Pseudo-Tetrahedral Rhodium(I) Complexes

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Dedicated to Prof. Ernesto Carmona on occasion of his 65 birthday

Abstract: A combination of four-electron donors, such as alkynes, with strongly donating and strong-field scorpionate ligands is appropriate to create pseudo-tetrahedral rhodium(I) environments, as found in $[Rh(PhBP_3)(HC\equiv CPh)]$, which promotes H–C bond activation and C–C coupling reactions under very smooth conditions.

The coordination chemistry of d^8-RhL$_4$ complexes is dominated by their strong propensity to adopt square-planar geometries. Nonetheless, some rare sawhorse (SH)[1] environments have also been reported, while the amazing compound $[Rh(trop_2SiMe)(C_2H_4)]$ remains the sole example for the related trigonal pyramid (TP) geometry.[2] In fact, SH and TP structures can be envisaged as derived formally from a trigonal bipyramid (*TBPY*) geometry lacking either one equatorial or one axial ligand, respectively. Noticeably, some of them have raised a very rich non-conventional chemistry,[3] including dinuclear C–H bond activation reactions,[4] and unusual electromeric rhodium radical complexes.[5] The above mentioned examples provide invaluable information on the parameters that control the electronic structure from a particular geometry and *viceversa*.[2] Some of these parameters are the ligand topology and bonding effects, such as strong π-donation, as verified by the unique square-planar (SP) iridium(II) and iridium(III) complexes based on pincer ligands,[6] or by the pseudo-tetrahedral metal environments created by the high-field scorpionate ligands $[PhB(CH_2PR_2)_3]^-$.[7] They strongly bind rhodium(I),[8] avoiding dissociation of one arm, which is generally observed for ligands such as the tris(pyrazolyl)borates,[9] and their fac-coordination make them ideal candidates to free rhodium from its natural trend to square-planarity. Pertinent to the present work is the seminal report from Bianchini,[10] which described the cationic triphos complexes $[Rh(MeC(CH_2PPh_2)_3)(RC\equiv CR)]BPh_4$ to be in a fast equilibrium between trigonal-bipyramidal and square-pyramidal geometries on the basis of spectroscopic studies. In this context, a rare iridium complex $[Ir(PMe_2Ph)_3(MeC\equiv CMe)]BF_4$ was reported to be between tetrahedral and square-pyramidal in the solid state.[11] Therefore, truly tetrahedral or pseudo-tetrahedral geometries are unknown in rhodium(I) chemistry so far,[12] and they are restricted to rhodium(–I) and rhodium(0) oxidation states.[13] Herein we report the synthesis, full characterization, preliminary reactivity studies, and electronic structure of d^8-RhL$_4$ complexes with a unique pseudo-tetrahedral geometry, which gives an insight into this very unusual coordination environment for mononuclear d^8-metal complexes of the second and third row.

Addition of phenylacetylene to a toluene solution of $[Rh(PhBP_3)(C_2H_4)(NCMe)]$ (**1**, PhBP$_3$ = $[PhB(CH_2PPh_2)_3]^-$),[8a] produced an immediate replacement of the ethylene and acetonitrile ligands to give $[Rh(PhBP_3)(HC\equiv CPh)]$ (**2**), which was isolated as dark-red monocrystals in excellent yield. In the structure of **2** (Figure 1),[14] the rhodium atom was found to be in a pseudo-tetrahedral geometry bonded to the three phosphorus atoms of PhBP$_3$ and to the C≡C bond of phenylacetylene in an η^2 fashion. Two Rh–P bond distances are longer than the third one (2.285 Å in average), while the Rh–C bond distances (2.029 Å in average) are quite short, suggesting that the acetylene is a four-electron donor in **2**.[15]

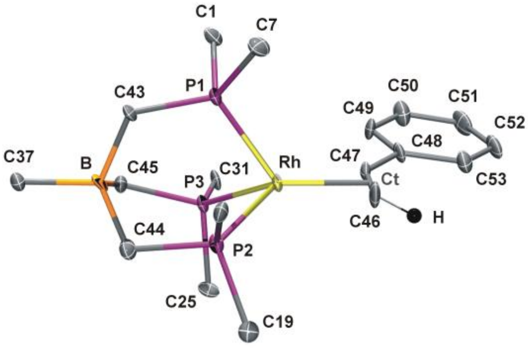

Figure 1. Structure (ORTEP at 50% level) of the complex $[Rh(PhBP_3)(HC\equiv CPh)]$ (**2**). (hydrogen atoms gave been omitted and only the C^{ipso} atoms of the phenyl groups from PhBP$_3$ are shown for clarity).

