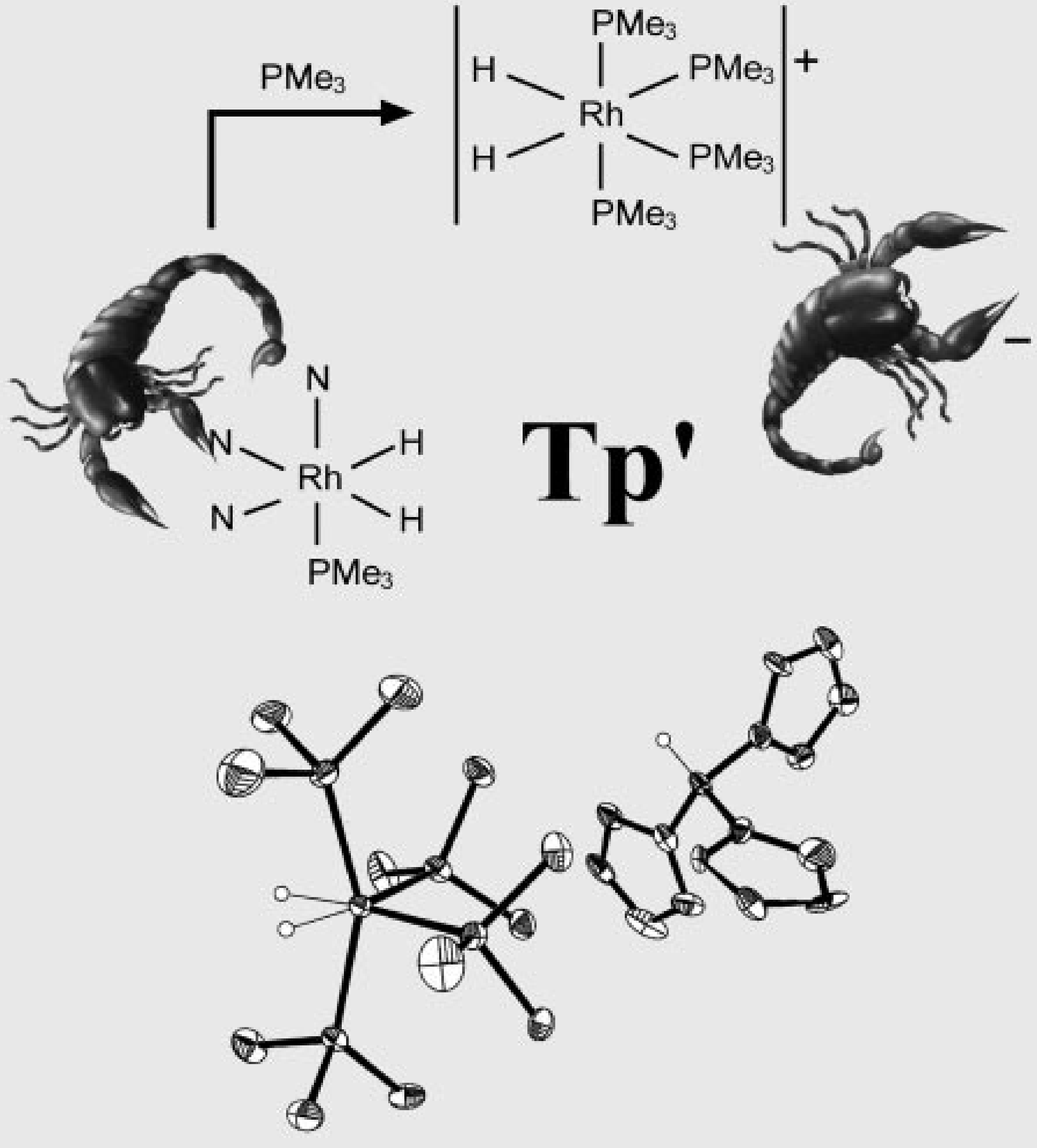
HOMOSCORPIONATES LIKE TO BE ANCHORED...



...BUT CAN BE DISENGAGED

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Step-by-Step Uncoordination of the Pyrazolyl Rings of Hydrotris(pyrazolyl)borate Ligands in Complexes of Rh^I and Rh^{III}

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Dedicated to Professor Rafael Uson on the occassion of his 75th birthday

Abstract: Compounds of rhodium(I) and rhodium(III) that contain ancillary hydrotris(pyrazolyl)borate ligands (Tp′) react with monodentate and bidentate tertiary phosphanes in a step-wise manner, with incorporation of P-donor atoms and concomitant replacement of the Tp′ pyrazolyl rings. Accordingly, $[Rh(\kappa^3\text{-}Tp^{Me_2})(C_2H_4)(PMe_3)]$ (**1b**), converts initially into $[Rh(\kappa^2\text{-}Tp^{Me_2})(PMe_3)_2]$ (**3**), and then into $[Rh(\kappa^1\text{-}Tp^{Me_2})(PMe_3)_3]$ (**2**) upon interaction with PMe_3 at room temperature, in a process which can be readily reversed under appropriate experimental conditions. Full disengagement of the Tp′ ligand is feasible to give Tp′ salts of rhodium(I) complex cations, for example, $[Rh(CO)(dppp)_2][Tp^{Me_2,4\text{-}Cl}]$ (**5**; dppp = $Ph_2P(CH_2)_3PPh_2$), or $[Rh(dppp)_2][Tp^{Me_2,4\text{-}Cl}]$ (**6**). Bis(hydride) derivatives of rhodium(III) exhibit similar substitution chemistry, for instance, the neutral complex $[Rh(Tp)(H)_2(PMe_3)]$ reacts at 20°C with an excess of PMe_3 to give $[Rh(H)_2(PMe_3)_4][Tp]$ (**9b**). Single-crystal X-ray studies of **9b**, conducted at 143 K, demonstrate the absence of bonding interactions between the $[Rh(H)_2(PMe_3)_4]^+$ and Tp ions, the closest Rh···N contact being at 4.627 Å.

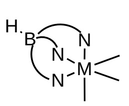
Keywords: coordination modes · N ligands · pyrazolylborates · rhodium

Introduction

The use of polydentate ligands has been of paramount importance for the development of coordination and organometallic chemistry. Even in those instances in which they seem to play an auxiliary role and behave as spectators, they anchor the metal and provide a rigid coordination environment, a property that frequently translates into enhanced thermodynamic stability, which is often accompanied by limited unwanted reactivity (e.g., towards O_2 or H_2).

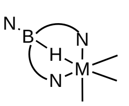
Variations in their coordination mode upon addition or removal of other ligands allow the metal to keep its formal electron count. These changes, which in the case of the cyclopentadienyl and related ligands are designated with the term ring-slippage,[1] usually have important consequences both in stoichiometric and catalytic reactions. A well-known organometallic example is the so-called "indenyl effect", responsible for the much higher substitution rates of $[M(C_9R_7)L_n]$ compounds (C_9R_7 = indenyl ligand), as compared to their $[M(C_5R_5)L_n]$ analogues.[2]

The hydrotris(pyrazolyl)borate ligands (Tp′) introduced by Trofimenko in 1966,[3] are versatile ligands[4] that bind predominantly in a facial, tripodal fashion (i.e., κ^3-*N,N′,N″*, structure **A**), and enforce near octahedral coordination to the



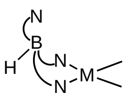
κ^3-*N,N′,N″*-Tp′

A



κ^3-*N,N′,B-H*-Tp′

B



κ^2-*N,N′*-Tp′

C

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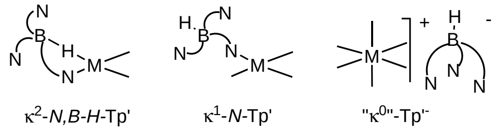
metal.[5] The non-classical, tridentate binding mode κ^3-*N,N′,B–H* (structure **B**) is also possible and has been demonstrated recently by spectroscopy and by X-ray methods.[6] Classical bidentate coordination, that is, κ^2-*N,N′* (structure **C**) is common in 16-electron, square-planar compounds;[4, 7] the alternative κ^2-*N,B–H* bonding mode has been proposed by some of us in the rhodium complex [Rh(Tp$^{Me_2,4\text{-}Cl}$)(CO)(PMePh$_2$)$_2$].[8] The Rh–H distance in this complex is somewhat longer than expected (2.35(3) Å) and the solution spectroscopic evidence for the Rh···H–B interaction is not fully conclusive. This and the much stronger Rh···H–B interaction found by Herberhold et al. in [Rh(Tp^{Me_2})(P(C$_7$H$_7$)$_3$)],[9] characterised by a Rh···H separation of 1.789(7) Å, and by ^1J(^{103}Rh,H) and ^1J(^{11}B,H) couplings of 19.6 and 71.6 Hz, respectively, suggest that the coordination in the Tp$^{Me_2,4\text{-}Cl}$ complex[8] should be considered as intermediate between the κ^2-*N,B–H*–Tp′ (structure **D**), and the monodentate κ^1-*N*-Tp′, (structure **E**). Prior to this work, the latter binding mode had only been demonstrated in some nickel complexes of the bulky Tp^{tBu} ligand.[7d, 10]



D **E** **F**

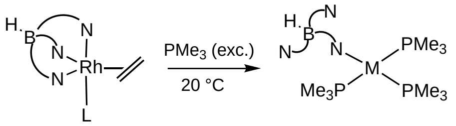
Corresponding variations in M–Cp′ binding have been known for many years.[1, 11] In a pioneer contribution, Casey and co-workers demonstrated the interconversion of η^5-C$_5$H$_5$, η^1-C$_5$H$_5$ and ionic "η^0"-C$_5$H$_5^-$ compounds in the course of the reaction of [Re(η^5-C$_5$H$_5$)(CH$_3$)(NO)(PMe$_3$)] with PMe$_3$, and proposed an η^3-C$_5$H$_5$ intermediate for the $\eta^5 \rightleftharpoons \eta^1$ exchange.[12] In contrast, at the outset of our work, direct unequivocal evidence for an ionic "κ^0"-Tp′$^-$ metal compound (structure **F**) had not yet been provided, although we later learnt that the compound [Re(O)$_2$(dmpe)$_2$][Tp] (dmpe = Me$_2$PCH$_2$CH$_2$PMe$_2$) had been prepared and structurally characterised by Santos and co-workers.[13] Moreover, the isolation of the complex salt [BiTm$_2$][NaTp$_2$] by addition of NaTp to the purported "[BiTm$_2$Cl$_2$]" (Tm = hydrotris(methimazolyl)borate) had been attributed to the proficiency of Tp as a ligand and to its unwillingness to act as a counterion.[14a] Herein we report our results on the study of the reactivity of various rhodium(I) and rhodium(III) compounds bearing Tp′ ligands toward monodentate and bidentate tertiary phosphanes. Stepwise changes in the denticity of the Tp′ group were observed, ranging from the common κ^3 facial coordination to the previously unreported "κ^0"-Tp′$^-$, that is, the uncoordinated situation. These changes take place under commonly used reaction conditions, stressing their probable implication in the stoichiometric and catalytic transformations undergone by compounds of these ligands. Part of this work has been published in preliminary form.[8, 15]

