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η^2-Bonded Hydrotris(3,5-dimethylpyrazolyl)borate in [Rh(HB(Me$_2$pz)$_3$)(CO)(PMe$_3$)]. X-ray Crystal Structure and Dynamic Exchange in Solution

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Owing to the possible η^2- and η^3-bonding modes for the hydrotris(pyrazolyl)borate ligand, 16- and 18-electron d^8 complexes can be observed.[1−3] Various substituents on the pyrazolyl groups can favor either the η^2- or the η^3- form, recently exemplified by two X-ray structures, one for the η^2-coordination, [Tp*Rh(CN-neopentyl)$_2$],[1] and the other for the η^3-mode, [Tp′Rh(NBD)][2] (Tp* = HB(3,5-Me$_2$pz)$_3$ and Tp′ = HB(3-Mepz)$_3$). However, in solution, NMR spectroscopy shows that the three pyrazolyls are equivalent, an observation that is consistent with either an η^3-structure or an η^2-geometry with a fast dynamic exchange between all the pyrazolyl groups. Infrared analysis of the ν_{CN} bands for the complex [Tp*Rh(CN-neopentyl)$_2$] allowed the authors to suggest an η^2-structure in solution. The complex [Tp*Rh(CO)$_2$], whose NMR spectrum presents a similar pyrazolyl pattern, has been shown by infrared spectroscopy to involve an η^2−η^3 isomerism in solution.[3]

We wish to report the preparation of [Tp*Rh(CO)(PMe$_3$)]. Its characterization by X-ray crystallography shows that the Tp* ligand is bidentate, the rhodium center being in a square-planar environment. Because a CO ligand has been substituted by a PMe$_3$ ligand, the three pyrazolyl groups are in different environments. Infrared measurements and a variable-temperature NMR study show that the complex is η^2-bonded in solution and that a dynamical exchange occurs between tetracoordinated isomers.

In their report, Powell *et al.*[4] mentioned that [Tp*Rh(CO)$_2$][4,5] reacts with phosphine or arsine ligands to afford yellow glasses whose elemental analyses and infrared data were consistent with a [Tp*Rh(CO)L] formula but whose broad and irreproducible NMR spectra were not assigned.[6,7] Here, addition in toluene of 1 equiv of PMe$_3$ to [Tp*Rh(CO)$_2$] was monitored by infrared spectroscopy: a ν_{CO} band at 1961 cm^{-1} appears very quickly whereas the two ν_{CO} bands of the starting material at 2053 and 1976 cm^{-1} decrease simultaneously. The reaction was complete within 10 min. From the toluene solution the complex [Tp*-Rh(CO)(PMe$_3$)] can be obtained quantitatively as a yellow powder by evaporation of the solvent under reduced pressure or with a 40% yield as bright yellow crystals by slow crystallization at −18 °C. ^{1}H NMR spectra recorded at 300 K show many signals which cannot be easily assigned. Moreover, recording the spectra over long durations showed a complex evolution of the NMR pattern.

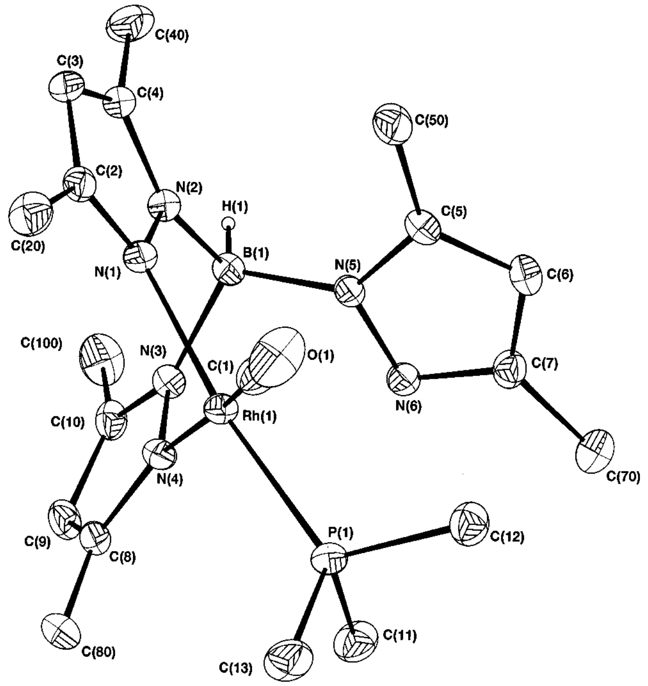

Figure 1. CAMERON view of [η^2-Tp*Rh(CO)(PMe$_3$)]. Thermal ellipsoids are drawn at the 30% probability level. Except for the hydrogen atom bonded to the boron, all the hydrogens have been omitted for clarity. Distances (Å) and angles (deg) of interest: Rh(1)−P(1) = 2.2447(9), Rh(1)−N(1) = 2.113(3), Rh(1)−N(4) = 2.101(3), Rh(1)−N(6) = 3.632(3), Rh(1)−C(1) = 1.797(4); P(1)−Rh(1)−N(1) = 170.79(8), P(1)−Rh(1)−N(4) = 95.81(8), N(1)−Rh(1)−N(4) = 83.6(1), P(1)−Rh(1)−C(1) = 85.9(1).

