case of a 6 × His-tag the more stable one (or ones) is formed more frequently instead. These two coordination bonds differ not only in stability, but also in the “energy landscape”[11] of their transition states, as revealed by the study we carried out on the dependence of their rupture forces on the force loading rate (to be published). This parameter, first introduced by Evans and Ritchie,[12] is equal to the product of the pulling velocity and the “effective” spring constant (the combination in series of the spring constant of the cantilever and of the molecular bridge).

This experiment, although not yet optimized, is casting a new light on our understanding of a bond that forms the basis for more and more important tools for molecular biology. These results make it possible not only to foresee the tremendous possibilities but also the possible problems and pitfalls of this very new and still developing SFM method for studying binding processes.

Experimental Section

The peptide HCys-(Gly)$_6$-(His)$_2$-OH was kindly provided by Prof. Peggion (Padova), and HCys-(Gly)$_6$-(His)$_6$-OH was synthesized by Tecnogen (Naples, Italy). Both were synthesized by solid-phase methods, and their purity was controlled by HPLC and MALDI-TOF MS. The Ni–nta Biacore chip was depleted of nickel(II) ions by incubation in 0.35 M ethylenediaminetetraacetic acid solution for 2 h; iron(III) or nickel(II) ions were reintroduced by treating the chip with a 100 mM solution of $FeCl_3$ or $NiCl_2$ and then rinsing with water. Si_3N_4 AFM cantilevers (DI, Santa Barbara, CA) were metalized by resistive deposition of Ti and then Au 99.99 % (thicknesses of 10–15 nm and 30–40 nm, respectively) at 10^{-6} Torr. The tips were then immediately immersed in a 1 mg mL^{-1} solution of the peptide in phosphate-buffered saline (PBS) at pH 7.4 for 30 min.

The spring constants of the cantilevers were determined from their thermal excitation[13] with a precision not higher than 30 %. Four cantilevers were used for the measurements. The values of their spring constants obtained by this method were in the range of 60 to 120 pN nm^{-1}. Force measurements were carried out in PBS with a Nanoscope III Multimode AFM (DI, Santa Barbara, CA).

Received: June 1, 1999 [Z13499]

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[1] E. Hochuli, H. Döbeli, A. Schacher, *J. Chromatogr.* **1987**, *411*, 177–184.

[2] a) L. Nieba, A. Krebber, A. Plückthun, *Anal. Biochem.* **1996**, *234*, 155–165, and references therein; b) A. M. Schmidt, H. N. Müller, A. Skerra, *Chem. Biol.* **1996**, *3*, 645–653.

[3] J. Crowe, H. Döbeli, R. Gentz, E. Hochuli, D. Stüber, *Methods in Molecular Biology*, *Vol. 31*, Humana Press, Totowa, NJ, **1994**, pp. 371–387, and references therein.

[4] a) V. T. Moy, E. L. Florin, H. E. Gaub, *Science* **1994**, *266*, 257–259; b) M. Grandbois, M. Beyer, M. Rief, H. Clausen-Schaumann, H. E. Gaub, *Science* **1999**, *283*, 1727–1730; c) J. Fritz, A. G. Katopodis, F. Kolbinger, D. Anselmetti, *Proc. Natl. Acad. Sci. USA* **1998**, *95*, 12283–12288; d) C. Bustamante, C. Rivetti, D. J. Keller, *Curr. Opin. Struct. Biol.* **1997**, *7*, 709–716; e) S. Izrailev, S. Stepaniants, M. Balsera, Y. Oono, K. Schulten, *Biophys. J.* **1997**, *72*, 1568–1581.

[5] B. Samorì, *Angew. Chem.* **1998**, *110*, 2318–2321; *Angew. Chem. Int. Ed.* **1998**, *37*, 2198–2200.

[6] In this experiment, the unbinding takes place under a rising force and in a time much shorter than those of protein separation processes. These forces are kinetic in nature.[4d,e, 11] Therefore, in these processes the bond ruptures may occur at lower forces than those we measured.

[7] M. Rief, F. Oesterhelt, B. Heymann, H. E. Gaub, *Science* **1997**, *275*, 1295–1297.

