Ruthenium Dihydridobis(pyrazolyl)borate Complexes Adopting a κ^3 N,N,H, κ^2 N,H, or κ^2 N,N Bonding Mode

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Ruthenium complexes containing the dihydridobis(3,5-bis(trifluromethyl)pyrazolyl)borate ligand $Bp^{(CF3)2}$ have been prepared and structurally characterized. Reaction of $(Bp^{(CF3)2})$-RuH(COD) (**1a**) with 2 equiv of bulky phosphines PR_3 under 3 bar of H_2 produces the hydrido-(dihydrogen) complexes $(Bp^{(CF3)2})RuH(H_2)(PR_3)_2$ (R = Cy, **2a**; R = ^{i}Pr, **3a**). X-ray structural analysis of **3a** confirms a κ^2 N,H bonding mode of the $Bp^{(CF3)2}$ ligand. In the absence of dihydrogen, the monohydride complex $(Bp^{(CF3)2})RuH(COD)(PCy_3)$ (**4a**) is isolated. Upon pressurization to 3 bar H_2, **4a** converts into $(Bp^{(CF3)2})RuH(H_2)(PCy_3)$ (**5a**) with rechelation of the pendant pyrazolyl ring and hydrogenation of the COD ligand. Addition of 2 equiv of PPh_3 or $Ppyl_3$ to **1a** under 3 bar of H_2 leads to the formation of the corresponding hydrido complexes $(Bp^{(CF3)2})RuH(PR_3)_2$ (R = Ph, **6a**; R = pyl, **7a**). Under similar conditions, **1a** reacts with 2 equiv of ^{t}BuNH$_2$ to produce the amine adduct $(Bp^{(CF3)2})RuH(^t BuNH_2)_2$ (**8a**). By addition of 1 equiv of MeI to **8a**, the iodo complex $(Bp^{(CF3)2})RuI(^t BuNH_2)_2$ (**9a**) is isolated and characterized by an X-ray structural determination. The analogous chloro complex $(Bp^{(CF3)2})RuCl(^t BuNH_2)_2$ (**10a**) can be prepared by stirring a dichloromethane solution of **8a** for 18 h. In the absence of dihydrogen, **1a** reacts with a large excess of ^{t}BuNH$_2$ to give $(Bp^{(CF3)2})RuH(COD)(^t BuNH_2)$ (**11a**). The structure with a κ^2 N,H coordination of the $Bp^{(CF3)2}$ ligand is confirmed by an X-ray determination. Using the more sterically demanding diisopropylamine in the same conditions used for the formation of **8a**, we could not isolate any complex. However upon N_2 atmosphere, the dinuclear species with a μ^2-bridging dinitrogen ligand $[(Bp^{(CF3)2})RuH(^i Pr_2NH)]_2(N_2)$ (**12a**) could be isolated and characterized by a single-crystal X-ray determination. Addition of mesitylene to **1a** produces the arene complex $(Bp^{(CF3)2})RuH(\eta^6\text{-}C_6H_3Me_3)$ (**13a**). The X-ray structure determination gave conclusive evidence for the κ^2 N,N bonding mode of the $Bp^{(CF3)2}$ ligand. When exposing **1a** to a CO atmosphere, the new acyl(dicarbonyl) complex $(Bp^{(CF3)2})Ru(COC_8H_{13})(CO)_2$ (**14a**) is isolated in very high yield. Its structure is fully characterized on the basis of 2D homonuclear and heteronuclear correlation NMR data and by an X-ray structural determination. Similar reactions have been performed using the nonfluorinated complex $(Bp^{Me2})RuH(COD)$ (**1b**) as starting material. The analogous complexes **2b**, **4b**−**6b**, and **14b** have been obtained. The variation of of the hapticity of the Bp ligand plays a crucial role in this chemistry, but the fluorinated substituents have a limited influence.

Introduction

Generation of an organometallic complex possessing vacant coordination sites is often required in several steps within a catalytic cycle. This might be achieved through the decoordination of a ligand but results in many cases in the decomposition of the catalyst. In this respect, the search for multidentate ligands able to coordinate to a metal center via different modes can be a useful alternative. A significant illustration of this concept is given by the mechanistic studies reporting on the alkane C−H bond activation by $Tp^{Me2}Rh$ complexes.[1] These systems involve dechelation and rechelation of one of the pyrazolyl arms of the hydridotris-(pyrazolyl)borate ligand. Hydridotris(pyrazolyl)borates (Tp) have been used for the synthesis of a wide variety of metal complexes,[2] and variation of the hapticity of the Tp ligand has been reported in several examples, among which the κ^3 N,N,N and κ^2 N,N bonding modes are the most common.[3] However very recently, rare examples of the κ^4 N,N,N,H,[4] the κ^3 N,N,H,[3a,5] the κ^2

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(1) (a) Bromberg, S. E.; Yang, H.; Asplund, M. C.; Lian, T.; McNamara, B. K.; Kotz, K. T.; Yeston, J. S.; Wilkens, M.; Frei, H.; Bergman, R. G.; Harris, C. B. *Science* **1997**, *278*, 260. (b) Wick, D. D.; Reynolds, K. A.; Jones, W. D. *J. Am. Chem. Soc.* **1999**, *121*, 3974.

(2) (a) Trofimenko, S. In *Scorpionates−The Coordination Chemistry of Polypyrazolylborate Ligands*; Imperial College Press: London, 1999. (b) Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943.

(3) Selected examples: (a) Takahashi, T.; Akita, M.; Hikichi, S.; Moro-oka, Y.*Organometallics* **1998**, *17*, 4884. (b) Burns, I. D.; Hill, A. F.; White, A. J. P.; Williams, D. J.; Wilton-Ely, J. D. E. T. *Organometallics* **1998**, *17*, 1552. (c) Oldham, W. J.; Heinekey, D. M. *Organometallics* **1997**, *16*, 467. (d) Bucher, U. E.; Currao, A.; Nesper, R.; Ruegger, H.; Venanzi, L. M.; Younger, E. *Inorg. Chem.* **1995**, *34*, 66.

(4) Takahashi, Y.; Hikichi, S.; Akita, M.; Moro-oka, Y. *Organometallics* **1999**, *18*, 2571.

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N,H,[6] the κ^1 N,[7] and the $\kappa^{0,7b}$ bonding modes have been reported and structurally characterized.

In comparison, complexes with dihydridobis(pyrazolyl)borate ligands (Bp), and in particular ruthenium complexes, have received little attention. In (Bp^{Me2})-RuH(COD), the Bp^{Me2} ligand adopts a κ^3 N,N,H bonding mode as evidenced by the X-ray structure determination,[8] whereas in BpRu(COMe)(CO)(PMe_3)$_2$ the Bp ligand adopts a κ^2 N,N bonding mode.[9] This latter mode is found in a whole series of Bp ruthenium compounds, among which the vinyl complex BpRu(CH=CH_2)(CO)-(PPh_3)$_2$ has been structurally characterized.[10]

The effect of the replacement of a methyl by a trifluoromethyl group on the acid−base properties of pyrazoles was already pointed out,[11] some years before the synthesis of the highly fluorinated hydridotris(3,5-bis(trifluromethyl)pyrazolyl)borate ligand ($Tp^{(CF3)2}$) and dihydridobis(3,5-bis(trifluromethyl)pyrazolyl)borate ligand ($Bp^{(CF3)2}$).[12] Relatively few complexes incorporating these ligands have been reported,[13] and the benefit of introducing such electron-withdrawing substituents remains relatively unclear.

We have previously shown that the hydridotris(pyrazolyl)borate ligand can stabilize dihydrogen ruthenium complexes, and we have for example isolated the bis(dihydrogen) complexes $TpRuH(H_2)_2$ (Tp = Tp^{Me2}, Tp^{iPrBr}). Their reactivity is characterized by the electrophilic character of the hydride and dihydrogen ligands.[14,15] This is very different from what is observed with the other bis(dihydrogen) complex $RuH_2(H_2)_2$-(PCy_3)$_2$, whose reactivity is dominated by substitution and hydrogen transfer reactions.[15,16] We were thus interested in exploring the potential use of Bp ligands in ruthenium chemistry. Preliminary results have been described in a communication,[17] and in this paper, we report further investigations of the reactions of ($Bp^{(CF3)2}$)-RuH(COD) (**1a**) ($Bp^{(CF3)2}$ = H_2B[3,5-(CF_3)$_2$-pz]$_2$) with phosphines, amines, arenes, and CO showing the capacity of the bis(pyrazolyl)borato ligand to adopt the κ^3 N,N,H, the κ^2 N,H, or the κ^2 N,N bonding mode. Similar reactions have been carried out with the nonfluorinated complex (Bp^{Me2})RuH(COD) (**1b**) (Bp^{Me2} = H_2B[3,5-(CH_3)$_2$-pz]$_2$), thus allowing the evaluation of the effect of the fluorine substituents.

Results and Discussion

All the reactions have been performed using ($Bp^{(CF3)2}$)-RuH(COD) (**1a**) or (Bp^{Me2})RuH(COD) (**1b**) as precursors. **1a** was obtained as a greenish solid in 75% yield by addition of NaH_2B[3,5-(CF_3)$_2$-pz]$_2$ to [$RuCl_2$(COD)]$_n$ in the presence of 1 equiv of NaOH, whereas **1b** was synthesized according to the procedure reported by Singleton et al.[8] **1a** has been fully characterized, and we have already mentioned in the preliminary communication[17] that **1a** and **1b** display the same geometry. As can be seen from their X-ray structures, the bis(pyrazolyl)borato ligand adopts the κ^3 N,N,H bonding mode.

In the absence of an X-ray determination, there are several NMR parameters that distinguish between the three possible modes of coordination of the Bp ligands. In the ^{1}H NMR spectra, the presence of a broad signal at high field (ca. 1 to −3 ppm) is characteristic of an agostic Ru−H−B interaction. However this resonance may be so broad that it can be difficult to detect it. The free B−H resonance is always extremely broad, but a bump can be observed around 4 ppm. In the absence of any fluxional behavior, the asymmetry of the two pyrazolyl rings' coordination will be reflected by the presence of two singlets in the 5.5−7 ppm region, and thus two singlets have to be observed for the κ^2 N,H bonding mode. This asymmetry will also be evidenced by two sets of signals in the ^{19}F NMR spectra. Additional information can be obtained by IR for the detection of an agostic Ru−H−B interaction. In our complexes, the free B−H band will be observed between 2500 and 2560 cm^{-1}, whereas the agostic Ru−H−B band is shifted to lower energies between 2060 and 2160 cm^{-1}. Comparison with previously reported examples of compounds with Bp or Tp ligands shows that the values highly depend on the nature of the other ligands around the metal. Thus, if it is possible to discriminate a free B−H from an agostic one, it is more difficult to analyze in detail the values of the latter, as band couplings with the hydride ligands can interfere.

Reactions with Phosphines. The reaction mainly depends on the steric properties of the phosphine, as can be seen from Scheme 1 for the reactions with **1a** and from Scheme 2 for the reactions with **1b**.

The reaction of **1a** with 2 equiv of a bulky phosphine, PCy_3 or P^iPr_3, in pentane under 3 bar of H_2 at room

(5) Corrochano, A. E.; Jalon, F. A.; Otero, A.; Kubicki, M. M.; Richard, P.*Organometallics* **1998**, *17*, 145.

(6) Malbosc, F.; Kalck, P.; Daran, J. C.; Etienne, M. *J. Chem. Soc., Dalton Trans.* **1999**, 271.

(7) (a) Gutierrez, E.; Hudson, S. A.; Monge, A.; Nicasio, M. C.; Paneque, M.; Carmona, E. *J. Chem. Soc., Dalton Trans.* **1992**, 2651. (b) Paneque, M.; Sirol, S.; Trujillo, M.; Gutierrez-Puebla, E.; Monge, M. A.; Carmona, E. *Angew. Chem., Int. Ed.* **2000**, *39*, 218.

