Rhodium diphosphite pincer complexes. Rare preferred *in-plane* olefin conformation in square-planar compounds†‡

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Square-planar ethylene rhodium derivatives bearing pincer diphosphite ligands have been prepared and characterized, they display a rare *in-plane* coordination which, based on DFT calculations, has been mainly attributed to steric effects.

The orientation of a coordinated olefin is an aspect of fundamental importance in organometallic chemistry with repercussion in processes involving olefin transformation like catalytic hydrogenation, hydroformylation or olefin metathesis among others.¹ The preferred alkene conformation has been explained as the result of an interplay between electronic and steric factors: the orientation of the proper metal-centred orbital back donating to the π^* olefin orbital and the steric repulsion between the alkene and adjacent ligands.² Thus, the overall preference is dependent on the geometry of the olefinic complex, and in the case of square-planar compounds, an *upright* (*u*) conformation has almost exclusively been observed.^{3–6} The preference of the *u* over the

in-plane (*ip*) conformation has been attributed to the higher steric interaction between the olefin and the two *cis* ligands in the latter structure. In comparison, electronic effects look to play a minor role, as the π component of the metal–olefin bond is of similar energy in both conformations.² From these arguments, it looks feasible that an arrangement of L ligands lowering encumbrance in the coordination plane while increasing in the axial direction, could favour the *ip* conformation. Indeed, we present in this contribution new diphosphites **2**, capable to act as pincer ligands in Rh complexes,⁷ which display these steric features and give rise to ethylene square-planar derivatives with an *ip* conformation. The series of complexes described herein are, in addition, the first Rh examples with diphosphite pincer ligands.⁸

Compounds **2** have been prepared from resorcinol and either flexible chlorophosphite **1a** or enantiomerically pure **1b** (Scheme 1). Reaction between **2** and Rh(Cl)(PPh₃)₃ led to compounds **3a** and **3b** (Scheme 2). This transformation involves dis-

Scheme 1 Synthesis of diphosphites **2**.

Scheme 2 Synthesis of pincer complexes.

placement of two PPh₃ ligands and cyclometallation of **2**, generating the corresponding anionic tridentate ligand (generically named here PCP). The PPh₃ in **3** is labile and can readily be displaced. Thus, carbonyl derivative **4a** is rapidly formed upon exposure of

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† The HTML version of this article has been enhanced with colour images.
‡ Electronic supplementary information (ESI) available: Representative experimental procedures, crystallographic information for **5a** and **5b**, computational details and calculated data for model compounds **I–VI**. See DOI: 10.1039/b617164h

a solution of **3a** to an atmosphere of CO. However, the displaced phosphine complicates isolation of **4a**. Most useful, addition of Se to the reaction mixture quenches the phosphine as $\text{P}(\text{Se})\text{Ph}_3$, which can be readily removed from the mixture. This protocol has also been applied to the preparation of ethylene derivatives **5a** and **5b**.^{9g}

An important characteristic of these PCP ligands is the acceptor character of the phosphite groups that causes a reduced back-donating ability of fragment Rh–PCP.¹⁰ This feature is evident in the IR spectrum of compound **5a**, that displays the $\nu(\text{CO})$ band at 2017 cm^{-1} , considerably shifted to higher energy (60 cm^{-1}) from that of an analogous Rh carbonyl bearing a pincer diphosphine.¹¹

Complexes **5** have been studied by X-ray diffraction (Fig. 1 and 2). The coordination of the PCP ligand in the pincer fashion is characterized by a $\text{P}(1)\text{--Rh--P}(2)$ angle of 155° . This angle is appreciably smaller than that found in complexes derived from pincer diphosphines, which usually cluster around 165° .¹² Also interesting, the biphenyl groups of **5a** have the same configuration (while they are conformationally flexible in solution) giving rise to a chiral structure. Another remarkable feature of the Rh–PCP fragment is its planarity, in contrast with the puckered structures usually produced by pincer diphosphines.¹³ This backbone pla-

narly is a common feature with other complexes described in the literature bearing oxygen atoms in the bridge.^{8,14} Most noteworthy, coordinated ethylene shows an unexpected *in-plane* conformation, with a small angle of 7.4° (**5a**) and 13.0° (**5b**) between planes defined by Rh–PCP and Rh– $\eta^2\text{-(C}_2\text{H}_4)$. The C=C bond length is similar for **5a** ($1.38\text{ \AA}$), while slightly lower for **5b** ($1.35\text{ \AA}$), to the mean value observed in other rhodium ethylene derivatives ($1.38\text{--}1.39\text{ \AA}$).¹²

Due to its C_2 symmetry, complex **5b** is not suitable to study ethylene rotation.¹⁵ To ascertain the participation of this process we have prepared the less-symmetric propene derivative **6b** by simply treating **5b** with an excess of propene (eqn. 1). Compound **6b** showed room temperature spectra consistent with an averaged C_2 symmetry, indicating olefin rotation. This process could not be frozen, as cooling of the sample down to 190 K did not split Bu^t signals in the ^1H or $^{13}\text{C}\{^1\text{H}\}$ spectra.