The topology of the tripodal ligand imposes P–Rh–P angles close to 90º and the three P–Rh–Ct angles (Ct is the middle point of the C≡C bond) were found to be almost identical (126º). Accordingly, Ct was found to be placed on the axis defined by the boron and rhodium atoms (axis(B,Rh)–Ct 179.8(2)º) (mol-1). A second independent molecule (mol-2) found in the crystal was slightly distorted in such a way that Ct is somewhat shifted from the B,Rh-axis (axis(B,Rh)–Ct, 177.0(2)º). This off-axis distortion makes the P1–Rh–Ct angle smaller (123.8(2)º) than the other two P–Rh–Ct angles. Nonetheless, an average symmetric species is observed by spectroscopic methods, which indicates the difference in energy between mol-1 and mol-2 to be quite small.

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The way in which the alkyne binds rhodium was firstly examined by using a fragment MO analysis of the 14-e model [Rh{MeB(CH$_2$PMe$_2$)$_3$}] and *bent*-HC≡CPh as found in the crystal structure of **2**. Figure 2 (left) shows the orbital splitting of the metallic fragment analyzed as an open-shell species, which becomes optimized for C_3 symmetry. This triplet state was found to be slightly more stable (in 3.22 kcal mol^{-1}) than the singlet state, but this difference can be meaningless because of the tendency of the B3LYP functional to stabilize high spin species.[16] The metallic fragment calculated as a closed-shell species also possesses five d-based MOs (Figure 2, center) and a low energy hybrid sp orbital (2a$_1$) that results from pyramidalization of rhodium imposed by the fac-P$_3$ ligand. It should be noted that the spin pairing produces two effects: a) a distortion of the framework that results in distinct Rh−P bond distances and P–Rh–P angles,[17] and reduces the symmetry from C_3 (triplet) to C_s (singlet); b) a drastic energy difference (2.37 eV) between the HOMO (2e$_a$) and LUMO (2e$_s$) that stabilizes the singlet state.

The two empty frontier orbitals (2a$_1$, and 2e$_s$ of parentage d$_{yz}$) in the singlet state match those of the filled $\pi_{||}$ and $\pi_{\perp}$ orbitals of the *bent*-C≡C bond. They form thus two bonding MOs, namely σ and π (Figure 2, right), which are filled with four electrons given by the alkyne, stabilizing a pseudo-tetrahedral geometry for an 18-e complex. A further match of the filled 2e$_a$ orbital with the empty $\pi_{||}$* orbital of the C≡C bond corresponds to a π-back donation.

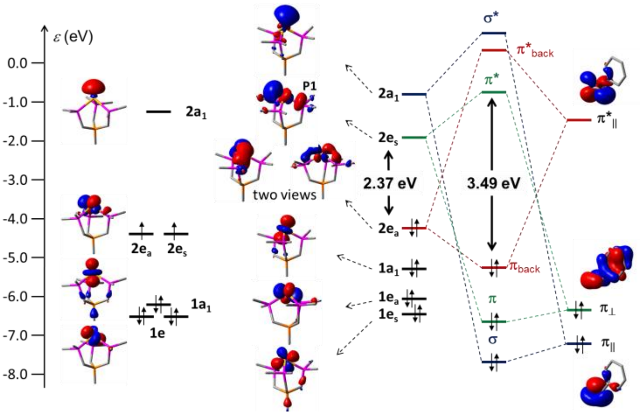


Figure 2. MOs for the model [Rh{MeB(CH$_2$PMe$_2$)$_3$}] in the triplet state (left; only one MO of the 1e and 2e sets is shown) and in the singlet sate (middle). MO correlation diagram of the singlet state and *bent*-HC≡CPh (right).