Abstract in Spanish: *La reacción de diversas fosfinas terciarias, mono o bidentadas, con compuestos de rodio(I) y rodio(III) transcurre a través de varias etapas sucesivas en las que se incorporan átomos donadores de fósforo, en sustitución de los anillos de pirazol del ligando Tp′. Así por ejemplo, en su reacción con PMe$_3$, a la temperatura ambiental, el complejo [Rh(κ^3-Tp^{Me_2})(C$_2$H$_4$)(PMe$_3$)] (**1b**) se convierte inicialmente en el [Rh(κ^2-Tp^{Me_2})(PMe$_3$)$_2$] (**3**), y con posterioridad en el [Rh(κ^1-Tp^{Me_2})(PMe$_3$)$_3$] (**2**), en un proceso reversible que puede invertirse si se emplean las condiciones experimentales apropiadas. Puede incluso llegarse a la expulsión del ligando Tp′ de la esfera de coordinación del metal, formándose en estos casos sales de complejos catiónicos de rodio(I) y del anión Tp′ como [Rh(CO)(dppp)$_2$][Tp$^{Me_2,4\text{-}Cl}$] (**5**) y [Rh(dppp)$_2$][Tp$^{Me_2,4\text{-}Cl}$] (**6**) (dppp = Ph$_2$P(CH$_2$)$_3$PPh$_2$). Los complejos de rodio(III) que contienen dos ligandos hidruro experimentan reacciones de sustitución análogas a las antes mencionadas, encontrándose por ejemplo que la interacción del compuesto neutro [Rh(Tp)(H)$_2$(PMe$_3$)] con un exceso de PMe$_3$, a 20°C, produce la especie [Rh(H)$_2$(PMe$_3$)$_4$][Tp] (**9b**). Los estudios de difracción de rayos X efectuados con esta sustancia a 143 K ponen de manifiesto la inexistencia de interacciones de enlace entre el catión [Rh(H)$_2$(PMe$_3$)$_4$]$^+$ y el anión Tp, encontrándose que la distancia Rh···N más corta es igual a 4.627 Å.*

Results and Discussion

Synthesis of phosphane complexes of rhodium(I) bearing the tris(pyrazolyl)borate ligands Tp^{Me_2} and Tp$^{Me_2,4\text{-}Cl}$: The following monodentate or bidentate tertiary phosphanes PMe$_3$, PMe$_2$Ph, PMePh$_2$ and Ph$_2$P(CH$_2$)$_3$PPh$_2$ (dppp) were treated with the complexes [Rh(Tp^{Me_2})(C$_2$H$_4$)L] (L = C$_2$H$_4$, **1a**; PMe$_3$, **1b**)[16a] and [Rh(Tp$^{Me_2,4\text{-}Cl}$)(CO)$_2$][16b] (**1c**). The choice of the rhodium(I) precursors was made for their simple and facile substitution chemistry.

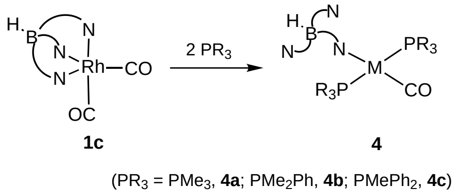
Treatment of [Tp^{Me_2}Rh(C$_2$H$_4$)L] (**1**) with an excess of PMe$_3$ (ca. 5 mol equiv) generates the new complex **2** instantaneously, in almost quantitative yield (Scheme 1). This transformation is applicable to complexes of other Tp′ and phosphane ligands. Scheme 2 shows the result of the addition of different PR$_3$ reagents to the complex **1c**, which contains an ancillary Tp$^{Me_2,4\text{-}Cl}$ group (only the κ^3 isomer of **1c** has been represented).[17]



1a,b (L = C$_2$H$_4$ or PMe$_3$) **2**

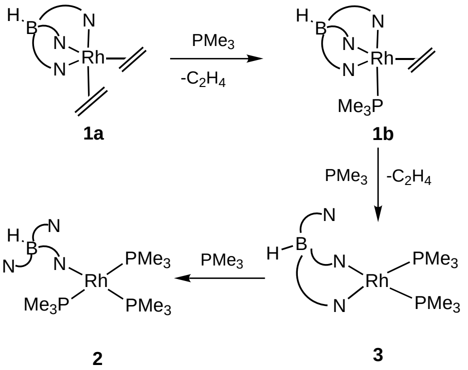
Scheme 1. Conversion of [Rh(Tp^{Me_2})(C$_2$H$_4$)L] (**1a** (L = C$_2$H$_4$) or **1b** (L = PMe$_3$)) into **2** in the presence of an excess of PMe$_3$ (ca. 5 mol equiv).

Not unexpectedly, the transformations represented in Schemes 1 and 2 proceed through the intermediacy of less-rich phosphane-containing complexes. Thus, when **1c** is treated with PMePh$_2$ (1 mol equiv), the monophosphane complex [Rh(Tp$^{Me_2,4\text{-}Cl}$)(CO)(PMePh$_2$)] is formed.[8] Similarly, in the Tp^{Me_2}-PMe$_3$ reaction system (Scheme 1), a bis(phosphane) derivative **3** is initially formed and can be isolated if a



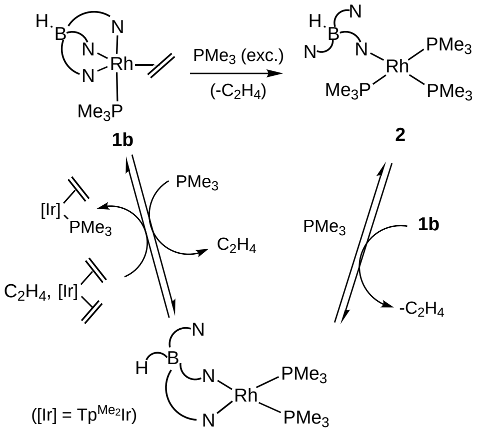
Scheme 2. The conversion of the complex **1c** containing an ancillary $Tp^{Me_2,4\text{-}Cl}$ group (only the κ^3-isomer of **1c** has been represented), into **4** by the addition of different PR_3 reagents.

solution that contains 1 mol equiv of PMe_3 is added dropwise to a solution of **1b**. Accordingly, the overall transformation of **1a** into **2** can be described as depicted in Scheme 3.



Scheme 3. Stepwise conversion of **1a** into **2** with variation in the coordination of the Tp^{Me_2} ligand from κ^3 to κ^1.

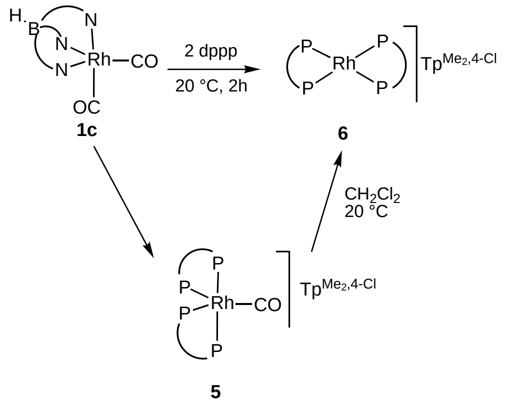
Experiments involving the complexes that participate in this reaction system demonstrate that both the κ^3 to κ^2 and the κ^2 to κ^1 rearrangements of the Tp^{Me_2} ligand are reversible (Scheme 4). In this way, compound **3**, which bears a κ^2-Tp^{Me_2} group, reacts with C_2H_4, in the presence of $[Tp^{Me_2}Ir(C_2H_4)_2]$ as the PMe_3 acceptor,[18] to regenerate the starting material $[Rh(\kappa^3\text{-}Tp^{Me_2})(C_2H_4)(PMe_3)]$ (**1b**). In turn, addition of solutions of **1b** to **2** cleanly produces complex **3**.



Scheme 4. Reversibility of some Tp^{Me_2} ligand denticity changes.

Even if the tris(phosphane) species **2** is unreactive toward additional PMe_3 under ambient conditions, at 120 °C further reaction takes place to give a species tentatively formulated as $[Rh(PMe_3)_4][Tp^{Me_2}]$ on the basis of the observation of a doublet at $\delta = -19.7$ ($^1J(Rh,P) = 146$ Hz) in the $^{31}P\{^1H\}$ NMR spectrum. These and other NMR parameters are similar to those reported for the somewhat analogous compound $[Rh(PMe_3)_4]Cl$.[19] The compound decomposes upon workup to give a complex mixture of species including the $[RhH_2(PMe_3)_4]^+$ ion.[19] Proper characterisation has proved unattainable thereby making this formulation uncertain.

The mono(carbonyl) derivatives **4** do not react cleanly with the corresponding PR_3, but the dicarbonyl precursor **1c** undergoes a smooth reaction with of $Ph_2P(CH_2)_3PPh_2$ (2 mol equiv; Scheme 5) giving first $[Rh(CO)(dppp)_2][Tp^{Me_2,4\text{-}Cl}]$ (**5**) and then $[Rh(dppp)_2][Tp^{Me_2,4\text{-}Cl}]$ (**6**), the latter resulting from the slow, spontaneous dissociation of CO from **5**. On a preparative scale, compound **6** is best obtained by the direct reaction of $[Rh(dppp)_2][Cl]$ with $KTp^{Me_2,4\text{-}Cl}$ (see Experimental Section).



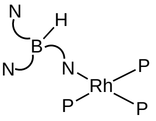
Scheme 5. Dissociation of the $Tp^{Me_2,4\text{-}Cl}$ ligand by action of the bidentate phosphane, dppp.

Solution and solid-state structural studies of compounds 2–6: As already indicated, the compound $[Rh(\kappa^2\text{-}Tp^{Me_2})(PMe_3)_2]$ (**3**) can be produced by the very slow, dropwise addition of solutions of PMe_3 to compound **1b**. Since the interaction of **3** with PMe_3 to give **2** is very fast, even microcrystalline samples of **3** were always contaminated with **2** and unreacted **1b** and have not been obtained in analytically pure form. Its characterisation by spectroscopic methods is, however, straightforward.

