

Interconversion of $\text{syn}-\{[(\text{Me}_3\text{C})_3\text{PRh}(\text{CO})]_2(\mu\text{-Cl})(\mu\text{-SR})\}$ and $\text{syn}-\{[(\text{Me}_3\text{C})_3\text{PRh}(\text{CO})]_2(\mu\text{-Cl})(\mu\text{-PR}_2)\}$ through exchange of bridging ligands. A case of sterically inactivated chloro bridges in dirhodium complexes

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Abstract

The transformation of $\text{syn}-\{[(\text{Me}_3\text{C})_3\text{PRh}(\text{CO})]_2(\mu\text{-Cl})(\mu\text{-SCMe}_3)\}$ to $\text{syn}-\{[(\text{Me}_3\text{C})_3\text{PRh}(\text{CO})]_2(\mu\text{-Cl})(\mu\text{-PPh}_2)\}$ by lithium diphenylphosphide in THF, and the conversion of $\text{syn}-\{[(\text{Me}_3\text{C})_3\text{PRh}(\text{CO})]_2(\mu\text{-Cl})(\mu\text{-PCMe}_3)_2\}$ into the above thiolato-bridged dirhodium complex by [(1,1-dimethylethyl)thio]trimethylsilane in hexane, provide examples of preferential exchange of thiolato- and phosphino-bridging ligands in dirhodium complexes containing sterically hindered chloro bridges.

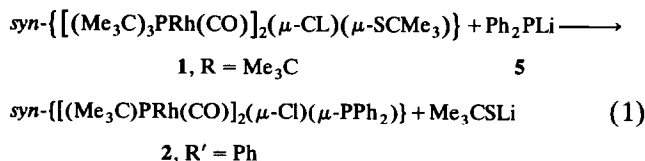
Key words: Rhodium; Interconversion

1. Introduction

The observations that dirhodium compounds of general formulas $\text{syn}-\{[(\text{Me}_3\text{C})_3\text{PRh}(\text{CO})]_2(\mu\text{-Cl})(\mu\text{-SR})\}$ (**1**) and $\text{syn}-\{[(\text{Me}_3\text{C})_3\text{PRh}(\text{CO})]_2(\mu\text{-Cl})(\mu\text{-PR}'_2)\}$ (**2**) are often more active catalysts than mono-rhodium complexes, [1,2] and more versatile than some dinuclear analogs with two thiolato- [3] or two phosphino-bridges [4], prompted our interest in the non-symmetrically bridged dirhodium compounds of type $[(\text{Me}_3\text{C})_3\text{PRh}(\text{CO})]_2(\mu\text{-SR})(\mu\text{-PR}'_2)$ (**3**). The ease with which many chloro-bridged dirhodium complexes are cleaved on the one hand, and the resistance of compounds with two thiolato- or phosphino-bridges towards such cleavage on the other hand [5], could suggest facile transformation of either **1** or **2** to **3**. Indeed, the feasibility of replacing chloro bridges in some dirhodium complexes containing one $\mu\text{-Cl}$ and one $\mu\text{-PR}_2$ ligand has already been demonstrated [6].

2. Results and discussion

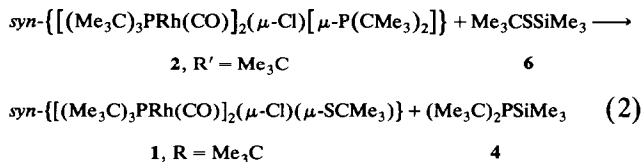
In the present study, we found, unexpectedly, that the chloro ligand in **1**, $\text{R} = \text{Me}_3\text{C}$ is not affected by the phosphination agents $(\text{Me}_3\text{C})_2\text{PSiMe}_3$ (**4**) and Ph_2PLi (**5**), and neither is the chloro bridge in **2**, $\text{R}' = \text{Me}_3\text{C}$ replaced by active thiolating agents [$\text{Me}_3\text{CSSiMe}_3$ (**6**), thiols or alkali thiolates]. Some of these reagents proved, however, to replace the non-halogen bridges, *i.e.* the thiolato and phosphino ligands. Compound **1**, $\text{R} = \text{Me}_3\text{C}$ (which is completely unreactive towards **4**) was transformed to **2**, $\text{R}' = \text{Ph}$ upon treatment with an equimolar amount of **5** in THF at room temperature for 4 h (eqn. (1)). The transformation was found to take place even at -20°C , although slowly.