The DFT computed optimized geometry of the model complex [Rh{MeB(CH$_2$PMe$_2$)$_3$}(HC≡CPh)] (**2a**) as a close-shell species (Figure 3, left) reproduces quite well the experimental data found for **2**, although it is slightly more distorted than mol-2 (calcd. axis(B,Rh)–Ct, 172.84º, P1–Rh–Ct, 119.59º; see Supporting Information). The off-axis distortion optimizes the overlap of the filled 2e$_a$ and empty $\pi_{||}$* orbitals (π back-donation), but on the light of the calculated and measured geometric data it is over weighed by the B3LYP functional. The representations and composition of the MOs of the model complex indicate such a strong mixing that direct comparison with the OMs of the fragment is difficult. Nonetheless, a clear example of MOs of each type is depicted in Figure 3. The HOMO-9 (of composition 33% Rh, 33% alkyne) corresponds to the σ-bond from the 2a$_1$ and $\pi_{||}$ OMs, while the LUMO (39% Rh, 29% alkyne) corresponds to the π* orbital derived from the interaction of 2e$_s$ with $\pi_{\perp}$. The antibonding character of the Rh–P1 bond in the LUMO and those of the Rh–P2 and Rh–P3 bonds in the HOMO account for the relatively shorter Rh–P1 bond distance found in the crystal structure of **2**. The LUMO+3 (40% Rh, 21% alkyne, π^*_{back}) corresponds to the antibonding MO from 2e$_a$ and $\pi_{||}$*. Basically, the geometric irregularity found for the metallic fragment in the singlet state is retained in the complex and the HOMO-LUMO splitting in **2a** (3.49 eV) is even bigger. Moreover, NBO analysis of **2a** gives a bond order of 1.99 for the C46–C47 bond, which is compatible with a strong donation from alkyne to rhodium, and an almost zero natural charge (−0.059) was calculated for the metal. Consequently, complex **2** is quite well represented as a Rh(I) complex with the alkyne η^2–coordinated to the metal through a double (σ and π) bond.

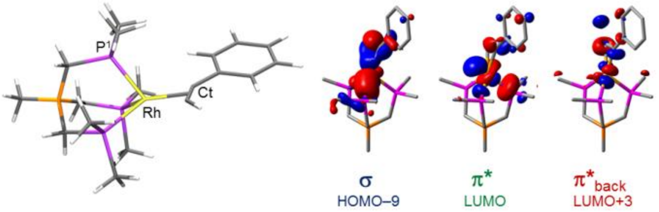


Figure 3. DFT geometry of the model [Rh(MeBP$_3$)(HC≡CPh)] (**2a**) (left), and representation of selected orbitals of **2a** (right).

For comparative purposes the optimized geometry for **2a** was calculated for the triplet state. It was found to be higher in energy than the singlet one (by 24.8 kcal/mol). Although still pseudo-tetrahedral, the coordination geometry and the disposition of the alkyne are quite different from those determined by X-ray diffraction. In particular, the alkyne is rotated and bound to the metal by one single carbon, since one of the Rh–C distances, 2.344 Å, is clearly nonbonding (see Supporting Information). In consequence, the pseudo-tetrahedral geometry of the alkyne complex is a result of the d-orbital splitting of the RhP$_3$ fragment as a closed-shell species generated by a strong-field ligand that leaves two empty metal orbitals able to accept four electrons from the alkyne.

A survey on the literature revealed that η^2-alkyne coordination to rhodium is dominated by a two-electron donicity stabilizing both, trigonal bipyramid (*TBPY*) and square-planar (*SP*) complexes. From the few examples crystallographically characterized, electronically saturated *TBPY* complexes are derived from 16-ev metal fragments such as ‘RhCl(PMe$_3$)$_3$’,[18] ‘RhCp’P^{i}Pr$_3$’[19] or ‘RhTp(L)’,[20] while T-shaped 14-ev fragments such as ‘Rh(X)(P^{i}Pr$_3$)$_2$’ (X = Cl, I)[21] and ‘Rh(acac)(olefin)’[22] bind alkynes to yield 16-ev *SP*-compounds. Functionalized alkynes like thioether-alkynylborates,[23] and P(C≡C)P pincer type ligands[24] also bind rhodium as two-electron donors. Consequently, complex **2** represents the first authenticate rhodium complex with the alkyne donating more than two electrons, which in turn, results in the unusual coordination environment for rhodium.

