

Crystal Structure of $[\text{Rh}_2(\mu^2\text{-O}_2\text{CMe})_2\{\mu^2\text{-(CH}_2\text{)PPh}_2\}\{\mu^2\text{-(C}_6\text{H}_4\text{)PPh}_2\}\cdot\text{PPh}_3]\cdot 2\text{CH}_2\text{Cl}_2$, a Compound with a Diphenylphosphinomethanide Group in a Bridging (P,C) Coordination

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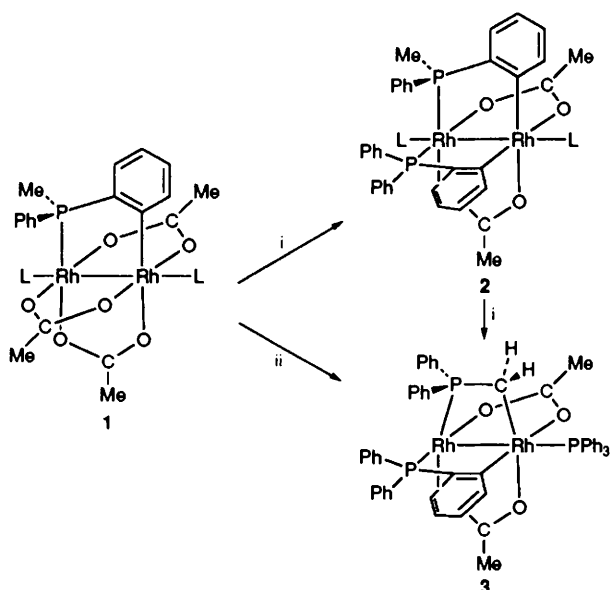
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The reaction of the monometallated compound $[\text{Rh}_2(\mu^2\text{-O}_2\text{CMe})_3\{\mu^2\text{-(C}_6\text{H}_4\text{)PMePh}\}\cdot(\text{HO}_2\text{CMe})_2]$ and two moles of PPh_3 yields $[\text{Rh}_2(\mu^2\text{-O}_2\text{CMe})_2\{\mu^2\text{-CH}_2\text{PPh}_2\}\{\mu^2\text{-(C}_6\text{H}_4\text{)PPh}_2\}\text{PPh}_3]\cdot 2\text{CH}_2\text{Cl}_2$ which according to the crystal structure contains an orthometallated triphenylphosphine and a diphenylphosphinomethanide group bridging the two rhodium atoms.

Some years ago Cotton *et al.*¹ reported that the reaction of rhodium tetraacetate and triphenylphosphine gives the compound $[\text{Rh}_2(\mu^2\text{-O}_2\text{CMe})_2\{\mu^2\text{-(C}_6\text{H}_4\text{)PPh}_2\}\cdot(\text{HO}_2\text{CMe})_2]$ where two acetate groups were replaced by two triphenylphosphine metallated at one *ortho* position of one phenyl ring. Since intramolecular C-H activation has been mainly described for monometallic systems² the above-mentioned example represented an interesting extension of this type of reactions to bimetallic systems. Further investigations showed that this type of compound can be prepared with a head-to-tail (H-T) or head-to-head (H-H)³ configuration and that acetic acid acts as catalyst for these reactions. The kinetics of a thermal and an acid-catalysed reaction has been studied.⁴ Reversible Rh-C bond cleavage has been studied for $[\text{Rh}_2(\mu^2\text{-O}_2\text{CMe})_3\{\mu^2\text{-(C}_6\text{H}_4\text{)PMePh}\}\cdot(\text{HO}_2\text{CMe})_2]$ in $\text{CD}_3\text{CO}_2\text{D}$ medium.⁵ Rhodium trifluoroacetate reacts faster than rhodium acetate with arylphosphines following the same reaction pathway.⁶ Morrison and Tocher⁷ reported on the reactivity of PMePh_2 or PMe_2Ph with dirhodium tetracarboxylates. In all cases metallation at the *ortho* aromatic carbon atoms of the phosphines was only observed and $[\text{Rh}_2(\mu^2\text{-O}_2\text{CR})_2\{\mu^2\text{-PC}\}_2\cdot(\text{HO}_2\text{CR})_2]$ compounds PC=bridging *ortho*-metallated group; R=Me, Bu^t were obtained.

