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Synthesis and Reactivity of the Ru^{III} Complexes [RuTp(PR$_3$)Cl$_2$] − Precursors for RuTp Dihydrogen Complexes

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The air-sensitive DMF-containing intermediate [RuTp(PR$_3$)(Cl)(DMF)] is formed by refluxing a DMF solution of [RuTp(COD)Cl] (**1**) in the presence of at least 1 equiv. of PR$_3$ (PR$_3$ = PPh$_3$, PPh$_2$*i*Pr, P*i*Pr$_3$, and PCy$_3$). On exposure to air in the presence of CCl$_4$, this complex is readily converted into the respective Ru^{III} complexes [RuTp(PR$_3$)Cl$_2$] (**2a**–**d**). These compounds are air-stable, readily accessible, permit easy variations as far as the electronic and steric properties of the PR$_3$ co-ligands are concerned, and are reducible to a variety of Ru^{II}Tp complexes. Treatment of **2** with NaBH$_4$ affords dihydrogen compounds of the type [RuTp(PR$_3$)(H)(η^2-H$_2$)]. Reduction of **2** can also be accomplished with Zn in the presence of CH$_3$CN and pyridine, which affords the diamagnetic Ru^{II} compounds [RuTp(PR$_3$)(CH$_3$CN)$_2$]$^+$ (**4a**–**c**) and [RuTp(PR$_3$)(py)Cl] (**5**). X-ray structures of representative complexes are presented.

Introduction

In our continuing systematic studies of the chemistry of ruthenium trispyrazolylborate (Tp) complexes[1] we have shown that [RuTp(PCy$_3$)(Cl)(DMF)] reacts with MeOH or EtOH in the presence of air to afford the Ru^{III} alkoxide complexes [RuTp(PCy$_3$)(Cl)(OR)] (R = Me, Et).[2] The formation of alkoxy compounds was restricted to very basic phosphanes, however, and failed, for instance, in the case of PPh$_3$. Nevertheless, these complexes turned out to be very useful precursors for a couple of new Ru^{II} complexes of the types [RuTp(PCy$_3$)(Cl)L] [L = CH$_3$CN, pyridine, CO, P(OMe)$_3$, PMe$_3$] and [RuTp(PCy$_3$)(Cl)(=C=CHR)] (R = Ph, COOEt, SiMe$_3$, *n*Bu). In the present contribution, we sought a synthetic route to obtain alternative Ru^{III}Tp precursors that are both air-stable, readily accessible, reducible to Ru^{II}Tp complexes, and permit easy variations as far as the PR$_3$ co-ligands are concerned. We report here the synthesis, characterization, and reactivity of the dichloro Ru^{III} complexes [RuTp(PR$_3$)Cl$_2$] (PR$_3$ = PPh$_3$, PPh$_2$*i*Pr, P*i*Pr$_3$, PCy$_3$). These compounds turned out to be valuable precursors for dihydrogen complexes of the type [RuTp(PR$_3$)(H)(η^2-H$_2$)] as well as other complexes containing the [RuTp(PR$_3$)]$^+$ fragment.

Results and Discussion

The synthesis of [RuTp(PR$_3$)Cl$_2$] (PR$_3$ = PPh$_3$, PPh$_2$*i*Pr, P*i*Pr$_3$, and PCy$_3$; **2a**–**d**) was performed as a one-pot reaction by refluxing a DMF solution of [RuTp(COD)Cl] (**1**) in the presence of PR$_3$ ($\geq$ 1 equiv.) to yield the air-sensitive DMF intermediate [RuTp(PR$_3$)(Cl)(DMF)]. On exposure to air in the presence of CCl$_4$, this complex is readily converted to afford, on workup, **2a**–**d** in 77–88% isolated yields (Scheme 1). No attempts were made to isolate the [RuTp(PR$_3$)(Cl)(DMF)] intermediate in this reaction sequence. It should be noted, however, that the PPh$_3$ and PPyr$_3$ (Pyr = pyrrolyl) compounds [RuTp(PPh$_3$)(Cl)(DMF)] and [RuTp(PPyr$_3$)(Cl)(DMF)] have recently been isolated and even crystallographically characterized.[3] Complexes **2a**–**d** are thermally robust orange solids that are stable to air both in the solid state and in solution. They are very soluble in most common organic solvents such as CH$_2$Cl$_2$, THF, or toluene. All complexes were characterized by elemental analysis. The NMR spectra suffer from severe line broadening due to the paramagnetic nature of these complexes. The measured magnetic moments, μ_{eff}, of **2a**–**2d** were determined at 295 K to be 1.89, 1.99, 1.90, and 1.40 μ_B, respectively, consistent with a d^5 (Ru^{III}) low-spin configuration with one unpaired electron. To further probe the electronic structure of **2a**–**d**, we examined their redox behavior by cyclic voltammetry. All four complexes display only one oxidation-reduction wave with $E_{1/2}$ values vs. NHE of 0.31 (PPh$_3$), 0.24 (PPh$_2$*i*Pr), 0.16 (P*i*Pr$_3$), and 0.12 V (PCy$_3$). These values correlate roughly with the increasing electron σ-donating abilities and decreasing π-accepting properties of the tertiary phosphanes, i.e., the relative stability of the Ru^{III} complexes follows the order PPh$_3$