(8) Albers, M. O.; Crosby, S. F. A.; Liles, D. C.; Robinson, D. J.; Shaver, A.; Singleton, E. *Organometallics* **1987**, *6*, 2014.

(9) Bellachioma, G.; Cardaci, G.; Gramlich, V.; Macchioni, A.; Pieroni, F.; Venanzi, L. M. *J. Chem. Soc., Dalton Trans.* **1998**, 947.

(10) Hill, A. F.; White, A. J. P.; Williams, D. J.; Wilton-Ely, J. D. E. T. *Organometallics* **1998**, *17*, 4249.

(11) Elguero, J.; Yranzo, G. I.; Laynez, J.; Jimenez, P.; Menendez, M.; Catalan, J.; de Paz, J. L. G.; Anvia, F.; Taft, R. W. *J. Org. Chem.* **1991**, *56*, 3942.

(12) (a) Dias, H. V. R.; Lu, H.-L.; Ratcliff, R. E.; Bott, S. G. *Inorg. Chem.* **1995**, *34*, 1975. (b) Dias, H. V. R.; Gorden, J. D. *Inorg. Chem.* **1996**, *35*, 318. (c) Renn, O.; Venanzi, L. M.; Marteletti, A.; Gramlich, V. *Helv. Chim. Acta* **1995**, *78*, 993.

(13) For example: (a) Del Ministro, E.; Renn, O.; Ruegger, H.; Venanzi, L. M.; Burckhardt, U.; Gramlich, V. *Inorg. Chim. Acta* **1995**, *240*, 631. (b) Dias, H. V. R.; Lu, H.-L.; Gorden, J. D.; Jin, W. *Inorg. Chem.* **1996**, *35*, 2149. (c) Dias, H. V. R.; Jin, W.; Kim, H.-J.; Lu, H.-L. *Inorg. Chem.* **1996**, *35*, 2317. (d) Dias, H. V. R.; Jin, W. *J. Am. Chem. Soc.* **1995**, *117*, 11381. (e) Dias, H. V. R.; Kim, H.-J. *Organometallics* **1996**, *15*, 5374. (f) Dias, H. V. R.; Jin, W. *Inorg. Chem.* **1996**, *35*, 267. (g) Dias, H. V. R.; Jin, W. *Inorg. Chem.* **1996**, *35*, 3687. (h) Dias, H. V. R.; Kim, H.-J.; Lu, H.-L.; Rajeshwar, K.; de Tacconi, N. R.; Derecskei-Kovacs, A.; Marynick, D. S. *Organometallics* **1996**, *15*, 2994. (i) Dias, H. V. R.; Lu, H.-L. *Inorg. Chem.* **1995**, *34*, 5380. (j) Dias, H. V. R.; Lu, H.-L.; Gorden, J. D.; Jin, W. *Inorg. Chem.* **1996**, *35*, 2149. (k) Dias, H. V. R.; Lu, H.-L.; Ratcliff, R. E.; Bott, S. G. *Inorg. Chem.* **1995**, *34*, 1975.

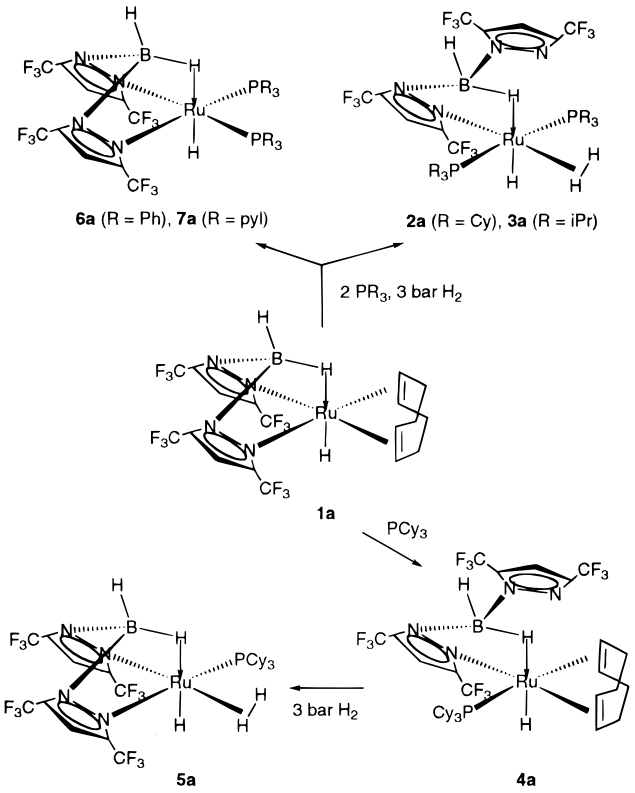
(14) (a) Moreno, B. Sabo-Etienne, S.; Chaudret, B.; Rodriguez, A.; Jalon, F.; Trofimenko, S. *J. Am. Chem. Soc.* **1995**, *117*, 7441. (b) *J. Am. Chem. Soc.* **1994**, *116*, 2635.

(15) Sabo-Etienne, S.; Chaudret, B. *Coord. Chem. Rev.* **1998**, *178−180*, 381, and references therein.

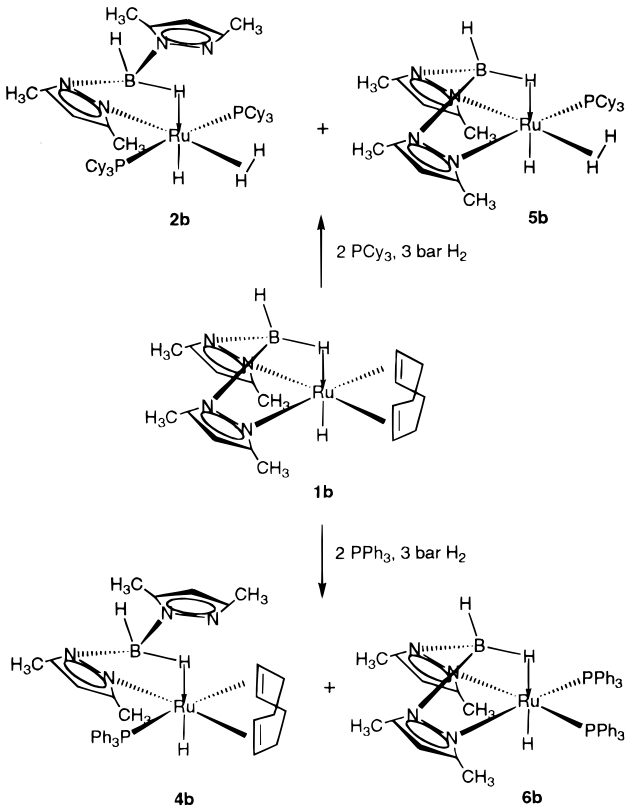
(16) (a) Delpech, F.; Sabo-Etienne, S.; Chaudret, B.; Daran, J. C.; Hussein, K.; Marsden, C. J.; Barthelat, J.-C. *J. Am. Chem. Soc.* **1999**, *121*, 6668. (b) Hussein, K.; Marsden, C. J.; Barthelat, J.-C.; Rodriguez, V.; Conejero, S.; Sabo-Etienne, S.; Donnadieu, B.; Chaudret, B. *Chem. Commun.* **1999**, 1315. (c) Delpech, F.; Sabo-Etienne, S.; Donnadieu, B.; Chaudret, B. *Organometallics* **1998**, *17*, 4926. (d) Guari, Y.; Sabo-Etienne, S.; Chaudret, B. *Eur. J. Inorg. Chem.* **1999**, 1047.

(17) Rodriguez, V.; Full, J.; Donnadieu, B.; Sabo-Etienne, S.; Chaudret, B. *New J. Chem.* **1997**, *21*, 847.

Scheme 1. Reactions of 1a with Phosphines



Scheme 2. Reactions of 1b with Phosphines



temperature, leads to hydrogenation of COD into cyclooctane and formation of the corresponding hydrido(dihydrogen) complexes $(Bp^{(CF3)2})RuH(H_2)(PR_3)_2$ (R = Cy, **2a**; R = ^{i}Pr, **3a**). We have already reported in a preliminary form the synthesis and characterization of **2a**.[17] The proposed structure is now fully confirmed by

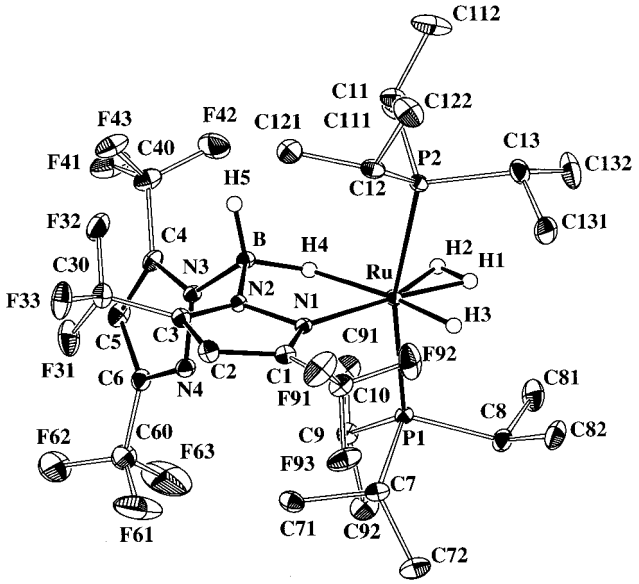


Figure 1. ZORTEP view of$(Bp^{(CF3)2})RuH(H_2)(P^iPr_3)_2$ (**3a**). Selected bond lengths (Å): Ru−H(1), 1.471(27); Ru−H(2), 1.597(28); Ru−H(3), 1.462(27); Ru−H(4), 1.840(25); H(1)−H(2), 0.994(35); B−H(4), 1.203(23); B−H(5), 1.048(25); Ru−N(1), 2.1480(19); Ru−P(1), 2.3595(8); Ru−P(2), 2.3650(8). Selected bond angles (deg): P(1)−Ru−P(2), 164.76(2); H(3)−Ru−H(4), 171.73(12); H(2)−Ru−H(1), 37.53(13); N(1)−Ru−P(2), 93.93(5); N(1)−Ru−P(1), 96.08(5).

comparison with the data obtained for the analogous triisopropylphosphine complex. In this case we were able to grow crystals, and the molecular structure of **3a** is depicted in Figure 1. Crystal data are reported in Table 1. The structure is approximately octahedral with two trans phosphine ligands (the P(1)−Ru−P(2) angle is 164.76(2)°). Coordination of these two bulky phosphines results in the modification of the κ^3 N,N,H to the κ^2 N,H of the $Bp^{(CF3)2}$ coordination mode. The $Bp^{(CF3)2}$ now has a pendant pyrazolyl ring bent back away from the ruthenium to reduce steric repulsion with the phosphine. The bidentate coordination of the $Bp^{(CF3)2}$ ligand is achieved through the coordination of the nitrogen of the second pyrazolyl ring with a Ru−N(1) distance of 2.1480(19) Å and an agostic B−H bond with a Ru−H(4) distance of 1.840(25) Å. The agostic B−H(4) distance (1.203(23) Å) is elongated compared to the noncoordinated one (1.048(25) Å). This agostic bond is trans to the hydride H(3), whereas the nitrogen of the coordinated pyrazolyl ring is trans to the dihydrogen ligand. The Ru−H bond lengths vary from 1.462(27) to 1.597(28) Å, and the dihydrogen ligand is characterized by a H(1)−H(2) distance of 0.994(35) Å.

