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Journal of Organometallic Chemistry 569 (1998) 189–194

Journal of Organo metallic Chemistry

Two dinuclear rhodium complexes with a non-A-frame and a distorted A-frame skeleton and two $^{i}Pr_2PCH_2P^{i}Pr_2$ molecules as bridging ligands[1]

Helmut Werner *, Matthias Manger, Matthias Laubender, Markus Teichert, Dietmar Stalke

Institut fürAnorganische Chemie der Universitat Würzburg, Am Hubland, D-97074 Würzburg, Germany

Received 13 April 1998

Abstract

The π-allyl(carbonyl)rhodium(I) complex $[Rh(\eta^3\text{-}C_3H_5)(CO)(\kappa^2\text{-}{}^{i}Pr_2PCH_2P^{i}Pr_2)]$ (**2**), which was obtained from $[Rh(\eta^3\text{-}C_3H_5)(\kappa^2\text{-}{}^{i}Pr_2PCH_2P^{i}Pr_2)]$ (**1**) and CO, reacted with H_2 at room temperature to give the dinuclear hydrido compound $[\{Rh(CO)(\mu\text{-}H)(\mu\text{-}{}^{i}Pr_2PCH_2P^{i}Pr_2)\}_2]$ (**3**) in nearly quantitative yield. The X-ray crystal structure analysis of **3** confirmed a distorted square-planar coordination sphere around both metal centers with one hydride and the CO group as well as the two phosphorus atoms of the bis(phosphino)methane ligands in *trans* disposition. The reaction of **1** with excess methylformiate led to the formation of the μ-carbonato complex $[\{Rh(CO)(\mu\text{-}{}^{i}Pr_2PCH_2PPr_2)\}_2(\mu\text{-}O_2CO)]$ (**4**) with an A-frame type skeleton. The carbonate ligand is possibly formed from HCO_2Me by initial C–H cleavage and subsequent hydrolysis of the resulting CO_2Me unit. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Rhodium; A-frame complexes; Bis(diisopropylphosphino)methane; Bridging hydrido ligands; Bridging carbonato ligands

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1. Introduction

Following the development of a new preparative route to bis(phosphino)methanes $R_2PCH_2PR'_2$ and their P,As and P,Sb analogues $R_2PCH_2ER'_2$ (E = As, Sb), we recently reported that these compounds behave both as monodentate and chelating bidentate ligands in rhodium chemistry [1–3]. While attempts to obtain π-allyl rhodium derivatives of the general composition $[Rh(\eta^3\text{-}C_3H_5)(\kappa^2\text{-}{}^{i}Pr_2PCH_2ER_2)]$ (R = ^{i}Pr, ^{t}Bu, Cy) failed, the bis(phosphino)methanes $^{i}Pr_2PCH_2PR_2$ reacted with the in situ generated species $[Rh(\eta^3\text{-}C_3H_5)(\eta^4\text{-}C_8H_{12})]$ [4] to give the chelate complexes $[Rh(\eta^3\text{-}C_3H_5)(\kappa^2\text{-}{}^{i}Pr_2PCH_2PR_2)]$ (R = ^{i}Pr, Cy, Ph) in excellent yield [5]. Treatment of these complexes with CO led in the initial step to the formation of 1:1 adducts $[Rh(\eta^3\text{-}C_3H_5)(CO)(\kappa^2\text{-}{}^{i}Pr_2PCH_2PR_2)]$ which possess a non-rigid structure in solution. The assumption, that the fluctional behavior is due to a π-σ-π rearrangement of the C_3H_5 ligand, prompted us to investigate the reactivity of the π-allyl(carbonyl)rhodium complexes towards hydrogen. From previous work it was known that on treatment of $[Rh(\eta^3\text{-}C_3H_5)(CO)(PPh_3)_2]$ with H_2 the dinuclear rhodium(0) compound $[\{Rh(CO)(PPh_3)_2\}_2]$ was formed whereas the reaction of $[Ir(\eta^3\text{-}C_3H_5)(CO)(PPh_3)_2]$ with H_2 gave the trishydridoiridium(III) compound $[IrH_3(CO)(PPh_3)_2]$, respectively [6].