[8] H. Li, M. Rief, F. Oesterhelt, H. E. Gaub, *Adv. Mater.* **1998**, *3*, 316–319.

[9] P. E. Marszalek, A. F. Oberhauser, Y. P. Pang, J. M. Fernandez, *Nature* **1998**, *396*, 661–664.

[10] E. L. Florin, V. T. Moy, H. E. Gaub, *Science* **1994**, *264*, 415–417.

[11] R. Merkel, P. Nassoy, A. Leung, K. Ritchie, E. Evans, *Nature* **1999**, *397*, 50–53, and references therein.

[12] E. Evans, K. Ritchie, *Biophys. J.* **1997**, *72*, 1541–1555.

[13] E. L. Florin, M. Rief, H. Lehmann, M. Ludwig, C. Dornmair, V. T. Moy, H. E. Gaub, *Biosensors Bioelectronics* **1995**, *10*, 895–901.

Denticity Changes of Hydrotris(pyrazolyl)borate Ligands in Rh^I and Rh^{III} Compounds: From κ^3- to Ionic “κ^0”-Tp′**

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Dedicated to Professor Swiatoslaw Trofimenko

The formally tridentate cyclopentadienyl and hydrotris(pyrazolyl)borate ligands are important auxiliary ligands in organometallic chemistry.[1, 2] Most often they act as spectators, and chemical transformation occurs at the metal center or at other coordinated ligands. However, in some instances they may have a noninnocent involvement by means of hapticity changes.

Variations in coordination mode are well documented for the cyclopentadienyl system (Cp′).[3, 4] Casey and co-workers demonstrated some years ago the interconversion of η^5-C_5H_5, η^1-C_5H_5, and ionic “η^0”-$C_5H_5^-$ compounds in the reaction of $[(\eta^5\text{-}C_5H_5)Re(NO)(CH_3)(PMe_3)]$ with PMe_3[5] and proposed an η^3-C_5H_5 intermediate for the $\eta^5 \rightleftharpoons \eta^1$ exchange. In contrast,

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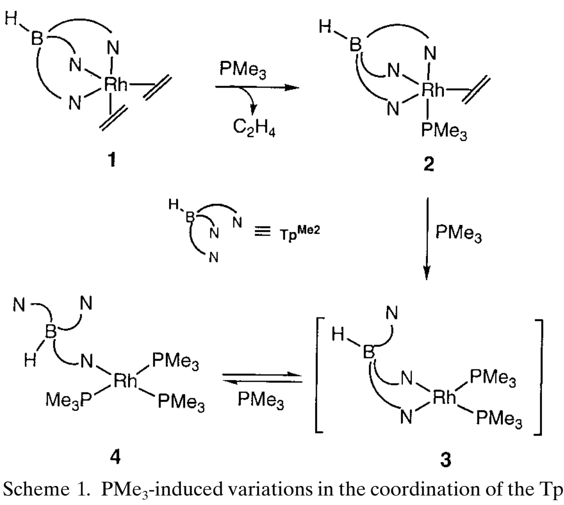
[**] Financial support from the DGESIC (projects PB96-0824, PB97-0733) and from the Junta de Andalucía is gratefully acknowledged.

the tris(pyrazolyl)borates (Tp′) bind predominantly in a facial, tripodal fashion,[2, 6] that is, κ^3-*N,N′,N″*-Tp′, and examples of κ^2-Tp′ML$_n$ complexes are rare except among 16-electron, square-planar species.[2, 7, 8] To our knowledge, the monodentate κ^1-*N*-Tp′ coordination mode is restricted to a series of closely related Ni complexes of the bulky hydrotris(3-*tert*-butylpyrazolyl)borate anion.[7, 9] During the course of this work, an interesting Rh compound that displays an unprecedented κ^2-*N,H*-Tp′ bonding mode was reported by Kalck, Etienne, and co-workers.[10]

As far as we are aware, direct, unequivocal evidence for an ionic "κ^0"-Tp′$^-$ metal compound has not yet been provided. Moreover, the recent isolation of the salt [Tm$_2$Bi][Tp$_2$Na], by addition of NaTp to the purported "[Tm$_2$BiCl]" (Tm = hydrotris(methimazolyl)borate), was attributed to the proficiency of Tp as a ligand and to its unwillingness to act as a counterion.[11] Here we report the interconversion of κ^3-*N,N′,N″*-, κ^2-*N,N′*-, κ^1-*N*- and "κ^0"-Tp′$^-$ rhodium compounds (Tp′ = Tp, Tp^{Me2} (Tp^{Me2} = hydrotris(3,5-dimethylpyrazolyl)borate)). We have authenticated the four coordination modes by X-ray crystallography on Rh^{I} and Rh^{III} complexes. That concerning the unprecedented "κ^0" mode is described herein.