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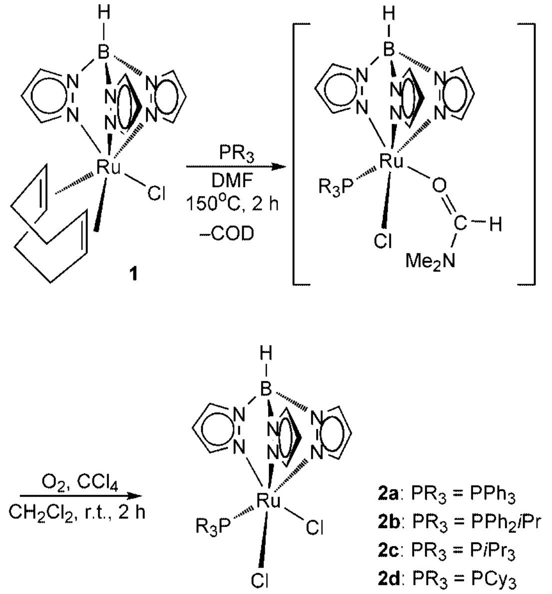
< PPh_2iPr < $PiPr_3$ ≈ PCy_3. Incidentally, the $E_{1/2}$ values decrease with increasing cone angles of the tertiary phosphane ligands.



Scheme 1.

The molecular structures of **2a**, **2b**, and **2d** are depicted in Figures 1, 2, and 3, respectively; selected bond lengths are reported in the captions. The coordination geometry of these complexes is approximately octahedral, and the bond lengths and angles in these three complexes are relatively uniform. Mean bond lengths for the three complexes are: Ru–Cl = 2.337(8) Å, Ru–N = 2.071(6) Å for N(2) and N(4), and Ru–N(6) = 2.112(4) Å; N(6) is *trans* to the phosphane, which exerts a *trans* effect, as shown by the Ru–N mean bond length elongation of 0.041 Å in comparison to the other Tp nitrogen atoms. The Ru–P bond lengths increase gradually from 2.364 Å in **2a** via 2.380 in **2b** to 2.417 Å in **2d**; this correlates with the electrochemical data. Another point of interest is the conformation of the PPh_3 ligand in **2a**, which instead of the frequent rotor (or propeller) has an irregular conformation, as can be shown by the Ru–P–

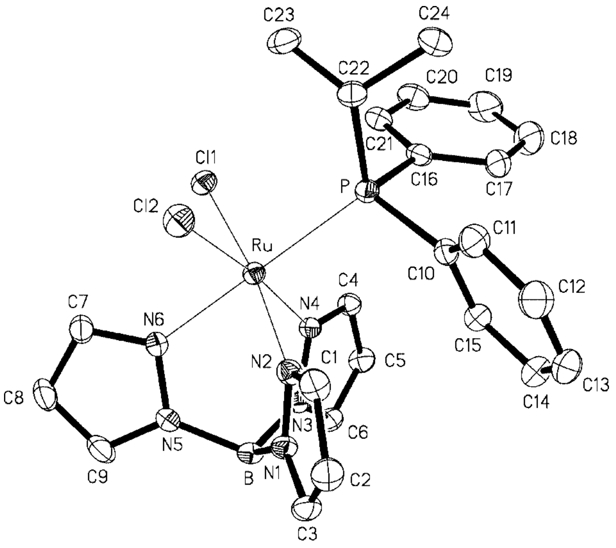


Figure 2. Structural view of $[RuTp(PPh_2iPr)Cl_2]$ (**2b**) showing 20% thermal ellipsoids (hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Ru–N(2) 2.073(2), Ru–N(4) 2.077(2), Ru–N(6) 2.115(2), Ru–P 2.3796(7), Ru–Cl(1) 2.3442(8), Ru–Cl(2) 2.3311(8); P–Ru–Cl(1) 92.92(3), P–Ru–Cl(2) 90.62(3), Cl(1)–Ru–Cl(2) 93.00(3).