The solid-state structure is retained in solution, as evidenced by the two sets of signals observed in ^{19}F NMR and by the ^{1}H NMR spectrum showing two singlets at 6.72 and 6.48 ppm for the pyrazolyl protons and a broad signal at −2.90 ppm for the agostic Ru−H−B hydride, whereas one triplet is found at − 13.58 ppm (J_{P-H} = 13.8 Hz) for the resonance of the hydride and dihydrogen ligands remaining in fast exchange at all accessible temperatures. The T_{1min} of 32 ms (250 K, 400 MHz) is characteristic of a hydrido(dihydrogen) formulation and is similar to the value obtained for the analogous complex $Tp^{Me2}RuH(H_2)(PCy_3)$.[14] Partial deuteration of **3a** was achieved by reacting **1a** with 2 equiv

Table 1. Crystallographic Data for Complexes 3a, 9a, and 11a

crystal parameters	3a	9a	11a
formula	$C_{28}H_{49}BF_{12}N_4P_2Ru$	$C_{18}H_{26}BF_{12}IN_6Ru$	$C_{22}H_{28}BF_{12}N_5Ru$
fw	843.53	793.23	702.37
cryst system	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a, Å	10.768(2)	9.7319(14)	10.1571(12)
b, Å	11.491(2)	10.9587(16)	22.365(3)
c, Å	17.015(4)	14.625(2)	12.6816(15)
α, deg	96.28(3)	110.068(17)	90
β, deg	102.87(3)	91.068(17)	106.745(13)
γ, deg	111.19(2)	109.031(17)	90
V, Å	1871.3(7)	1371.0(3)	2758.6(6)
temp, K	160(2)	160(2)	160(2)
no. of data/restraints/params	5000/131/465	4037/661/438	3908/133/393
abs corr [32]	numerical	numerical	numerical
$T_{min} - T_{max}$	0.55−1.0	0.66−1.0	0.75−1.0
goodness of fit on F^2	1.028	0.984	1.022
R1 [$I > 2\sigma(I)$]	0.0273	0.0226	0.0279
wR2	0.0653	0.0505	0.0683

of P^iPr_3 in pentane under 3 bar of D_2 at room temperature. The resulting solid shows for the hydrido(dihydrogen) resonance a complex multiplet at −13.6 ppm with an apparent J_{H-D} value of 6.5 Hz, thus leading to a J_{H-D} calculated value of 19.5 Hz. Estimation of the d_{HH} distance from the J_{H-D} value using the equation developed by Morris[18] leads to 1.09 Å, in good agreement with the X-ray data. These data show that **3a** is a stretched dihydrogen complex. We have already reported hydrido(dihydrogen) ruthenium complexes presenting the same characteristics.[19] Several authors have used the ν_{B-H} values as a criterium to distinguish the κ^n-Tp denticity.[5,7b,20] In particular, the κ^3 mode is characterized by higher values. Our result seems to follow this trend, as the ν_{B-H} for the free B−H is shifted from 2555 cm^{-1} in the case of **1a** to 2514 and 2498 cm^{-1} for **2a** and **3a**, respectively.

In the absence of dihydrogen, stirring a pentane solution of **1a** with 1.5 equiv of PCy_3 at room temperature for 4 days results in the formation of $(Bp^{(CF3)2})$-RuH(COD)(PCy_3) (**4a**). This complex was isolated as a pale green solid and characterized by IR and NMR spectroscopy. Dechelation of one pyrazolyl ring allowing PCy_3 coordination is evidenced by ^1H and ^{19}F NMR data, very similar to the data obtained for **2a**. The hydride resonates as a doublet at −7.66 ppm (J_{P-H} = 21.4 Hz), and a broad band at −0.40 ppm is attributed to the agostic Ru−H−B. Remarkably when **4a** is pressurized under 3 bar H_2, rechelation of the pendant pyrazolyl ring can be obtained and the new hydrido(dihydrogen) complex $(Bp^{(CF3)2})RuH(H_2)(PCy_3)$ (**5a**) can be isolated with a κ^3 N,N,H $Bp^{(CF3)2}$ coordination mode. In this complex, the agostic Ru−H−B gave an extremely broad signal centered at 0.3 ppm, whereas the hydride and dihydrogen ligands are in fast exchange at all accessible temperatures and appear as a doublet at −12.72 ppm (J_{P-H} = 17.9 Hz) in the ^1H NMR spectrum. The T_{1min} of 25 ms, measured at 260 K at 400 MHz, is very close to the one found for **2a** and indicative of a hydrido(dihydrogen) formulation. Comparison of the ν_{B-H} value for the free B−H (2546 cm^{-1}) with those obtained in the case of **1a** and **3a** is also in favor of the κ^3 mode.

As can be seen from the reactions leading to **2a**, **3a**, or **5a**, the use of a bulky phosphine allows the stabilization of a dihydrogen complex. On the contrary, when phosphines displaying smaller cone angles are added to **1a** in the same conditions, coordination of the two phosphines in a cis position is now allowed and monohydride complexes are thus obtained. Addition of 2 equiv of PPh_3 or $Ppyl_3$ to a pentane solution of **1a** under 3 bar of H_2 at room temperature leads to the formation of the corresponding hydrido complexes $(Bp^{(CF3)2})RuH(PR_3)_2$ (R = Ph, **6a**; R = pyl, **7a**). Thus, hydrogenation of COD into cyclooctane allows the coordination of two phophine ligands, the $Bp^{(CF3)2}$ ligand keeping its κ^3 N,N,H $Bp^{(CF3)2}$ coordination mode. The hydride appears in the ^1H NMR spectrum as a triplet at −16.16 ppm for **6a** and is shifted at lower field for **7a** (−14.31 ppm), in agreement with the presence of the π-acceptor $Ppyl_3$ phosphine. In these reactions, the steric factor is predominant since the use of the two phosphines, PPh_3 and $Ppyl_3$, with very different electronic properties but with the same cone angle (145°),[21] results in the formation of similar hydrido complexes, whereas bulky phosphines allow the stabilization of the dihydrogen compounds **2**, **3**, and **5**.

When the nonfluorinated precursor **1b** is used (Scheme 2), addition of 2 equiv of PCy_3 under 3 bar of H_2 leads to a mixture of two complexes, $(Bp^{Me2})RuH(H_2)(PCy_3)_2$ (**2b**) and $(Bp^{Me2})RuH(H_2)(PCy_3)$ (**5b**), that we have characterized by comparison with the spectroscopic data of **2a** and **5a**, respectively. **2b** and **5b** are formed in a 2:3 ratio, and any attempt to separate them has failed. Using 2 equiv of PPh_3 also leads to a mixture of compounds $(Bp^{Me2})RuH(COD)(PPh_3)$ (**4b**) and (Bp^{Me2})-$RuH(PPh_3)_2$ (**6b**) in 1:2 ratio. They were characterized by comparison with the spectroscopic data of **4a** and **6a**, respectively. Thus in each case, the use of two different phosphines leads to a mixture of two compounds with a κ^2 N,H and a κ^3 N,N,H $Bp^{(CH3)2}$ coordination mode. As observed with the $Bp^{(CF3)2}$ derivatives, dihydrogen complexes can be stabilized only in the presence of a bulky phosphine, P^iPr_3 or PCy_3. Apart from the chemical

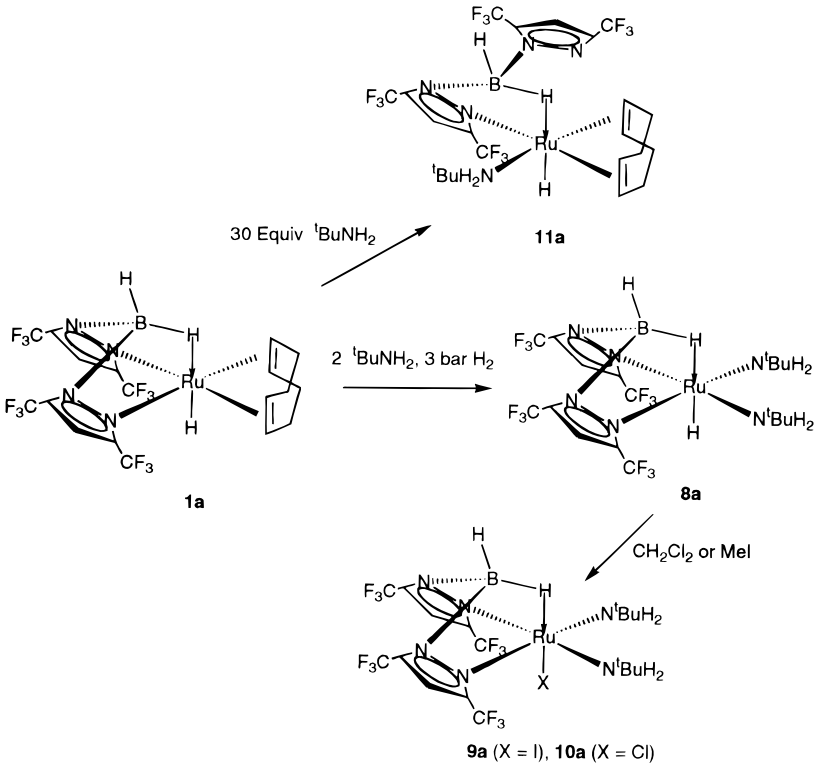
(18) Maltby, P. A.; Schlaf, M.; Steinbeck, M.; Lough, A. J.; Morris, R. H.; Klooster, W. T.; Koetzle, T. F.; Srivastava, R. C. *J. Am. Chem. Soc.* **1996**, *118*, 5396.

(19) (a) Guari, Y.; Sabo-Etienne, S.; Chaudret, B. *Organometallics* **1996**, *15*, 3471. (b) Guari, Y.; Sabo-Etienne, S.; Chaudret, B. *J. Am. Chem. Soc.* **1998**, *120*, 4228.

(20) Akita, M.; Ohta, K.; Takahashi, Y.; Hikichi, S.; Moro-oka, Y. *Organometallics* **1997**, *16*, 4121.

(21) (a) Moloy, K. G.; Petersen, J. L. *J. Am. Chem. Soc.* **1995**, *117*, 7696. (b) Rodriguez, V.; Donnadieu, B.; Sabo-Etienne, S.; Chaudret, B. *Organometallics* **1998**, *17*, 3809.

Scheme 3. Reactions of 1a with Amines



shift of the pyrazolyl protons shifted at higher field in the case of the $Bp^{(CH3)2}$ ligand, no significant modification is observed when comparing the data for these two series of compounds (**2a**, **5a** with **2b**, **5b** and **4a**, **6a** with **4b**, **6b**, respectively). In particular, no significant change is observed for the T_{1min} values for the hydrido(dihydrogen) complexes **2a**,**b** (27 and 28 ms at 400 MHz) and **5a**,**b** (25 and 23 ms at 400 MHz), demonstrating that introduction of electron-withdrawing substituents has little effect on the dihydrogen stretching and therefore that the Bp ligands are not π-acceptors. It should be noted that the use of a dihydridobis(pyrazolyl)borate ligand allows the formation of the bisphosphine complexes **2a**,**b**, whereas with the bulkier hydridotris(pyrazolyl)borate ligand we could obtain only monophosphine complexes.[14] Moreover comparison of the T_{1min} values obtained for the monophosphine complexes **5a**,**b** (ca. 24 ms at 400 MHz) with the analogous Tp^{Me2} complex $Tp^{Me2}RuH(H_2)(PCy_3)$ (22 ms at 250 MHz corresponding to 35 ms at 400 MHz) indicates that replacement of the agostic B−H coordination by nitrogen coordination of the third pyrazolyl ring of the Tp^{Me2} ligand has a noticeable influence on the H−H bond of the dihydrogen ligand.[14] The more electron-rich Tp^{Me2} ligand induces a lengthening of the H−H bond.