In this paper we describe the synthesis and structural characterization of two new dinuclear rhodium(I) compounds which are obtained from $[Rh(\eta^3\text{-}C_3H_5)(\kappa^2\text{-}{}^{i}Pr_2PCH_2P^{i}Pr_2)]$ (**1**) and $[Rh(\eta^3\text{-}C_3H_5)(CO)(\kappa^2\text{-}{}^{i}Pr_2PCH_2P^{i}Pr_2)]$ (**2**) as starting materials and which contain two bis(diisopropylphosphino)methane molecules as bridging ligands.

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* Corresponding author. Fax: +49 931 8884605.

[1] Dedicated to Professor Akira Nakamura in honour of his pioneering work in organometallic chemistry.

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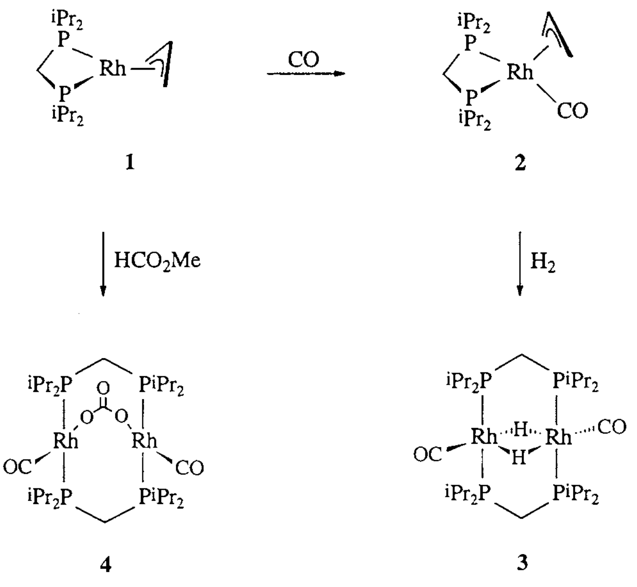
PII S0022-328X(98)00787-6

2. Results and discussion

If a slow stream of H_2 is passed through a solution of **2** in hexane/benzene (4:1), a deep red solution is formed from which upon evaporation of the solvent a deep red, relatively low-melting solid was isolated in nearly quantitative yield. The ^{1}H-NMR spectrum of the crude reaction mixture confirmed that propene is generated as a by-product. While the IR spectrum of the red solid indicated the presence of a metal bonded CO group, the ^{31}P-NMR spectrum unexpectedly displays a signal at δ 71.7 with an AA′A″A‴XX′-pattern (separation of the major lines 134.4 Hz) which is typical for compounds of the general composition $[\{Rh_2(\mu\text{-}Ph_2PCH_2PPh_2)_2\}X_nL_m]$ [7]. The ^{1}H-NMR spectrum of the new compound reveals that the allylic moiety has been replaced and a metal bonded hydrido ligand is present. The corresponding signal at δ -9.85 appears as a triplet with a rather large Rh,H coupling of 19.6 Hz. Since similar data were found for the hydrido bridged complex $[\{Rh(\mu\text{-}H)(CO)(\mu\text{-}Ph_2PCH_2PPh_2)\}_2]$, prepared by Eisenberg et al. from $[\{RhCl(CO)(\mu\text{-}Ph_2PCH_2PPh_2)\}_2]$ and $NaBH_4$ [8], we concluded that the reaction of **2** with H_2 affords the corresponding dinuclear hydridorhodium(I) complex **3** containing $^iPr_2PCH_2P^iPr_2$ as a bridging ligand.