Treatment of either [Tp^{Me2}Rh(C$_2$H$_4$)$_2$] (**1**) or [Tp^{Me2}Rh(C$_2$H$_4$)(PMe$_3$)] (**2**)[12] with an excess of PMe$_3$ (ca. 5–6 equiv; 20 °C, < 1 h) induces quantitative formation of the new complex **4**, isolable as yellow crystals (Scheme 1). The putative intermediate bis-phosphane complex cannot be detected in the course of this reaction, but it can be generated by the slow dropwise addition of one molar equivalent of PMe$_3$ to solutions of **2**. Compound **3** is always contaminated with small amounts of **2** and **4** and has not been isolated in analytically pure form. Its characterization by spectroscopic methods is, however, straightforward.[13] Since the reaction of the tris-phosphane complex **4** with the bis-ethene derivative **1** gives a mixture of **2** and **3**, the interconversion of the κ^1- and κ^2-Tp^{Me2}Rh^I complexes shown in Scheme 1 is reversible. Complete displacement of the coordinated Tp^{Me2} ligand appears possible, although more forcing conditions are needed (120 °C, 6 h). Like other [Rh(PMe$_3$)$_4$]X (X = BPh$_4$, PF$_6$) salts,[14] [Rh(PMe$_3$)$_4$]Tp^{Me2} cannot be isolated and decomposes during workup. This precluded its full characterization.



Scheme 1. PMe$_3$-induced variations in the coordination of the Tp^{Me2} ligand in Rh^I complexes.

A single crystal of the tris-phosphane complex **4** was subjected to an X-ray study[15] (Figure 1). The long Rh···H(B) separation of 2.59(4) Å seems to indicate no significant B–H···Rh interaction and therefore κ^1-Tp^{Me2} coordination. However, in view of the error associated with the determination of this bonding parameter and of the somewhat similar, albeit shorter, Rh···H separation of 2.35(3) Å[10] in the related complex [(κ^2-*N,H*-Tp$^{Me2,4\text{-}Cl}$)Rh(CO)(PPh$_3$)$_2$] (Tp$^{Me2,4\text{-}Cl}$ = hydrotris(3,5-dimethyl-4-chloropyrazolyl) borate), it seems advisable to defer the assignment of the Tp^{Me2} coordination mode in **4** until more data are available. The ^{31}P{^{1}H} NMR spectrum of **4** in [D$_8$]toluene at 20 °C can be interpreted in terms of an AB$_2$X spin system (X = ^{103}Rh) in which the AB$_2$ portion almost approaches a first-order situation (δ(P$_A$) = −5.8, δ(P$_B$) = −14.1; ^2J(P$_A$,P$_B$) = 48, ^1J(P$_A$,Rh) = 158, ^1J(P$_B$,Rh) = 133 Hz). However, at −80 °C the two *trans* phosphane ligands become inequivalent, and a large ^2J(P,P) coupling of 340 Hz can be readily computed by spin-simulation techniques. The low-temperature spectrum is in accord with an asymmetric structure, but in view of literature precedent[8a, 10, 16–18] the presence in solutions of **4** of isomeric complexes that feature different coordination modes of the Tp^{Me2} ligand (see above) cannot be excluded.