Reactions with Amines. Catalytic hydroamination is an important process, but N−H activation via oxidative addition of amines to late-transition metal complexes remains relatively little explored.[22] It was thus tempting to study the reactivity of **1a** toward amines. All the reactions we have performed by using different amines led either to decomposition or to compounds in which the amine acts as a classical two-electron donor ligand (see Scheme 3). For example, treating a pentane solution of **1a** under 3 bar of dihydrogen with 2 equiv of $^tBuNH_2$ results in a mixture of different complexes, among which we could isolate an orange solid $(Bp^{(CF3)2})RuH(^tBuNH_2)_2$ (**8a**) in 30% yield. Several mono- or dinuclear complexes were obtained in very small quantities, and they display interesting structures that will be described elsewhere. **8a** also features κ^3 N,N,H coordination of the $Bp^{(CF3)2}$ ligand, as for **6a** and **7a**. The pyrazolyl rings appear equivalent, as one singlet is observed at 6.30 ppm in the ^1H NMR spectrum. The $^tBuNH_2$ ligand is characterized by a singlet at 0.56 ppm for the ^{t}Bu protons and by an AB signal at 1.24 and 3.33 ppm (J_{H-H} = 12 Hz) for the amine hydrogens. This AB pattern is mostly attributed to a restricted rotation of the $^tBuNH_2$ ligand around the metal. As a result of the presence of the two basic amine ligands, the hydride resonates at very high field (−26.04 ppm). No reaction was observed when H_2 was bubbled for 30 min through a C_6D_6 solution of **8a**.

By addition of 1 equiv of MeI to **8a**, we could isolate the corresponding iodo complex $(Bp^{(CF3)2})RuI(^tBuNH_2)_2$ (**9a**) and suitable crystals were obtained, allowing an X-ray structural determination (see Figure 2). Crystal data are reported in Table 1. **9a** also features κ^3 N,N,H coordination of the $Bp^{(CF3)2}$ ligand. The ruthenium is in an octahedron environment with the axial positions occupied by the iodide and the agostic H(12) hydrogen atom, whereas the equatorial positions are occupied by four nitrogen atoms, i.e., N(1) and N(2) of the two amines and N(11) and N(21) of the Bp ligand. The H(12)−Ru−I angle is 175.30(12)° and the N(11)−RuN(2) and N(21)−Ru−N(1) angle are 176.56(10)° and 176.14(10)°, respectively. The distances Ru−N(1) and Ru−N(2) are 2.157(3) and 2.158(3) Å, thus slightly shorter than the Ru−N distances reported for other

(22) Muller, T. E.; Beller, M. *Chem. Rev.* **1998**, *98*, 675.

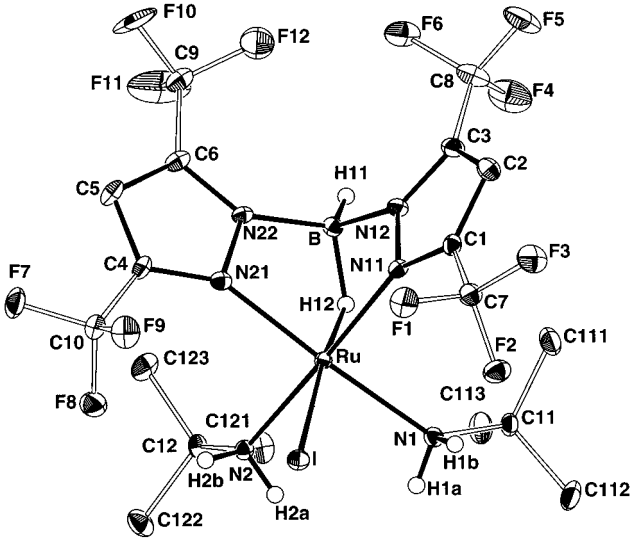


Figure 2. ZORTEP view of $(Bp^{(CF3)2})RuI(^tBuNH_2)_2$ (**9a**). Selected bond lengths (Å): Ru−H(12), 1.667(32); B−H(12), 1.291(34); B−H(11), 0.971(33); Ru−N(1), 2.157(3); Ru−N(2), 2.158(3); Ru−N(11), 2.100(3); Ru−N(21), 2.082-(3); Ru−I, 2.7195(6). Selected bond angles (deg): N(21)−Ru−N(1), 176.14(10); N(11)−Ru−N(2), 176.56(10); H(12)−Ru−I, 175.30(12); N(2)−Ru−N(1), 91.50(13); N(21)−Ru−N(11), 87.74(11); N(21)−Ru−N(2), 90.25(12); N(11)−Ru−N(1), 90.34(12); N(1)−Ru−I, 83.82(8); N(21)−Ru−I, 99.77(7).

amine ruthenium complexes.[23] The Ru−I distance of 2.7195(6) Å is similar to previously reported data.[24] Comparison of the distances involving the agostic hydrogen in **9a** and **3a** (B−H(12) 1.291(34) Å and Ru−H(12) 1.667(32) Å for **9a** and B−H(4) 1.203(23) Å and Ru−H(4) 1.840(25) Å for **3a**) is in favor of a stronger agostic interaction in **9a**.

The amine hydrogens resonate, as for **8a**, as two doublets but at lower field, δ 4.67 and δ 3.42. The most important difference for the Bp ligand concerns the agostic BH, which is now trans to the iodide and observed at very high field at δ −15.9, in agreement with a strong agostic interaction. The analogous chloro complex $(Bp^{(CF3)2})RuCl(^tBuNH_2)_2$ (**10a**) can be prepared by stirring for 18 h a dichloromethane solution of **8a**. **10a** and **9a** display the same NMR data. Any attempt to generate an amido complex from **9a** or **10a**, in particular by addition of $NaNH_2$ and a THF solution of NH_3, has failed. [25]

In the absence of dihydrogen, stirring a pentane solution of **1a** with a large excess of $^tBuNH_2$ gives rise to the immediate formation of a blue solution, from which a blue solid could be isolated and characterized as $(Bp^{(CF3)2})RuH(COD)(^tBuNH_2)$ (**11a**). The structure with a κ^2 N,H coordination of the $Bp^{(CF3)2}$ ligand, as already reported for the hydrido(dihydrogen) complex **3a**, is confirmed by an X-ray determination. Crystal data are reported in Table 1, and the molecular structure is shown in Figure 3. In the absence of dihydrogen, the COD ligand cannot be hydrogenated and remains coordinated to the ruthenium, as observed in the case of the analogous phosphine complex **4a** (see above) obtained when adding PCy_3 to **1a** in the absence of

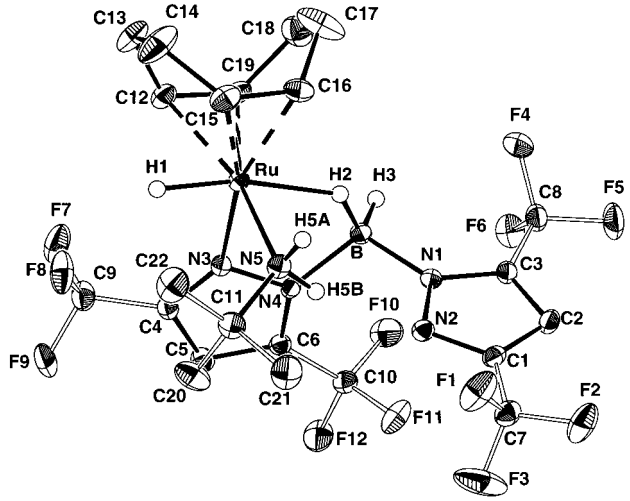


Figure 3. ZORTEP view of $(Bp^{(CF3)2})RuH(COD)(^tBuNH_2)$ (**11a**). Selected bond lengths (Å): Ru−H(1), 1.54(3); Ru−H(2), 1.90(3); B−H(2), 1.19(3); B−H(3), 1.08(3); Ru−N(3), 2.122(2); Ru−N(5), 2.196(2). Selected bond angles (deg): N(3)−Ru−N(5), 91.50(10); H(1)−Ru−H(2), 167.2(14).

dihydrogen. Dechelation of one pyrazolyl ring is thus favored to allow amine coordination.

Using the more sterically demanding diisopropylamine in the same conditions used for the formation of **8a**, we could not isolate any complex. However under an N_2 atmosphere, yellow crystals could be isolated and characterized by a single-crystal X-ray determination as a dinuclear species $[(Bp^{(CF3)2})RuH(^iPr_2NH)]_2(N_2)$ (**12a**) with a μ^2-bridging dinitrogen ligand. Crystal data are reported in Table 2, and the molecular structure is shown in Figure 4. Two $[(Bp^{(CF3)2})RuH(^iPr_2NH)]$ units are symmetrically bridged by the dinitrogen molecule. The $Bp^{(CF3)2}$ ligands keep a κ^3 N,N,H coordination with the agostic hydrogen trans to the hydride. The two ruthenium are connected by a linear dinitrogen ligand, characterized by a N−N distance of 1.138(8) Å. This value falls in the range characteristic of an end-on bridging dinitrogen ligand (1.1−1.2 Å).[26] The overall geometry of **12a** is in particular similar to the one reported for the dinuclear ruthenium complex $\{(NN'N)-RuCl_2)\}_2(\mu^2-N_2)$ containing the tridentate NN′N ligand, 2,6-bis[(dimethylamino)methyl]pyridine).[27] In our compound the perpendicular twisting of the two $Bp^{(CF3)2}$ ligands is also in favor of an efficient back-donation from the ruthenium to the π^* orbitals of the dinitrogen ligand. The ^1H NMR spectrum shows a singlet at very high field (δ −22.59) for the hydrides, and restricted Ru−N rotation of the amine ligand is again observed. The reactivity of **12a** will be the subject of future studies.

Arene Coordination: k^2 N,N Bonding Mode of the $Bp^{(CF3)2}$ Ligand. We have already reported that addition of benzene to **1a** under 3 bar of dihydrogen results in hydrogenation of COD into cyclohexane and coordination of benzene to the metal center to produce $(Bp^{(CF3)2})RuH(\eta^6-C_6H_6)$.[17] Addition of mesitylene to **1a**

(23) Joslin, F. L.; Johnson, M. P.; Mague, J. T.; Roundhill, D. M. *Organometallics* **1991**, *10*, 2781.
(24) Chaudret, B.; Chung, G.; Eisenstein, O.; Jackson, S. A.; Lahoz, F. J.; Lopez, J. A. *J. Am. Chem. Soc.* **1991**, *113*, 2314.
(25) Kaplan, A. W.; Ritter, J. C. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1998**, *120*, 6828.
(26) (a) Hidai, M.; Mizobe, Y. *Chem. Rev.* **1995**, *95*, 1115. (b) Leigh, G. J. *Acc. Chem. Res.* **1992**, *25*, 177.
(27) Abbenhuis, R. A. T. M.; del Rio, I.; Bergshoef, M. M.; Boersma, J.; Veldman, N.; Spek, A. L.; van Koten, G. *Inorg. Chem.* **1998**, *37*, 1749.