The result of the X-ray crystal structure analysis of **3** (Fig. 1) confirms the structural proposal outlined in Scheme 1. The molecule contains a crystallographic center of symmetry which is the midpoint of the four-membered Rh_2H_2 plane. Due to the bridging coordination mode of the hydrido ligands, the geometry around both metal centers is distorted square-planar [P(1)–Rh(1)–P(2) 157.51(2)°, H(1)–Rh(1)–C(1) 164.7(9)°] with one hydrido ligand and the carbonyl group as well as two phosphorus atoms of the bis(phosphino)methane ligands in *trans* disposition, respectively. The bond angle P(1A)–C(20)–P(2) is 115.09(12)° (Table 1) and thus quite similar to that in bridging $Ph_2PCH_2PPh_2$ (dppm) ligands [9] and in free $Cy_2PCH_2PCy_2$ [10]. The Rh(1)–Rh(1A) distance of **3** [2.837(1) Å] is somewhat longer than in the cationic complex $[Rh_2(CO)_2(\mu\text{-}Ph_2PCH_2PPh_2)_2(\mu\text{-}H)(\mu\text{-}CO)]^+$ [2.731(2) Å] [11] where a Rh–Rh single bond is postulated. However, the intraligand distance between the phosphorus atoms [P(1)–P(2A) 3.12 Å] is significantly longer than the Rh(1)–Rh(1A) distance indicating that a rather strong Rh–Rh interaction is present in **3**. The Rh(1)–H(1) distance of 1.77(3) Å is almost identical to that of structurally related complexes containing a Rh–



Scheme 1.

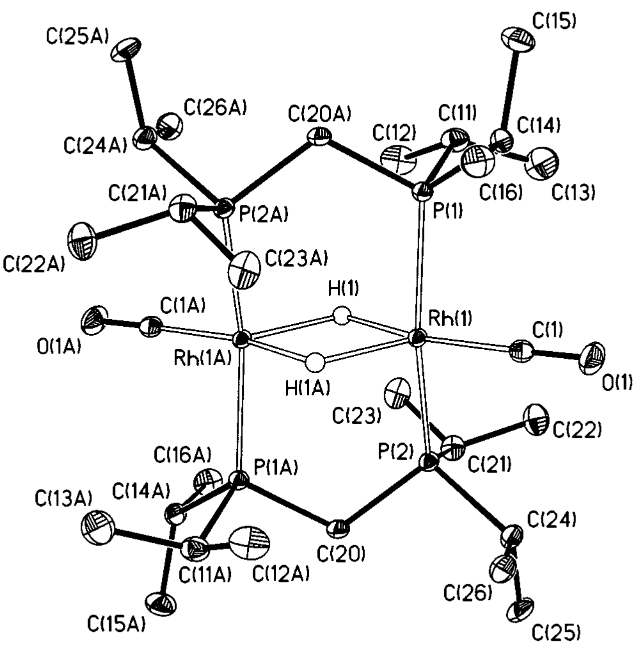


Fig. 1. Molecular structure of compund **3**; anisotropic displacement parameters are depicted at the 50% probability level.

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

Rh(1)-Rh(1A)	2.837(1)	Rh(1)–C(1)	1.839(3)
Rh(1)–H(1)	1.77(3)	C(1)–O(1)	1.161(3)
Rh(1)–P(1)	2.292(1)	P(1A)–C(20)	1.852(2)
Rh(1)–P(2)	2.294(1)	P(2)–C(20)	1.849(3)
Rh(1)–H(1)–Rh(1A)	103.0(9)	H(1)–Rh(1)–P(1)	84.0(9)
P(1)–Rh(1)–P(2)	157.51(2)	H(1)–Rh(1)–P(2)	85.5(9)
H(1)–Rh(1)–C(1)	164.7(9)	P(1)–Rh(1)–C(1)	91.71(8)
Rh(1)–C(1)–O(1)	178.3(2)	P(2)–Rh(1)–C(1)	93.28(8)
P(1)–Rh(1)–Rh(1A)	93.01(2)	P(1A)–C(20)–P(2)	115.09(12)
P(2)–Rh(1)–Rh(1A)	90.99(3)		