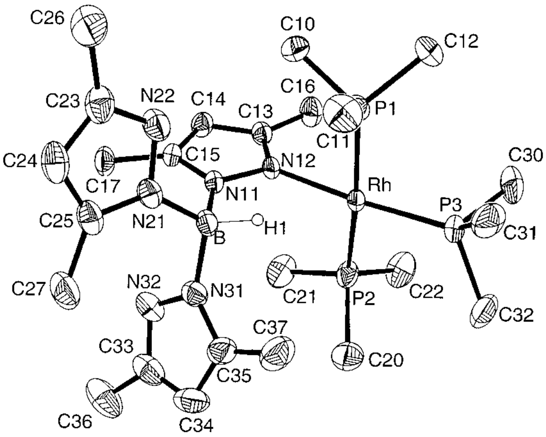
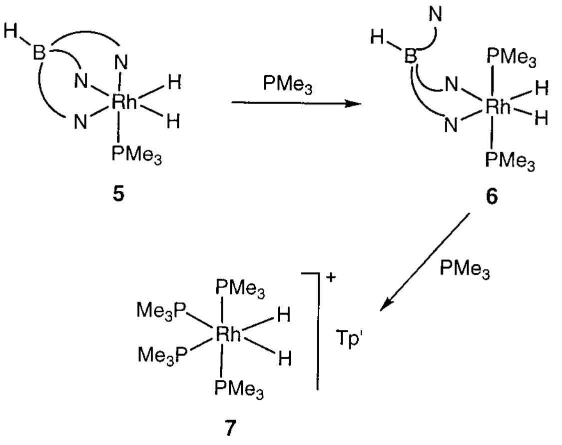


Figure 1. Molecular structure of **4**. Selected bond lengths [Å] and angles [°]: Rh–N12 2.116(2), Rh–P1 2.3209(8), Rh–P2 2.3057(8), Rh–P3 2.2206(9); N12-Rh-P1 86.14(6), N12-Rh-P2 86.89(6), P3-Rh-P2 93.69(3), P3-Rh-P1 92.78(3).

The bis-hydrido complex [(κ^3-Tp^{Me2})Rh(H)$_2$(PMe$_3$)] (**5a**)[12] undergoes similar reactions when heated in the presence of PMe$_3$ (Scheme 2). The κ^2-Tp^{Me2} bis-phosphane compound **6a** is initially formed[19] (50 °C, 2 h), but additional stirring at 50 °C for 8 h gives a compound formulated as [Rh(H)$_2$(PMe$_3$)$_4$]Tp^{Me2} (**7a**). The NMR parameters of the [Rh(H)$_2$(PMe$_3$)$_4$]$^+$ cation of **7a** are identical to those already reported,[14, 20] and match exactly those corresponding to the species that is generated by the reaction of [Rh(H)$_2$(PMe$_3$)$_4$]Cl[14] with KTp^{Me2}.



(Tp' = Tp^{Me2}: **5a**, **6a**, **7a**; Tp: **5b**, **7b**)

Scheme 2. Changes in the denticity of Tp and Tp^{Me2} in Rh^{III} hydrido complexes. The reactions proceed at 50 °C for Tp′ = Tp^{Me2}, and at room temperature for Tp′ = Tp.

Whereas this proposal could not be confirmed by X-ray studies, the analogous complex [Rh(H)$_2$(PMe$_3$)$_4$]Tp (**7b**) of the unsubstituted tris(pyrazolyl)borate ligand can be isolated as white crystals from the reaction of [(κ^3-Tp)Rh(H)$_2$(PMe$_3$)] (**5b**) with PMe$_3$ (ca. 5–6 equiv).[21] As shown in Figure 2, there is no bonding interaction[22] between the Rh^{III} center and the Tp$^-$anion; the closest Rh⋯N contact is to one of the N atoms of the Tp ligand of another asymmetric unit (4.627 Å). It is therefore clear that the overall transformation shown in Scheme 2 provides the first examples of metal salts of the hydrotris(pyrazolyl)borate anions Tp^{1-}. Moreover, our results constitute the first observation of a stepwise change in the denticity of Tp′ ligands from κ^3 to "κ^0". Such changes in Tp′ coordination modes may have important implications in stoichiometric and catalytic transformations of M–Tp′ compounds.