Table 2. Crystallographic Data for Complexes 12a, 13a, and 14a

crystal parameters	12a	13a	14a
formula	$C_{32}H_{38}B_2F_{24}N_{12}Ru_2$	$C_{19}H_{17}BF_{12}N_4Ru$	$C_{21}H_{17}BF_{12}N_4O_3Ru$
fw	1270.50	641.25	713.27
crystal system	monoclinic	monoclinic	orthorhombic
space group	*P*2/*c*	$P2_1/n$	$Pca2_1$
a, Å	12.340(2)	10.384(2)	23.922(5)
b, Å	14.324(2)	12.668(2)	9.574(2)
c, Å	27.001(3)	18.141(2)	11.463(2)
α, deg	90	90	90
β, deg	93.09(2)	103.27(2)	90
γ, deg	90	109.03(2)	90
V, Å	4765(1)	2322.5(5)	2625.4(9)
temp, K	160(2)	160(2)	160(2)
no. of data/restraints/params	6795/208/689	3593/0/349	3946/1/391
abs corr[32]	none	numerical	numerical
$T_{min} - T_{max}$		0.69−1.0	0.56−1.0
goodness of fit on F^2	1.167	1.038	1.014
R1 [$I > 2\sigma(I)$]	0.0422	0.0210	0.0425
wR2	0.0926	0.0510	0.1029
absolute structure param[36]			0.03(4)

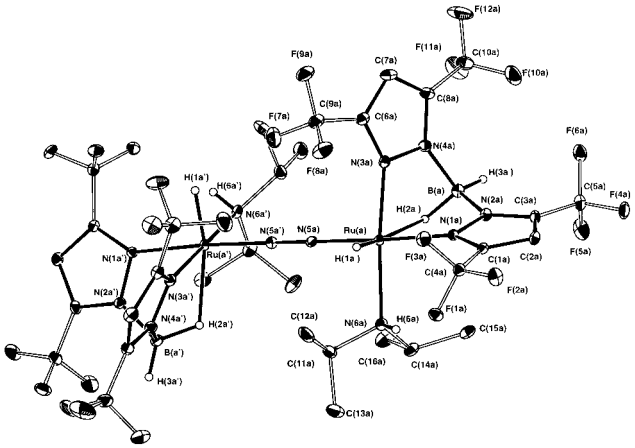


Figure 4. ZORTEP view of $[(Bp^{(CF3)2})RuH(^iPr_2NH)]_2(N_2)$ **(12a).** Selected bond lengths (Å): Ru(a)−H(1a), 1.49(5); Ru(a)−H(2a), 2.13(4); B(a)−H(2a), 1.17(4); B(a)−H(3a), 0.98 (5); Ru(a)-N(1a), 2.065 (4); Ru(a)-N(3a), 2.055 (4); Ru(a)-N(6a), 2.202(4); Ru(a)−N(5a), 1.916(4); N(5a)−N(5a′), 1.138(8). Selected bond angles (deg): N(5a)−Ru(a)−N(1a), 176.08(16); N(5a′)−N(5a)−Ru(a), 179.5(3); H(1a)−Ru(a)−H(2a), 167 2); N(3a)−Ru(a)−N(6a), 175.01(16); N(3a)−Ru(a)−N(1a), 83.99(15); N(5a)−Ru(a)−N(6a), 90.60(16); N(1a)−Ru(a)−N(6a), 92.02(16).

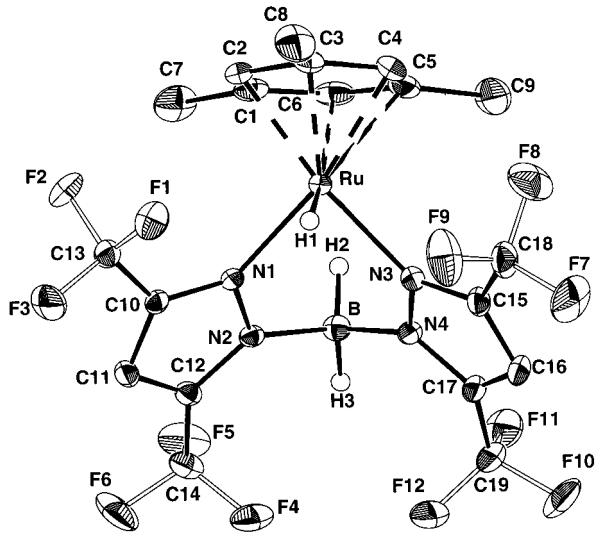
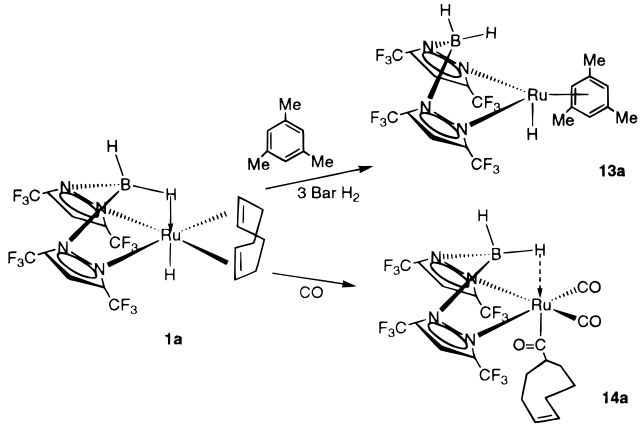


Figure 5. ZORTEP view of$(Bp^{(CF3)2})RuH(\eta^6\text{-}C_6H_3Me_3)$ (**13a**). Selected bond lengths (Å): Ru−H(1), 1.51(2); B−H(2), 1.12(2); B−H(3), 1.07(2); Ru−N(1), 2.1074 (17); Ru−N(3), 2.1101(16). Selected bond angles (deg): N(1)−Ru−N(3), 85.37(6); N(1)−Ru−H(1), 81.4(10); N(3)−Ru−H(1), 82.0(9).

produces the corresponding complex $(Bp^{(CF3)2})RuH(\eta^6\text{-}C_6H_3Me_3)$ (**13a**) (see Scheme 4). This complex was isolated as pale yellow crystals, and the X-ray structure determination gave conclusive evidence for the κ^2 N,N bonding mode of the $Bp^{(CF3)2}$ ligand. Crystal data are reported in Table 2, and the molecular structure is depicted in Figure 5. In this complex, the ruthenium reaches an 18-electron configuration without any agostic B−H−Ru bond. The two B−H bond distances are 1.12-(2) and 1.07(2) Å, thus shorter than the agostic B−H bonds previously described in **1a**, **3a**, **9a**, **11a**, and **12a** (from 1.17 to 1.29 Å). No geometrical distortion within the $Bp^{(CH3)2}$ ligand is observed, as can be seen from the N(1)−Ru−N(3) angles (85.37(6)° in **13a** and 84.2(1)° in **1a**). The ^1H NMR spectrum shows a singlet at 4.44 ppm for the aromatic protons of the mesitylene ligand, in agreement with an arene coordination to the metal center.

When the Bp^{Me2} ligand is used, the reaction is not straightforward and a mixture of unidentified compounds is observed.

Scheme 4. Reactions of 1a with Mesitylene and CO



CO Activation. From all the reactions described above, one can see that in **1a** the COD ligand is strongly bound to the Ru. Its hydrogenation by using an H_2 pressure is the best way to allow its substitution.

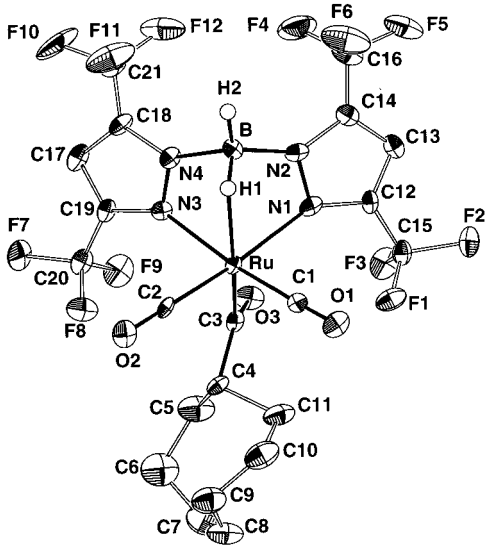


Figure 6. ZORTEP view of $(Bp^{(CF3)2})Ru(CO)_2(COC_8H_{13})$ (**14a**). Selected bond lengths (Å): Ru−H(1), 2.11(5); B−H(1), 1.03(5); B−H(2), 1.01(5); Ru−N(1), 2.426(6); Ru−N(3), 2.123(5); Ru−C(1), 1.793(6); Ru−C(2), 2.096(7); Ru−C(3), 1.968(6); C(1)−O(1), 1.084(7); C(2)−O(2), 1.282(8); C(3)−O(3), 1.130(7); C(3)−C(4), 1.538(9); C(4)−C(5), 1.345(7); C(5)−C(6), 1.632(13); C(6)−C(7), 1.537(14); C(7)−C(8), 1.106(10); C(8)−C(9), 1.471(13); C(9)−C(10), 1.602(13); C(10)−C(11), 1.440(11); C(11)−C(4), 1.581(11). Selected bond angles (deg): N(3)−Ru−C(1), 171.4(2); N(1)−Ru−C(2), 172.5(2); H(1)−Ru−C(3), 163.5(15); Ru−C(1)−O(1), 177.4(6); Ru−C(2)−O(2), 179.5(4); Ru−C(3)−O(3), 107.2(5); C(1)−Ru−C(3), 82.7(2); C(3)−Ru−C(2), 93.3(2); C(1)−Ru−C(2), 103.2(2).

However, when exposing **1a** to a CO atmosphere, the new acyl(dicarbonyl) complex $(Bp^{(CF3)2})Ru(COC_8H_{13})(CO)_2$ (**14a**) can be isolated in very high yield (see Scheme 4). It was fully characterized by spectroscopic data, and the X-ray structural determination confirms its structure shown in Figure 6. The crystal data are reported in Table 2. The ^1H and ^{13}C NMR resonances of the acyl ligand were fully assigned on the basis of 2D homonuclear and heteronuclear correlation spectra. The acyl carbon resonates at δ 231.7, whereas only one signal is observed at δ 197.4 for the two carbonyls. The cyclooctenyl ligand is characterized by eight resonances, i.e., five for the 5 CH_2 carbons between δ 24−31, two for the free olefinic carbons at δ 131.7 (J_{C-H} = 156 Hz) and 129.7 (J_{C-H} = 157 Hz), and one for the CH at 69.4 (J_{C-H} = 132 Hz). The two pyrazolyl ligands are unequivalent, as can be seen from the two singlets at δ 6.19 and 6.17 in the ^1H spectrum and the two sets of signals in the ^{19}F NMR spectrum. This nonequivalence is also reflected by the X-ray data, showing two abnormally different Ru−N distances, Ru−N(1) 2.426(6) Å and Ru−N(3) 2.123(5) Å. As a consequence, the values concerning the two carbonyls trans to these nitrogens are also different. Remarkably, the acyl presents a CO distance (1.130(7) Å) between the ones obtained for the two carbonyls (1.084(7) and 1.282(8) Å). This is also the case for the corresponding Ru−C distances: 1.968(6) Å for the acyl Ru−C(3) and 2.096(7) and 1.793(6) Å for Ru−C(2) and Ru−C(1), respectively. It is worth comparing our data with those obtained for the previously reported acyl ruthenium complexes, $Cp^*Ru(COC_{10}H_{13})(CO)_2$ [28] and $[Ru(COPh)(CO)(CNCMe_3)_2(PMe_2Ph)_2]^+$.[29] In these cases, the acyl ligand shows Ru−C distances of 2.090(6) and 2.128(10) Å and C=O distances of 1.211(7) and 1.241(12) Å, respectively. In addition, the O=C−Ru angles are 117.9(5)° and 120.2(8)°, whereas in **14a** it is reduced to 107.2(5)°. However the Ru−O(3) distance is too long (2.54 Å) to consider the acyl as an η^2-bonded ligand. Finally, it should be noted that an agostic B−H bond should allow the ruthenium to reach an 18-electron configuration. The H(1) is indeed located in the right position; however, the Ru−H(1) and B−H(1) distances of 2.11(57) and 1.03(5) Å indicate a very weak interaction by comparison with the data reported above for the complexes with a κ^3 or a κ^2 structure. Thus it seems that we have a rather unusual situation with the $Bp^{(CF3)2}$ ligand adopting a bonding mode intermediate between a κ^3 and a κ^2 structure, characterized by elongated Ru−N(3) and Ru−H(1) distances. This could be responsible for the different values measured for the two carbonyls.