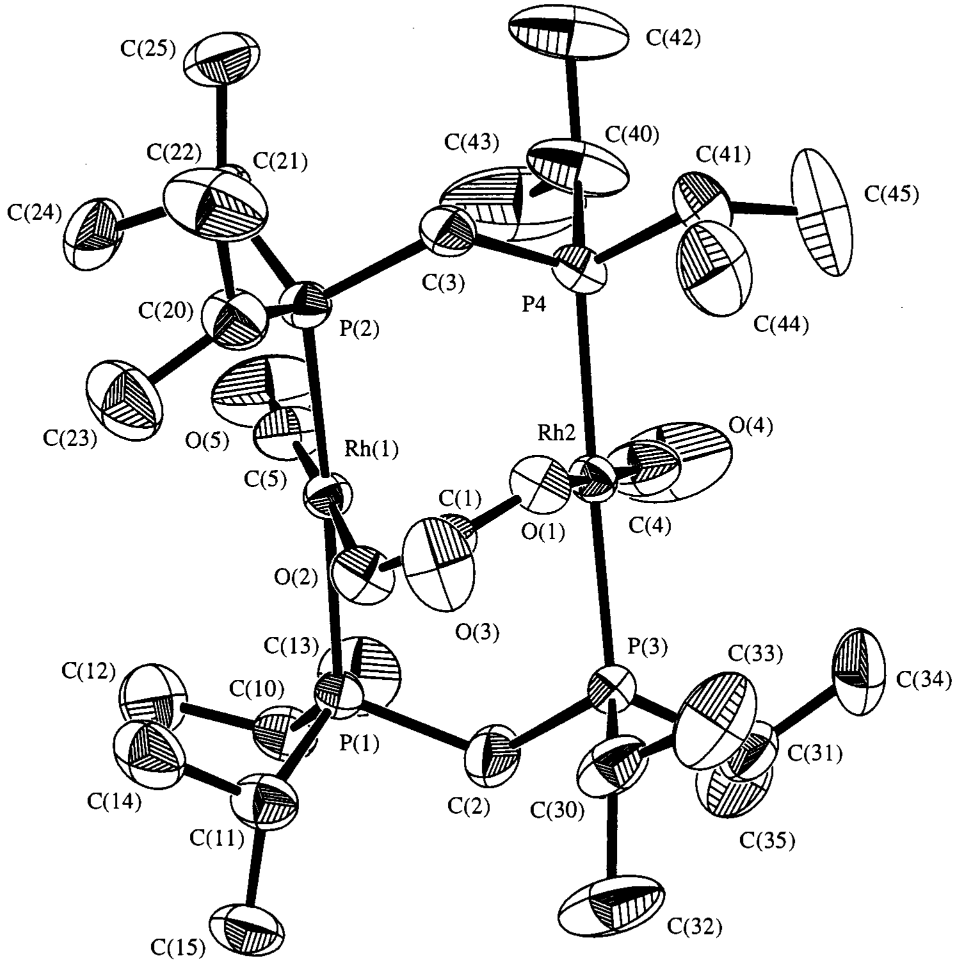


Fig. 2. Molecular structure of compound **4**; anisotropic displacement parameters are depicted at the 50% probability level.

H–Rh moiety [12]. The bond distances of the Rh–CO as well as of the $Rh_2(\mu\text{-}^iPr_2PCH_2P^iPr_2)_2$ unit are nearly the same as in corresponding carbonyl complexes with dppm as a ligand ([7]a, [12]c,d,e) and thus need no further comment.

With regard to the mechanism of formation of **3** from the mononuclear precursor **2** we assume that in the initial step of the reaction one molecule of H_2 is oxidatively added to the σ-allylic isomer $[Rh(\eta^1\text{-}C_3H_5)(CO)(\kappa^2\text{-}^iPr_2PCH_2P^iPr_2)]$ of **2**. Subsequent elimination of propene generates a square-planar carbonyl(hydrido)rhodium complex which, due to the ring strain of the chelating bis(phosphino)methane ligand, probably undergoes a dissociation of one P^iPr_2 fragment. Dimerization of the resulting intermediate could yield the final product.