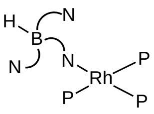
The proposed κ^2-N,N'-Tp^{Me_2} binding relies upon the observation of a $\nu(B{-}H)$ infrared absorption[20] at 2450 cm^{-1} and a $^{11}B\{^1H\}$ NMR resonance[21] at $\delta = -5.6$. These data compare well with those expected for complexes that exhibit κ^2-Tp′ binding[20] and differ significantly from those associated with the κ^3 structures. The latter exhibit $\nu(B{-}H)$ around 2515 cm^{-1} and δ $^{11}B\{^1H\}$ at about -9.[16a]

Although the X-ray studies discussed below may be interpreted as indicative of a weak $Rh\cdots H{-}B$ interaction in compounds **4**, there is no clear spectroscopic evidence in support of such a bonding in solution. Conceivably the four complexes **2** and **4a**–**4c** should have similar structures, as supported by their similar spectroscopic properties. In the foregoing discussion **2** will be used as a representative example. At the outset of this work, only one family of compounds, exemplified by the X-ray characterised [Ni(Tp^{tBu})(C_6H_4-*p*-Me)($(PMe_3)_2$)], had been demonstrated to contain a κ^1-*N*-Tp′ group, but $^{11}B\{^1H\}$ NMR data were not provided.[10, 7d] Despite the dearth of information available, the observation of the $^{11}B\{^1H\}$ NMR resonance of **2** at $\delta = -2.0$ argues in favour of κ^1-*N* binding. This shift adjusts into the trend expected for the $\kappa^3 \rightarrow \kappa^2 \rightarrow \kappa^1$ exchange (recall that κ^3- and κ^2-Tp^{Me_2} coordinations are associated with approximate δ $^{11}B\{^1H\}$ ranges of -9.8 to -8.4 and -7.0 to -5.9, respectively [21]) and, moreover, it is very close to the $\delta = -1.8$ value reported for the 18-electron complex [Ru(Tp)(quin)(η^6-*p*-MeC_6H_4*i*Pr)][22] (quin = quinolin-8-olate), recently characterised by Kirchner and co-workers as containing a κ^1-Tp ligand.

All of the compounds **2** and **4** present a plethora of weak IR absorptions associated with ν(B–H). Taking **2** as the archetype, bands in the proximity of 2425, 2390 and 2355 cm^{-1} (along with other weaker absorptions) have been recorded. These absorptions undergo insignificant variations from Nujol mull to KBr disk or THF solutions, in the latter case in the temperature range 20 to -85 °C (four main peaks are observed (KBr) for **4a** and **4b** between ca. 2440 and 2260 cm^{-1}). Nonetheless, this complexity is not uncommon[22] and may be due to different reasons,[23] which include the existence of κ^3 and κ^2 isomers in the crystal cell.[20] With respect to the possibility of κ^2-*N,B–H* binding, the lowest energy band of **2** at 2355 cm^{-1} indicates that an appreciable interaction of this kind does not exist in this complex. For comparative purposes, the analogous band of [Rh(Tp^{Me_2})($P(C_7H_7)_3$)][9] appears at 1822 cm^{-1} and that of [Ru(Tp)^{Me_2}(Me)(C_8H_{12})][6a] at 1870 cm^{-1}. In both cases a strong M···H–B interaction has been demonstrated. A structure of type **G**, which actually corresponds to the solid-state structure (vide infra) could possibly have lower ν(B–H) than one of type **H**. In summary, we suggest that solid-state effects and possibly the co-crystallisation of molecules with different Tp^{Me_2} conformations (or even coordination) could account for the multiplicity of ν(B–H). As discussed below, two kinds of crystals of **2**, characterised by different cell parameters and distribution of the pz′ rings of Tp^{Me_2}, have been obtained and examined by X-ray crystallography.



G



H

The room-temperature $^{31}P\{^1H\}$ NMR spectrum (202.5 MHz) of **2** in [D_8]toluene consists of a doublet of triplets centred at δ -5.82 ($^1J(P_A,Rh) = 158$; $^2J(P_A,P_M) = 48$ Hz) and a doublet of doublets at $\delta = -14.15$ ($^1J(P_M,Rh) = 133$ Hz), as expected for an AM_2X spin system (X = ^{103}Rh). Lowering the temperature (-80 °C) results in the inequivalency of the *trans* PMe_3 groups and, consequently, in the observation of a strong $^2J(P_A,P_M)$ coupling of 340 Hz. The low-temperature spectrum is in accord with a rigid asymmetric structure in which the plane perpendicular to the P-Rh-P vector (see Figure 1 below) is no longer a plane of symmetry. This may result from restricted conformational mobility of the Tp′ ligand in the sterically crowded coordination environment. A similar situation is found for the monocarbonyl derivatives **4**, since they all have *trans*, non-equivalent PR_3 groups at -90 °C ($^2J(P_A,P_M) = 320$–330 Hz) that equilibrate at ambient temperature to give the expected doublet ($\delta = -6.5$; $^1J(P,Rh) = 116$ Hz, data for **4a**).

In agreement with the proposed ionic formulation, equivalence of the three pz′ rings of compounds **5** and **6** is observed. IR and ^{11}B NMR data ($\nu(B-H) = 2433$ cm^{-1}; $\delta = -0.7$, data for **6**) are inconclusive in this regard[15] (vide infra), but conductivity measurements for **6** provide a value of $\Lambda_M = 56$ $cm^2\Omega^{-1}mol^{-1}$ (CH_3CN, 20 °C), similar to that obtained for the analogous chloride, [Rh(dppp)$_2$]Cl[24] ($\Lambda_M = 58$ $cm^2\Omega^{-1}mol^{-1}$). This value is lower than that found for related salts of the BPh_4^- ion (e.g., $\Lambda = 79$ for [Rh($P(OMe)_3)_4$]BPh_4[25]), and also than expected for a 1:1 electrolyte in acetonitrile ($\Lambda = 120$–160).[26] Notwithstanding the above, it cannot be considered surprising if allowance is made of both the large size of the ions of **6** and the propensity of Tp'^- anions to act as ligands.[3, 14a]

Compound **5** is dynamic in solution; its room-temperature $^{31}P\{^1H\}$ NMR spectrum consists of just one doublet. Below -60 °C a rigid structure is obtained that gives a pattern of lines corresponding to an A_2M_2X spin system (X = ^{103}Rh), so that under these conditions a trigonal-bipyramid geometry with an equatorial CO group (see Scheme 5) can be proposed. Similar data have been reported for analogous cations.[27]

As for **6**, mass spectroscopy analyses in electrospray of its acetonitrile solutions are consistent with the formula [Rh(dppp)$_2$][$Tp^{Me_2,4-Cl}$]. The cation is clearly observed at *m*/*z* 927.3 in positive mode, whereas the anion [$Tp^{Me_2,4-Cl}$] appears at *m*/*z* 399.1 in negative mode, in agreement with the expected theoretical spectrum. The room-temperature $^{31}P\{^1H\}$ NMR spectrum of **6** does not correspond to a square-planar structure in which the four phosphorus atoms are expected to be equivalent as previously observed for analogous cations.[28] Two doublets of triplets associated with an A_2M_2X spin system, typical of a five-coordinate trigonal-bipyramidal geometry, are in fact observed. Such a structure has already been observed by Pignolet et al.[28] at low temperature for the solvated [Rh(dppp)$_2$][BF_4] species, particularly in acetone. In our case, taking into account 1) that CD_2Cl_2 is a very weakly coordinating solvent, 2) that such a solvated species should also be observed for [Rh(dppp)$_2$][Cl] and 3) that the conductivity measurements are lower than for a 1:1 electrolyte, we propose an ion-pair for **6**. The influence of the Tp'^- counterion in close vicinity of the rhodium(I) complex cation may induce the adoption of a geometry close to a trigonal bipyramid.

To ascertain the coordination mode of the Tp′ ligand in the molecules of complexes **2** and **4** in the solid state, we carried out X-ray crystallographic studies on compounds **2**, **4a**, and **4c**.[8] Crystals of **5** and **6** suitable for this structural determination have not been isolated. Figures 1–3 show the struc-

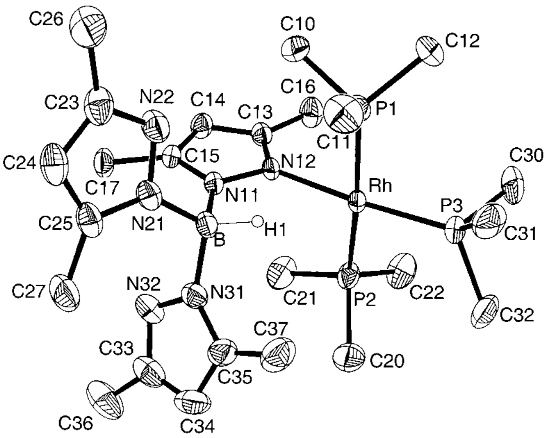


Figure 1. Molecular structure of compound **2**.

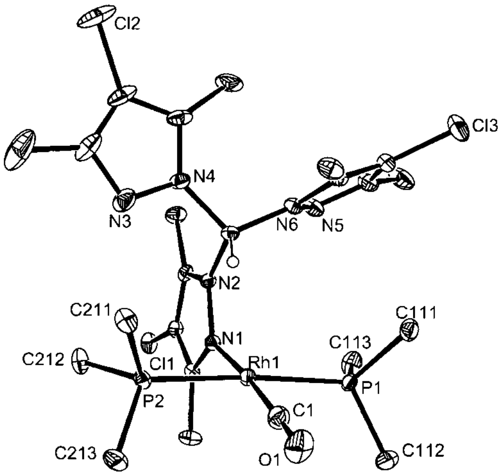


Figure 2. ORTEP view of molecule **4a** with atom labelling scheme. Ellipsoids are drawn at 30% probability.