An X-ray crystal structure determination was undertaken.[8] As shown in the CAMERON[9] view of the molecule in Figure 1, the rhodium center is in a square-planar environment, although the square plane is slightly distorted. Thus, the hydrotris(3,5-dimethylpyrazolyl)borate ligand is bonded to rhodium in an η^2-mode. The rhodium−phosphorus distance is 2.2447(9) Å, within classical range.[10] The Rh−N(4) distance of 2.101(3) Å

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(6) When this paper was submitted, a paper of Purwoko and Lees appeared describing briefly the preparation of [Tp*Rh(CO)(PPh$_3$)] characterized only by infrared and UV−visible spectroscopy: Purwoko, A. A. ; Lees, A. J. *Inorg. Chem.* **1996**, *35*, 675.

(7) One reviewer has informed us that C. K. Ghosh (from W. A. G. Graham's group) described the complexes [Tp*Rh(CO)L] with L = PMe$_3$, PMe$_2$Ph, PMePh$_2$, PPh$_3$, and PMeEtPh and their dymanic NMR behavior. This work was reported in his thesis (Edmonton, Canada, 1988) but was never published. In the meantime where this paper was submitted, we have prepared the complexes with L = PCy$_3$, PMe$_2$ Ph, PMePh$_2$, PPh$_3$, P(OMe)$_3$, and P(OPh)$_3$.

(8) Anal. Calcd for [Tp*Rh(CO)(PMe$_3$)] (C$_{19}$H$_{31}$BN$_6$OPRh): C, 45.26; H, 6.22; N, 16.67. Found: C, 45.48; H, 6.22; N, 16.60. Crystal data: monoclinic, space group $P2_1/c$; a = 16.473(2) Å, b = 8.898(2) Å, c = 17.058(2) Å, β = 110.41(1)°, V = 2343.6(8) Å^3, ρ_{calc} = 1.46 g·cm^{-3} for Z = 4. A total of 4581 independent reflections were collected. The structure was solved using direct methods techniques. R = 0.0276 for 3388 independent reflections with $I > 3\sigma(I)$.

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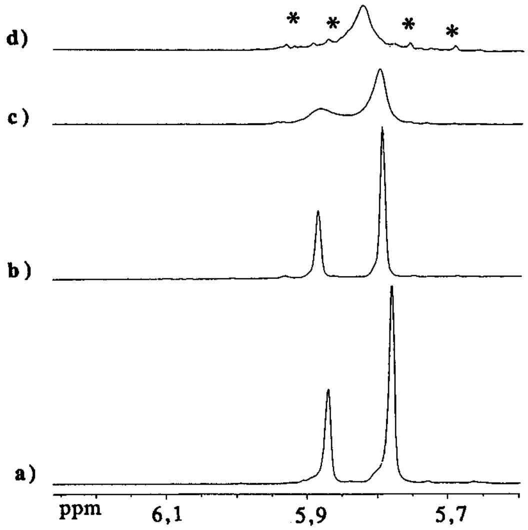

Figure 2. ^{1}H NMR signals of the pyrazolyl C-H recorded at (a) 183 K, (b) 233 K, (c) 283 K, and (d) 300 K. Peaks with asterisks are due to decomposition products.

compares well with those published for [HB(3,5-$Me_2pz)_2$(3,5-Me_2pzH)Rh$(CO)_2$] (2.070(4) and 2.093(4) Å), where each nitrogen donating ligand is trans to a CO ligand.[3] The Rh−N(1) distance of 2.113(3) Å is slightly longer than the Rh−N(4) distance, although not significantly different within experimental errors, due to the trans influence of the PMe_3 ligand. The two N(1)−Rh−P and N(4)−Rh−C(1) angles, of 170.79(8) and 173.1(1)°, respectively, are in agreement with a small distortion of the square-planar basal structure, but the rhodium atom is in fact in the mean coordination {N(1)N(4)C(1)P(1)} plane. The Rh−N(6) distance is 3.632(3) Å, and the lone pair points away from the rhodium atom, the N(6)-containing pyrazolyl plane, making an angle of 137.32° with the square plane.