The π-allyl complex **1**, which on treatment with CO smoothly affords the carbonyl derivative **2**, was also investigated with respect to its reactivity towards methylformiate. Recent work by Milstein has shown that $[RhCl(PMe_3)_3]$ (which like **1** is also a 16-electron species) reacts with HCO_2Me to give in the initial step by oxidative addition *mer*-$[RhHCl(CO_2Me)(PMe_3)_3]$. This six-coordinate hydridorhodium(III) compound slowly looses methanol as well as one PMe_3 ligand and finally yields *trans*-$[RhCl(CO)(PMe_3)_2]$ [13]. Methylformiate thus behaves as a source of CO and on treatment with **1** could possibly give **2**.

However, the attempts to prepare **2** from **1** and HCO_2Me failed. If a solution of **1** in benzene was treated with an equimolar amount of methylformiate, an orange-red solution was formed which owing to the ^{31}P-NMR spectrum contained a mixture of compounds including the starting material **1**. The use of an excess of HCO_2Me led to a different result. From the resulting deep red solution red crystals of **4** were obtained, the IR spectrum of which displayed a C≡O stretch for a metal-bonded carbonyl ligand at 1945 cm^{-1} and two bands at 1613 and 1445 cm^{-1} assigned to the stretching frequencies of a carbonate group. In the ^{31}P-NMR spectrum of **4** only one signal appears at δ 43.6 with a splitting pattern that is very similar to that of **3**.

Since the spectroscopic data of the new complex did not allow to make a convincing structural proposal, an X-ray crystal structure analysis of **4** was carried out. The result is shown in Fig. 2. The molecule consists of two Rh(CO) fragments which are bridged by two $^{i}Pr_2PCH_2P^{i}Pr_2$ and one carbonate ligand. Although the Rh(1)–O(2)–C(1)–O(1)–Rh(2) unit is somewhat twisted, the (OC)Rh(μ-O_2CO)Rh(CO) skeleton resembles a capital letter A similar to the situation found in $[\{Rh(CO)(\mu\text{-dppm})\}_2(\mu\text{-}O_2CCF_3)]^+$ ([7]d) and other dinuclear rhodium(I) complexes [14]. The geometry around both metal centers is almost exactly square-planar with bond angles between 82.96(7)° and 94.8(1)° (Table 2). Due to the twisting of the RhOCORh five-membered ring, the two RhCO units lie not in the same plane, the dihedral angle between the [O(4), C(4), Rh(2), Rh(1)] and [O(5), C(5), Rh(1), Rh(2)] planes being 21.7(2)°. The Rh–Rh distance of 2.974(1) Å is ca. 0.14 Å longer than in **3** but nearly identical to that in the cation $[\{Rh(CO)(\mu\text{-dppm})\}_2(\mu\text{-}O_2CCF_3)]^+$ (2.982 Å) ([7]d). The bond lengths Rh(1)–O(2) and Rh(2)–O(1) are significantly shorter than in carbonato complexes in which the CO_3^{2-} ligand forms a chelate bond to one metal center [15]. The two distances C(1)–O(1) and C(1)–O(2) lie between those of a C–O single and a C=O double bond indicating a partial degree of π-electron delocalization in the bridging carbonate unit.

The question of how compound **4** is formed from **1** and how the CO_3^{2-} and CO ligands are generated from methylformiate can not be answered conclusively. There is of course ample precedence for the formation of carbonyl complexes from HCO_2Me [13,16] but proof for the generation of a carbonate ligand from formic acid or methylformiate is rare. One possibility is that a metal-bonded CO_2Me unit is transformed in the presence of traces of water into a O_2COH ligand which by deprotonation gives coordinated CO_3^{2-}. We note that Yoshida et al. found that the dihydridorhodium(III) compound $[RhH_2(\kappa^2\text{-}O_2COH)(P^{i}Pr_3)_2]$ reacts with CO to produce the dinuclear carbonato-bridged complex $[\{Rh(CO)\ (P^{i}Pr_3)_2\}_2(\mu\text{-}O_2CO)\}]$ ([15]b).

