at -50°C and saturated with CO. The solution was slowly warmed to r.t. and stirred for 1 h. The solvent was evaporated in vacuo and the residue recrystallized from 15 ml of pentane. After the solution was stored at -20°C for 12 h, red crystals precipitated which were washed with small amounts of pentane (-20°C) and dried in vacuo; yield 70 mg (78%), m.p. (dec.) 108°C . Anal. Calc. for $\text{C}_{44}\text{H}_{51}\text{O}_5\text{PRh}_2$: C, 58.94; H, 5.73; Rh, 22.95. IR (C_6D_6): $\nu(\text{CO})$ 1822, $\nu(\text{CO}_{\text{acac}})$ 1584, 1516 cm^{-1} . ^1H NMR (C_6D_6 , 200 MHz): 7.53, 7.13 (both m, 8H, *ortho*-H of *p*-tol), 7.02, 6.91, 6.73, 6.62 [all d, $J(\text{H},\text{H}) = 8.4$ Hz, 8H, *meta*-H of *p*-tol], 5.46, 4.96 (both s, 2H, CH of acac), 2.22, 2.12, 1.98, 1.26 (all s, 12H, CH_3 of acac), 1.91, 1.79 (both s, 12H, CH_3 of *p*-tol), 0.76 [d, $J(\text{P},\text{H}) = 9.1$ Hz, 9H, PCH_3]. ^{31}P NMR (C_6D_6 , 81.0 MHz): -5.2 [dd, $^1J(\text{Rh},\text{P}) = 129.7$, $^3J(\text{Rh},\text{P}) = 7.6$ Hz]. Found: C, 59.26; H, 5.41; Rh, 22.21%.

Crystal data for **6**: Crystals were obtained from pentane at -20°C . $\text{C}_{44}\text{H}_{51}\text{O}_5\text{PRh}_2$, $M_r = 896.64$; triclinic, space group $P\bar{1}$ (no. 2), $Z = 2$, $a = 10.7783(18)$ Å, $b = 13.895(3)$ Å, $c = 14.795(2)$ Å, $\alpha = 78.38(2)^\circ$, $\beta = 74.634(19)^\circ$, $\gamma = 74.42(2)^\circ$, $V = 2037.7(6)$ Å³, $D_{\text{calc}} = 1.461$ g cm⁻³, $\lambda = 0.71073$ Å, $T = 173(2)$ K, $\mu(\text{Mo K}\alpha) = 0.892$ mm⁻¹. Crystal size $0.21 \times 0.19 \times 0.18$ mm³; $2\theta_{\text{max}} = 50.06^\circ$; 21,424 reflections were measured, 6772 of these were independent ($R_{\text{int}} = 0.0649$) and employed in the structure refinement (481 parameters). The R values are $R_1 = 0.0412$ and $wR_2 = 0.0947$ [$I > 2\sigma(I)$] and $R_1 = 0.0590$ and $wR_2 = 0.1015$ (all data); reflex/parameter ratio = 14.1; min/max residual electron density: $0.927/-1.461$ e Å⁻³. Data were collected on a IPDS diffractometer from Stoe. A semi-empirical absorption correction was applied. The structure was solved by direct methods (SHELXS-97) [10] and refined against F^2 by least-squares (SHELXS-97) [11]. All non-hydrogen atoms were refined anisotropically. The positions of all hydrogen atoms were calculated according to ideal geometry (distance C–H 0.95 Å) and used only in structure factor calculations.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structure analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 232920 for compound **3**. Copies of this information may be obtained free of charge on application to the

Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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