Monomerisation of $[Rh_2(1,3\text{-bis-(diphenylphosphino)-propane})_2(\mu_2\text{-Cl})_2]$ detected by pulsed gradient spin echo spectroscopy and ^{31}P NMR monitoring of metathesis experiments

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A pulsed gradient spin echo experiment on $[Rh_2(1,3\text{-bis-(diphenylphosphino)-propane})_2(\mu_2\text{-Cl})_2]$ complex has been conducted in order to shed light on the supposed monomerisation process of $[Rh_2(diphosphine)_2(\mu_2\text{-Cl})_2]$ complexes in solution. Such a process should generate a 14-electron [Rh(diphosphine)Cl] complex, which has only been postulated to date. Metathesis experiments on $[Rh_2(1,3\text{-bis-(diphenylphosphino)-propane})_2(\mu_2\text{-Cl})_2]$ and $[Rh_2(bis[2\text{-(diphenylphosphino)phenyl]ether})_2(\mu_2\text{-Cl})_2]$ complexes, analysed by ^{31}P NMR, reveal that monomerisation of $[Rh_2(diphosphine)_2(\mu_2\text{-Cl})_2]$ complexes is not restricted to the case of 1,3-bis-(diphenylphosphino)propane.

Keywords: diphosphine, Rh(I), diffusion-ordered spectroscopy, pulsed gradient spin echo spectroscopy

Neutral dimeric Rh(I) complexes stabilised by diphosphine ligands $[Rh_2(PP)_2(\mu_2\text{-Cl})_2]$ (PP = diphosphine) have interesting applications, mainly in catalysis. Recent examples include the hydrogenation of prochiral olefins,[1–3] the formation of C–C bonds mediated by hydrogen,[4–6] the addition of carboxylic acids to alkynes,[7–10] CO gas-free hydroformylation,[11–12] carbonylations[13] and many others. As suggested by several authors, the reactivity of these complexes should be strongly dependent on a dissociative process, which should generate a monomeric, highly reactive 14-electron complex of the type [Rh(PP)Cl] (Scheme 1).

The formation of this kind of intermediate has been proposed by us in the case of bis-[2-(diphenylphosphino) phenyl]ether[14] (DPEPhos) and by other authors in the case of 1,4-bis-(diphenylphosphino)ethane (DPPE) and 1,4-bis-(diphenylphosphino)butane[15] (DPPB), MeO-2,2′-bis-(diphenylphosphanyl)-1,1'-biphenyl[16] (MeO-BIPHEP) and PPh_3.[17] However, to the best of our knowledge, the generation of [Rh(PP)Cl] has been only postulated or even only calculated, but never observed directly.

The aim of the present study is to present some insights about the existence of the equilibrium reported in Scheme 1 in the case of PP = DPPP and DPEPhos through a diffusion-ordered NMR spectroscopy experiment and metathesis experiments followed by ^{31}P NMR.

Results and discussion

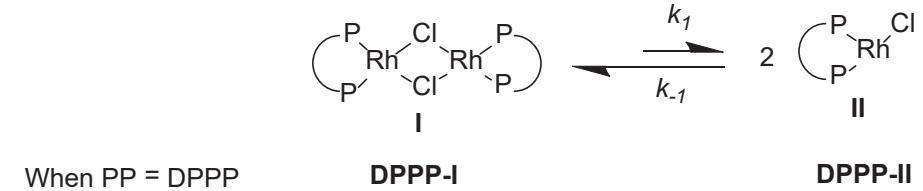
Complex $[Rh_2(DPPP)_2(\mu_2\text{-Cl})_2]$ (DPPP-I) was prepared by a variation of Bosnich´s procedure.[18] A solution containing DPPP-I (10 mg) in deuterated tetrahydrofuran (THF) (1 mL) was used for the NMR study. ^{31}P NMR experiments showed a doublet at δ 31.9 ppm with a J_{P-Rh} of 184 Hz, while ^{1}H and ^{13}C NMR spectroscopy indicated the presence of only one kind of species in solution. For a detailed characterisation of $[Rh_2(DPPP)_2(\mu_2\text{-Cl})_2]$, see ref.19. The detection of the supposed monomer [Rh(DPPP)Cl] (DPPP-II) by routine NMR experiments can be complicated by the rate of the equilibrium reported in Scheme 1, currently unknown. Attempts to quantify such an equilibrium have been made by flash photolysis of the carbonyl complex $[Rh(PPh_3)_2Cl(CO)]$.[20]

The only NMR characterisation of a tri-coordinate complex of this type was the proposed synthesis and characterisation of $[Rh(PCy_3)_2Cl]$ tri-coordinated complexes.[21] Comparison with the ^{31}P NMR spectrum of the corresponding dimer $[Rh_2(PCy_3)_4(\mu_2\text{-Cl})_2]$ revealed a slight change in the value of J_{P-Rh}. However the monomerisation of the $[Rh_2(PCy_3)_4(\mu_2\text{-Cl})_2]$ complex was not observed or proved.