Table 2
Selected bond distances (Å) and bond angles (°) with estimated S.D. for compound **4**.

Rh(1)–Rh(2)	2.974(1)	Rh(1)–O(2)	2.058(2)
Rh(1)–P(1)	2.326(1)	Rh(2)–O(1)	2.060(2)
Rh(1)–P(2)	2.348(1)	C(1)–O(1)	1.301(4)
Rh(2)–P(3)	2.329(1)	C(1)–O(2)	1.292(4)
Rh(2)–P(4)	2.324(1)	C(1)–O(3)	1.237(4)
Rh(1)–C(5)	1.781(3)	P(1)–C(2)	1.843(3)
Rh(2)–C(4)	1.772(3)	P(3)–C(2)	1.815(3)
C(5)–O(5)	1.157(4)	P(2)–C(3)	1.842(3)
C(4)–O(4)	1.150(4)	P(4)–C(3)	1.827(3)
P(1)–Rh(1)–P(2)	172.30(3)	C(4)–Rh(2)–P(3)	89.6(1)
O(2)–Rh(1)–C(5)	176.3(1)	C(4)–Rh(2)–P(4)	93.9(1)
Rh(1)–C(5)–O(5)	178.6(3)	O(2)–Rh(1)–P(1)	82.96(7)
P(3)–Rh(2)–P(4)	175.58(3)	O(2)–Rh(1)–P(2)	90.74(7)
O(1)–Rh(2)–C(4)	177.4(1)	O(1)–Rh(2)–P(3)	92.35(7)
Rh(2)–C(4)–O(4)	177.8(4)	O(1)–Rh(2)–P(4)	84.11(7)
O(2)–Rh(1)–Rh(2)	76.97(6)	O(1)–C(1)–O(2)	119.4(3)
O(1)–Rh(2)–Rh(1)	77.12(6)	O(1)–C(1)–O(3)	120.4(3)
C(5)–Rh(1)–P(1)	94.8(1)	O(2)–C(1)–O(3)	120.2(3)
C(5)–Rh(1)–P(2)	91.3(1)	P(1)–C(2)–P(3)	120.0(2)
		P(2)–C(3)–P(4)	117.7(2)

In conclusion, the present investigation has shown that bis(diisopropylphosphino)methane like dppm can act as a bridging ligand toward rhodium(I). The common feature of the two isolated complexes **3** and **4**, which were both characterized crystallographically, is the presence of a non-planar $Rh_2(CO)_2(\mu\text{-}^{i}Pr_2PCH_2P^{i}Pr_2)_2$ building block that is completed either by two hydrido or by one carbonato bridge. Thus two stable dinuclear species, one with a non-A-frame and the other with a distorted A-frame structure, results. It should be mentioned that prior to our work Fryzuk and coworkers [17] prepared from $[Rh(\eta^3\text{-}CH_2Ph)(\kappa^2\text{-}^{i}Pr_2PCH_2P^{i}Pr_2)]$ and hydrogen the hydrido complex $[\{RhH_2(\mu\text{-}H)\}_2\ (\mu\text{-}^{i}Pr_2PCH_2P^{i}Pr_2)_2]$ which also contains two $^{i}Pr_2PCH_2P^{i}Pr_2$ bridging ligands. However, in contrast to **3** and **4** this compound has rhodium(III) as the metal centers.

3. Experimental section

All experiments were carried out under an atmosphere of argon by using Schlenk techniques. The starting material **1** was prepared according to a published method [5]. IR: Perkin-Elmer 1320, NMR: Bruker AC 200 and AMX 400. Decomposition points were determined by DTA.

