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

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Square-planar ethylene rhodium derivatives bearing pincer diphosphate 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 diphosphate pincer ligands.

Compounds 2 have been prepared from resorcinol and either flexible chlorophosphite 1a or enantiomerically pure 2b (Scheme 1). Reaction between 2 and Rh(Cl)(PPh3)3 led to compounds 3a and 3b (Scheme 2). This transformation involves dis-
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 P(Se)Ph3, which can be readily removed from the mixture. This protocol has also been applied to the preparation of ethylene derivatives 5a and 5b.54 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 $\nu$(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 P(1)–Rh–P(2) angle of 155.37(3). This angle is appreciably smaller than that found in complexes derived from pincer diphosphines, which usually cluster around 165$.11$ 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 characterized by a P(1)–Rh–P(2) angle of 155.490(13). This backbone planarity is a common feature with other complexes described in the literature bearing oxygen atoms in the bridge.4,14

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–$\eta^1$-(C$_2$H$_4$)$_2$. The C–C bond length is similar for 5a (1.38 Å), while slightly lower for 5b (1.35 Å), to the mean value observed in other rhodium ethylene derivatives (1.38–1.39 Å).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* signals in the $^1$H or $^{13}$C($^1$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)(C$_2$H$_4$)(PH$_3$)$_2$ (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...
of optimization of the \( u \) conformer converge into the \( ip \) one. The structural parameters of \( \text{VI} - ip \) are in good agreement with the experimental data obtained for \( 5a \). For instance, the computed parameters around the Rh–C\(_6\)H\(_5\) 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 \( \text{IV–VI} \) 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 \( \text{IV} \) and \( \text{V} \) (Fig. 4). Otherwise, for model complex \( \text{VI} \) the \( \text{Bu}^+ \) groups significantly reduce the available space of the cavity in the axial direction and while an \( \text{in-plane} \) ethylene perfectly matches in the pocket, it is not possible to fit a perpendicular one without a significant distortion of the Rh–PCP fragment.

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 \( \text{Bu}^+ \) 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. \( \text{Cu}_{3} \text{H}_{12} \cdot \text{Cu} \cdot \text{H}_{2} \cdot \text{O} \cdot \text{P} \cdot \text{Rh} \cdot M = 1189.33 \), monoclinic, \( P2_1/c \), \( \alpha = 17.2239(5), \beta = 19.2234(6), \gamma = 20.3456(6) \) Å, \( V = 6675.63(3) \) Å\(^3\), \( T = 100 \) K, \( Z = 4, \mu = 0.351 \) mm\(^{-1}\), 153626 reflections collected, 20.381 independent (\( R(\text{int}) = 0.0346 \)), \( R = 0.0311, wR = 0.0797 \) (\( I > 2 \sigma (I) \)).

\( \text{Cu}_{3} \text{H}_{12} \cdot \text{O} \cdot \text{P} \cdot \text{Rh} \cdot M = 1004.98 \), orthorhombic, \( P2_12_12_1 \), \( a = 18.8544(18), b = 26.636(3) \) Å, \( V = 5227.6(9) \) Å\(^3\), \( T = 100 \) K, \( Z = 4, \mu = 0.436 \) mm\(^{-1}\), 45,841 reflections collected, 11402 independent (\( R(\text{int}) = 0.0496 \)), \( R = 0.0352, wR = 0.0717 \) (\( I > 2 \sigma (I) \)).

CCDC reference numbers 625416 and 625417. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b617164h.

3. A family of formally tetracoordinated \( \text{Pd} \) and \( \text{Pt} \) allyl complexes have shown olefin coordination \( \text{in-plane} \), however, due to the small bite angle of the allyl ligand, definition of their structure is not unambiguous and both square-planar and planar-trigonal geometries have been proposed for them.
6. Forced alkene coordination \( \text{in-plane} \) has been observed in diolfin compounds with mutually perpendicular \( \text{C=C} \) bonds: M. H. Rakowsky, J. C. Woolcock, L. L. Wright, D. B. Green, M. F. Rettig and R. M. Wing, Organometallics, 1987, 6, 1211.
12. For QUEST3D-search details see ESI†.