A possible way to gain more information about the existence of the equilibrium reported in Scheme 1 and to collect direct evidence of the *in situ* formation of DPPP-II is by means of pulsed gradient spin echo (PGSE) diffusion NMR spectroscopy. Diffusion-ordered spectroscopy (DOSY) experiments have already been used in the past for the characterisation of reactive organometallic intermediates in solution.[22,23]

In this regard, when an evolving system is considered, the interpretation of the DOSY map can be difficult. In particular, in the case of fast exchange between two species in solution, the distinction between the two different coefficients of diffusion (D) is not guaranteed.[24] Having this limitation in mind, a ^{31}P DOSY experiment has been performed on a solution of DPPP-I in deuterated THF, with the aim of distinguishing between DPPP-I and DPPP-II on the basis of their different hydrodynamic radii (Fig. 1).[25]

The DOSY map relative to DPPP-I in THF reveals two different species with distinct values of D ($D_1 = 1.24 \times 10^{-9}$ m^2 s^{-1} and $D_2 = 1.42 \times 10^{-9}$ m^2 s^{-1}), which give the same signal in the ^{31}P NMR (δ 31.9 ppm). Due to the supposed fast equilibrium between DPPP-I and DPPP-II, the values for D reported in the DOSY map could be shifted with respect to the real ones, as previously reported.[26] In fact, the contribution of a fast equilibrium to the variation of I_0 (the signal amplitude in the absence of an external gradient), which will affect the increasing gradient strength, is not considered. As



Scheme 1 Monomerisation of $[Rh_2(DPPP)_2(\mu_2\text{-Cl})_2]$ complex.

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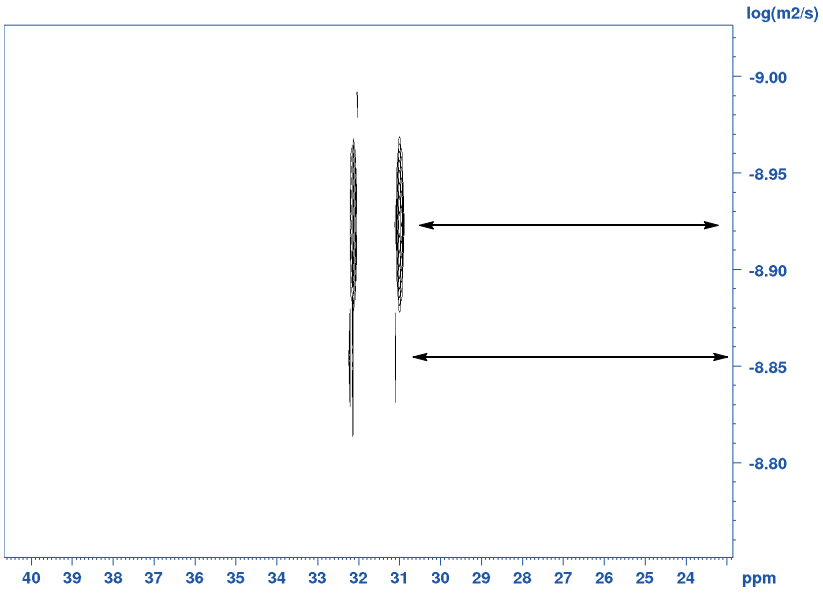

Fig. 1 DOSY map of a solution of complex DPPP-I in deuterated THF at room temperature.