3.1. Preparation of *$[\{Rh(CO)(\mu\text{-}H)(\mu\text{-}^{i}Pr_2PCH_2P^{i}Pr_2)\}_2]$ (3)*

A degassed solution of 250 mg (0.59 mmol) of **2** in 10 ml of hexane/benzene (4:1) was treated with H_2 at −20°C and upon warming to room temperature stirred for 45 min. A change of color from orange-yellow to deep red occurred and an orange-red solid precipitated. The solvent was removed in vacuo, the residue was washed three times with 5-ml portions of pentane and dried. Yield 194 mg (86%); m.p. 40°C (decomposition). Anal. found: C, 44.58; H, 8.03. $C_{28}H_{62}O_2P_4Rh_2$ calc.: C, 44.22; H, 8.21. IR (C_6H_6): ν(C≡O) 1890 cm^{-1}. ^1H-NMR (400 MHz, C_6D_6): δ 1.96 (m, 8H, PC*H*CH$_3$), 1.75 (m, 4H, PCH$_2$P), 1.22 (m, in $^1H\{^{31}P\}$ d, J(HH) = 7.0 Hz, 24H, PCHC*H*$_3$), 1.16 (m, in $^1H\{^{31}P\}$ d, J(HH) = 6.9 Hz, 24H, PCHC*H*$_3$), −9.85 (br m, in $^1H\{^{31}P\}$ t, J(RhH) = 19.6 Hz, 2H, RhHRh). ^{31}P-NMR (81.0 MHz, $C_6D_5CD_3$): δ 71.7 (m, AA′A′A‴XX′-pattern, separation of the most intensive lines 134.4 Hz).

*3.2. Preparation of $[\{Rh(CO)(\mu\text{-}^{i}Pr_2PCH_2P^{i}Pr_2)\}_2(\mu\text{-}O_2CO)]$ (**4**)*

A solution of 129 mg (0.33 mmol) of **1** in 7 ml of hexane was treated with 0.8 ml (11.2 mmol) HCO_2Me and stirred for 3 h at room temperature. A red solution was formed which was brought to dryness in vacuo. The residue was dissolved in 3 ml of toluene/hexane (1:2) at ca. 50°C, and the solution was then slowly cooled to -78°C. Upon storing for 18 h red crystals were obtained, which were filtered, washed twice with 3-ml portions of pentane (0°C) and dried in vacuo. Yield: 52 mg (39%); m.p. 54°C (decomposition). Anal. found: C, 42.85; H, 7.12. $C_{29}H_{60}O_5P_4Rh_2$ calc.: C, 42.56; H, 7.39. IR (C_6H_6): ν(C≡O) 1945 cm^{-1}, $\nu(OCO_{asym})$ 1613 cm^{-1}, $\nu(OCO_{sym})$ 1445 cm^{-1}. ^1H-NMR (400 MHz, C_6D_6): δ 2.46 (m, 6H, PC*H*CH_3 and PCH_2P), 1.84 (m, 2H, PCH_2P), 1.52 (dvt, $N = 15.7$, $J(HH) = 8.0$ Hz, 12H, PCHC*H*$_3$), 1.22 (dvt, $N = 14.6$, $J(HH) = 7.3$ Hz, 12H, PCHC*H*$_3$), 1.13 (dvt, $N = 13.3$, $J(HH) = 6.9$ Hz, 12H, PCHC*H*$_3$), 1.10 (dvt, $N = 12.8$, $J(HH) = 6.5$ Hz, 12H, PCHC*H*$_3$). ^{31}P-NMR (81.0 MHz, $C_6D_5CD_3$): δ 43.6 (m, AA′A′A‴XX′- pattern, separation of the most intensive lines 131.0 Hz).