The analogous complex $(Bp^{Me2})Ru(COC_8H_{13})(CO)_2$ (**14b**) could be obtained by exposing **1b** to 3 bar of CO. It should be noted that **14a**,**b** are produced in good yields. Their formation implies olefin insertion of one C=C double bond of the COD into the Ru−H bond and then CO insertion to obtain the acyl ligand. Unfortunately we could not identify any intermediate. A similar reaction was reported with a hydrido norbornadiene complex: the acyl complex $RuCl(COC_7H_9)(CO)_2(PPh_3)_2$ was obtained after treatment of $RuHCl(C_7H_8)(PPh_3)_2$ with CO.[30]

Reduction of Ketones. We have already mentioned the lack of reactivity of **1a** with $HBF_4{\cdot}Et_2O$ in agreement with an acidic behavior.[17] In this context, we have shown that the analogous $Tp^{Me2}RuH(COD)$ is active for the hydrogenation of ketones.[31] We have tested the activity of **1a** using the same conditions. The reactions were done in heptane at 80 °C under 3 bar of H_2 using a molar ratio of catalyst to substrate of 1:100. Reduction of cyclohexanone was obtained in 60% yield after 2 h (92% with $Tp^{Me2}RuH(COD)$), and total conversion was observed after 4 h. In the case of acetone, 76% conversion was reached after 15 h (63% with $Tp^{Me2}RuH(COD)$ after 2 h), whereas we did not observe any conversion of acetophenone after 19 h (6% with $Tp^{Me2}RuH(COD)$ after 15 h). Thus it appears that **1a** and $Tp^{Me2}RuH(COD)$ have a comparable activity, **1a** being slightly less active.

Conclusion

We have shown that $(Bp^{(CF3)2})RuH(COD)$ (**1a**) is a valuable starting material for $(Bp^{(CF3)2})Ru$ complexes. Hydrogenation is the easiest way to force COD elimination, and the new compounds are available in high yields. We have demonstrated that this Bp ligand has the capacity to coordinate to the metal in three different modes, κ^3 N,N,H, κ^2 N,H, or κ^2 N,N. This is exemplified

(28) Eisenstadt, A.; Frolow, F.; Efraty, A. *J. Chem. Soc., Dalton Trans.* **1982**, 1013.
(29) Dauter, Z.; Mawby, R. J.; Reynolds, C. D.; Saunders: D. R.; Hansen, L. K. *J. Chem. Soc., Dalton Trans.* **1987**, 27.
(30) Dekleva, T.; James, B. R. *J. Chem. Soc., Chem. Commun.* **1983**, 1350.
(31) Vicente, C.; Shul'pin, G. B.; Moreno, B.; Sabo-Etienne, S.; Chaudret, B. *J. Mol. Catal.* **1995**, *98*, L5.

by the preparation, in the absence of dihydrogen, of the monohydride complex ($Bp^{(CF3)2}$)RuH(COD)(PCy_3) (**4a**) with a κ^2 N,H bonding mode of the Bp ligand, whereas under H_2 the hydrido(dihydrogen) complex ($Bp^{(CF3)2}$)-RuH(H_2)(PCy_3) (**5a**) is formed with rechelation of the pendant pyrazolyl ring and hydrogenation of the COD ligand. It should be noted that stabilization of dihydrogen complexes is again favored by the use of bulky phosphines. From all the results presented in this paper, it can be seen that the diagnostic of the presence of an agostic Ru−H−B bond and the estimation of its strength has to be ascertained by different criteria (X-ray data, NMR, IR).

Disappointingly, no specific properties can be attributed to the use of fluorinated substituents since a similar chemistry has been observed when using the nonfluorinated Bp^{Me2} ligand. This is also illustrated by the comparable catalytic activity with the analogous Tp^{Me2}RuH(COD) complex. However, reactions are cleaner and stabilization is enhanced, allowing the isolation of a new series of complexes.

Experimental Section

All reactions and workup procedures were performed under argon using conventional vacuum line and Schlenck tube techniques. All solvents were freshly distilled from standard drying agents and thoroughly degassed under argon before use. Microanalysis were performed by the Laboratoire de Chimie de Coordination Microanalytical Service. Infrared spectra were obtained as Nujol mulls on a Perkin-Elmer 1725 FT-IR spectrometer. NMR spectra were acquired on Bruker AC 200, AM 250, or AMX 400 spectrometers. $RuCl_3 \cdot 3H_2O$ was purchased from Johnson Matthey Ltd. The following chemicals were prepared according to published procedures: Na[H_2B-(3,5-$(CF_3)_2$-pz)$_2$] ($NaBp^{(CF3)2}$),[12] tri-*n*-pyrrolylphosphine ($Ppyl_3$),[21a] ($Bp^{(Me)2}$)RuH(COD).[8]

($Bp^{(CF3)2}$)RuH(COD) (1a). Ethanol (60 mL) was added to [$RuCl_2$(COD)]$_n$ (1.27 g, 4.52 mmol), Na[H_2B(3,5-$(CF_3)_2$-pz)$_2$] (2.00 g, 4.52 mmol), and sodium hydroxide (0.18 g, 4.52 mmol). This mixture was heated at 80 °C for 1 h. The green mixture was allowed to cool and was filtered. Removal of the solvent to a volume of 30−40 mL produced a green precipitate, which was collected by filtration. The green solid was washed with ethanol (2 × 3 mL) and dried under vacuum. Filtrates were stored at −15 °C, and a small additional amount of green crystals was obtained. Yield: 75%.

IR (Nujol): 2555, 2128, 2028 cm^{-1} (B−H, Ru−H). ^{1}H NMR (C_6D_6, 200 MHz): δ 6.00 (s, 2H, H of pyrazolyl rings), 3.80 (m, 2H, CH═CH), 3.01 (m, 2H, CH═CH), 2.19 (m, 2H, H^{exo} of COD), 2.07 (m, 2H, H^{exo} of COD), 1.59 (m, 2H, H^{endo} of COD), 1.42 (m, 2H, H^{endo} of COD), −7.30 (s, 1H, RuH). ^{1}H NMR (C_7D_8, 400 MHz, 243 K): δ 4.9 (br, 1H, BH), −4.7 (br, 1H, Ru−H−B), −7.30 (s, 1H, RuH). ^{13}C{^{1}H} NMR (C_7D_8, 100 MHz, 243 K): δ 145.10 (q, J_{C-F} = 39.9 Hz, *C*CF_3), 139.05 (q, J_{C-F} = 41.5 Hz, *C*CF_3), 120.59 (q, J_{C-F} = 274.1 Hz, CF_3), 119.71 (q, J_{C-F} = 270.9, CF_3), 108.3 (s, CH of pyrazolyl rings), 74.2 (s, CH of COD), 72.33 (s, CH of COD), 32.58 (s, CH_2 of COD), 30.17 (s, CH_2 of COD). ^{19}F{^{1}H} NMR (C_6D_6, 188 MHz): δ −61.36, −61.96. DCI.MS (carrier gas NH_3): *m/e* 646 (100%, M + NH_3), 645 (68%, M − H + NH_3), 629 (22%, M^+), 628 (19%, M − H). Anal. Calcd for $C_{18}H_{17}BF_{12}N_4Ru$: C 34.35, H 2.73, N 8.90. Found: C 34.35, H 2.55, N 8.69.

($Bp^{(CF3)2}$)RuH(H_2)(PCy_3)$_2$ (2a). A solution of ($Bp^{(CF3)2}$)RuH-(COD) (150 mg, 0.24 mmol) and tricyclohexylphosphine (134 mg, 0.48 mmol) in pentane (10 mL) was introduced into a Fischer−Porter bottle and pressurized to 3 bar of H_2. The reaction mixture was stirred for 18 h at room temperature, over which time a white precipitate separated. It was filtered off, washed three times with pentane (1 mL), and dried under vacuum. Yield: 80%.

IR (Nujol): 2514, 2149 and 2007 cm^{-1} (B−H, Ru−H). ^{1}H NMR (C_6D_6, 200 MHz): δ 6.76 (s, 1H, H of pyrazolyl ring (not linked to Ru)), 6.53 (s, 1H, H of pyrazolyl ring (linked to Ru)), 5.0 (vbr, BH), 1.85−0.84 (m, 66H, PCy_3), −2.70 (br, 1H, Ru−H−B), −13.59 (t, J_{P-H} = 13 Hz, RuH(H_2)). T_{1min} at 270 K (δ −13.59, 400 MHz) 27 ms. ^{19}F{^{1}H} NMR (C_6D_6, 188 MHz): δ −60.55, −61.38, −63.65, −63.74. ^{31}P{^{1}H} NMR (C_6D_6, 81 MHz): δ 51.2, 46.4 (J_{P-P} = 251 Hz). Anal. Calcd for $C_{46}H_{73}$-$BF_{12}N_4P_2Ru$: C 50.96, H 6.80, N 5.17. Found: C 50.93, H 6.19, N 5.04.

($Bp^{(CF3)2}$)RuH(H_2)(P^iPr_3)$_2$ (3a). A solution of ($Bp^{(CF3)2}$)RuH-(COD) (150 mg, 0.24 mmol) and triisopropylphosphine (134 mg, 0.48 mmol) in pentane (10 mL) was introduced into a Fischer−Porter bottle and pressurized to 3 bar of H_2. The reaction mixture was stirred for 18 h at room temperature. The resulting blue solution was evaporated to dryness, and 2 mL of ethanol was added. After filtration, the solid was dissolved in 2 mL of pentane. After cooling overnight, the complex was isolated as white crystals. Yield: 71%.

IR (Nujol): 2498, 2143 and 2008 cm^{-1} (B−H, Ru−H). ^{1}H NMR (C_6D_6, 200 MHz): δ 6.72 (s, 1H, H of pyrazolyl ring (not linked to Ru)), 6.48 (s, 1H, H of pyrazolyl ring (linked to Ru)), 5.0 (vbr, BH), 2.00 (m, 6H, CH of P^iPr_3), 0.89 (m, 36H, CH_3 of P^iPr_3), −2.90 (br, 1H, Ru−H−B), −13.58 ppm (t, J_{P-H} = 13.8 Hz, RuH(H_2)); T_{1min} at 250 K (δ −13.59, 400 MHz) 32 ms. ^{19}F-{^{1}H} NMR (C_6D_6, 188 MHz): δ −61.02, −61.78, −63.83, −64.25. ^{31}P{^{1}H} NMR (C_6D_6, 81 MHz): δ 58.1, 55.0 (J_{P-P} = 252 Hz). Anal. Calcd for $C_{28}H_{49}BF_{12}N_4P_2Ru$: C 39.86, H 5.81, N 6.64. Found: C 40.14, H 5.61, N 6.68.

($Bp^{(CF3)2}$)RuH(COD)(PCy_3) (4a). A solution of ($Bp^{(CF3)2}$)-RuH(COD) (150 mg, 0.24 mmol) and tricyclohexylphosphine (101 mg, 0.36 mmol) in pentane (10 mL) was stirred for 4 days at room temperature. The resulting blue solution was evaporated to dryness, and 2 mL of ethanol was added. A pale green solid precipitated. It was filtered off, washed with 2 mL of pentane, and dried under vacuum. Yield: 74%.

IR (Nujol): 2520, 2095 and 1973 cm^{-1} (B−H, Ru−H). ^{1}H NMR (C_6D_6, 200 MHz): δ 6.81 (s, 1H, H of pyrazolyl ring (not linked to Ru)), 6.25 (s, 1H, H of pyrazolyl ring (linked to Ru)), 4.67, 4.49, 3.56, 3.13 (m, 4H, CH═CH), 2.40−0.80 (m, 8H of COD and 33H of PCy_3), −0.40 (br, 1H, Ru−H−B), −7.66 (d, J_{P-H} = 21.4 Hz, RuH). ^{31}P{^{1}H} NMR (C_6D_6, 81 MHz): δ 33.4 (s). ^{19}F{^{1}H} NMR (C_6D_6, 188 MHz): δ −60.84, −61.40, −63.71, −64.12. Anal. Calcd for $C_{36}H_{50}N_4BF_{12}PRu$: C 47.53, H 5.55, N 6.16. Found: C 47.42, H 5.51, N 6.05.