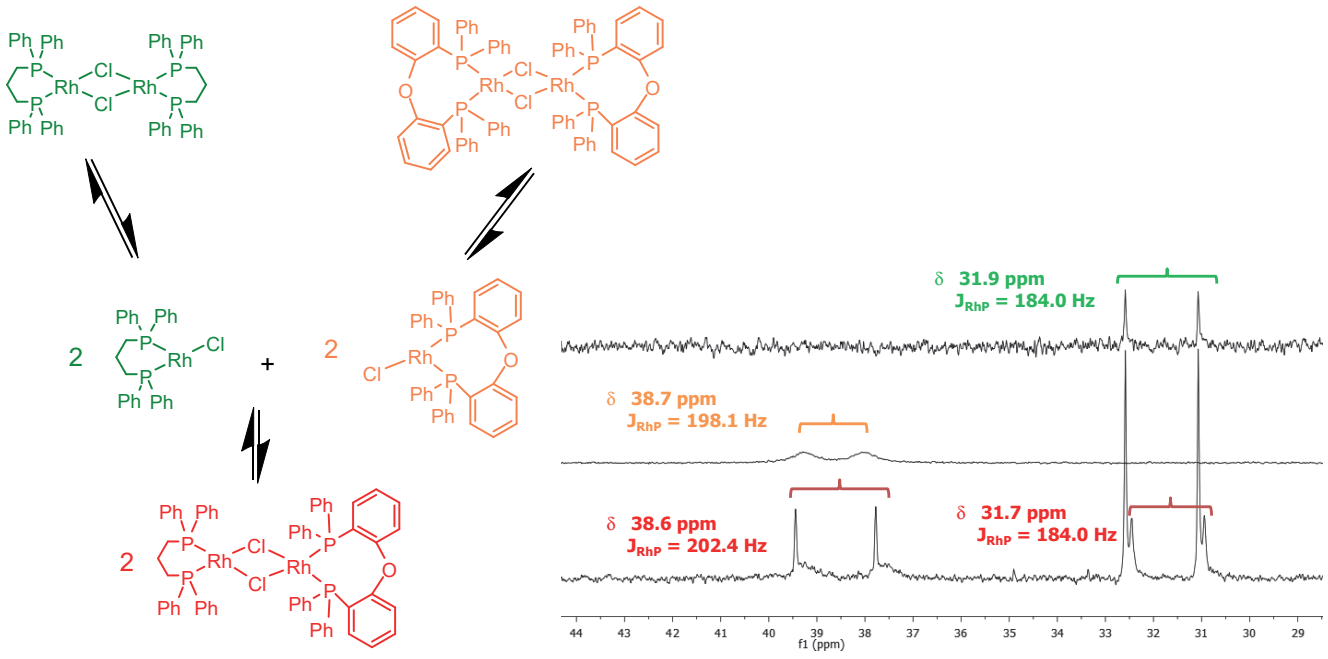

Fig. 2 Metathesis between $[Rh_2(DPPP)_2(\mu_2\text{-}Cl)_2]$ and $[Rh_2(DPEPhos)_2(\mu_2\text{-}Cl)_2]$; ^{31}P NMR in THF/benzene-d_6.

a consequence of this, when the kinetic rate of the equilibrium considered is fast enough to be comparable with the time of the DOSY measurements, the detection of intermediate reactive species can fail. Fortunately, in the case of the DPPP-I complex, it was possible to distinguish between two different species present in solution with different thermodynamic radii.

Metathesis experiment

If the DOSY map shows the presence of two species when $[Rh_2(DPPP)_2(\mu_2\text{-}Cl)_2]$ is dissolved in THF, it does not give us any information about the monomeric or dimeric nature of the species. Very recently, an easy experiment to demonstrate the *in situ* monomerisation of dimeric $[Rh_2(PP)_2(\mu_2\text{-}Cl)_2]$ complexes has been designed. $[Rh_2(DPPP)_2(\mu_2\text{-}Cl)_2]$ (DPPP-I) and $[Rh_2(DPPE)_2(\mu_2\text{-}Cl)_2]$ (DPPE-I) were dissolved in THF and the *in situ* formation of the mixed complex $[Rh_2(DPPP)(DPPE)(\mu_2\text{-}Cl)_2]$ (DPPP-DPPE-I) was observed by ^{31}P NMR.[27] The experiment represented indirect evidence of the monomerisation of $[Rh_2(PP)_2(\mu_2\text{-}Cl)_2]$ (PP = DPPP or DPPE) in aprotic solvents.

In order to increase the number of examples of such transformations and to expand the synthetic possibilities of the [Rh(DPPP)Cl] (DPPP-II) complex, an analogous experiment with DPPP-I and $[Rh_2(DPEPhos)_2(\mu_2\text{-}Cl)_2]$ (DPEPhos-I) has been performed. Equimolar quantities of DPPP-I and DPEPhos-I, mixed and dissolved in a mixture of THF/benzene-d_6, were analysed by ^{31}P NMR, which revealed the *in situ* formation of the metathesis complex DPPP-DPEPhos-I (Fig. 2). (Note: A combination of THF and benzene was used to enhance the solubility of the mixture of complexes $[Rh_2(DPEPhos)_2(\mu_2\text{-}Cl)_2]$ and $[Rh_2(DPPP)_2(\mu_2\text{-}Cl)_2]$.)