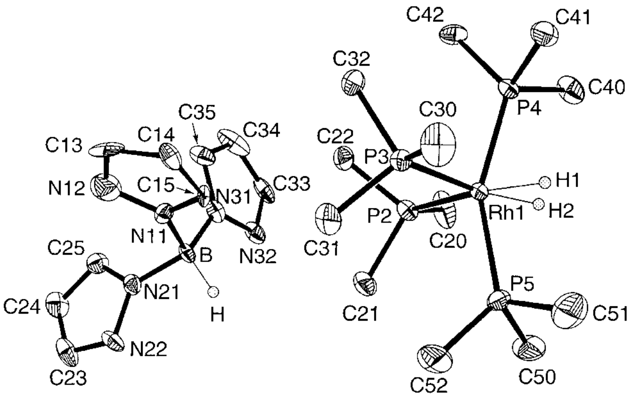


Figure 2. Molecular structure of **7b**. Selected bond lengths [Å] and angles [°]: Rh1–H1 1.57(7), Rh1–H2 1.53(9), Rh1–P(2) 2.362(2), Rh1–P3 2.358(2), Rh1–P4 2.310(2), Rh1–P5 2.296(2); P3-Rh1-P2 98.70(7), P5-Rh1-P4 154.72(7).

Before closing, some comments on the application of the ν(B–H)[17] and δ(^{11}B{^{1}H})[18] criteria to ascertain the κ^n-Tp′ denticity in the above complexes appear appropriate. Referring for convenience and simplicity to the Tp^{Me2} derivatives, the ν(B–H) stretching frequencies of **2** (2518 cm^{-1}) and **3** (2450 cm^{-1}) are in accord with the proposed κ^3-Tp^{Me2} (in the case of **2**) and κ^2-Tp^{Me2} coordination modes (for **3**). The ^{11}B{^{1}H} NMR chemical shifts of $\delta = -8.8$ (**2**) and -5.6 (**3**) also point in the same direction.[18] The situation is, however, more complex for the κ^1-Tp^{Me2} compound **4**. Comparison of its ^{11}B{^{1}H} chemical shift of $\delta = -2.0$ with those of **2** and **3** shows the trend expected for $\kappa^3 \rightarrow \kappa^2 \rightarrow \kappa^1$ exchange. However, the IR spectrum of **4** (KBr disk, Nujol mull, and solution in THF, in the latter case in the temperature range 20 to −85 °C) contains three bands in the proximity of 2425 (shoulder for spectra in THF), 2390, and 2355 cm^{-1}. It seems reasonable that the proposed κ^1 coordination mode in **4** is only one of several possible isomeric forms, and that other isomers, such as κ^2-*N,H* or κ^2-*N,N′*, are responsible for the multiplicity of the ν(B–H) bands. In solution these putative structures could equilibrate rapidly on the NMR time scale. This interesting aspect of the chemistry of **4** is presently under investigation and will be addressed in detail in a full paper. Finally, the "κ^0" complex **7a** displays ν(B–H) at 2431 cm^{-1} and has a δ(^{11}B) value of about −2.0. Hence, a distinction between the κ^1- and "κ^0" formulations for our compounds does not appear possible purely on the basis of B–H stretching frequencies and ^{11}B chemical shifts.

Experimental Section

4: A solution of [Tp^{Me2}Rh(C$_2$H$_4$)$_2$] (0.114 g, 0.25 mmol) in THF (15 mL) at −30 °C was treated with a solution of PMe$_3$ in THF (1.5 mL, 1 M, 1.5 mmol). After stirring for 1 h at room temperature, the solution was analyzed by ^{31}P NMR spectroscopy, which showed quantitative formation of the title compound. The volatile materials 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 **4** were obtained (0.12 g, 42 % yield). IR (Nujol): $\tilde{\nu} = 2425$, 2390, 2355, 2335(sh) cm^{-1} (B–H); ^{1}H NMR (C$_6$D$_6$, 25 °C): $\delta = 5.93$, 5.85 (br s, 2:1, 3 H, 3 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, 3 PMe$_3$); ^{13}C{^{1}H} NMR (C$_6$D$_6$, 25 °C): $\delta = 146.6$, 143.6, 145.3, 148.1 (2:2:1:1, C$_q$ (pz)), 106.3, 104.6 (2:1, 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 (C$_6$D$_6$, 25 °C): $\delta = -5.8$ (dt, ^1J(P,Rh) = 158 Hz, ^2J(P,P) = 48 Hz), −14.1 (dd, ^1J(P,Rh) = 133 Hz, ^2J(P,P) = 48 Hz); ^{11}B{^{1}H} NMR (C$_6$D$_6$, 25 °C): $\delta = -2.0$; elemental analysis calcd for C$_{24}$H$_{49}$BN$_6$P$_3$Rh: C 45.9, H 7.9, N 13.4; found: C 45.7, H 7.8, N 13.7.