*3.3. Crystal structure analysis of **3***

Crystals were obtained by cooling a saturated solution of **3** in toluene (from 50 to -25°C). Crystal structure determination of **3**: $C_{28}H_{62}O_2P_4Rh_2$, $M_r = 760.48$; monoclinic, space group $C2/c$, $Z = 4$, $a = 18.441(4)$ Å, $b = 11.618(2)$ Å, $c = 16.101(3)$ Å, $\beta = 98.09(3)°$, $V = 3415.3(11)$ Å^3, $D_c = 1.479$ g cm^{-3}, $F(000)$ 1584, $\lambda = 0.71073$ Å, T = 133(2) K, $\mu(Mo\text{-}K_\alpha) = 1.177$ mm^{-1}, min/max transmission: 0.734/0.944. Crystal size $0.28 \times 0.23 \times 0.05$ mm^3; $4.46° < 2\Theta < 55.08°$; 12315 reflections were measured, 3855 unique of these were independent ($R_{int} = 0.0345$) and employed in the structure refinement (175 parameters). The R-values are $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.0277$ $[I > 2\sigma(I)]$ and $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[wF_o^4]\}^{1/2} = 0.0546$ (all data); min/max residual electron density: $-0.473/-0.477$ eÅ^{-3}. The bridging hydrogen atom bonded to rhodium was refined freely with isotropic displacement parameter. Data were collected on a Huber-Stoe-Siemens four cycle diffractometer with Siemens CCD area detector using an oil-coated shock-cooled crystal in an oil drop [18]. Data integration was performed with the program SAINT. A semiempirical absorption correction was applied [19]. The structure was solved by direct methods (SHELXS-97) [20] and refined against F^2 by least-squares (SHELXL-97) [21]. All non-hydrogen atoms were refined anisotropically. For the hydrogen atoms a riding model was employed. Crystallographic data (excluding structure factors) for **3** have been deposited with the Cambridge Crystallographic Data Centre [22]. Any request to the CCDC for this material should quote the full literature citation and the reference number CCDC-102392.

*3.4. Crystal structure analysis of **4***

Crystals were grown from benzene at room temperature. Crystal structure determination of **4**: $C_{29}H_{60}O_5P_4Rh_2$, $M_r = 818.47$; monoclinic, space group $P2_1/c$ (no. 14), $Z = 4$, $a = 12.288(4)$ Å, $b = 15.180(3)$ Å, $c = 20.055(7)$ Å, $\beta = 93.76(2)°$, $V = 3733(2)$ Å^3, $D_c = 1.456$ g cm^{-3}, $\mu(Mo\text{-}K_\alpha) = 1.077$ mm^{-1}. Crystal size $0.75 \times 0.63 \times 0.5$ mm^3; 7171 reflection were measured, 6558 of these were independent ($R_{int} = 0.0124$), 5998 regarded as being observed $[I > 2\sigma(I)]$ and employed in the structure refinement (377 parameters). The R-values are $R_1 = \Sigma|F_o| - |F_c||/\Sigma|F_o| = 0.0322$ $[I > 2\sigma(I)]$ and $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[wF_o^4]\}^{1/2} = 0.0749$ (all data); reflex to parameter ratio 17.40; min/max residual electron density $+0.838/-0.700$ eÅ^{-3}. Data were collected on a Enraf Nonius CAD4 diffractometer, $Mo\text{-}K_\alpha$ radiation (0.71073 Å), graphite monochromator, T = 293(2) K, Ω/Θ-scan, max $2\Theta = 50°$. LP- and empirical absorption correction was applied (Ψ-scans, minimum transmission 82.97%). The structure was solved by direct methods (SHELXS-86) [20] and refined against F^2 by least-squares (SHELXL-93) [23]. Crystallographic data (excluding structure factors) for **3** have been deposited with the Cambridge Crystallographic Data Centre [22]. Any request to the CCDC for this material should quote the full literature citation and the reference number CCDC-102392.

Acknowledgements

We gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft (SFB 347), the Fonds der Chemischen Industrie (Doktorandenstipendium for M. M.) and Degussa AG. M. T. thanks the Volkswagenstiftung and D. S. wishes to thank axe-Analytical X-Ray Systems, Karlsruhe, for support. Moreover, we gratefully acknowledge valuable experimental assistance by G. Canepa.

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