($Bp^{(CF3)2}$)RuH(H_2)(PCy_3) (5a). A solution of ($Bp^{(CF3)2}$)RuH-(COD)(PCy_3) (200 mg, 0.23 mmol) in toluene (10 mL) was introduced into a Fischer−Porter bottle and pressurized to 3 bar of H_2. The reaction mixture was stirred for 5 h at 60 °C. The resulting yellow solution was evaporated to dryness, and 2 mL of ethanol was added. A pale yelow solid precipitated. It was filtered off and dried under vacuum. Yield: 72%.

IR (Nujol): 2546, 2064 and 1988 cm^{-1} (B−H, Ru−H). ^{1}H NMR (C_6D_6, 200 MHz): δ 6.13 (s, 2H, H of pyrazolyl rings), 1.80−0.84 (m, 33H, H of PCy_3), −12.72 (d, J_{P-H} = 17.9 Hz, RuH(H_2)); T_{1min} at 260 K, C_7D_8 (δ −12.55, 400 MHz) 25 ms. ^{19}F{^{1}H} NMR (C_6D_6, 188 MHz): δ −61.43, −63.00. ^{31}P{^{1}H} NMR (C_6D_6, 81 MHz): δ 73.1 (s). Anal. Calcd for $C_{28}H_{40}BF_{12}N_4$-PRu: C 41.85, H 5.03, N 6.97. Found: C 41.04, H 4.61, N 6.06.

($Bp^{(CF3)2}$)RuH(PPh_3)$_2$ (6a). A solution of ($Bp^{(CF3)2}$)RuH-(COD) (120 mg, 0.19 mmol) and triphenylphosphine (100 mg, 0.38 mmol) in pentane (10 mL) was introduced into a Fischer−Porter bottle. This mixture was pressurized to 3 bar of H_2 and stirred for 17 h at room temperature, over which time a yellow solid precipitated. It was filtered off, washed twice with pentane (2 mL), and dried under vacuum. Yield: 90%.

IR (Nujol): 2537, 2109 and 2027 cm^{-1} (B−H, Ru−H). ^{1}H NMR (C_6D_6, 200 MHz): δ 7.50 (m, 12H, PPh_3), 6.81 (m, 18H, PPh_3), 5.76 (s, 2H, H of pyrazolyl rings), −16.16 (t, J_{P-H} = 28

Hz, 1H, RuH). ^{19}F NMR (C_6D_6, 188 MHz): δ −61.14, −62.46. ^{31}P{^{1}H} NMR (C_6D_6, 81 MHz): δ 68.97 (s). Anal. Calcd for $C_{46}H_{35}BF_{12}N_4P_2Ru$: C 52.83, H 3.38, N 5.36. Found: C 52.89, H 3.32, N 5.15.

(Bp$^{(CF3)2}$)RuH(Ppyl$_3$)$_2$ (7a). A solution of (Bp$^{(CF3)2}$)RuH(COD) (120 mg, 0.19 mmol) and tri-*n*-pyrrolylphosphine (Ppyl$_3$) (87 mg, 0.38 mmol) in pentane (8 mL) was introduced into a Fischer−Porter bottle. This mixture was pressurized to 3 bar of H_2 and stirred for 17 h at room temperature. Removal of the solvent produced a white solid, which was washed with pentane (2 mL) and dried under vacuum. Yield: 76%.

IR (Nujol): 2566, 2099 and 1953 cm^{-1} (B−H, Ru−H). ^{1}H NMR (C_6D_6, 200 MHz): δ 6.46 (m, 12H, Ppyl$_3$), 5.97 (m, 12H, Ppyl$_3$), 5.90 (s, 2H, H of pyrazolyl rings), −14.31 (t, J_{P-H} = 34 Hz, 1H, RuH). ^{19}F{^{1}H} NMR (C_6D_6, 188 MHz): δ −61.53, −62.89. ^{31}P{^{1}H} NMR (C_6D_6, 81 MHz): δ 132.0 (s). Anal. Calcd for $C_{34}H_{29}BF_{12}N_{10}P_2Ru$: C 41.69, H 2.99, N 14.30. Found: C 41.75, H 2.71, N 13.52.

(Bp$^{(CF3)2}$)RuH(^{t}BuNH$_2$)$_2$ (8a). A solution of (Bp$^{(CF3)2}$)RuH(COD) (500 mg, 0.795 mmol) and *tert*-butylamine (185.5 μL, 1.75 mmol) in pentane (30 mL) was introduced into a Fischer−Porter bottle and pressurized to 3 bar of H_2. The reaction mixture was stirred for 20 h at room temperature, over which time an orange solid precipitated. It was filtered off, washed with pentane (2 mL), and dried under vacuum. Yield: 30%.

IR (Nujol): 2540, 2085 and 1929 cm^{-1} (B−H, Ru−H). ^{1}H NMR (C_6D_6, 200 MHz): δ 6.30 (s, 2H, H of pyrazolyl rings), 4.75 (br, BH), 3.33 (d, 2H, J_{H-H} = 12 Hz, NH$_2$), 1.24 (d, 2H, J_{H-H} = 12 Hz, NH$_2$), 0.56 (s, 18H, ^{t}Bu), −26.04 (s, 1H, RuH). ^{19}F{^{1}H} NMR (C_6D_6, 188 MHz): δ −61.27, −62.15. Anal. Calcd for $C_{18}H_{27}BF_{12}N_6Ru$: C 32.40, H 4.08, N 12.59. Found: C 32.54, H 3.45, N 12.44.

(Bp$^{(CF3)2}$)RuI(^{t}BuNH$_2$)$_2$ (9a). A solution of (Bp$^{(CF3)2}$)RuH(^{t}BuNH$_2$)$_2$ (30 mg, 0.045 mmol) and methyliodide (2.8 μL, 0.045 mmol) in toluene (5 mL) was stirred for 18 h at room temperature. After cooling to 0 °C a yellow solid precipitated. It was filtered off and dried under vacuum. Yield: 80%.

^{1}H NMR (C_6D_6, 200 MHz): δ 6.15 (s, 2H, H of pyrazolyl rings), 4.67 (d, 2H, J_{H-H} = 13 Hz, NH$_2$), 3.8 (br, BH), 3.42 (d, 2H, J_{H-H} = 13 Hz, NH$_2$), 0.78 (s, 18H, H of ^{t}Bu), −15.90 (br, 1H, Ru−H−B). ^{19}F NMR (C_6D_6, 188 MHz): δ −59.16 (s, C(5)-CF_3), −61.66 (s, C(3)CF_3). Anal. Calcd for $C_{18}H_{26}BF_{12}N_6IRu$: C 27.26, H 3.30, N 10.60. Found: C 27.49, H 2.89, N 10.47. IR (Nujol): 2551 and 1690 cm^{-1} (B−H).

(Bp$^{(CF3)2}$)RuCl(^{t}BuNH$_2$)$_2$ (10a). A solution of (Bp$^{(CF3)2}$)RuH(^{t}BuNH$_2$)$_2$ (30 mg, 0.045 mmol) in dichloromethane (5 mL) was stirred for 18 h at room temperature. After cooling to 0 °C an orange solid precipitated. The solid was filtered off and dried under vacuum. Yield: 70%.

^{1}H NMR (C_6D_6, 200 MHz): δ 6.14 (s, 2H, H of pyrazolyl rings), 4.64 (d, 2H, J_{H-H} = 13 Hz, NH$_2$), 3.06 (d, 2H, J_{H-H} = 13 Hz, NH$_2$), 0.81 (s, 18H, H of ^{t}Bu), −18 (br, Ru−H−B). ^{19}F-{^{1}H} NMR (C_6D_6, 188 MHz): δ −60.93, −61.76. Anal. Calcd for $C_{18}H_{26}BF_{12}N_6ClRu$: C 30.81, H 3.73, N 11.98. Found: C 31.08, H 3.17, N 11.68.

(Bp$^{(CF3)2}$)RuH(COD)(^{t}BuNH$_2$) (11a). A solution of (Bp$^{(CF3)2}$)-RuH(COD) (90 mg, 0.143 mmol) and *tert*-butylamine (455 μL, 4.29 mmol) in pentane (10 mL) was stirred for 40 min at room temperature. The resulting blue solution was filtered off and evaporated to dryness to give a blue solid. Yield: 90%.

IR (Nujol): 2522, 2157 and 2021 cm^{-1} (B−H, Ru−H). ^{1}H NMR (C_6D_6, 200 MHz): δ 6.67 (s, 1H, H of pyrazolyl ring (not linked to Ru), 6.17 (s, 1H, H of pyrazolyl ring (linked to Ru), 3.98 (d, 1H, J_{H-H} = 12 Hz, NH), 3.54 (m, 1H, CH=CH), 2.79 (m, 1H, CH=CH), 2.64 (m, 1H, CH=CH), 2.47 (m, 1H, CH=CH), 2.15 (m, 4H, H^{exo} of COD), 1.47 (m, 4H, H^{endo} of COD), 0.95 (s, 9H, H of ^{t}Bu), 0.59 (d, 1H, J_{H-H} = 12 Hz, NH), −5.44 (s, 1H, RuH). ^{19}F{^{1}H} NMR (C_6D_6, 188 MHz): δ −61.27, −62.15. Anal. Calcd for $C_{22}H_{28}BF_{12}N_5Ru$: C 37.62, H 4.02, N 9.97. Found: C 37.53, H 3.92, N 9.77.

[(Bp$^{(CF3)2}$)RuH(^{i}Pr$_2$NH)]$_2$(μ-N$_2$) (12a). A solution of (Bp$^{(CF3)2}$)RuH(COD) (200 mg, 0.318 mmol) and diisopropylamine (98.1 μL, 0.70 mmol) in pentane (10 mL) was introduced into a Fischer−Porter bottle and pressurized to 3 bar of H_2. The reaction mixture was stirred for 20 h at room temperature and was filtered off into a new Fischer−Porter bottle. The solution was pressurized to 3 bar of N_2 and stirred for 20 h at room temperature. After cooling to 0 °C, a yellow solid precipitated. The solid was filtered off, washed with pentane (3 mL), and dried under vacuum. Yield: 32%.

IR (Nujol): 2541 and 2068 cm^{-1} (B−H, Ru−H). ^{1}H NMR (C_6D_6, 250 MHz): δ 6.20 (s, 2H, H of pyrazolyl rings), 6.12 (s, 2H, H of pyrazolyl rings), 4.50 (br, BH), 2.67 (m, 2H, CH of ^{i}Pr), 2.40 (m, 2H, CH of ^{i}Pr), 2.20 (d, 6H, J_{H-H} = 7 Hz, CH$_3$ of ^{i}Pr), 2.11 (d, 2H, NH), 1.12 (d, 6H, J_{H-H} = 6 Hz, CH$_3$ of ^{i}Pr), 0.59 (d, 6H, J_{H-H} = 7 Hz, CH$_3$ of ^{i}Pr), 0.27 (d, 6H, J_{H-H} = 6 Hz, CH$_3$ of ^{i}Pr), −22.59 (s, 1H, RuH). ^{19}F{^{1}H} NMR (C_6D_6, 188 MHz): δ −61, −63.14. Anal. Calcd for $C_{32}H_{40}B_2F_{24}N_{12}Ru_2$: C 30.20, H 3.17, N 13.21. Found: C 30.22, H 3.24, N 12.94.

(Bp$^{(CF3)2}$)RuH(η^6-C$_6$H$_3$Me$_3$) (13a). A solution of (Bp$^{(CF3)2}$)-RuH(COD) (150 mg, 0.24 mmol) in 2 mL of mesitylene was introduced into a Fischer−Porter bottle and presurized to 3 bar of H_2. The reaction mixture was stirred for 17 h at room temperature. The resulting blue solution was evaporated to dryness, and 10 mL of pentane was added. After cooling to −15 °C for 2 days, the complex was isolated as pale yellow crystals. Yield: 75%.