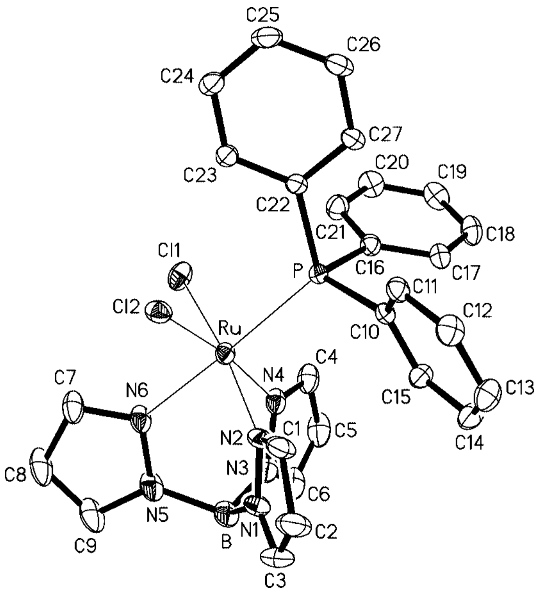


Figure 1. Structural view of $[RuTp(PPh_3)Cl_2]$ (**2a**) showing 30% thermal ellipsoids (hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Ru–N(2) 2.079(2), Ru–N(4) 2.069(2), Ru–N(6) 2.106(2), Ru–P 2.3642(6), Ru–Cl(1) 2.3236(6), Ru–Cl(2) 2.3368(6); P–Ru–Cl(1) 90.08(2), P–Ru–Cl(2) 90.28(2), Cl(1)–Ru–Cl(2) 95.80(2).

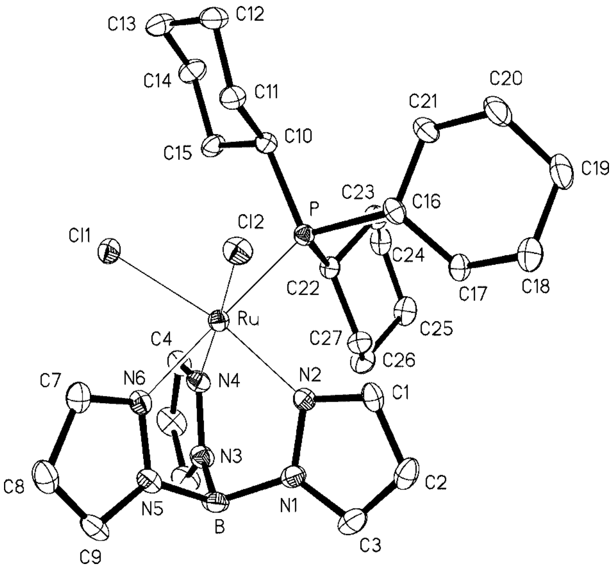
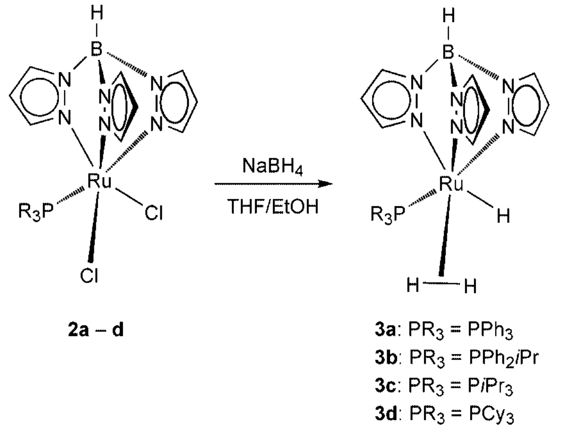


Figure 3. Structural view of $[RuTp(PCy_3)Cl_2]\cdot CH_2ClCH_2Cl$ (**2d**$\cdot CH_2ClCH_2Cl$) showing 40% thermal ellipsoids (hydrogen and CH_2ClCH_2Cl atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Ru–N(2) 2.065(2), Ru–N(4) 2.063(2), Ru–N(6) 2.114(2), Ru–P 2.4168(8), Ru–Cl(1) 2.3459(8), Ru–Cl(2) 2.3433(8), P–Ru–Cl(1) 95.36(3); P–Ru–Cl(2) 89.11(3), Cl(1)–Ru–Cl(2) 92.79(3).