In order to supply additional information about the rare case of *ip* conformation shown in the X-ray structures of **5**, we have performed DFT calculations (B3LYP, TZVP basis set; see ESI for details[†]) with selected model complexes (Fig. 3). As a reference, the structure of the simplest model *trans*-Rh(Ph)(C₂H₄)(PH₃)₂ (**I**) has been optimized in both *u* and *ip* conformations. As expected, the *u* conformation is considerably more stable by *ca.* 11 kcal mol^{-1} . In addition, *u* and *ip* conformers of pincer model complexes **II** and **III** have also been optimized. Interestingly, the energy difference between the two conformers of these models is quite small (about 1 kcal mol^{-1}). This fact reflects that the reduction in the P–Rh–P angle, caused by the pincer backbone, stabilizes the *ip* conformation and then disrupts the regular preference for the *u* conformer. Likewise, very small energy differences (less than 1 kcal mol^{-1}) in favour of the *ip* conformation were observed for **IV** and **V**. Finally, for model **VI**, the closest to complex **5a**, different conformations for the ethylene ligand were explored as starting geometries. However, the only conformation that appears as a stationary point corresponds to the *ip* isomer. All our attempts

Fig. 1 ORTEP view of complex **5a**. H atoms (except for ethylene ligand) and solvent molecule have been omitted for clarity. Selected bond lengths ($\text{\AA}$) and angles ($^\circ$): Rh–P(1) = $2.2076(3)$, Rh–P(2) = $2.2165(3)$, Rh–C(1) = $2.0233(12)$, Rh–C(63) = $2.2353(14)$, Rh–C(64) = $2.2184(14)$, C(64)–C(63) = $1.377(2)$, P(1)–Rh–P(2) = $155.490(13)$.

Fig. 2 ORTEP view of complex **5b**. H atoms (except for ethylene ligand) and solvent molecule have been omitted for clarity. Selected bond lengths ($\text{\AA}$) and angles ($^\circ$): Rh–P(1) = $2.2237(7)$, Rh–P(2) = $2.2096(7)$, Rh–C(1) = $2.019(3)$, Rh–C(55) = $2.228(3)$, Rh–C(56) = $2.230(3)$, C(55)–C(56) = $1.353(4)$, P(1)–Rh–P(2) = $155.37(3)$.

Fig. 3 Model complexes analyzed.

of optimization of the *u* conformer converge into the *ip* one. The structural parameters of **VI-*ip*** are in good agreement with the experimental data obtained for **5a**. For instance, the computed parameters around the Rh–C₂H₄ moiety (Rh–C, 2.285 Å, and C–C 1.373 Å) agrees well with the experimental values found for **5a**. Additionally, the calculation reproduces remarkably well structural features of **5** like the planarity of the backbone or the value of the P–Rh–P angle (computed: 155.1°). A comparison of the structures of the models **IV–VI** shows a practically superimposable structure of the common part of the Rh–PCP fragment (see ESI†). Thus, the cavity around the remaining coordination position is very similar along the series of complexes. In this pocket it is therefore possible to accommodate an ethylene ligand in either *u* or *ip* conformation both for **IV** and **V** (Fig. 4). Otherwise, for model complex **VI** the Bu^t groups significantly reduce the available space of the cavity in the axial direction and while an *in-plane* ethylene perfectly matches in the pocket, it is not possible to fit a perpendicular one without a significant distortion of the Rh–PCP fragment.

Fig. 4 Space-filling views: **V-*ip*** (top), **V-*u*** (middle) and **VI-*ip*** (bottom).

We have described herein a family of Rh pincer diphosphite complexes. The olefinic derivatives show in the solid-state a rare *ip* conformation, while olefin rotation in solution is observed. Calculations by DFT methods suggest that the reduction of the P–Rh–P angle releasing hindrance in the coordination plane and the presence of bulky Bu^t groups pointing towards the axial

direction favour this unusual conformation. Further studies about the coordination properties of these ligands and their application in homogeneous catalysis are currently under way.

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Notes and references

§ Crystal data. **5a**–C₃H₁₂: C₆₉ H₉₉ O₆ P₂ Rh, *M* = 1189.33, monoclinic, *P*2₁/*c*, *a* = 17.2239(5), *b* = 19.2234(6), *c* = 20.3456(6) Å, *V* = 6675.6(3) Å³, *T* = 100 K, *Z* = 4, *μ* = 0.351 mm^{−1}, 153626 reflections collected, 20 381 independent (*R*(int) = 0.0346), *R*1 = 0.0311, *wR*2 = 0.0797 (*I* > 2σ(*I*)). **5b**. C₅₆ H₇₁ O₆ P₂ Rh, *M* = 1004.98, orthorhombic, *P*2₁2₁2₁, *a* = 10.4092(11), *b* = 18.8544(18), *c* = 26.636(3) Å, *V* = 5227.6(9) Å³, *T* = 100 K, *Z* = 4, *μ* = 0.436 mm^{−1}, 45 841 reflections collected, 11 402 independent (*R*(int) = 0.0496), *R*1 = 0.0352, *wR*2 = 0.0717 (*I* > 2σ(*I*)). CCDC reference numbers 625416 and 625417. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b617164h

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