Infrared spectra recorded in KBr dispersions exhibit a strong ν_{CO} band at 1961 cm^{-1}. CH_2Cl_2 solutions at room temperature display a single ν_{CO} band at 1969 cm^{-1}, the 8 cm^{-1} difference being due to the solvent effect. These observations are consistent with a square-planar structure both in the solid state and in solution.

The [η^2-Tp*Rh(CO)(PMe_3)] complex was dissolved in CD_2Cl_2 and analyzed by ^{1}H NMR spectroscopy at 183 K. Whereas the spectra were expected to show six signals for the methyl groups and three signals for the CH's of the three distinct pyrazolyl groups, two pyrazolyls appeared equivalent. At 233 K the pattern is quite the same, the signals being sharper. In the ^{1}H NMR spectrum the PMe_3 ligand shows a doublet at 1.20 ppm, the methyl groups of the pyrazolyls present four signals of 2:2:1:1 intensities at 1.91, 2.20, 2.29, and 2.31 ppm, and the CH's of the pyrazolyl rings show two signals of relative intensities 2:1 at 5.79 and 5.88 ppm. Thus, a complete NMR analysis involving two-dimensional correlations ^{1}H−^{13}C GE-HMQC{^{13}C,^{31}P} ^1J, long range (LR), and ^{31}P−^{103}Rh{^{103}Rh,^{1}H} ^1J was performed at 233 K. The variable-temperature spectra are consistent with an exchange phenomenon in which two pyrazolyls are made equivalent. Figure 2 displays the illustrative C−H region.

We could consider that the nonbonded pyrazolyl is readily detected by the signals at 2.29 and 2.31 (CH_3 groups) and 5.88 ppm (CH). However, this would mean that the dynamic behavior would involve a tetrahedral rhodium transition state leading to the two square-planar isomers with either N(1) or N(4) trans to PMe_3. At any time the N(6) nitrogen atom would be involved in the exchange. As tetrahedral species are not common in the rhodium chemistry, we prefer to consider an exchange phenomenon between two square planes in which the dangling pyrazolyl is exchanged with a coordinated pyrazolyl. Presumably the N(1)-containing one is involved since the Rh−N(1) bond distance is longer than Rh−N(4) in the solid state and the PMe_3 ligand exerts a greater trans effect than CO. The transition state would just require the N(6) coordination affording a trigonal bipyramid. A simple rotation of the N(6)-containing pyrazolyl group along the B(1)−N(5) bond suffices for the approach of N(6) toward the rhodium center. Then, a rotation along B(1)−N(2) would remove the N(1) atom. Such a flip−flop movement entails *a priori* a lower energy level than the N(4)−N(6) exchange. Thus, the ^{1}H signals at 2.29, 2.31, and 5.88 ppm would belong to the N(4)-pyrazolyl which remains trans to the CO ligand in both situations. So, we propose exchange of square-planar environments through a five-coordinate transition state in which all three pyrazolyl groups are attached to rhodium. At 283 K all the signals broaden, and at 300 K only one broad peak is observed for the C−H groups. Thus, the first exchange moves toward another one, which makes the C_3−H, C_6−H, and C_9−H protons equivalent. The fast-exchange limit was not reached, since the [Tp*Rh(CO)(PMe_3)] complex was transformed in several species which obscured the phenomenon observed. Decomposition of [Tp′Rh(COD)], although slower, was previously reported, affording dinuclear pyrazolyl-bridged complexes.[2] Nevertheless, this second exchange phenomenon would make the three pyrazolyl groups equivalent on the NMR time scale. As, at room temperature, the infrared data are consistent with a square-planar structure, we prefer to explain our observations by an exchange between square-planar species with trigonal-bipyramidal intermediates rather than to consider a Berry pseudorotation mechanism. Indeed, if the Rh−N(4) bond cleavage and the N(4)−N(6) exchange are superimposed on the N(1)−N(6) exchange, then the three pyrazolyls become equivalent by the flip−flop movements.

In conclusion, the CO substitution with PMe_3 in [Tp*Rh$(CO)_2$] proceeds very easily under ambient conditions. The [Tp*Rh(CO)(PMe_3)] complex thus obtained presents a square-planar geometry in which the hydrotris(pyrazolyl)borato ligand is η^2-bonded to the rhodium center as evidenced by the X-ray crystal structure. In solution, this geometry is still observed but due to a nonrigidity phenomenon, the nonbonded pyrazolyl is exchanged with the coordinated pyrazolyls.

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Supporting Information Available: Text giving the preparation method for [Tp*Rh(CO)(PMe_3)] and the details of its structure determination, tables of atomic coordinates, bond distances and angles, and anisotropic thermal parameters, and relevant spectra of the NMR analyses (11 pages). An X-ray crystallographic file, in CIF format, is also available. Access and ordering information is given on any current masthead page.

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