Complex **2**, $\text{R}' = \text{Me}_3\text{C}$, was converted into the thio-

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lato-bridged compound **1**, R = Me₃C when treated with **6** in boiling hexane (eqn. (2)).



The structure of the dirhodium complex obtained in reaction **1** was established by: (i) its ¹H NMR spectrum, which consists of a doublet of the tris-*tert*-butylphosphine at 1.425 ppm (*J*(H,P) = 11.5 Hz), and multiplets at 7.050, 8.089 and 8.399 ppm of the aromatic ring protons, (ii) its ³¹P NMR spectrum which shows a tt pattern of the bridging atom at -3.06 ppm (*J*(P,P) = 233 Hz, *J*(P,Rh) = 90 Hz), indicating the *syn* orientation of the P(CMe₃)₃ groups that appear as a dd at 81.77 ppm (*J*(P,Rh) = 117 Hz); (iii) ¹H-³¹P decoupling and ³¹P-³¹P DQF-COSY measurements; (iv) elemental analysis; and (v) two independent syntheses from [Rh(CO)₂(μ-Cl)]₂ and P(CMe₃)₃ followed by reaction of the intermediate [(Me₃C)₃PRh(CO)(μ-Cl)]₂ so formed with either **5** or Ph₂PSiMe₃ (**7**) (see Experimental details).

The product formed in reaction **2** was compared directly with an authentic sample of **1**, R = Me₃C (the identity of which had been previously determined by an X-ray diffraction study [1a]).

We attribute the resistance of the bridging chlorine atom in **1** and **2** (R = Me₃C) towards displacement by the various thiolating and phosphination agents to the steric effect of the *syn*-oriented tris-*tert*-butylphosphine ligands, which practically encapsulate the small chlorine atom and shield it from external attack. This shielding also accounts for the resistance of compounds **1** and **2** towards cleavage (even at elevated temperatures) during various catalytic processes [1,2].

3. Experimental details

All experiments were performed under dried oxygen-free argon by use of standard Schlenk and vacuum techniques. Solvents were dried by standard methods, and distilled under argon before use. Infrared spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer. NMR spectra were recorded on Bruker WP 200 SY and AMX 400 spectrometers; ¹H and ³¹P chemical shifts are reported in ppm relative to TMS and 85% H₃PO₄, respectively.

Tetracarbonyl-*di-μ*-chlorodirhodium was purchased from Johnson Matthey, UK, and freshly sublimed before use. *syn*-{Dicarbonyl-*μ*-chloro[*μ*-(2-methyl-2-propanethiolato)bis[tris(1,1-dimethylethyl)phosphine]dirho-

dium (**1**, R = Me₃C) [1a], *syn*-[*μ*-[bis(1,1-dimethylethyl)phosphino]dicarbonyl-*μ*-chlorobis-[tris(1,1-dimethylethyl)phosphine]dirhodium (**2**, R' = Me₃C) [2], [bis(1,1-dimethylethyl)(trimethylsilyl)phosphine (**4**) [2], lithium diphenylphosphide (**5**) [7], [(1,1-dimethylethyl)thio]trimethylsilane (**6**) [8], and diphenyl(trimethylsilyl)phosphine (**7**) [7] were prepared by published methods.