We have recently found⁸ that $[\text{Rh}_2(\mu^2\text{-O}_2\text{CMe})_3\{\mu^2\text{-(C}_6\text{H}_4\text{)PMePh}\}\cdot(\text{HO}_2\text{CMe})_2]$ **1** reacts with PPh_3 giving $[\text{Rh}_2(\mu^2\text{-O}_2\text{CMe})_2\{\mu^2\text{-(C}_6\text{H}_4\text{)PMePh}\}\{\mu^2\text{-(C}_6\text{H}_4\text{)PPh}_2\}\cdot(\text{HO}_2\text{CMe})_2]$ **2**, a compound with a H-H configuration, in moderated yield. We report here that **1**, in chloroform solution, reacts at room



Scheme 1 Reagents and conditions: i, PPh₃; ii, 2PPh₃ (L = MeCO₂H; solvent: CHCl₃; room temperature)

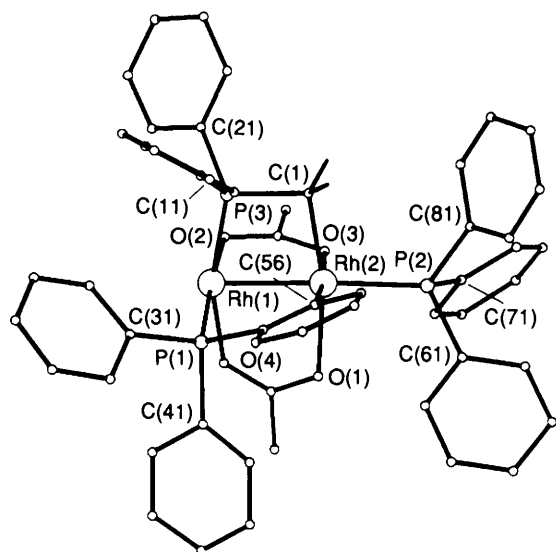


Fig. 1 The molecular structure of **3**, selected bond lengths (Å): Rh(1)–Rh(2) 2.532(2), Rh(1)–P(1) 2.211(4), Rh(1)–P(3) 2.240(4), Rh(1)–O(4) 2.117(9), Rh(1)–O(2) 2.111(9), Rh(2)–P(2) 2.297, Rh(2)–O(1) 2.228(9), Rh(2)–O(3) 2.169(9), Rh(2)–C(1) 2.06(1), Rh(2)–C(56) 2.05(1).

temperature with 2 moles of PPh₃ giving [Rh₂(μ²-O₂CMe)₂{μ²-(CH₂)PPh₂}{μ²-(C₆H₄)PPh₂}PPh₃] **3** as a major product. This compound is also obtained in good yield by reacting **2** with 1 mole of PPh₃ under the same conditions. Compound **3**⁺ is also formed with low yield in the preparation reaction of **2** from **1** and equimolar amounts of PPh₃.

† **Synthesis of 3**: **1** (100 mg, 0.14 mmol) and PPh₃ (74 mg, 0.28 mmol) were dissolved in CHCl₃ under argon atmosphere. The resulting brown-red solution was stirred for 2 h and the solvent removed under reduced pressure. The crude solid was transferred to a chromatography column packed with silica gel. Elution with CH₂Cl₂-hexane-acetone 5 : 5 : 1 separated a major yellow band containing **3**.

Spectroscopic data of 3 (*J* in Hz): ³¹P{¹H} NMR δ Pa 35.8, ¹J_{Rh-Pa} 154.3, ²J_{Pa-Pb} 8.6, ³J_{Pa-Pc} 36.5; δ Pb 17.4, ¹J_{Rh-Pb} 143.1, ²J_{Rh-Pb} 29.3, ³J_{Pc-Pb} 19.2; δ Pc 12.1, ¹J_{Rh-Pc} 134.3, ²J_{Rh-Pc} 17.7. ¹H NMR spectrum: 1.14 (3 H, CH₃, s), 1.16 (3 H, CH₃, s), 5.24 (2 H, CH₂Cl₂), 5.8–8.2 (39 H, arom, m). ¹³C {¹H} NMR: -5.2 (CH₂, m, metallated), 22.2 (CH₃, s), 22.9 (CH₃, s), 53.4 (CH₂, CH₂Cl₂, s), 120.5–145.9 (m, arom), 162.4 (m, arom), 178.1 (OCO, s), 178.3 (OCO, s).