C_{ipso}–C torsion angles of 63.6°, 66.8°, and –19.9° for phenyl rings C(10)–C(15), C(16)–C(21), and C(22)–C(27),[4] whereas the PPh_3 orientation relative to the $RuTpCl_2$ moiety is defined by an angle of 0.2° for N(2)–Ru–P–C(10). These data suggest that the phenyl ring C(22)–C(27) is in an approximately bisecting orientation and fits with C(23)–H(23) in between the two chlorine atoms (Figure 1). It is interesting to note that this appears to be a preferred configuration rather than merely a packing effect as the crystal structures of two solvates of **2a**, one with $ClCH_2CH_2Cl$ and one with Et_2O, have essentially the same complex conformation although they crystallize in entirely different lattices ($ClCH_2CH_2Cl$ solvate: orthorhombic, space group $P2_12_12_1$; Et_2O solvate: triclinic, space group $P\bar{1}$).

Complexes **2** turned out to be useful reagents for the preparation of dihydrogen compounds of the types [RuTp(PR_3)(H)(η^2-H_2)]. Thus, treatment of **2a**–**d** with $NaBH_4$ affords the diamagnetic Ru^{II} compounds [RuTp(PR_3)(H)(η^2-H_2)] (**3a**–**d**) in high yields (Scheme 2). All these compounds are thermally robust solids that slowly decompose in the presence of air both in the solid state and in solution. Characterization was accomplished by elemental analysis as well as ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy. Complexes **3a**–**d** show a doublet resonance for the hydride signal at all accessible temperatures in the range δ = –9.31 to –10.53 ppm (Table 1). The integration ratios toward the other ligands are in agreement with the presence of three metal-bound hydrogen atoms in all complexes. The presence of a dihydrogen ligand in **3b**–**d** is confirmed by the small T_{1min} for the hydride signal, as shown in Table 1. Measurement of the relaxation time T_{1min} has been reported previously for **3a**.[5] Irreversible isomerization to the ruthenium(IV) trihydride form [RuTp(PR_3)$(H)_3$] has not been observed, at variance with what commonly happens in related CpRu or Cp*Ru systems.[6]



Scheme 2.

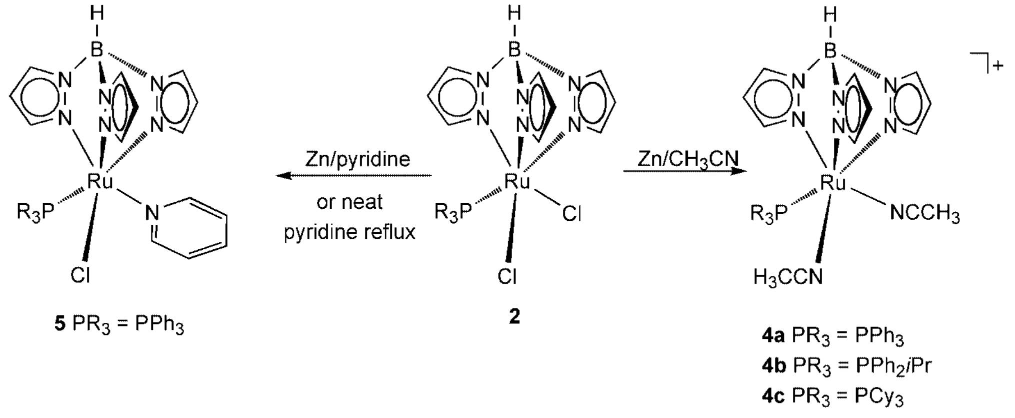
Table 1. Selected spectroscopic properties of complexes [RuTp(PR_3)(H)(η^2-H_2)] **3a**–**d**.

	^1H NMR δ [ppm]	$^2J_{H,P}$ [Hz]	$^{31}P\{^1H\}$ NMR δ [ppm]	T_{1min} [ms]	T [K]
3a	–9.31	18.1	75.4	34[a] (400 MHz)	216
3b	–9.68	18.2	82.4	41 (300 MHz)	235
3c	–10.53	18.1	82.2	24 (300 MHz)	200
3d	–10.41	17.6	76.5	27 (300 MHz)	227

[a] Ref.[5]

It should be noted that this type of dihydrogen complex has also been prepared by different methods utilizing precursors such as [Ru(PCy_3)$_2$$(H)_2$HI],[7] [RuTp($PPh_3$)($CH_3CN$)H],[5] [RuTp(P*i*$Pr_2$Me)($CH_3CN$)Cl],[8] and [RuTp*(COD)H].[9]