Complex **2** maintains in solution the symmetric structure found in the solid state. The signals in the ^{1}H and ^{13}C{^{1}H} NMR spectra coming from the HC≡ proton and the C≡C carbons are largely low-field shifted (δ = 10.04, and δ = 164.9, 151.8 ppm, respectively), as found typically for alkynes behaving as four-electron donors (Figures S5-S6).[15] The three phosphorus nuclei from the $PhBP_3$ ligand remain equivalent even at –70 ºC. This fluxional behavior has to be attributed to a free rotation of the alkyne around the Rh–Ct axis. Indeed, calculation of this motion in the 0-120º range in 10º steps leads to a very low activation barrier of 0.9 kcal mol^{-1} (Figure 4). This low-energy barrier is associated to an almost continuous overlap of the orbitals involved in the metal-alkyne bond all along the move, avoiding thus a bond cleavage. The easy rotation of the alkyne corroborates our above description of the complex and excludes an expectedly more rigid metallacyclopropene-Rh(III) resonant structure.[25] Most probably, the original complexes reported by Bianchini,[10] having similar spectroscopic data, are better described as pseudo-tetrahedral, as found for **2,** and undergoing a fast rotation around the Rh–Ct axis.

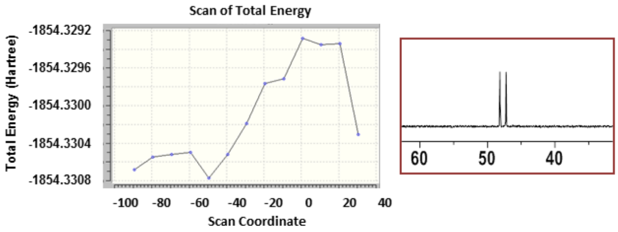
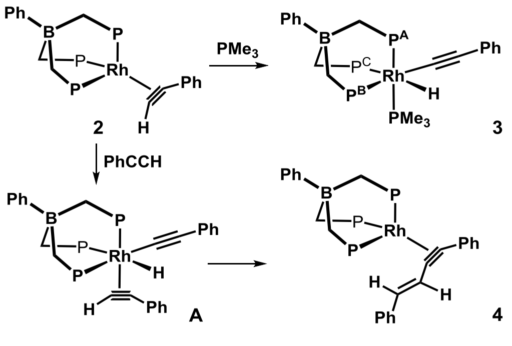


Figure 4. $^{31}P\{^1H\}$ NMR spectrum of complex $[Rh(PhBP_3)(PhC{\equiv}CH)]$ (**2**) in CD_2Cl_2 at −80 ºC (right). Total energy (in hartree) *versus* scan coordinate for the rotation of the alkyne around the Rh-Ct axis in the model $[Rh\{MeB(CH_2PMe_2)_3\}(HC{\equiv}CPh)]$ (**2a**) (left).

The deep colour of **2** is mainly due to spin allowed transitions to the LUMO, which result in bands in the Vis-UV spectrum ca. 530 and 380 nm (Figures S12-S13) according to TD-DFT calculations. Complex **2** was found to be a reactive complex despite of being electronically saturated (18-ve), a fact that could be related to the low-lying LUMO (π*, Figure 3 right), which is pointing toward a possible vacant site. Thus, complex **2** easily reacts with hydrogen under atmospheric pressure to give $[\{Rh(PhBP_3)(H)(\mu\text{-}H)\}_2]$[8a] and ethylbenzene (quantitative by NMR). Moreover, addition of a two-electron donor such as PMe_3 triggers a C–H activation reaction to give the alkynylhydrido rhodium(III) complex $[Rh(PhBP_3)(C{\equiv}CPh)(H)PMe_3]$ (**3**, Scheme 1), which was isolated as an off-white solid.



Scheme 1. Synthesis of complexes **3** and **4**.