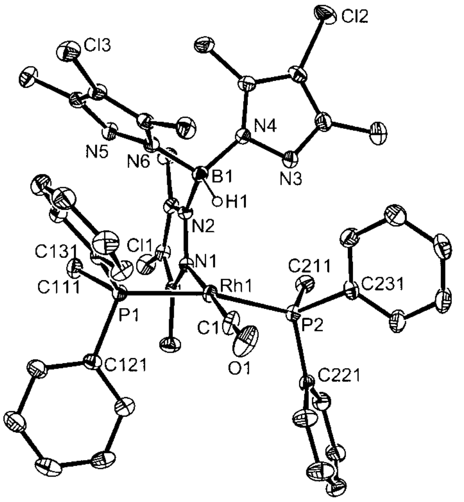


Figure 3. ORTEP view of molecule **4c** with atom labelling scheme. Ellipsoids are drawn at 30% probability.

tures of of the above-mentioned complexes and the appropriate crystal data are summarised in Tables 1 and 2. Crystals of **2** and **4a** are monoclinic, belonging to the space groups $P2_1/c$ and $P2_1$, respectively. Compound **4c** crystallise in the space group $P\bar{1}$. Leaving aside for the time being the question of the purported Rh···H–B interaction, as the values of the selected bond angles and lengths included in the respective part of Table 3 indicate, the coordination sphere of the Rh center is best described in the three cases as a somewhat distorted square-planar geometry. In compounds **4** the two phosphanes are mutually *trans* and direct the CO group to the coordination site *trans* to the Tp′-N atom. In **2**, this site is occupied by the third PMe_3, which forms angles very close to the ideal 90° value with the other two PMe_3 groups.

As already discussed, there is no spectroscopic evidence indicative of the existence in solution of a Rh···H–B bonding interaction. In the solid state, two structural parameters may be used to discriminate in favour or against this possibility: the Rh···H separation and the length of the B–H bond, allegedly involved in such an interaction. Rh···H distances in **2**, **4a**, and **4c** are 2.59(4), 2.41(2) and 2.35(3) Å, respectively. The B–H hydrogen is located for each complex in a position that would correspond to the apex of a hypothetical square pyramid, and while this consideration could be taken in support of some Rh···H–B bonding, the long Rh···H distances indicate that if this interaction exists it must be very weak. Comparison with M···H distances in complexes that exhibit strong M···H–B interactions points toward that conclusion too. Thus, in the complex $[Rh(\kappa^2\text{-}N,B\text{-}H\text{-}Tp^{Me_2})\{P(C_7H_8)_3\}]$ the two independent molecules that exist in the unit cell[9] have Rh···H distances of 1.789(7) and 1.899(7) Å, whereas in Ru^{II} complexes featuring κ^3-*N*,*N*′,*B*–*H*-Tp′ binding[6] the Ru···H–B separations span the range 1.77–1.96 Å.

Application of the second aforementioned criterium, namely the lengthening of the B–H bond, reinforces these arguments. B–H distances in **2** and **4a** (1.13(2) Å) and in **4c** (1.17(3) Å) are characteristic of normal bonds between these atoms (in $Al(BH_4)_3$ the terminal and bridging B–H bonds have lengths of 1.196 and 1.283 Å, respectively[29]). Additionally, in the above-mentioned Rh[9] and Ru[6] complexes, which display strong M···H–B interactions, the B–H bond length is in the interval 1.20–1.30 Å.

Before closing this section it should be mentioned that with the aim of clarifying the reasons of the complexity of the ν(B–H) infrared region of compounds **2** and **4**, crystals from different crops of compound **2** were studied by X-ray methods. A second kind of crystal of this complex (**2′** from now on) was found to belong to the space group *Pbcn* in the orthorhombic system and was characterised by different cell parameters. However, the main bond lengths and angles are very similar to those of **2**; the principal difference between the molecules **2** and **2′** is the slightly different conformation of the pz′ rings (see Supporting Information for more details).

Complexes of rhodium(III): The changes in the Tp′ ligand denticity described in the preceeding sections for the complexes of rhodium(I) can be extended to compounds of rhodium(III). For example, treatment of the peroxo derivative $[Rh(\kappa^3\text{-}Tp^{Me_2})(O_2)(PMe_3)]$[16a] with an excess of PMe_3 at 50 °C, allows the incorporation of a second molecule of phosphane, with concomitant dissociation of one of the pyrazolyl rings and formation of complex **7** (Scheme 6). In accord with the proposed κ^3 to κ^2 Tp^{Me_2} coordination change, ν(B–H) and δ

Table 1. Crystal data and structure refinement for compounds **2**, **7**, **8** and **9b**.

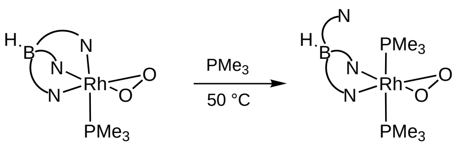
	2	**7**	**8**	**9b**
formula	$C_{24}H_{49}BN_6P_3Rh$	$C_{21}H_{40}BN_6O_2P_2Rh$	$C_{21}H_{42}BN_6P_2Rh$	$C_{21}H_{48}BN_6P_4Rh$
M_r	628.32	584.25	554.27	622.25
T [K]	148(2)	148(2)	293(2)	143(2)
λ [Å]	0.71073	0.71073	0.71073	0.71073
crystal system	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/c$	$P2_1$	$P2_1/c$	$P\bar{1}$
a [Å]	12.5927(9)	9.2876(14)	9.497(4)	9.4968(13)
b [Å]	12.3861(9)	11.034(2)	11.290(5)	9.7223(13)
c [Å]	20.773(2)	13.621(2)	25.984(10)	9.8279(13)
α [°]	90	90	90	60.891(2)
β [°]	93.6140(10)	93.320(3)	91.81(2)	85.285(2)
γ [°]	90	90	90	80.050(2)
V [Å^3]	3233.6(4)	1393.5(4)	2785(2)	780.9(2)
Z	4	2	4	4
ρ_{calcd} [mg m^{-3}]	1.291	1.392	1.324	1.323
μ [mm^{-1}]	0.699	0.756	0.747	0.772
$F(000)$	1320	608	1164	326
crystal size [mm]	0.2 × 0.35 × 0.35	0.10 × 0.10 × 0.2	0.4 × 0.6 × 1.0	0.08 × 0.1 × 0.14
θ range [°]	2.55–26.52	2.73–26.59	1.57–23.30	3.00–26.40
limiting indices	$-13 \leq h \leq 13$	$-9 \leq h \leq 11$	$-10 \leq h \leq 10$	$-11 \leq h \leq 10$
	$-9 \leq k \leq 15$	$-9 \leq k \leq 15$	$-12 \leq k \leq 11$	$-12 \leq k \leq 7$
	$-5 \leq l \leq 25$	$-5 \leq l \leq 25$	$-23 \leq l \leq 28$	$-12 \leq l \leq 12$
reflections collected	9001	4071	10547	3680
independent reflections	5245 ($R_{int} = 0.0223$)	3233 ($R_{int} = 0.0424$)	3985 ($R_{int} = 0.0550$)	3210 ($R_{int} = 0.0261$)
absorption correction	none	SADABS	none	SADABS
refinement method	full-matrix least-squares on F^2			
data/restraints/parameters	5245/0/335	3233/1/310	3985/0/304	3210/3/322
goodness-of-fit on F^2	0.967	0.986	1.026	0.750
final R indices [$I > 2\sigma(I)$]	$R1 = 0.0329$, $wR2 = 0.0733$	$R1 = 0.0525$, $wR2 = 0.0853$	$R1 = 0.0532$, $wR2 = 0.1246$	$R1 = 0.0417$, $wR2 = 0.0925$
R indices (all data)	$R1 = 0.0510$, $wR2 = 0.0807$	$R1 = 0.0840$, $wR2 = 0.0959$	$R1 = 0.0802$, $wR2 = 0.1352$	$R1 = 0.0522$, $wR2 = 0.0998$
largest diff peak/hole [e Å^{-3}]	0.435/−0.644	0.406/−0.481	1.925/−0.463	0.439/−0.571

Table 2. Crystal data and structure refinement for compound **4a**.

formula	$C_{22}H_{37}BCl_3N_6OP_2Rh$
M_r	683.60 g
shape (colour)	box (yellow)
size [mm]	0.56 × 0.56 × 0.28
crystal system	monoclinic
space group	$P2_1$
a [Å]	10.7035(16)
b [Å]	12.3711(13)
c [Å]	13.2127(19)
β [°]	113.81(2)
V [Å^3]	1600.7(3) Å^3
Z	2
$F(000)$	698
ρ_{calcd} [g cm^{-3}]	1.418
μ (Mo$_{K\alpha}$) [cm^{-1}]	9.092
2θ range [°]	$5.3 < 2\theta < 51.9$
reflections collected	12340
unique reflections	6028
merging factor R(int)	0.0273
reflections observed [$I > 2\sigma(I)$]	5898
R	0.0273
Rw	0.0310
$(\Delta/\sigma)_{max}$	0.081
$\Delta\rho_{min}/\Delta\rho_{max}$	−0.69/1.95
Flack parameter	0.00(2)
goodness-of-fit	0.978
parameters	331

Table 3. Selected bond lengths [Å] and angles [°] for compounds **2**, **4a** and **4c**.

2		**4a**		**4c**	
Rh–P1	2.3209(8)	Rh1–P1	2.3122(7)	Rh1–P1	2.3273(8)
Rh–P2	2.3057(8)	Rh1–P2	2.3117(7)	Rh1–P1	2.3317(8)
Rh–P3	2.2206(9)	Rh1–C1	1.805(3)	Rh1–C1	1.802(4)
Rh–N12	2.116(2)	Rh1–N1	2.117(2)	Rh1–N1	2.105(3)
Rh–H1	2.59(4)	Rh1–H1	2.41(2)	Rh1–H1	2.35(3)
B1–H1	1.14(4)	B1–H1	1.13(2)	B1–H1	1.17(3)
		O1–C1	1.157(3)	O1–C1	1.150(5)
P1-Rh-P2	171.65(3)	P1-Rh1-P2	176.09(2)	P1-Rh1-P2	167.54(3)
P1-Rh-N12	86.14(6)	P1-Rh1-N1	91.40(5)	P1-Rh1-N1	89.97(7)
P2-Rh-N12	86.89(6)	P2-Rh1-N1	90.76(5)	P2-Rh1-N1	90.21(7)
P1-Rh-P3	92.78(3)	P1-Rh1-C1	88.79(8)	P1-Rh1-C1	89.93(11)
P2-Rh-P3	93.69(3)	P2-Rh1-C1	88.74(8)	P2-Rh1-C1	89.46(11)
N12-Rh-P3	174.16(7)	N1-Rh1-C1	174.39(11)	N1-Rh1-C1	178.01(14)
		Rh1-C1-O1	179.1(3)	Rh1-C1-O1	178.7(4)

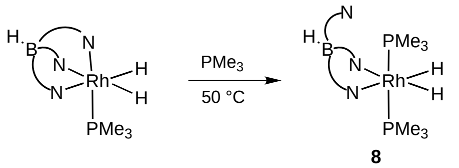


7

Scheme 6. Formation of complex **7** by treatment of the peroxo derivative [Rh(κ^3-Tp^{Me_2})(O_2)(PMe_3)] with an excess of PMe_3 at 50 °C.