Reduction of complexes **2** can also be accomplished with Zn in the presence of suitable ligands. Thus, treatment of **2** with Zn in neat CH_3CN affords the cationic diamagnetic Ru^{II} compounds [RuTp(PR_3)$(CH_3CN)_2$]$^+$ (**4a**–**c**) with either $ZnCl_4^{2-}$ as counterion or, if the reaction is performed in the presence of $NaBPh_4$, with BPh_4^- as counterion (Scheme 3). Similarly, reduction of **2** in the presence of pyridine (5 equiv.) yields the neutral complex [RuTp(PR_3)(py)Cl] (**5**). It is noteworthy that if **2** is refluxed in neat pyridine for 2 h, clean reduction to **5** also takes place in the absence of Zn powder. It was not possible to obtain the cationic bispyridine complex [RuTp(PR_3)$(py)_2$]$^+$ under these reaction conditions. Compounds **4** and **5** are thermally robust solids that are stable to air both in the solid state and in solution. Characterization was accomplished by elemental analysis and ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy; no unusual features were observed.



Scheme 3.

The structures of $[RuTp(PPh_2iPr)(CH_3CN)_2]_2(ZnCl_4)$ (**4b**) and $[RuTp(PPh_3)(py)Cl]$ (**5**) were determined by X-ray crystallography. The molecular structures are depicted in Figures 4 and 5, respectively; important bond lengths are reported in the caption. Complex **4b** is closely related in terms of stereochemistry and ligand disposition to complex **2b**, including the *trans* influence of the phosphane on the Ru–N(6) bond (Figure 4). Complex **5** is remarkable in having PPh_3 with a very regular propeller-like conformation, as can be seen by the three Ru–P–C_{ipso}–C torsion angles of –46.3°, –47.4°, and –54.1°. With this conformation and N(2)–Ru–P–C(10), the phenyl rings C(10)–C(15) and C(16)–C(21) exhibit stabilizing intramolecular π-π stacking interactions with one pyrazole and the pyridine ring.

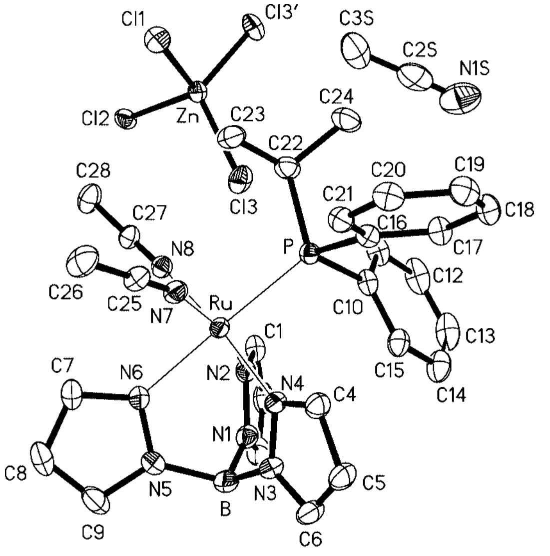


Figure 4. Structural view of $[RuTp(PPh_2iPr)(CH_3CN)_2]_2[ZnCl_4]\cdot CH_3CN$ (**4b**·CH_3CN) showing 30% thermal ellipsoids (hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Ru–N(2) 2.064(2), Ru–N(4) 2.078(2), Ru–N(6) 2.113(2), Ru–P 2.3234(5), Ru–N(7) 2.028(8), Ru–N(8) 2.029(2), Zn–Cl(1) 2.258(1), Zn–Cl(2) 2.290(1), Zn–Cl(3) 2.307(1), Zn–Cl(3′) 2.238(2); P–Ru–N(7) 96.37(5), P–Ru–N(8) 92.90(4), N(7)–Ru–N(8) 90.54(6).

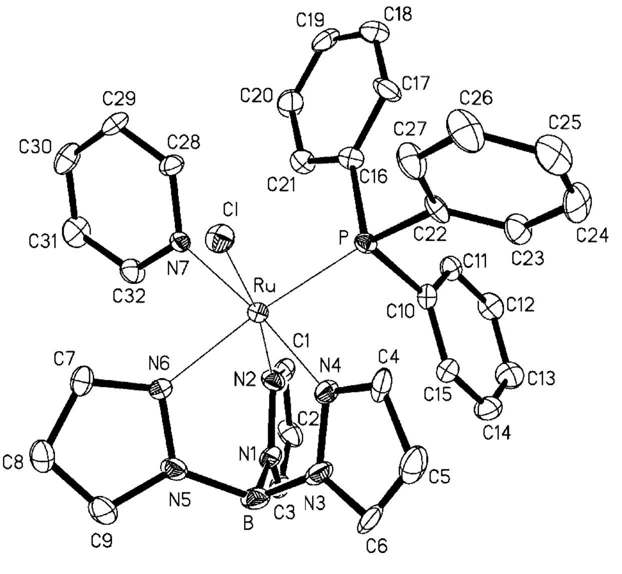


Figure 5. Structural view of $[RuTp(PPh_3)(py)(Cl)]\cdot solv$ (**5**·solv) showing 30% thermal ellipsoids (hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Ru–N(2) 2.072(6), Ru–N(4) 2.063(7), Ru–N(6) 2.111(5), Ru–P 2.294(2), Ru–Cl 2.428(2), Ru–N(7) 2.080(7); P–Ru–Cl 98.44(6), P–Ru–N(7) 96.7(2), Cl–Ru–N(7) 86.2(2).