Relevant signals correspond to the hydride ligand (δ = –8.74 ppm, dddt) and to the acetylide carbons (δ = 111.5 (≡CPh), 109.5 (RhC≡) ppm) in the ^1H and $^1H,^{13}C$-hmbc NMR spectra, respectively. The expected ABCMX spin system ($M = PMe_3$, $X = {}^{103}Rh$) is clearly observable in the $^{31}P\{^1H\}$ NMR spectrum of **3** (Figures S7-S9). Although no intermediates were detected, even monitoring the reaction at –70 ºC in d_8-toluene, it is reasonable to suppose that the reaction stars with coordination of PMe_3 to **2** to give the *TBPY*-Rh(I) complex $[Rh(PhBP_3)(HC{\equiv}CPh)(PMe_3)]$, which is followed by the oxidative-addition of the C–H bond.[26]

Addition of a second mol of HC≡CPh to **2** allows a further reaction, in which most probably the acetylene becomes initially coordinated, as observed for PMe_3; the product was found to be the dark-red complex $[Rh(PhBP_3)(PhC{\equiv}C–CH{=}CHPh)]$ (**4**), which contains *trans*-1,4-phenyl-but-3-ene-1-yne (the phenylacetylene dimerization product) bound to rhodium through the C≡C bond (Scheme 1). A full spectroscopic study as well as DFT calculations on the model compound $[Rh(MeBP_3)(PhC{\equiv}C–CH{=}CHPh)]$ (**4a**) agree with the η^2-alkyne-rhodium(I) formulation depicted in Scheme 1 (see Figures S3, S10-S11 and Table S1). Hence, complex **4** represents a second example of a Rh(I) complex in a pseudo-tetrahedral environment.

Assuming complex **A** (similar to **3**) to be the first intermediate in the synthesis of **4**, the reaction would proceed through insertion of the alkyne into the Rh–H bond to give an alkynyl(vinyl)Rh species followed by a reductive elimination step to the enyne. Such type of C–C coupling between alkynyl and vinyl moieties promoted by rhodium has been previously observed.[27] In addition, the alkyne exchange reaction:

$$\mathbf{4a} + HC{\equiv}CPh \rightarrow \mathbf{2a} + PhC{\equiv}C\text{–}CH{=}CHPh,$$

which would close a plausible catalytic cycle for the dimerization of phenylacetylene, is exoergic with an estimated value of $\Delta G^0 = -3.13$ kcal mol^{-1}. Indeed, preliminary essays indicated the reaction to be catalytic. Thus, the enyne was quantitatively obtained in 4h by warming phenylacetylene at 80 ºC in the presence of complex **1** as catalyst (in 5% molar ratio). No additives were required, and **4** was the sole rhodium complex observed at the end of the catalysis. Moreover, the reaction was found to be regioselective to the *trans*-enyne (82 %),[28] and the catalytic activity for the non-optimized process is comparable (or even better) to that of related rhodium catalysts.[27],[29]

In conclusion, we have verified that 18-electron rhodium(I) complexes in pseudo-tetrahedral environments are accessible and isolable compounds. Moreover, our results indicate that combination of a strongly donating tripod ligand with a four-electron donor in the coordination sphere seems to play a decisive role in the stabilization of this unknown geometry for rhodium(I). A deeper investigation on the generality of this idea is currently underway.

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Keywords: rhodium • pseudo-tetrahedral • trisphosphaneborate • alkynes • stereochemistry

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Catch Phrase ———————————

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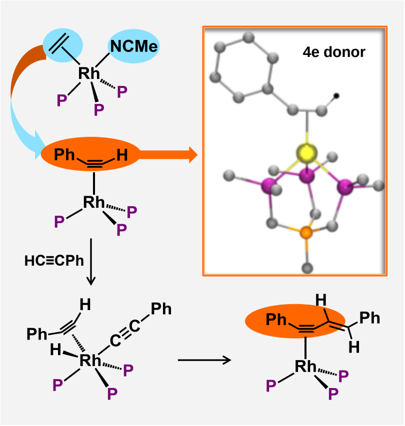
Pseudo-Tetrahedral Rhodium(I) Complexes



Combination of four electron π-donors, such as alkynes, with strongly donating scorpionate ligands in the coordination sphere is appropriate to create pseudo-tetrahedral rhodium(I) environments. Such type of geometry was unknown in rhodium(I) chemistry The complex shown in the Figure promotes H–C bond activation and C–C coupling reactions under very smooth conditions. Code color: Rh (yellow), P (purple), C (grey), B (orange).