$^{11}B\{^1H\}$ vary from 2520 cm^{-1} and $\delta = -9.1$ in the monophosphane complex[16a] to 2475 cm^{-1} and $\delta = -6.4$ in the new species **7**. A second, lower energy IR band is observed at 2405 cm^{-1}. This band appears also in the spectrum of the analogous bis(hydride) compound **8**, discussed below, but at present we can offer no reasonable explanation for its existence.

Reaction of the known complex $[Rh(\kappa^3\text{-}Tp^{Me_2})(H)_2(PMe_3)]$[16a] with PMe_3 under analogous conditions produces the bis(phosphane) derivative **8** (Scheme 7). As for **7**, only the stereoisomer that has *trans* PMe_3 ligands is formed.



Scheme 7. Conversion of the known complex $[Rh(\kappa^3\text{-}Tp^{Me_2})(H)_2(PMe_3)]$ into the bis(phosphane) derivative **8** in the presence of PMe_3.

Complexes **7** and **8** were readily characterised by NMR spectroscopy (see Experimental Section). The ^1H NMR spectrum of **8** shows a high-field quartet at $\delta = -17.22$ caused by the two equivalent hydrides that have accidentally equal coupling to the two ^{31}P and the ^{103}Rh nuclei (20.8 Hz). The hydride ligands are also responsible for the two IR bands appearing at 2070 and 2045 cm^{-1}, whereas a higher energy absorption at 2485 cm^{-1} (accompanied, as indicated above, by a second one at 2400 cm^{-1}) suggests $\kappa^2\text{-}Tp^{Me_2}$ coordination. In agreement with this proposal, the $^{11}B\{^1H\}$ resonance appears at $\delta = -6.0$.

As Figures 4 and 5 show, the $\kappa^2\text{-}Tp^{Me_2}$ coordination in **7** and **8** persists in the solid state. Structural parameters have normal values and compare well with those obtained for related compounds. However, in light of the earlier discussion dedicated to the rhodium(I) derivatives, it is worth pointing out that: 1) the B–H bond lengths of **7** and **8** are 1.04(9) and 1.06(5) Å, respectively, and 2) the two Rh–H functionalities of **8** have identical bond lengths of 1.53(9) and 1.57(7) Å, evidently much shorter than the Rh···H–B separations found in **2**, **4a**, and **4c** (see Tables 3 and 4).

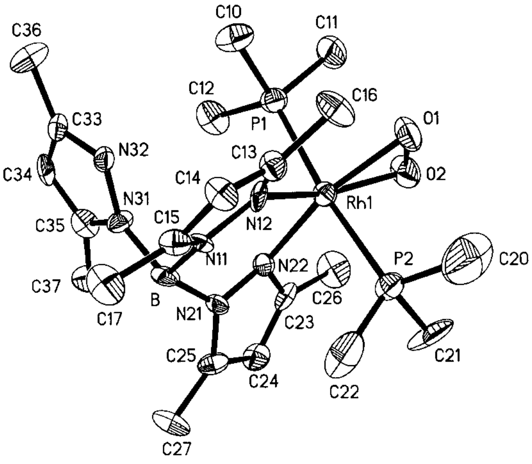


Figure 4. Molecular structure of compound **7**.

Table 4. Selected bond lengths [Å] and angles [°] for compounds **7**, **8** and **9b**.

7		8		9b	
Rh1–O1	1.9995(6)	Rh–H1	1.60(6)	Rh1–H1	1.57(7)
Rh1–O2	2.012(7)	Rh–H2	1.60(7)	Rh1–H2	1.53(9)
Rh1–N12	2.100(7)	Rh–N12	2.182(5)	Rh1–P2	2.362(2)
Rh2–N22	2.118(7)	Rh–N22	2.198(5)	Rh1–P3	2.358(2)
Rh1–P1	2.329(3)	Rh–P1	2.296(2)	Rh1–P4	2.310(2)
Rh1–P2	2.330(3)	Rh–P2	2.276(2)	Rh1–P5	2.296(2)
O1–O2	1.466(8)	B–H(B)	1.06(5)		
B–H(B)	1.04(9)				
O1-Rh1-O2	42.9(2)	H1-Rh-H2	73(3)	H1-Rh1-H2	74(4)
N12-Rh1-N22	91.3(3)	N12-Rh-N22	91.3(2)	P4-Rh1-P5	154.72(7)
P1-Rh1-P2	174.01(12)	P1-Rh-P2	167.93(6)	P2-Rh1-P3	98.70(7)

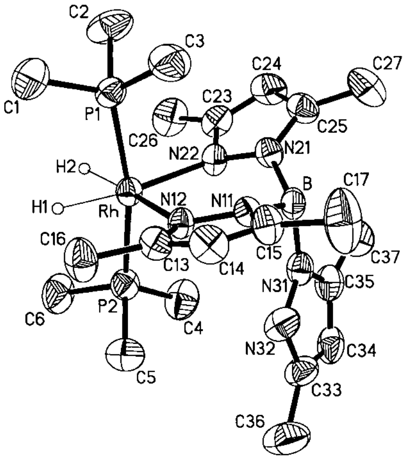
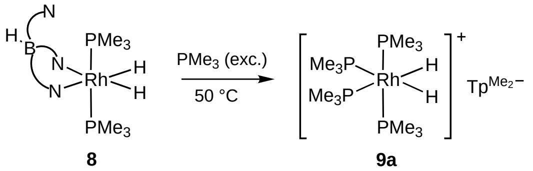


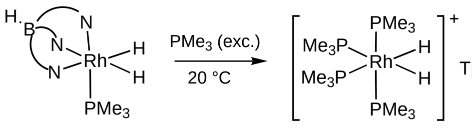
Figure 5. Molecular structure of compound **8**.



Scheme 8. Conversion of the hydride **8** into the known cation **9a** ($[Rh(H)_2(PMe_3)_4]^+$) by forcing the coordination of two additional molecules of PMe_3.

No further changes with time are observed in the reaction system that leads to **7**, but the hydride **8** can be forced to coordinate two additional molecules of PMe_3 to form ultimately the known $[Rh(H)_2(PMe_3)_4]^+$ ion,[19] postulated to exist in these solutions as the salt of the Tp^{Me_2-} ion (Scheme 8). The $^{11}B\{^1H\}$ NMR spectrum of the reaction mixture consists of a signal at about $\delta = -2.0$, whilst the ν(B–H) absorption appears at 2430 cm^{-1}. As already noted[15] the ν(B–H) and δ $^{11}B\{^1H\}$ criteria[20, 21] appear to be meaningless for the uncomplexed Tp′ anions. As for the $[Rh(H)_2(PMe_3)_4]^+$ counterion, its NMR properties are coincident with those already reported.[19] Moreover, they match exactly those corresponding to the species that forms when $[Rh(PMe_3)_4]Cl$[19] is treated with KTp^{Me_2}.

Despite the fact that **9a** seems to form in high yields, our efforts to obtain analytically pure samples of this compound proved fruitless. Nevertheless, the bis(hydride) complex of the unsubstituted Tp ligand, $[Rh(Tp)(H)_2(PMe_3)]$, reacts at room temperature with an excess of PMe_3 to produce **9b** (Scheme 9), with no observable intermediates. In contrast to **9a**, crystalline samples of **9b** of analytical purity can be obtained by crystallisation from THF at −20 °C. Besides resonances due to $[Rh(H)_2(PMe_3)_4]^+$, solutions of **9b** in [D$_6$]acetone display three ^1H signals at $\delta = 7.36$ (d), 7.28 (d)



9b

Scheme 9. Conversion of the bis(hydride) complex of the unsubstituted Tp ligand, $[TpRh(H)_2(PMe_3)]$ into **9b**.

and 5.92 (dd), each corresponding to 3 H (^3J(H,H) = 2.0 Hz) assigned to the pyrazolyl protons, along with a broad quartet at $\delta = 4.97$, attributed to the BH proton (^1J(H,B) = 114 Hz). In the IR spectrum ν(B–H) appears at 2475 cm^{-1} and it is, once more, of no significance with regard to the ν(B–H) coordination rule. Figure 6 shows the result of a single-crystal X-ray study carried out at 143 K. As can be seen, there is no bonding interaction between $[Rh(H)_2(PMe_3)_4]^+$ and Tp$^-$; the closest Rh···N contact is to one of the N atoms of the Tp ligand of another asymmetric unit (4.627 Å). Compound **9b** is the first structurally authenticated example of a metal salt of a hydrotris(pyrazolyl)borate anion.

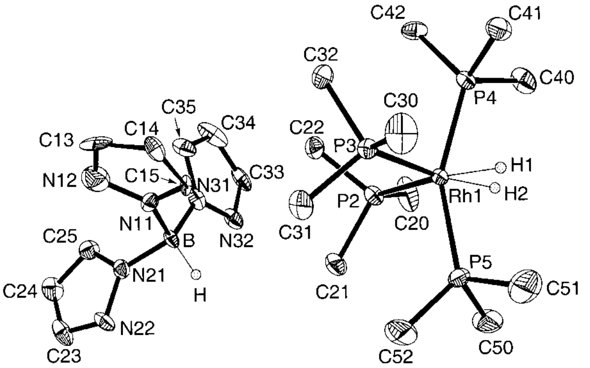


Figure 6. Molecular structure of compound **9b**.

In summary, the intensive research developed by many research groups around the world in recent years on the chemistry of M–Tp′ compounds, the main results of which are collected in a monograph and several review articles,[4] has provided evidence that this extremely versatile ligand family can exhibit a rich variety of coordination modes. In mononuclear compounds of simple Tp^R ligands that do not contain agostic[30] or metallated[31, 32] groups, these modes rank from the tridentate κ^3 to the uncoordinated "κ^0". Four donor functions, the three N atoms in the 2-pyrazolyl positions plus the B–H bond, compete for a maximum of three coordination sites of the metal, giving rise to two different modes of tridentate binding (structures **A** and **B**), two of bidentate (**C** and **D**) and one monodentate (**E**). Additionally, as reported in this contribution, full disengagement is also feasible (formulation **F**).

The work herein discussed, and the independent research of Santos and co-workers,[13b] demonstrate unequivocally that these variations can occur as a consequence of the chemical action of common, widely used phosphane reagents under ordinary reaction conditions (1 atm, 20–100 °C). It is therefore evident that these coordination changes can have important consequences in the stoichiometric and the catalytic reactions promoted by the M–Tp′ compounds.