In summary, we have described a facile synthesis of a series air-stable dichloro Ru^{III} complexes of the type $[RuTp(PR_3)Cl_2]$. These compounds are readily reduced to Ru^{II} complexes containing the $[RuTp(PR_3)]^+$ fragment. The use of $NaBH_4$ as reducing agent gives the dihydrogen complexes $[RuTp(PR_3)(H)(\eta^2\text{-}H_2)]$, while with Zn in the presence of CH_3CN and pyridine, respectively, complexes $[RuTp(PR_3)(CH_3CN)_2]^+$ and $[RuTp(PR_3)(py)Cl]$ are obtained.

Experimental Section

General: All manipulations were performed under an inert atmosphere of purified argon by using Schlenk techniques. All chemicals were standard reagent grade and used without further purification. The solvents were purified according to standard procedures.[10] The deuterated solvents were purchased from Aldrich and dried with 4-Å molecular sieves. [RuTp(COD)Cl] (**1**) was prepared according to the literature method.[11] ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded with Bruker Avance-250, -300, and -400 spectrometers and are referenced to $SiMe_4$ and H_3PO_4 (85%), respectively.

[RuTp(PPh₃)Cl₂] (2a): A suspension of **1** (150 mg, 0.33 mmol) and PPh_3 (89.1 mg, 0.34 mmol) in DMF (4 mL) was heated at reflux for 2 h. After removal of the solvent, the remaining residue was dissolved in CH_2Cl_2 and CCl_4 (2 mL) was added. After stirring of the solution for 2 h at room temperature, the volume of the solution was reduced to about 1 mL and the product was precipitated by addition of Et_2O and petroleum ether. The residue was collected on a glass-frit, washed with Et_2O, and dried in vacuo. Yield: 183 mg (86%). $C_{27}H_{25}BCl_2N_6PRu$ (647.30): calcd. C 50.10, H 3.89, N 12.98; found C 50.21, H 3.91, N 12.41. $\mu_{eff} = 1.89\ \mu_B$.

[RuTp(PPh₂*i*Pr)Cl₂] (2b): This complex was prepared analogously to **2a** using **1** (150 mg, 0.33 mmol) and PPh_2iPr (77.6 mg, 0.34 mmol) as starting materials. Yield: 174 mg (88%). $C_{24}H_{27}BCl_2N_6PRu$ (613.28): calcd. C 47.00, H 4.44, N 13.70; found C 47.11, H 4.35, N 13.88. $\mu_{eff} = 1.99\ \mu_B$.

[RuTp(P*i*Pr₃)Cl₂] (2c): This complex was prepared analogously to **2a** using **1** (150 mg, 0.33 mmol) and $PiPr_3$ (64.9 µL, 0.34 mmol) as starting materials. Yield: 156 mg (87%). $C_{18}H_{31}BCl_2N_6PRu$ (545.24): calcd. C 39.65, H 5.73, N 15.41; found C 39.55, H 5.40, N 15.53. $\mu_{eff} = 1.99\ \mu_B$.

[RuTp(PCy₃)Cl₂] (2d): This complex was prepared analogously to **2a** using **1** (150 mg, 0.33 mmol) and PCy_3 (95.3 mg, 0.34 mmol) as starting materials. Yield: 169 mg (77%). $C_{27}H_{43}BCl_2N_6PRu$ (665.44): calcd. C 48.73, H 6.51, N 12.63; found C 48.60, H 6.91, N 12.70. $\mu_{eff} = 1.40\ \mu_B$.