7b: A solution of PMe$_3$ in THF (0.6 mL, 1 M, 0.6 mmol) was added to a solid sample of [TpRh(H)$_2$(PMe$_3$)] (0.03 g, 0.07 mmol). The mixture was heated at 50 °C for 30 min, after which ^{31}P NMR spectroscopy revealed quantitative transformation into a new compound. The solvent was evaporated in vacuo, and the residue extracted with THF. After filtration and concentration under reduced pressure, the solution was cooled to −20 °C to yield white crystals of **7b** in about 40 % yield. IR (Nujol): $\tilde{\nu} = 2474$ (B–H), 1955 cm^{-1} (Rh–H); ^{1}H NMR ([D$_6$]acetone, 25 °C): $\delta = 7.36$, 7.28, 5.92 (d, d, t, ^1J(H,H) = 2.0 Hz, 3 H each, 9 CH$_{Tp}$), 4.97 (q, 1:1:1:1, ^1J(H,B) = 113.6, 1 H, BH), 1.60 (pseudo-t, J(H,P)$_{app}$ = 3.2 Hz, 18 H, 2 *trans*-PMe$_3$), 1.53 (d, ^2J(H,P) = 7.0 Hz, 18 H, 2 *cis*-PMe$_3$), −10.57 (dtd, ^2J(H,P) = 136.6, 20.2, ^1J(H,Rh) = 15.0 Hz, 2 H, 2 Rh–H); ^{13}C{^{1}H} NMR ([D$_6$]acetone, 25 °C): $\delta =$ 138.7, 133.4, 102.6 (CH$_{Tp}$), 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{^{1}H} NMR ([D$_6$]acetone, 25 °C): $\delta = -13.0$ (dt, ^1J(P,Rh) = 96, ^2J(P,P) = 27 Hz), 23.9 (dt, ^1J(P,Rh) = 87, ^2J(P,P) = 27 Hz); ^{11}B{^{1}H} NMR ([D$_6$]acetone, 25 °C): $\delta = -1.2$; elemental analysis calcd for **7b** (C$_{21}$H$_{48}$BN$_6$P$_4$Rh): C 40.5, H 7.7, N 13.5; found: C 40.2, H 7.5, N 13.6.

Received: August 3, 1999 [Z13823]

[1] a) F. A. Cotton, G. Wilkinson, C. A. Murillo, M. Bochmann, *Advanced Inorganic Chemistry*, Wiley-Interscience, New York, **1999**; b) F. Bottomley, L. Sutin, *Adv. Organomet. Chem.* **1988**, *28*, 339; c) R. Poli, *Chem. Rev.* **1991**, *91*, 509.

[2] a) S. Trofimenko, *Chem. Rev.* **1993**, *93*, 943; b) G. Parkin, *Adv. Inorg. Chem.* **1995**, *42*, 291; c) N. Kitajima, W. B. Tolman, *Prog. Inorg. Chem.* **1995**, *43*, 418.

[3] See, for example: a) H. Werner, H.-J. Kraus, *Angew. Chem.* **1979**, *91*, 1013; *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 948; b) B. W. Hames, P. Legzdins, D. T. Martin, *Inorg. Chem.* **1978**, *17*, 3644; c) M. D. Butts, R. G. Bergman, *Organometallics* **1994**, *13*, 1899; d) W. D. Jones, V. L. Kuykendall, A. D. Selmeczy, *Organometallics* **1991**, *10*, 1577.

[4] J. M. O'Connor, C. P. Casey, *Chem. Rev.* **1987**, *87*, 307.

[5] C. P. Casey, J. M. O'Connor, K. J. Haller, *J. Am. Chem. Soc.* **1985**, *107*, 1241.