IR (Nujol): 2550, 2453 and 1994 cm^{-1} (B−H, Ru−H). ^{1}H NMR (C_6D_6, 200 MHz): δ 6.39 (s, 2H, H of pyrazolyl rings), 4.44 (s, 3H of mesitylene), 1.53 (s, 9H, Me of mesitylene), −4.88 (s, 1H, RuH). ^{19}F{^{1}H} NMR (C_6D_6, 188 MHz): δ −60.97, −61.72. Anal. Calcd for $C_{19}H_{17}BF_{12}N_4Ru$: C 35.58, H 2.68, N 8.74. Found: C 35.78, H 2.24, N 8.63.

(Bp$^{(CF3)2}$)Ru(COC$_8$H$_{13}$)(CO)$_2$ (14a). A solution of (Bp$^{(CF3)2}$)-RuH(COD) (120 mg, 0.19 mmol) in pentane (12 mL) was introduced into a Fischer−Porter bottle and pressurized to 1 bar of CO. The reaction mixture was stirred for 15 h at room temperature. The resulting yellow solution was evaporated to 4 mL, and after cooling overnight to − 30 °C, the complex was isolated as white crystals. Yield: 76%.

IR (Nujol): 2564 (B−H), 2060, 1995 (CO), 1691 (C=O) cm^{-1}. ^{1}H NMR (C_6D_6, 400 MHz): δ 6.19 (s, 1H, H of pyrazolyl rings), 6.17 (s, 1H, H of pyrazolyl rings), 5.76 (m, 1H,^{8} CH=CH), 5.63 (m, 1H,^{7} CH=CH), 4.3 (br, BH), 3.21 (m, 1H,^{4} C$_8$H$_{13}$), 2.59 (m, 1H,^{11} C$_8$H$_{13}$), 2.34 (m, 2H,^{5,6} C$_8$H$_{13}$), 2.04 (m, 1H^6 and 2H,^{9} C$_8$H$_{13}$), 1.73 (m, 3H^{5,10,11}, C$_8$H$_{13}$), 1.50 (m, 1H,^{10} C$_8$H$_{13}$). ^{13}C-{^{1}H} gated NMR (C_6D_6, 100 MHz): δ 231.7 (C=O), 197.4 (CO), 145.0 (q, J_{C-F} = 40.3 Hz, *C*CF$_3$), 140.0 (q, J_{C-F} = 41.3 Hz, *C*CF$_3$), 131.7 (d, $^1J_{C-H}$ = 155.8 Hz, C,^{8} C$_8$H$_{13}$), 129.7 (d, $^1J_{C-H}$ = 156.8 Hz, C,^{7} C$_8$H$_{13}$), 120.1 (q, J_{C-F} = 270.4 Hz, CF$_3$), 119.4 (q, J_{C-F} = 271.8, CF$_3$), 109.2 (d,$^1J_{C-H}$ = 188.0 Hz, CH of pyrazolyl rings), 69.4 (d, $^1J_{C-H}$ = 131.1 Hz, C,^{4} C$_8$H$_{13}$), 30.7 (t,$^1J_{C-H}$ = 129.4 Hz, C,^{5} C$_8$H$_{13}$), 29.9 (t,$^1J_{C-H}$ = 126.6 Hz, C,^{11} C$_8$H$_{13}$), 28.7 (t,$^1J_{C-H}$ = 122.2 Hz, C,^{10} C$_8$H$_{13}$), 26.8 (t,$^1J_{C-H}$ = 125.3 Hz, C,^{9} C$_8$H$_{13}$), 24.2 (t,$^1J_{C-H}$ = 131.1 Hz, C,^{6} C$_8$H$_{13}$). ^{19}F-{^{1}H} NMR (C_6D_6, 188 MHz): δ −61.66, −61.68, −62.34, −62.42. Anal. Calcd for $C_{21}H_{17}BN_4F_{12}O_3Ru$: C 35.37, H 2.41, N 7.86. Found: C 35.36, H 2.29, N 7.89.

(Bp$^{(Me)2}$)RuH(H$_2$)(PCy$_3$)$_2$ (2b) and (Bp$^{(Me)2}$)RuH(H$_2$)-(PCy$_3$) (5b). A solution of (Bp$^{(Me)2}$)RuH(COD) (80 mg, 0.193 mmol) and PCy$_3$ (185.5 μL, 1.75 mmol) in pentane (10 mL) was introduced into a Fischer−Porter bottle and pressurized to 3 bar of H_2. The reaction mixture was stirred for 18 h at room temperature, over which time a white solid precipitated. It was filtered off, washed twice with pentane (1 mL), and dried under vacuum. The solid was shown by NMR data to be a mixture of **2b** and **5b** in a 2:3 ratio.

2b. ^{1}H NMR (C_6D_6, 200 MHz): δ 6.03 (s, 1H, H of pyrazolyl rings), 5.78 (s, 1H, H of pyrazolyl rings), 2.58 (s, 3H, Me), 2.45 (s, 3H, Me), 2.37 (s, 3H, Me),), 1.95 (s, 3H, CH$_3$ Me), −3.2 (br, Ru−H−B), −12.93 (t, 3H, J_{P-H} = 14 Hz, RuH(H$_2$)); T_{1min} at

253 K (δ −12.95, 300 MHz) 21 ms. $^{31}P\{^1H\}$ NMR (C_6D_6, 81 MHz): δ 51.98.

5b. ^1H NMR (C_6D_6, 200 MHz): δ 5.54 (s, 2H, H of pyrazolyl rings), 2.25 (s, 6H Me), 2.14 (s, 6H, Me), −12.60 (d, 3H, J_{P-H} = 17 Hz, RuH(H_2)); T_{1min} at 253 K (δ −12.65, 300 MHz) 17 ms. $^{31}P\{^1H\}$ NMR (C_6D_6, 81 MHz): δ 75.57 (s).

($Bp^{(Me)2}$)RuH(PPh_3)(COD) (4b) and ($Bp^{(Me)2}$)RuH(PPh_3)$_2$ (6b). A solution of ($Bp^{(Me)2}$)RuH(COD) (90 mg, 0.218 mmol) and triphenylphosphine (114.2 mg, 0.433 mmol) in pentane (10 mL) was introduced into a Fischer−Porter bottle and pressurized to 3 bar of H_2. The reaction mixture was stirred for 17 h at room temperature. The solution was then filtered off. Evaporation to dryness gave a yellow solid, which was washed with 10 mL of ether. The resulting white solid was dried under vacuum. It was shown to be, by NMR data, a mixture of **4b** and **6b** in a 1:1.8 ratio.

4b. ^1H NMR (C_6D_6, 200 MHz): δ 7.73−7.01(m, 30H, PPh_3), 5.42 (s, 1H, H of pyrazolyl rings), 5.12 (s, 1H, H of pyrazolyl rings), 4.25 (br, BH), 3.55, 3.04, 2.68, 2.64 (m, 4H, CH=CH), 2.5−0.5 (m, 8H, COD), 2.18 (s, 3H, Me), 2.12 (s, 3H, Me), 2.09 (s, 3H, Me), 1.62 (s, 3H, Me), −0.59 (br, Ru−H−B), −12.06 (d, 1H, J_{P-H} = 27 Hz, RuH). $^{31}P\{^1H\}$ NMR (C_6D_6, 81 MHz): δ 73.47 (s).

6b. ^1H NMR (C_6D_6, 200 MHz): δ 5.09 (s, 2H, H of pyrazolyl rings), 2.11 (s, 6H, Me), 1.65 (s, 6H, Me), −16.90 (t, H, J_{P-H} = 27.5 Hz, RuH). $^{31}P\{^1H\}$ NMR (C_6D_6, 81 MHz): δ 70.83 (s).

($Bp^{(Me)2}$)Ru(COC_8H_{13})(CO)$_2$ (14b). A solution of ($Bp^{(CH3)2}$)-RuH(COD) (46 mg, 0.11 mmol) in pentane (5 mL) was introduced into a Fischer−Porter bottle and pressurized to 3 bar of CO. The reaction mixture was stirred for 18 h at room temperature. The resulting solution was filtered off and evaporated to dryness to give a yellow solid. Yield: 63%.

IR (Nujol): 2042, 1974 and 1735 cm^{-1} (CO). ^1H NMR (C_6D_6, 200 MHz): δ 5.63 (m, 2H, C_8H_{13}), 5.40 (s, 1H, H of pyrazolyl ring), 5.38 (s, 1H, H of pyrazolyl ring), 3.23 (m, 1H, C_8H_{13}), 2.12 (s, 3H, Me), 2.10 (s, 3H, Me), 1.97 (s, 6H, Me), 2.3−1.5 (m, 10H, C_8H_{13}). Anal. Calcd for $C_{21}H_{29}BN_4O_3Ru$: C 50.71, H 5.88, N 11.26. Found: C 50.63, H 5.33, N 11.08.

Crystal Data. Data were collected at low temperature on a Stoe imaging plate diffraction system (IPDS), equipped with an Oxford Cryosystems Cryostream cooler device and using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The final unit cell parameters were obtained by least-squares refinement of a set of 5000 reflections, and crystal decay was monitored by measuring 200 reflections by image. No fluctuation of the intensity was observed over the course of the data collection. Numerical correction absorptions[32] were applied for the structures **3a**, **9a**, **11a**, **13a**, and **14a**, by using a set of symmetry equivalent reflections selected with the criterion [$I > 3\sigma(I)$] such that all directions of reciprocal space are equally represented. All the structures have been solved by direct methods using SIR92[33] and refined by least-squares procedures on F^2 with the aid of (SHELXL97),[34] by minimizing the function $\sum w(F_o^2 - F_c^2)^2$, where F_o and F_c are respectively the observed and calculated structure factors. The atomic scattering factors were taken from International Tables for X-Ray Crystallography.[35] Hydrogens were located on a difference Fourier maps and refined in a riding model, except for the hydrides and other specific hydrogen atoms, which were isotropically refined without any restraint applied on interatomic distances or angles. For all the structures non-hydrogen atoms were anisotropically refined, and in the last cycles of refinement a weighting scheme was used, where weights are calculated from the following formula: $w=1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$. The structure of **14a** has been solved in the enantiomorph group $Pca2_1$. The absolute configuration was assigned without ambiguity on the basis of the refinement of the Flack enantiopole parameter X.[36] This parameter is sensitive to the polarity of the structure and was found close to 0 (0.03(4)), which clearly indicates the correctness of the enantiomer which has been refined. Drawing of the molecules were performed with the program ZORTEP,[37] with 50% probability displacement ellipsoids for non-hydrogen atoms. Further details on the crystal structure investigation are available on request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB−Cambridge, UK, on quoting the full journal citation.

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Supporting Information Available: X-ray structural information. An X-ray crystallographic file in CIF format is available. This material is available free of charge via the Internet at http://pubs.acs.org.

OM000199O

(32) X-SHAPE (revision 1.01) July 1996. *A Crystal Optimisation For numerical Correction* STOE and Cie. (X-SHAPE is based on the Program "HABITUS" by Dr Wolfang Herrendorf, Institüt für Anorganische Chemie, Universitât GIESSEN).

(33) Altomare, A.; Cascarano, G.; Giacovazzo, G.; Guagiardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 435.

(34) Sheldrick, G. M. *SHELXL97. Program for the refinement of Crystal Structures*. University of Göttingen, Germany, 1997.

(35) *International tables for X-ray crystallography*; Kynoch Press: Birmingham, England, 1974; Vol IV.

(36) Flack H D *Acta Crystallogr.* **1983**, *A39*, 876.

(37) Zolnaï, L. *ZORTEP, Graphical Program for X-ray Structures Analysis;* University of Heidelberg, Germany, 1998.