Experimental Section

All preparations and manipulations were carried out under oxygen-free nitrogen or argon following conventional Schlenk techniques. Solvents were rigorously dried and degassed before use. The light petroleum used had a b.p. of 40–60 °C. The complexes $[Rh(Tp)(C_2H_4)_2]$,[33] $[Rh(Tp^{Me_2})(C_2H_4)_2]$,[16a] $[Rh(Tp^{Me_2})(C_4H_6)]$,[16a] $[Rh(Tp^{Me_2})(C_2H_4)(PMe_3)]$,[16a] $[Rh(Tp^{Me_2})(O_2)(PMe_3)]$,[16a] $[Rh(Tp^{Me_2,4-Cl})(CO)_2]$,[16b] $[Rh(Tp^{Me_2})(H)_2(PMe_3)]$,[16a] $[Rh(H)_2(PMe_3)_4]Cl$,[19] $[Rh(PMe_3)_4]Cl$,[19] $[Rh(dppp)_2]Cl$,[24] and the salts $KHB(pz)_3$ (KTp),[34] $KHB(3,5\text{-}Me_2\text{-}pz)_3$ (KTp^{Me_2})[34a] and $KHB(3,5\text{-}Me_2\text{-}4\text{-}Cl\text{-}pz)_3$ ($KTp^{Me_2,4-Cl}$)[7a] were prepared according to literature procedures. Compound $[Rh(Tp)(H)_2(PMe_3)]$ was prepared following the procedure described for the analogous Tp^{Me_2} derivative in ref. [16a]. Microanalyses were by the Microanalytical Services of the Instituto de Investigaciones Químicas (Sevilla) and the Ecole Nationale Supérieure de Chimie de Toulouse. In a series of analogous compounds, only some of them were analysed. Infrared spectra were recorded on Perkin–Elmer model 1710 and Bruker Vector 22 spectrometers; NMR spectra were recored on Bruker AC 250, AMX 300 and DRX 400 spectrometers. The ^{1}H and ^{13}C{^{1}H} resonances of the solvent were used as the internal standard, but the chemical shifts are reported with respect to TMS. ^{31}P and ^{11}B NMR shifts were referenced to external 85 % H_3PO_4 and $BF_3 \cdot OEt_2$, respectively. Mass spectra were obtained by the Mass Spectrometry Service of the Université Paul Sabatier (Toulouse) with a Perkin–Elmer Sciex API 365 – MS/MS spectrometer. Conductivity measurements were done on a Philips GM 4249 conductimeter.

$[Rh(\kappa^1\text{-}Tp^{Me_2})(PMe_3)_3]$ (2): Although this compound can be prepared by the same procedure starting from either $[Rh(Tp^{Me_2})(C_2H_4)_2]$, $[Rh(Tp^{Me_2})(C_2H_4)(PMe_3)]$ or the butadiene $[Rh(Tp^{Me_2})(C_4H_6)]$, the preparation reported here uses the latter precursor, because it provides cleaner results. A solution of $[Rh(Tp^{Me_2})(C_4H_6)]$ (0.20 g, 0.44 mmol) in THF (15 mL) at room temperature was treated with a solution of PMe_3 in THF (2.2 mL, 1 M, 2.2 mmol). After stirring for 2 h at room temperature, the reaction was analysed by ^{31}P NMR spectroscopy; this indicated the quantitative formation of **2**. The volatiles were removed in vacuo and the residue was dissolved in petroleum ether (20 mL). After filtration and concentration, the solution was cooled to −20 °C and yellow crystals of **2** were obtained (0.117 g, 0.19 mmol, 42 %). ^{1}H NMR (300 MHz, [D$_6$]benzene, 25 °C): $\delta = 5.93, 5.85$ (br s, 2:1, 3 H; CH$_{pz}$), 2.40, 2.36, 2.28, 2.18 (br s, 2:1:1:2, 18 H; 6 Me$_{pz}$), 0.96 (m, 27 H; PMe$_3$); ^{13}C{^{1}H} NMR (75.5 MHz, [D$_6$]benzene, 25 °C): $\delta = 148.1, 146.6, 145.3, 143.6$ (1:2:1:2; Cq$_{pz}$), 106.3, 104.6 (1:2; CH$_{pz}$), 21.4 (d, ^1J(C,P) = 27 Hz; PMe$_3$), 17.7 (pseudo t, J(C,P)$_{app}$ = 13 Hz; 2 *trans*-PMe$_3$), 15.1, 14.1, 12.7, 11.5 (1:2:1:2; Me$_{pz}$); ^{31}P{^{1}H} NMR (121.5 MHz, [D$_6$]benzene, 25 °C): $\delta = -5.8$ (dt, ^1J(P,Rh) = 158 Hz, ^2J(P,P) = 48 Hz), −14.1 (dd, ^1J(P,Rh) = 133 Hz); ^{11}B{^{1}H} NMR (96 MHz, [D$_6$]benzene, 25 °C): $\delta = -2.0$; IR (Nujol): $\tilde{\nu} = 2425, 2390, 2355, 2335$ cm^{-1} (sh) (B–H); elemental analysis calcd (%) for $C_{24}H_{49}BN_6P_3Rh$ (628.33): C 45.9, H 7.9, N 13.4; found: C 45.7, H 7.8, N 13.7.

$[Rh(\kappa^2\text{-}Tp^{Me_2})(PMe_3)_2]$ (3):

Route A: A solution of $[Rh(Tp^{Me_2})(C_2H_4)(PMe_3)]$ (0.25 g, 0.5 mmol) in THF (20 mL) at room temperature was stirred vigorously, and a solution of PMe_3 in THF (0.45 mL, 1 M, 0.45 mmol) was added dropwise. After stirring for 40 minutes at room temperature, the volatiles were removed in vacuo and NMR analyses revealed the presence of species **3** with 80–90 % purity.

Route B: A solution of complex $[\{Rh(\mu\text{-}Cl)(C_2H_4)_2\}_2]$ (0.058 g, 0.15 mmol) in THF (10 mL) was treated with a solution of PMe_3 in THF (0.6 mL, 1 M, 0.6 mmol). After stirring for 2 h at room temperature, a solution of KTp^{Me_2} (0.101 g, 0.3 mmol) in THF (6 mL) was added. After stirring for a further 1.5 h at room temperature, the solution was filtred through celite, the volatiles were removed in vacuo and the residue analysed by NMR spectroscopy. It contained compound **3** in about 70 % purity. Attempts to purify or crystallise the compound failed. ^{1}H NMR (300 MHz, [D$_6$]benzene, 25 °C): $\delta = 5.96, 5.59$ (br s, 1:2, 3 H; CH$_{pz}$), 2.37, 2.31, 2.30, 2.12 (br s, 1:2:2:1, 18 H; Me$_{pz}$), 0.99 (br pseudo t, J(H,P)$_{app}$ = 4.0 Hz, 18 H; PMe$_3$); ^{13}C{^{1}H} NMR (75.5 MHz, [D$_6$]benzene, 25 °C): $\delta = 152.4, 148.0, 146.0, 149.3$ (1:2:2:1; Cq$_{pz}$), 105.5, 104.8 (1:2; CH$_{pz}$), 19.5 (pseudo t, J(C,P)$_{app}$ = 14 Hz; PMe$_3$), 16.5, 14.4, 13.5, 13.0 (2:1:2:1; Me$_{pz}$); ^{31}P{^{1}H} NMR (121.5 MHz, [D$_6$]benzene, 25 °C) $\delta = -2.4$ (d, ^1J(P,Rh) = 171 Hz); ^{11}B{^{1}H} NMR (96 MHz, [D$_6$]benzene, 25 °C): $\delta = -5.6$; IR (Nujol): $\tilde{\nu} = 2452$ cm^{-1} (B–H).

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[Rh(κ^1-Tp$^{\mathrm{Me_2,4\text{-}Cl}}$)(CO)(PR$_3$)$_2$] (PR$_3$ = PMe$_3$, 4a; PMe$_2$Ph, 4b; PMePh$_2$, 4c):

Compound ***4a***: Pure PMe$_3$ (0.121 mL) was added to a solution of [Rh(Tp$^{\mathrm{Me_2,4\text{-}Cl}}$)(CO)$_2$] (0.34 g, 0.61 mmol) in pentane (30 mL) at 0 °C. The reaction was instantaneous and a new ν(CO) band was observed at 1974 cm^{-1} by IR spectroscopy. After filtration, yellow crystals were obtained from the filtrate at room temperature (0.37 g, 0.54 mmol, 90 %). ^{1}H NMR (250 MHz, [D$_2$]dichloromethane, 25 °C): δ = 2.16 (br s, 9H; Me$_{\mathrm{pz}}$), 1.82 (s, 9H; Me$_{\mathrm{pz}}$), 1.19 (pseudo t, J(H,P)$_{\mathrm{app}}$ = 3.2 Hz, 18H; 2 *trans*-PMe$_3$); ^{1}H NMR (400 MHz, [D$_2$]dichloromethane, −50 °C): δ = 2.24, 2.09, 1.80, 1.69 (s, 1:2:2:1, 18H; Me$_{\mathrm{pz}}$), 1.13 (br s, 18H; PMe$_3$); ^{31}P{^{1}H} NMR (162 MHz, [D$_2$]dichloromethane, 25 °C): δ = −6.5 (d, ^1J(P,Rh) = 116 Hz); ^{31}P{^{1}H} NMR (162 MHz, [D$_8$]toluene, −90 °C): δ = −2.62 (ABX system, ^2J(P$_A$,P$_B$) = 330.7 Hz, ^1J(P$_A$,Rh) = 114.3 Hz, ^1J(P$_B$,Rh) = 116.4 Hz); ^{11}B{^{1}H} NMR (128 MHz, [D$_2$]dichloromethane, 25 °C): δ = 0.27; ^{103}Rh NMR (12.64 MHz, [D$_2$]dichloromethane, 25 °C): δ = −312 (2 lines, A$_2$X system); IR (KBr): $\tilde{\nu}$ = 2390–2145 (B–H) (4 main peaks at 2390, 2354, 2304, 2259), 1963 cm^{-1} (CO).

Compound ***4b***: Pure PMe$_2$Ph (0.054 mL, 0.38 mmol) was added to a solution of [Rh(Tp$^{\mathrm{Me_2,4\text{-}Cl}}$)(CO)$_2$] (0.10 g, 0.19 mmol) in pentane (30 mL) at 0 °C. The reaction was instantaneous and a new ν(CO) band at 1982 cm^{-1} was observed by IR spectroscopy. After filtration, the volatiles were removed under vacuo and the residue washed with cold heptane (0.07 g, 0.11 mmol, 60 %). ^{1}H NMR (200 MHz, [D$_6$]benzene, 25 °C): δ = 7.45–7.03 (m, 10H; PPh), 2.09, 1.23 (s, 18H; Me$_{\mathrm{pz}}$), 1.07 (br s, 12H; PMe$_2$); ^{31}P{^{1}H} NMR (81 MHz, [D$_6$]benzene, 25 °C): δ = 1.13 (d, ^1J(P,Rh) = 120.4 Hz); IR (KBr): $\tilde{\nu}$ = 2394–2300 (v br) (B–H), 1978 cm^{-1} (CO).