The results reported point to an equilibrium dimer–monomer even in the case of complex DPEPhos-I, as previously calculated by density functional theory (DFT) computations.[14]

Conclusions

For the first time, a ^{31}P DOSY experiment has been employed to detect the formation of the complex [Rh(DPPP)Cl], a highly reactive intermediate considered responsible for the catalytic activity of $[Rh_2(DPPP)_2(\mu_2\text{-}Cl)_2]$ but never before directly observed. Metathesis experiments involving $[Rh_2(DPPP)_2(\mu_2\text{-}Cl)_2]$ and $[Rh_2(DPEPhos)_2(\mu_2\text{-}Cl)_2]$ showed the formation of $[Rh_2(DPPP)(DPEPhos)(\mu_2\text{-}Cl)_2]$, confirming the *in situ* monomerisation of both starting complexes.

Experimental

All manipulations were carried out under argon using standard Schlenk techniques. THF, dichloroethane, benzene and xylene were distilled from sodium and MeOH was distilled from magnesium. Subsequent removal of traces of oxygen from deuterated THF was carried out through the application of six freeze–thaw cycles. The rhodium precursor $[Rh_2(cod)_2(\mu_2\text{-}Cl)_2]$ (98%) was purchased from Strem. DPPP and DPEPhos were purchased from Sigma Aldrich (98%) and were recrystallised from MeOH.

NMR experiments

^{1}H NMR and ^{31}P NMR spectra were obtained on a Bruker AV-300 or AV-400 spectrometer at 297–298 K and were referenced internally to the deuterated solvent. For $^{31}P\{^1H\}$ NMR spectra, 85% H_3PO_4 was used as external standard. Data processing was performed by Topspin software (version 3.5) (Bruker). All of the NMR spectra were recorded at 297 K (24 °C) unless otherwise indicated.

Diffusion-ordered spectroscopy

For the DOSY experiment, 32 spectra with a TD = 32 k were collected. For each experiment, 64 scans were acquired using a Δ = 0.07 s and a δ = 1 ms. The pulse gradients were incremented from 2% to 98% of the maximum gradient strength in a linear ramp. The temperature was set at 297 K (24 °C). In the PGSE diffusion experiment, $[Rh_2(DPPP)_2(\mu_2\text{-}Cl)_2]$ (0.01 mmol) was dissolved in deuterated THF (1 mL) and the resulting solution was subjected to a DOSY experiment.

Synthesis of $[Rh_2(DPPP)_2(\mu_2\text{-}Cl)_2]$

A solution of DPPP (29.7 mg, 0.072 mmol) in xylene (1.5 mL) was added dropwise to a solution of $[Rh_2(cod)_2(\mu_2\text{-}Cl)_2]$ (35.5 mg, 0.036 mmol) in xylene (1 mL) at 70 °C. The temperature was raised to 110 °C and the resulting red mixture was stirred for 3 h. The solvent was removed under vacuum at 110 °C and the residue dried under vacuum overnight in order to remove traces of free cod. The product was recrystallised from THF/*n*hexane to give a red powder: Yield 95%; ^{1}H NMR (300 MHz, THF-d_8): δ (ppm) 1.65–1.78 (m, 4H), 2.15 (s, br, 8H), 7.05 (t, J = 7.20 Hz, 16H), 7.15 (t, J = 7.25 Hz, 8H), 7.64–7.70 (m, 16H); ^{31}P NMR (300 MHz, THF-d_8): δ (ppm) 31.9 (d, J_{P-Rh} = 184.0 Hz).

Synthesis of $[Rh_2(DPEPhos)_2(\mu_2\text{-}Cl)_2]$

A dry, argon-flushed Schlenk tube was charged with $[Rh_2(COD)_2(\mu_2\text{-}Cl)_2]$ (23.6 mg, 0.0479 mmol), DPEPhos (51.5 mg, 0.0957 mmol) and 1,2-dichloroethane (DCE) (1 mL) under argon. The resulting solution was stirred at r.t. for 30 min and then layered with diethyl ether and stored under argon. A red crystalline precipitate formed in a few hours. The solvent was removed and the crystals were washed with diethyl ether: ^{1}H NMR (300 MHz, benzene-d_6): δ (ppm) 6.44–7.94 (m, 28H); ^{31}P NMR (300 MHz, benzene-d_6): δ (ppm) 38.7 (d, J_{P-Rh} = 198 Hz).

Metathesis experiment

THF (2 mL) was added to a Schleck tube containing $[Rh_2(DPPP)_2(\mu_2\text{-}Cl)_2]$ (0.02 mmol) and $[Rh_2(DPEPHOS)_2(\mu_2\text{-}Cl)_2]$ (0.02 mmol). To a portion of the THF solution (0.5 mL), benzene-d_6 (0.5 mL) was added, and the resulting mixture was monitored by ^{31}P NMR.

Received 4 June 2018; accepted 19 July 2018
Paper 1805455
https://doi.org/10.3184/174751918X15333065984578
Published online: 9 August 2018

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