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Interconversion of *syn*-{[$(Me_3C)_3PRh(CO)]_2(\mu$-Cl)(μ-SR)} and *syn*-{[$(Me_3C)_3PRh(CO)]_2(\mu$-Cl)(μ-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 *syn*-{[$(Me_3C)_3PRh(CO)]_2(\mu$-Cl)(μ-$SCMe_3$) to *syn*-{[$(Me_3C)_3PRh(CO)]_2(\mu$-Cl)(μ-PPh_2) by lithium diphenylphosphide in THF, and the conversion of *syn*-{[$(Me_3C)_3PRh(CO)]_2(\mu$-Cl)[μ-$P(CMe_3)_2$]} 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 *syn*-{[$(Me_3C)_3PRh(CO)]_2(\mu$-Cl)(μ-SR)} (**1**) and *syn*-{[$(Me_3C)_3PRh(CO)]_2(\mu$-Cl)(μ-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 [$(Me_3C)_3PRh(CO)]_2(\mu$-SR)(μ-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 μ-Cl and one μ-PR_2 ligand has already been demonstrated [6].

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2. Results and discussion

In the present study, we found, unexpectedly, that the chloro ligand in **1**, R = Me_3C is not affected by the phosphination agents $(Me_3C)_2PSiMe_3$ (**4**) and Ph_2PLi (**5**), and neither is the chloro bridge in **2**, R′ = Me_3C replaced by active thiolating agents [$Me_3CSSiMe_3$ (**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**, R = Me_3C (which is completely unreactive towards **4**) was transformed to **2**, R′ = 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.

$$\underset{\textbf{1},\ R = Me_3C}{syn\text{-}\{[(Me_3C)_3PRh(CO)]_2(\mu\text{-CL})(\mu\text{-}SCMe_3)\}} + \underset{\textbf{5}}{Ph_2PLi} \longrightarrow \underset{\textbf{2},\ R' = Ph}{syn\text{-}\{[(Me_3C)PRh(CO)]_2(\mu\text{-Cl})(\mu\text{-}PPh_2)\}} + Me_3CSLi \quad (1)$$

Complex **2**, R′ = Me_3C, was converted into the thio-

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lato-bridged compound **1**, R = Me_3C when treated with **6** in boiling hexane (eqn. (2)).

$$\underset{\textbf{2},\ R' = Me_3C}{syn\text{-}\{[(Me_3C)_3PRh(CO)]_2(\mu\text{-}Cl)[\mu\text{-}P(CMe_3)_2]\}} + \underset{\textbf{6}}{Me_3CSSiMe_3} \longrightarrow$$

$$\underset{\textbf{1},\ R = Me_3C}{syn\text{-}\{[(Me_3C)_3PRh(CO)]_2(\mu\text{-}Cl)(\mu\text{-}SCMe_3)\}} + \underset{\textbf{4}}{(Me_3C)_2PSiMe_3} \quad (2)$$

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 ^{31}P 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 $P(CMe_3)_3$ groups that appear as a dd at 81.77 ppm (J(P,Rh) = 117 Hz); (iii) ^1H–^{31}P decoupling and ^{31}P–^{31}P DQF-COSY measurements; (iv) elemental analysis; and (v) two independent syntheses from $[Rh(CO)_2(\mu\text{-}Cl)]_2$ and $P(CMe_3)_3$ followed by reaction of the intermediate $[(Me_3C)_3PRh(CO)(\mu\text{-}Cl)]_2$ so formed with either **5** or Ph_2PSiMe_3 (**7**) (see Experimental details).

The product formed in reaction 2 was compared directly with an authentic sample of **1**, R = Me_3C (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 = Me_3C) 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 ^{31}P chemical shifts are reported in ppm relative to TMS and 85% H_3PO_4, 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]dirhodium (**1**, R = Me_3C) [1a], *syn*-[μ-[bis(1,1-dimethylethyl)phosphino]]dicarbonyl-μ-chlorobis-[tris(1,1-dimethylethyl)phosphine]dirhodium (**2**, R′ = Me_3C) [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 $(Me_3C)_3P$ in 3 ml of *n*-hexane was injected into a solution of 432 mg (1.11 mmol) of $[Rh(CO)_2(\mu\text{-}Cl)]_2$ 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 (C_6D_6 200 MHz): δ 1.425 (d, 54H, J(H,P) = 11.5 Hz, CH_3); 7.050 (m, 4H, Ar*H*); 8.089 (m, 4H, Ar*H*); 8.399 (m, 2H, ArH). $^{31}P\{^1H\}$ NMR (C_6D_6 162 MHz): δ −3.06 (tt, J(P,P) = 233 Hz, J(P,Rh) = 90 Hz, μ-*P*Ph_2); 81.77 [dd, J(P,P) = 233 Hz, J(P,Rh) = 117 Hz, $(Me_3C)P$]. Anal. Found: C, 50.93; H, 6.85; Cl, 4.55. $C_{38}H_{64}ClO_2P_3Rh_2$ (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 $(Me_3C)_3P$ in 5 ml THF was added to a solution of 284 mg (0.72 mmol) of $[Rh(CO_2)(\mu\text{-}Cl)]_2$ 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 Ph_2PLi 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 = Me_3C 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**, R' = Ph and 15% of the unchanged starting complex, **1**.

3.3. Reaction of 2, R' = Me_3C 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**, R' = Me_3C [freshly prepared from 0.77 mmol of $[Rh(CO)_2(\mu\text{-}Cl)]_2$, 1.48 mmol of $(Me_3C)_3P$ 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**, R = Me_3C 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(H,P) = 12 Hz, PCCH_3); 2.116 (s, 9H, SCCH_3). $^{31}P\{^1H\}$-NMR (C_6D_6 162 MHz): δ 89.16 (d, J(P,Rh) = 140 Hz) [1a].

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