[RuTpH(H₂)(PPh₃)] (3a): $NaBH_4$ (28 mg, 0.75 mmol) was added to a solution of **2a** (100 mg, 0.15 mmol) in THF (5 mL) and EtOH (1 mL) and the reaction mixture was stirred at room temperature for 2 h. The solution was then evaporated to dryness and the residue was redissolved in THF. Insoluble materials were removed by filtration and the solution was again evaporated to dryness to yield a white solid, which was dried under vacuum. Yield: 84 mg (97%). $C_{27}H_{28}BN_6PRu$ (579.41): calcd. C 55.97, H 4.87, N 14.50; found C 56.10, H 4.76, N 14.60. ^{1}H NMR (C_6D_6, 20 °C): δ = 7.70–7.51 (m, 7 H, Ph, Tp), 7.25–7.18 (m, 2 H, Tp), 7.15–6.99 (m, 12 H, Ph, Tp), 5.93–5.79 (m, 3 H, Tp), –9.31 (d, $^2J_{H,P}$ = 18.1 Hz, 3 H, H, H$_2$) ppm. ^{31}P{^{1}H} NMR (C_6D_6, 20 °C): δ = 75.4 ppm.

[RuTpH(H$_2$)(PPh$_2$*i*Pr)] (3b): This complex was prepared analogously to **3a** using **2b** (100 mg, 0.16 mmol) and NaBH$_4$ (31 mg, 0.82 mmol) as starting materials. Yield: 76 mg (87%). $C_{24}H_{30}BN_6PRu$ (545.40): calcd. C 52.85, H 5.54, N 15.41; found C 52.77, H 5.49, N 15.50. ^{1}H NMR (C_6D_6, 20 °C): δ = 7.71–7.46 (m, 6 H, Tp), 7.20–6.86 (m, 10 H, Ph), 5.95–5.69 (m, 3 H, Tp), 2.24–2.03 (m, 1 H, CH), 1.24 (dd, $^3J_{H,P}$ = 14.1, $^3J_{H,H}$ = 7.0 Hz, 6 H, CH$_3$), –9.68 ppm (d, $^2J_{H,P}$ = 18.1 Hz, 3 H, H,H$_2$); T_{1min}: 41 ms (–38 °C, [D$_8$]toluene, 300 MHz). ^{31}P{^{1}H} NMR (C_6D_6, 20 °C): δ = 82.4 ppm.

[RuTpH(H$_2$)(P*i*Pr$_3$)] (3c): This complex was prepared analogously to **3a** using **2c** (100 mg, 0.18 mmol) and NaBH$_4$ (34 mg, 0.90 mmol) as starting materials. Yield: 71 mg (83%). $C_{18}H_{34}BN_6PRu$ (477.36): calcd. C 45.29, H 7.18, N 17.61; found C 45.17, H 7.23, N 17.69. ^{1}H NMR (C_6D_6, 20 °C): δ = 8.13–7.40 (m, 6 H, Tp), 6.25–5.82 (m, 3 H, Tp), 2.12–1.88 (m, 3 H, CH), 1.09 (dd, $^3J_{H,P}$ = 12.6, $^3J_{H,H}$ = 7.1 Hz, 18 H, CH$_3$), –10.53 ppm (d, $^2J_{H,P}$ = 18.1 Hz, 3 H, H, H$_2$); T_{1min}: 24 ms (–73 °C, CD$_2$Cl$_2$, 300 MHz). ^{31}P{^{1}H} NMR (C_6D_6, 20 °C): δ = 82.2 ppm.

[RuTpH(H$_2$)(PCy$_3$)] (3d): This complex was prepared analogously to **3a** using **2d** (100 mg, 0.15 mmol) and NaBH$_4$ (28 mg, 0.75 mmol) as starting materials. Yield: 80 mg (89%). $C_{27}H_{46}BN_6PRu$ (597.55): calcd. C 54.27, H 7.76, N 14.06; found C 54.20, H 7.69, N 14.00. ^{1}H NMR (C_6D_6, 20 °C): δ = 8.16–7.49 (m, 6 H, Tp), 6.32–5.86 (m, 3 H, Tp), 3.60–3.36 (m, 3 H, CH), 2.12–0.95 (m, 30 H), –10.41 ppm (d, $^2J_{H,P}$ = 17.6 Hz, 3 H, H, H$_2$); T_{1min}: 27 ms (–46 °C, CD$_2$Cl$_2$, 300 MHz). ^{31}P{^{1}H} NMR (C_6D_6, 20 °C): δ = 76.5 ppm.