3.1. *syn*-[Dicarbonyl-*μ*-chlorobis[tris(1,1-dimethylethyl)phosphine](*μ*-diphenylphosphino)]dirhodium (**2**, R' = Ph)

3.1.1. Method A

A solution of 448 mg (2.22 mmol) of (Me₃C)₃P in 3 ml of *n*-hexane was injected into a solution of 432 mg (1.11 mmol) of [Rh(CO)₂(μ-Cl)]₂ in 30 ml of the same solvent. The mixture was refluxed for 40 min during which the color changed from light yellow to deep orange. The mixture was cooled to 50°C and a solution of 343 mg (1.33 mmol) of **7** in 7 ml of *n*-hexane was added. After 2h refluxing, the tan solution was cooled and concentrated under reduced pressure. The remaining liquid was decanted off, and the precipitate washed several times with cold *n*-hexane then dried at 0.05 T. Yield 490 mg (50%) of pale yellow **2**, R' = Ph; m.p. 134–136°C (dec.). IR (KBr disk): ν (CO) 1950, 1955 cm⁻¹. ¹H NMR (C₆D₆, 200 MHz): δ 1.425 (d, 54H, *J*(H,P) = 11.5 Hz, CH₃); 7.050 (m, 4H, ArH); 8.089 (m, 4H, ArH); 8.399 (m, 2H, ArH). ³¹P{¹H} NMR (C₆D₆, 162 MHz): δ -3.06 (tt, *J*(P,P) = 233 Hz, *J*(P,Rh) = 90 Hz, *μ*-PPh₂); 81.77 [dd, *J*(P,P) = 233 Hz, *J*(P,Rh) = 117 Hz, (Me₃C)P]. Anal. Found: C, 50.93; H, 6.85; Cl, 4.55. C₃₈H₆₄ClO₂P₃Rh₂ (887.13) calcd: C, 51.44; H, 7.22; Cl, 4.00%.

3.1.2. Method B

A solution of 290 mg (1.44 mmol) of (Me₃C)₃P in 5 ml THF was added to a solution of 284 mg (0.72 mmol) of [Rh(CO)₂(μ-Cl)]₂ in 15 ml of the same solvent, and the mixture refluxed for 40 min. The solution was cooled to 20°C and 550 μl of a 1.3 M Ph₂PLi in THF (0.72 mmol) diluted with 8 ml of the same solvent was added from a syringe. The mixture was stirred at room temperature for 16 h and the solvent removed under reduced pressure. The residue was digested with 5 ml of benzene and the insoluble LiCl filtered off. Evaporation of the solvent at room temperature afforded 302 mg (47%) of **2**, R' = Ph, having the same physical properties as the sample obtained by method A.

3.2. Reaction of **1**, R = Me₃C with **5**

To a stirred solution of 300 mg (0.38 mmol) of **1**, R = Me₃C in 20 ml THF was added dropwise during

30 min 8 ml of THF containing 98 mg (0.4 mmol) of Ph_2PLi . The olive-brown solution was stirred at room temperature for 4 h. The solvent was removed under reduced pressure and the residue digested with 5 ml of benzene. The extract was filtered and evaporated to dryness, to give 134 mg of light-tan material that was shown by NMR spectroscopy, to consist of 85% of **2**, $\text{R}' = \text{Ph}$ and 15% of the unchanged starting complex, **1**.

3.3. Reaction of **2**, $\text{R}' = \text{Me}_3\text{C}$ with **6**

A solution of 114 mg (0.77 mmol) of **6** in 5 ml of *n*-hexane was added to a solution of **2**, $\text{R}' = \text{Me}_3\text{C}$ [freshly prepared from 0.77 mmol of $[\text{Rh}(\text{CO})_2(\mu\text{-Cl})_2]$, 1.48 mmol of $(\text{Me}_3\text{C})_3\text{P}$ and 0.83 mmol of **4** [2]] in 6 ml of the same solvent. The mixture was refluxed for 2 h, cooled and concentrated. The solvent was decanted, and the resulting precipitate washed twice with 5 ml of hexane to give 150 mg (25%) of pure **1**, $\text{R} = \text{Me}_3\text{C}$ as pale-yellow crystals; m.p. 117–120°C (dec.). IR (KBr disk): ν (CO) 1972, 1963 cm^{-1} . ^1H NMR (C_6D_6 200 MHz): δ 1.410 (d, 54H, $J(\text{H},\text{P}) = 12$ Hz, PCClH_3); 2.116 (s, 9H, SCCH_3). $^{31}\text{P}\{^1\text{H}\}$ -NMR (C_6D_6 162 MHz): δ 89.16 (d, $J(\text{P},\text{Rh}) = 140$ Hz) [1a].

Acknowledgments

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