Compound ***4c***: Pure PMePh$_2$ (0.34 mL, 1.82 mmol) was added to a solution of [Rh(Tp$^{\mathrm{Me_2,4\text{-}Cl}}$)(CO)$_2$] (0.51 g, 0.90 mmol) in pentane (30 mL) at room temperature. After stirring for 15 min, the solution was cooled at 0 °C for 5 min, then filtered. From the filtrate, orange-yellow crystals were obtained at 0 °C (0.55 g, 0.59 mmol, 66 %). ^{1}H NMR (400 MHz, [D$_8$]toluene, 25 °C): δ = 7.9–7.2 (m, 20H; PPh$_2$), 2.12, 2.38 (v br, 18H; Me$_{\mathrm{pz}}$), 1.82 (br s, 6H; PMe); ^{1}H NMR (400 MHz, [D$_2$]dichloromethane, −40 °C): δ = 7.69–7.33 (m, 20H; PPh$_2$), 2.13, 1.95, 1.84, 1.43 (s, 2:1:1:2, 18H; Me$_{\mathrm{pz}}$), 1.50 (br s, 6H; PMe); ^{13}C{^{1}H} NMR (100 MHz, [D$_2$]dichloromethane, −40 °C): δ = 190.9 (dt, ^1J(C,Rh) = 69.0 Hz, ^2J(P,C) = 16.4 Hz; CO), 144.4, 143.9, 143.1, 139.6, 107.9, 106.4 (1:2:1:2:1:2; Cq$_{\mathrm{pz}}$), 135.1 (pseudo t, J(C,P)$_{\mathrm{app}}$ = 2.3 Hz, Cq (PPh$_2$)), 134.1 (pseudo t, J(C,P)$_{\mathrm{app}}$ = 2.3 Hz, Cq (PPh$_2$)), 132.4 (pseudo t, J(C,P)$_{\mathrm{app}}$ = 6.6 Hz), 131.2 (pseudo t, J(C,P)$_{\mathrm{app}}$ = 6.0 Hz), 130.0, 129.4, 128.1 (pseudo t, J(C,P)$_{\mathrm{app}}$ = 4.6 Hz), 127.9 (pseudo t, J(C,P)$_{\mathrm{app}}$ = 4.5) (CH (PPh$_2$)), 12.6, 11.0, 9.8, 8.5 (1:2:1:2; Me$_{\mathrm{pz}}$), 11.3 (pseudo t, J(C,P)app = 14 Hz; 2 *trans*-PMe); ^{31}P{^{1}H} NMR (162 MHz, [D$_2$]dichloromethane, −40 °C): δ = 19.5 (d, ^1J(P,Rh) = 125.6 Hz); ^{31}P{^{1}H} NMR (162 MHz, [D$_2$]dichloromethane, 25 °C): δ = 19.1 (d, ^1J(P,Rh) = 127.9 Hz); ^{31}P{^{1}H} NMR (162 MHz, [D$_8$]toluene, −90 °C): δ = 24.7 (ABX system, ^1J(Rh,P) = 128 Hz, ^2J(P,P) = 320 Hz); ^{11}B{^{1}H} NMR (128 MHz, [D$_2$]dichloromethane, 25 °C): δ = 0.37; ^{103}Rh NMR (12.62 MHz, [D$_2$]dichloromethane, −40 °C): δ = 344 (d, ^1J(P,Rh) = 208 Hz); IR (KBr): $\tilde{\nu}$ = 2443–2196 (B–H) (4 main peaks at 2443, 2406, 2364, 2340), 1978 cm^{-1} (CO); elemental analysis calcd (%) for C$_{42}$H$_{45}$BN$_6$OP$_2$Cl$_3$Rh (931.9): C 54.1, H 4.9, N 9.0; found: C 53.9, H 5.0, N 8.9.

[Rh(CO)(dppp)$_2$][Tp$^{\mathrm{Me_2,4\text{-}Cl}}$] (5): A solid sample of dppp (0.25 g, 0.6 mmol) was added to a solution of [Rh(Tp$^{\mathrm{Me_2,4\text{-}Cl}}$)(CO)$_2$] (0.17 g, 0.3 mmol) in dichloromethane (20 mL). After stirring at room temperature for 15 minutes, a new ν(CO) band at 1948 cm^{-1} was observed by IR spectroscopy. The solvent was removed in vacuo and the residue washed with diethyl ether to yield compound **5** in almost quantitative yield. Attempts to recrystallise the compound failed, since this derivative slowly loses CO in solution to yield compound **6**. ^{1}H NMR (400 MHz, [D$_2$]dichloromethane, 25 °C): δ = 7.37 (m, 40H; Ph), 2.12 (s, 9H; Me$_{\mathrm{pz}}$), 1.88 (s, 9H; Me$_{\mathrm{pz}}$), the methylene groups were not located; ^{31}P{^{1}H} NMR (162 MHz, [D$_2$]dichloromethane, 25 °C): δ = 10.4 (d, ^1J(P,Rh) = 132 Hz); ^{31}P{^{1}H} NMR (162 MHz, [D$_2$]dichloromethane, −90 °C): δ = 3.0 (dt, ^1J(P,Rh) = 126 Hz, ^2J(P,P) = 46 Hz); 15.80 (dt, ^1J(P,Rh) = 139 Hz); ^{1}H NMR (400 MHz, [D$_2$]dichloromethane, −90 °C): δ = 8.19–6.05 (m, 40H; Ph), 2.06 (s, 9H; Me$_{\mathrm{pz}}$), 1.75 (s, 9H; Me$_{\mathrm{pz}}$); ^{11}B{^{1}H} NMR (128 MHz, [D$_2$]dichloromethane, 25 °C): δ = −0.7; IR (KBr): $\tilde{\nu}$ = 2429 (br) (B–H), 1942 cm^{-1} (CO).

[Rh(dppp)$_2$][Tp$^{\mathrm{Me_2,4\text{-}Cl}}$] (6): A solid sample of KTp$^{\mathrm{Me_2,4\text{-}Cl}}$ (0.27 g, 0.62 mmol) was added to a solution of [Rh(dppp)$_2$]Cl (0.60 g, 0.62 mmol) in dichloromethane (10 mL). The mixture was stirred for 2 h at room temperature. After filtration, the solvent was removed under vacuum and the residue washed with diethyl ether. The yield was quantitative. [Rh(dppp)$_2$][Tp$^{\mathrm{Me_2,4\text{-}Cl}}$] could also be obtained by keeping [Rh(CO)(dppp)$_2$][Tp$^{\mathrm{Me_2,4\text{-}Cl}}$] in solution for a few days with periodical removal of CO under vacuum. ^{1}H NMR (400 MHz, [D$_2$]dichloromethane, 25 °C): δ = 7.85–6.95 (m, 40H; Ph), 2.58 (br pseudo t, J(H,P)$_{\mathrm{app}}$ = 14.3 Hz, 4H; PC*Ha*HbCHcHdCHe*Hf*P$_{trans}$), 2.38–2.19 (m, 4H; P$_{cis}$CHa*Hb*C*Hc*Hd), 2.16 (s, 9H; Me$_{\mathrm{pz}}$), 1.92 (s, 9H; Me$_{\mathrm{pz}}$), 1.58 (br quintet, J(H,H) = 11.9 Hz, 2H, PCH$_2$CHc*Hd*CH$_2$), 0.57 (br tq, J(H,H) = 14.3, 2.4 Hz, 2H; C*He*HfP$_{trans}$); ^{13}C{^{1}H} NMR (100.6 MHz, [D$_2$]dichloromethane, 25 °C): δ = 143.0 (Cq$_{\mathrm{pz}}$), 139.9 (Cq$_{\mathrm{pz}}$), 134.5–128.2 (Cq, CH PPh$_2$), 106.0 (Cq–Cl pz), 28.8 (filled in d, ^1J(P,C) = 28.9 Hz, ^1J(C,H) = 130.5 Hz; P$_{cis}$CH$_2$ dppp), 20.0 (pseudo t, J(P,C)$_{\mathrm{app}}$ = 14.4 Hz, ^1J(C,H) = 130.3 Hz; CH$_2$P$_{trans}$ dppp), 18.9 (^1J(C,H) = 131.3 Hz; PCH$_2$*C*H$_2$ dppp), 11.9 (Me$_{\mathrm{pz}}$), 10.2 (Me$_{\mathrm{pz}}$); ^{31}P{^{1}H} NMR (162 MHz, [D$_2$]dichloromethane, 25 °C): δ = −7.28 (dt, ^1J(P,Rh) = 84.7 Hz, ^2J(P,P) = 30 Hz; P$_{trans\text{-ax.}}$), 20.08 (dt, ^1J(P,Rh) = 122.7 Hz; P$_{cis\text{-eq.}}$); ^{11}B{^{1}H} NMR (128 MHz, [D$_2$]dichloromethane, 25 °C): δ = −0.7; ^{103}Rh NMR (12.66 MHz, [D$_2$]dichloromethane, 25 °C): δ = 1225.1 (6 main lines, similar to the simulation of an A$_2$M$_2$X system); IR (KBr): $\tilde{\nu}$ = 2430 cm^{-1} (br) (B–H); MS (pos. ES, NCMe): *m*/*z* (%): 927.3 (100) [Rh(dppp)$_2$]$^+$; MS (neg. ES, NCMe): *m*/*z* (%): 399.1 (100) [Tp$^{\mathrm{Me_2,4\text{-}Cl}}$]$^-$, 401.1 (99); elemental analysis calcd (%) for C$_{69}$H$_{71}$BN$_6$P$_4$Cl$_3$Rh · CH$_2$Cl$_2$: C 59.5, H 5.2, N 5.9; found: C 58.8, H 5.1, N 5.6.