[6] For an early discussion of the tendency of Tp′ ligands to coordinate in a tridentate fashion and to impose nearly octahedral coordination geometry on the metal center, see a) M. D. Curtis, K. B. Shiu, W. M. Butler, *J. Am. Chem. Soc.* **1986**, *108*, 1550; b) M. D. Curtis, K. B. Shiu, W. M. Butler, J. C. Huffman, *J. Am. Chem. Soc.* **1986**, *108*, 3335.

[7] E. Gutiérrez, S. A. Hudson, A. Monge, M. C. Nicasio, M. Paneque, C. Ruiz, *J. Organomet. Chem.* **1998**, *551*, 215.

[8] a) U. E. Bucher, A. Currao, R. Nesper, H. Rüegger, L. M. Venanzi, E. Younger, *Inorg. Chem.* **1995**, *34*, 66; b) R. G. Ball, C. K. Ghosh, J. K. Hoyano, A. D. McMaster, W. A. G. Graham, *J. Chem. Soc. Chem. Commun.* **1989**, 341; c) V. Chauby, C. Serra Le Berre, P. Kalck, J.-C. Daran, G. Commenges, *Inorg. Chem.* **1996**, *35*, 6354.

[9] E. Gutiérrez, S. A. Hudson, A. Monge, M. C. Nicasio, M. Paneque, E. Carmona, *J. Chem. Soc. Dalton Trans.* **1992**, 2651.

[10] F. Malbosc, P. Kalck, J.-C. Daran, M. Etienne, *J. Chem. Soc. Dalton Trans.* **1999**, 271.

[11] J. Reglinski, M. D. Spicer, M. Garner, A. R. Kennedy, *J. Am. Chem. Soc.* **1999**, *121*, 2317.

[12] a) M. Paneque, S. Taboada, E. Carmona, *Organometallics* **1996**, *15*, 2678; b) A. Monge, M. C. Nicasio, M. Paneque, P. J. Pérez, A. Pizzano, M. L. Poveda, L. Rey, C. Ruiz, S. Sirol, S. Taboada, M. Trujillo, E. Carmona, *Inorg. Chem.*, in press.

[13] [κ^2-Tp^{Me2}Rh(PMe$_3$)$_2$] (**3**): IR (Nujol mull): $\tilde{\nu} = 2450\,\text{cm}^{-1}$ (BH); ^{31}P{^{1}H} NMR (C$_6$D$_6$, 25 °C): $\delta = -2.4$ (d, ^1J(P,Rh) = 171 Hz); ^{11}B{^{1}H} NMR (C$_6$D$_6$, 25 °C) $\delta = -5.6$.

[14] A. R. Jones, F. M. Real, G. Wilkinson, A. M. R. Galas, M. B. Hursthouse, K. M. A. Malik, *J. Chem. Soc. Dalton Trans.* **1980**, 551.

[15] a) X-ray data for **4**: a crystal having approximate dimensions 0.20 × 0.35 × 0.35 mm was mounted on a Brucker-Siemens Smart CCD diffractometer equipped with a low-temperature device and a normal-focus 2.4-kW sealed-tube X-ray source (Mo$_{K\alpha}$ radiation, $\lambda = 0.71067$ Å) operating at 50 kV and 20 mA. Data were collected over a quadrant by a combination of two exposure sets. Each exposure of 10 s covered 0.3° in ω. The unit cell dimensions were determined by a least-squares refinement on reflections with $I > 2\sigma$ and $6° < 2\theta < 52°$. The crystal-to-detector distance was 6.05 cm. Coverage of the unique set was over 92% complete to at least 23° in θ. The first 50 frames were recollected at the end of the data collection to monitor crystal decay. The intensities were corrected for Lorentzian and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for Rh and P were taken from the *International Tables for X-Ray Crystallography*.[23] The structure was solved by Multan and Fourier methods. Full-matrix least-square refinement was carried out by minimizing $w(F_o^2 - F_c^2)^2$. Hydrogen atoms were included in their calculated positions, except for that coordinated to B, which was located in a Fourier synthesis and refined isotropically. Refinement was performed on F^2 for all reflections. Weighted R factors (Rw) and all goodness of fits were based on F^2, and conventional R factors (R) on F. Most of the calculations were carried out with SMART[24] software for data collection and reduction, and SHELXTL[24] for structure solution and refinements. Crystal data: $M_r = 628.32$; monoclinic, space group $P2_1/c$, $a = 12.5927(9)$ Å, $b = 12.3861(9)$, $c = 20.773(2)$ Å, $\beta = 93.6140(10)°$, $V = 3233.6(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.291\,\text{g cm}^{-3}$, $F(000) = 1320$, $T = 148(2)$ K. Of the 9001 reflections collected, 5245 were unique ($R_{int} = 0.0223$). Final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0329$, $wR_2 = 0.0733$. b) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications nos. CCDC-132889 (**4**) and CCDC-132888 (**7b**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[16] Y. Takahashi, M. Akita, S. Hikighi, Y. Moro-oka, *Organometallics* **1998**, *17*, 4884.