Single crystals of **3**, suitable for X-ray crystallography, were grown by slow evaporation of a dichloromethane solution and the structure was confirmed by an X-ray structure determination[‡] (Fig. 1). The structure consists on discrete dinuclear rhodium units [Rh–Rh 2.532(2) Å] containing four bridging groups, two acetate ligands, one metallated triphenylphosphine and one metallated methyl-diphenylphosphine. The two phosphines are in a H–H configuration. One molecule of PPh₃ coordinates the less sterically hindered axial position. The relevant feature of this structure is that the PMePh₂ ligand is metallated at the Me group, and the diphenylphosphino-methanide group forms a four-membered Rh–P–C–Rh metalocycle. The formation of **3**, starting from **1** or **2**, involves cleavage of the Rh–C(aromatic) bond of the metallated PMePh₂ group, followed by metallation at one aliphatic C–H bond of the same ligand (Scheme 1). One intermediate species can be detected by monitoring the 1–3 reaction by ³¹P NMR spectroscopy at low temperature; however, its structural assignment is uncertain.

To our knowledge, the P,C bridging coordination mode observed for the methanide group in compound **3** had not been previously found for any of the different monophosphinomethanide compounds that have been reported up to date.⁹ Such a novel bridging mode has been only reported for a diplatinum complex with a bis-diphenylphosphinomethanide ligand.¹⁰

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References

- 1 A. R. Chakravarty, F. A. Cotton, D. A. Tocher and J. H. Tocher, *Organometallics*, 1985, **4**, 8.
- 2 D. Ryabov, *Chem. Rev.*, 1990, **90**, 403.
- 3 P. Lahuerta, J. Payá, E. Peris, A. Aguirre, S. García-Granda and F. Gómez-Beltrán, *Inorg. Chim. Acta*, 1992, **192**, 43.
- 4 P. Lahuerta, E. Peris, M. Sanaú, G. González and M. Martínez, *J. Chem. Soc., Dalton Trans.*, in the press.
- 5 P. Lahuerta and E. Peris, *Inorg. Chem.*, 1992, **31**, 4547.
- 6 P. Lahuerta, M. A. Ubeda, J. Payá, S. García-Granda, F. Gómez-Beltrán and A. Anillo, *Inorg. Chim. Acta*, 1993, **205**, 91.
- 7 E. C. Morrison and D. A. Tocher, *J. Organomet. Chem.*, 1991, **408**, 105; *Inorg. Chim. Acta*, 1989, **157**, 139.
- 8 M. V. Borrachero, F. Estevan, P. Lahuerta, J. Payá and E. Peris, *Polyhedron*, 1993, **12**, 1715.
- 9 H. H. Karsch and H. Schmidbauer, *Z. Naturforsch.*, 1977, **32b**, 762; H. H. Karsch, H. F. Klein, C. G. Kreiter and H. Schmidbauer, *Chem. Ber.*, 1974, **107**, 3692; N. E. Schre, L. S. Benner and B. E. Labelle, *Inorg. Chem.*, 1981, **20**, 3200; T. Cuenca, J. C. Flores, P. Royo, A. M. Larssonneur, R. Choukroun and F. Dahan, *Organometallics*, 1992, **11**, 777; J. Ruiz, V. Riera, M. Vivanco, S. García-Granda and A. García-Fernández, *Organometallics*, 1992, **11**, 4077.
- 10 M. P. Brown, A. Yavari, L. Manojlovic-Muir and M. W. Muir, *J. Organomet. Chem.*, 1983, **256**, C19.

‡ **Crystal data**: C₅₃H₄₇O₄P₃Rh₂·2CH₂Cl₂, *M*_r = 1216.55, yellow prisms, 0.23 × 0.23 × 0.13 crystal size, monoclinic, space group *P*2₁/*c*, *a* = 19.930(8), *b* = 15.29(2), *c* = 16.84(2) Å, β = 90.1(1)°, *V* = 5129(9) Å³, *Z* = 4, *D*_c = 1.58 g cm⁻³, *T* = 200 K; 9712 reflections measured, range 0 < θ < 25 and -23 < *h* < 23, 0 < *k* < 18, 0 < *l* < 20, 8988 unique reflections (*R*_{int} = 0.054) and 4749 observed with *i* > 3σ(*I*); μ = 9.80 cm⁻¹, *F*(000) = 2296 final *R* = 0.061, *R*_w = 0.061 (605 parameters, and ω = 1[σ²(*F*_o) + 0.001*F*_o²]; maximum shift/error 0.04, ρ_{max} = 1.8, ρ_{min} = -0.9 e Å⁻³, ρ = residual electron density. Mo-Kα radiation (λ = 0.71073 Å) graphite monochromated; Enraf-Nonius CAD4 (ω-2θ scan technique). Semiempirical and empirical absorption corrections were applied. The structure was solved by direct methods (SHELXS86) and anisotropically refined (SHELXS76, local version). Drawing made using the PLUTO program. All calculations made on a MicroVax-3400 at the Scientific Computer Center of the University of Oviedo. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data centre. See Notice to Authors, Issue No. 1.