[Rh(κ^2-Tp$^{\mathrm{Me_2}}$)(O$_2$)(PMe$_3$)$_2$] (7): An excess of PMe$_3$ (0.3 mL, 3 mmol) was added to a solution of [Rh(Tp$^{\mathrm{Me_2}}$)(O$_2$)(PMe$_3$)] (0.05 g, 0.09 mmol) in THF (5 mL). After stirring for 5 h at 50 °C, the solution was taken to dryness, and the residue extracted with a 1:1 mixture of petroleum ether/diethyl ether. Compound **7** was obtained as orange crystals upon cooling to −20 °C. Yield: 70 %; ^{1}H NMR (300 MHz, [D$_6$]benzene, 25 °C): δ = 5.76 (s, 3H, 3 CH$_{\mathrm{pz}}$), 2.41, 2.31, 2.18, 2.02 (s, 2:1:2:1, 18H; 6 Me$_{\mathrm{pz}}$), 1.28 (d, 9H, ^2J(H,P) = 6.8 Hz; PMe$_3$), 0.58 (d, 9H, ^2J(H,P) = 6.5 Hz; PMe$_3$); ^{13}C{^{1}H} NMR (100 MHz, [D$_6$]benzene, 25 °C): δ = 152.4, 147.7, 147.5, 141.7 (2:2:1:1; Cq$_{\mathrm{pz}}$), 107.9, 104.5 (2:1; CH$_{\mathrm{pz}}$), 15.5, 13.7, 13.6, 12.3 (2:2:1:1; Me$_{\mathrm{pz}}$), 10.7 (dd, ^1J(C,P) = 17, ^2J(C,Rh) = 10 Hz; PMe$_3$), 9.9 (dd, ^1J(C,P) = 19, ^2J(C,Rh) = 9 Hz; PMe$_3$); ^{31}P{^{1}H} NMR (162 MHz, [D$_6$]benzene, 25 °C): AB part of an ABX spin system centered at δ = −4.0 (J(A,Rh) = 96 Hz, J(B,Rh) = 99 Hz); J(A,B) could not be computed from the spectrum because the smallest signals of the AB spin system were not located; ^{11}B{^{1}H} NMR (96 MHz, [D$_6$]benzene, 25 °C): δ = −6.4; IR (Nujol): $\tilde{\nu}$ = 2477, 2405 cm^{-1} (B–H); elemental analysis calcd (%) for C$_{21}$H$_{40}$BN$_6$O$_2$P$_2$Rh (584.25): C 43.2, H 6.8, N 14.4; found: C 43.3, H 6.6, N 14.5.

[Rh(κ^2-Tp$^{\mathrm{Me_2}}$)(H)$_2$(PMe$_3$)$_2$] (8): An excess of PMe$_3$ was added (0.1 mL, 1 mmol) to a solution of [Rh(Tp$^{\mathrm{Me_2}}$)(H)$_2$(PMe$_3$)] (0.05 g, 0.10 mmol) in THF (10 mL). The mixture was heated at 50 °C for 2 h, after which time the solvent was evaporated and the residue extracted with Et$_2$O (15 mL). Concentration and cooling to −20 °C yielded yellow crystals of compound **8** (0.05 g, 90 %). Since the precursor of compound **8**, [Rh(Tp$^{\mathrm{Me_2}}$)(H)$_2$(PMe$_3$)], is obtained from [Rh(Tp$^{\mathrm{Me_2}}$)(C$_2$H$_4$)(PMe$_3$)], which is highly sensitive to oxygen,[16a] a small impurity of the peroxo derivative **7** is very often present when **8** is prepared, hence analytically pure samples of **8** were not obtained. ^{1}H NMR (400 MHz, [D$_6$]benzene, 25 °C): δ = 5.84, 5.74 (s, 2:1, 3H; CH$_{\mathrm{pz}}$), 2.41, 2.32, 2.15, 1.73 (s, 2:2:1:1, 18H; CH$_{3\mathrm{pz}}$), 1.13 (d, ^2J(H,P) = 5.5 Hz, 9H; PMe$_3$), 0.55 (d, ^2J(H,P) = 4.8 Hz, 9H; PMe$_3$), −17.22 (q, ^1J(H,Rh) = ^2J(H,P) = 20.8 Hz, 2H; Rh,H); ^{13}C{^{1}H} NMR (100 MHz, [D$_6$]benzene, 25 °C): δ = 151.0, 150.0, 146.0, 141.4 (2:2:1:1; Cq$_{\mathrm{pz}}$), 107.0, 105.6 (2:1; CH$_{\mathrm{pz}}$), 19.3 (dd, ^1J(C,P) = 19 Hz, ^3J(C,P) = 12 Hz; PMe$_3$), 18.0 (dd, ^1J(C,P) = 17 Hz, ^3J(C,P) = 11 Hz; PMe$_3$), 17.0, 14.3, 14.0, 11.3 (2:2:1:1; CH$_{3\mathrm{pz}}$); ^{31}P{^{1}H} NMR (162 MHz, [D$_6$]benzene, 25 °C): AB part of an ABX spin system centered at δ = −4.0 (J(A,Rh) = J(B,Rh) = 107 Hz); J(A,B) could not be computed from the spectrum because the smallest signals of the AB spin system were not located; ^{11}B{^{1}H} NMR (96 MHz, [D$_6$]benzene, 25 °C): δ = −6.0; IR (Nujol): $\tilde{\nu}$ = 2484, 2400 (B–H), 2068, 2045 cm^{-1} (Rh–H).

[Rh(H)$_2$(PMe$_3$)$_4$][Tp$^{\mathrm{Me_2}}$] (9a):

Route A: PMe$_3$ (1 mL, 10 mmol) was added to a solution of [Rh(Tp$^{\mathrm{Me_2}}$)(H)$_2$(PMe$_3$)] (0.05 g, 0.1 mmol) in THF (10 mL). The mixture was heated at 50 °C for 8 h. The solvent was evaporated under vacuum and the residue, analysed by ^{31}P{^{1}H} NMR spectroscopy, contained **9a** in almost quantitative yield.

Route B: This compound was alternatively obtained by the addition of the stoichiometric amount of KTp^{Me_2} to a solution in acetone of $[Rh(H)_2(PMe_3)_4]Cl$; after stirring for 2 h, the mixture was filtered through Celite and the solvent removed under vacuum to yield compound **9a** in almost quantitative yield (NMR). All attempts to purify this compound by crystallisation proved unsuccessful. ^1H NMR (300 MHz, $[D_6]$acetone, 25 °C): $\delta = 5.42$ (s, 3H; 3 CH_{pz}), 2.01, 2.00 (s, 1:1, 18H; 6 CH_{3pz}), 1.58 (pseudo t, $J(H,P)_{app} = 2.3$ Hz, 18H; 2 *trans*-PMe_3), 1.52 (pseudo d, $J(H,P)_{app} = 7.0$ Hz, 18H; 2 *cis*-PMe_3), -10.58 (dtd, $^2J(H,P) = 136.6$, 20.2 Hz, $^1J(Rh,H) = 15.0$ Hz, 2H; Rh–H); $^{13}C\{^1H\}$ NMR (75 MHz, $[D_6]$acetone, 25 °C): $\delta = 145.4$, 142 9 (1:1; Cq_{pz}), 103.6 (CH_{pz}), 25.4 (pseudo t, $J(C-P)_{app} = 18$ Hz, *trans*-PMe_3), 22.0 (filled in d, $J(C-P)_{app} = 25$ Hz, 2 *cis*-PMe_3), 14.6, 14.1 (1:1, Me_{pz}); $^{31}P\{^1H\}$ NMR (121.5 MHz, $[D_6]$benzene, 25 °C): $\delta = -23.4$ (br dt, $^1J(P,Rh) = 85$ Hz, $^2J(P,P) = 27$ Hz), -13.0 (dt, $^1J(P,Rh) = 96$ Hz); $^{11}B\{^1H\}$ NMR (96 MHz, $[D_6]$benzene, 25 °C): $\delta = -2.0$; IR (Nujol): $\tilde{\nu} = 2448$ (B–H), 1956 cm^{-1} (Rh–H).

$[Rh(H)_2(PMe_3)_4][Tp]$ (9b): A solution of PMe_3 in THF (0.6 mL, 1 M, 0.6 mmol) was added to a solution of $[Rh(Tp)(H)_2(PMe_3)]$ (0.03 g, 0.07 mmol) in THF (2 mL). After stirring at 50 °C for 30 min, the solvent was stripped off, the residue extracted with THF (5 mL) and the resulting solution concentrated and cooled to −20 °C to yield colourless crystals of compound **9b**. ^1H NMR (300 MHz, $[D_6]$acetone, 25 °C): $\delta = 7.36$, 7.28, 5.92 (d, d, t, $^3J(H,H) = 2.0$ Hz, each 3H; 9 CH_{pz}), 4.97 (q, $^1J(B,H) = 113.6$ Hz, 1H; BH(Tp)), 1.60 (pseudo t, $J(H,P)_{app} = 3.2$ Hz, 18H; 2 *trans*-PMe_3), 1.53 (d, $^2J(H,P) = 7.0$ Hz, 18H; 2 *cis*-PMe_3), -10.57 (dtd, $^2J(H,P) = 136.6$, 20.2 Hz, $^1J(H,Rh) = 15.0$ Hz, 2H; 2 Rh–H); $^{13}C\{^1H\}$ NMR (75 MHz, $[D_6]$acetone, 25 °C): $\delta = 138.7$, 133,4, 102.6 (CHpz), 25.3 (pseudo t, $J(C,P)_{app} = 17$, Hz; 2 *trans*-PMe_3), 21.9 (filled in d, $J(C,P)_{app} = 27$ Hz; 2 *cis*-PMe_3); $^{31}P\{^1H\}$ NMR (121.5 MHz, $[D_6]$acetone, 25 °C): $\delta = -13.0$ (dt, $^1J(P,Rh) = 96$ Hz, $^2J(P,P) = 27$ Hz), -23.9 (dt, $^1J(P,Rh) = 87$ Hz, $^2J(P,P) = 27$ Hz); $^{11}B\{^1H\}$ NMR (96 MHz, $[D_6]$acetone, 25 °C): $\delta = -1.2$. IR (Nujol): $\tilde{\nu} = 2474$ (B–H), 1955 cm^{-1} (Rh–H); elemental analysis calcd (%) for $C_{21}H_{48}BN_6P_4Rh$: C 40.5, H 7.7, N, 13.5; found: C 40.2, H 7.5, N 13.6.

Crystal structure determinations of compounds 2, 4a, 7, 8 and 9b: Detailed information about the crystal structure determinations of compounds **2**, **4a**, **7**, **8** and **9b** is given as Supporting Information. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-132889 (**2**), CCDC-154691 (**2′**), CCDC-156684 (**4a**), CCDC-186/1279 (**4c**), CCDC-154693 (**7**), CCDC-154692 (**8**) and CCDC-132888 (**9b**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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