[17] M. Akita, K. Ohta, Y. Takahashi, S. Hikichi, Y. Moro-Oka, *Organometallics* **1997**, *16*, 4121.

[18] T. O. Northcutt, R. J. Lachicotte, W. D. Jones, *Organometallics* **1998**, *17*, 5148.

[19] [(κ^2-Tp^{Me2})Rh(H)$_2$(PMe$_3$)$_2$] (**6a**): IR (Nujol): $\tilde{\nu} = 2484$ (B–H), 2068, 2045 cm^{-1} (Rh–H); ^{1}H NMR (C$_6$D$_6$, 25 °C): $\delta = 5.84$, 5.74 (s, 2:1, 3H, 3CH$_{pz}$), 2.41, 2.32, 2.15, 1.73 (s, 2:2:1:1, 18H 6Me$_{pz}$), 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, 2Rh–H); ^{13}C{^{1}H} NMR (C$_6$D$_6$, 25 °C): $\delta = 151.0$, 150.0, 146.0, 141.4 (2:2:1:1, C$_q$ (pz)), 107.0, 105.6 (2:1, CH$_{pz}$), 19.3 (dd, ^1J(C,P) = 19, ^3J(C,P) = 12 Hz; PMe$_3$), 18.0 (dd, ^1J(C,P) = 17, $^3J_{CP}$ = 11 Hz, PMe$_3$), 17.0, 14.3, 14.0, 11.3 (2:2:1:1; Me$_{pz}$); ^{31}P{^{1}H} NMR (C$_6$D$_6$, 25 °C): AB part of an ABX spin system centered at $\delta = -4.0$, J(A,Rh) = J(B,Rh) = 107 Hz; J(AB) could not be computed from the spectrum because the smallest signals of the AB spin system were not located; ^{11}B{^{1}H} NMR (C$_6$D$_6$, 25 °C): $\delta = -6.0$.

[20] R. R. Schrock, J. A. Osborn, *J. Am. Chem. Soc.* **1971**, *93*, 2397.

[21] While this manuscript was being prepared, we learned that related Rh^I complexes containing a "κ^0"-Tp′ group (Tp′ = Tp^{Me2}, 4-^{Cl}) can be obtained from [Tp′Rh(CO)$_2$] and PMePh$_2$ or Ph$_2$P(CH$_2$)$_3$PPh$_2$: P. Kalck, personal communication.

[22] X-ray data for **7b**: the X-ray structural determination of **7b** was carried out on a crystal of approximate dimensions 0.08 × 0.10 × 0.14 mm by the same procedure as for compound **4**[15a] but in this case data were collected over an hemisphere of the reciprocal space by combination of three exposure sets. The H atoms coordinated to Rh were located in Fourier synthesis and refined isotropically. Crystal data: $M_r = 622.25$; triclinic, space group $P1$, $a = 9.4968(13)$, $b = 9.7223(13)$, $c = 9.8279(13)$ Å, $\alpha = 60.891(2)$, $\beta = 85.285(2)$, $\gamma = 80.050(2)°$, $V = 780.9(2)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.323\,\text{g cm}^{-3}$, $F(000) = 326$, $T = 143(2)$ K. Of the 3680 reflections collected, 3210 were unique ($R_{int} = 0.0261$). Final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0417$, $wR_2 = 0.0925$.[15b]

[23] *International Tables for X-Ray Crystallography*, Kynoch Press: Birmingham, U. K., **1974**.

[24] SHELXTL, Siemens Energy & Automation Inc., Analytical Instrumentation, **1996**.