[RuTp(PPh$_3$)(CH$_3$CN)$_2$]$_2$(ZnCl$_4$) (4a): Zn powder (98 mg, 1.5 mmol) was added to a solution of **2a** (100 mg, 0.15 mmol) in acetonitrile and the reaction mixture was stirred at room temperature for 2 h. Insoluble materials were then removed by filtration. The volume of the solution was then reduced to about 1 mL and the product was precipitated by addition of Et$_2$O. The pale-yellow residue was collected on a glass frit, washed with Et$_2$O, and dried under vacuum. Yield: 174 mg (76%) $C_{62}H_{62}B_2Cl_4N_{16}P_2Ru_2Zn$ (1524.2): calcd. C 48.86, H 4.10, N 14.70; found C 48.75, H 4.02, N 14.78. ^{1}H NMR (CD$_3$CN, 20 °C): δ = 8.12–8.04 (m, 1 H, Tp), 7.93–7.80 (m, 3 H, Tp), 7.59–7.44 (m, 3 H, Ph), 7.43–7.33 (m, 6 H, Ph), 7.23–7.04 (m, 6 H, Ph), 6.85–6.74 (m, 2 H, Tp), 6.44–6.36 (m, 1 H, Tp), 6.04–5.93 (m, 2 H, Tp), 2.33 (s, 6 H, C*H$_3$*CN) ppm. ^{13}C{^{1}H} NMR (CD$_3$CN, 20 °C): δ = 146.8–127.0 (Ph, Tp), 125.8 (CH$_3$*C*N), 107.8 (d, $J_{C,P}$ = 1.5 Hz, Tp), 107.4 (Tp), 104.8 (Tp), 5.1 (CH$_3$CN) ppm. ^{31}P{^{1}H} NMR (CD$_3$CN, 20 °C): δ = 51.9 ppm.

[RuTp(PPh$_2$*i*Pr)(CH$_3$CN)$_2$]$_2$(ZnCl$_4$) (4b): This complex was prepared analogously to **4a** using **2b** (100 mg, 0.16 mmol) and zinc powder as starting materials. Yield: 156 mg (67%). $C_{56}H_{66}B_2Cl_4N_{16}P_2Ru_2Zn$ (1456.14): calcd. C 46.19, H 4.57, N 15.39; found C 46.23, H 4.61, N 15.42. ^{1}H NMR (CD$_3$CN, 20 °C): δ = 8.08–7.95 (m, 1 H, Tp), 7.83–7.64 (m, 3 H, Tp), 7.48–6.97 (m, 10 H, Ph), 6.89–6.82 (m, 1 H, Tp), 6.41–6.30 (m, 1 H, Tp), 5.96–5.80 (m, 2 H, Tp), 3.30–3.06 (m, 1 H, CH), 2.51 (6 H, C*H$_3$*CN), 1.33 (dd, $^3J_{H,P}$ = 14.5, $^3J_{H,H}$ = 6.9 Hz, 6 H, CH$_3$) ppm. ^{13}C{^{1}H} NMR (CD$_3$CN, 20 °C): δ = 154.0–127.4 (Ph, Tp), 126.3 (CH$_3$*C*N), 106.3 (d, $J_{C,P}$ = 3.1 Hz, Tp), 106.3 (Tp), 25.4 (CH), 18.3 (CH$_3$), 4.0 (CH$_3$CN) ppm. ^{31}P{^{1}H} NMR (CD$_3$CN, 20 °C): δ = 54.3 ppm.

[RuTp(PCy$_3$)(CH$_3$CN)$_2$]BPh$_4$ (4c): NaBPh$_4$ (56.6 mg, 0.165 mmol) and Zn powder (98 mg, 1.5 mmol) were added to a solution of **2d** (100 mg, 0.15 mmol) in acetonitrile and the reaction mixture was stirred at room temperature for 2 h. Insoluble materials were removed by filtration. The volume of the solution was then reduced to about 1 mL and the product was precipitated by addition of Et$_2$O. The pale-yellow residue was collected on a glass frit, washed with Et$_2$O, and dried in vacuo. Yield: 126 mg (89%). $C_{51}H_{63}B_2N_8PRu$ (941.78): calcd. C 65.04, H 6.74, N 11.90; found C 64.97, H 6.78, N 11.89. ^{1}H NMR (CD$_3$CN, 20 °C): δ = 7.91–7.79 (m, 3 H, Tp), 7.78–7.70 (m, 1 H, Tp), 7.67–7.55 (m, 2 H, Tp), 7.38–7.14 (m, 8 H, Ph), 7.09–6.92 (m, 8 H, Ph), 6.90–6.74 (m, 4 H, Ph), 6.37–6.22 (m, 3 H, Tp), 2.43 (6 H, C*H$_3$*CN), 2.26–2.05 (m, 3 H, Cy), 1.82–1.56 (m, 18 H, Cy), 1.54–1.32 (m, 4 H, Cy), 1.31–1.02 (m, 8 H, Cy) ppm. ^{13}C{^{1}H} NMR (CD$_3$CN, 20 °C): δ = 146.1–121.7 (Ph, Tp, CH$_3$*C*N), 106.5 (Tp), 106.2 (d, $J_{C,P}$ = 2.1 Hz, Tp), 34.6 (d, $^1J_{C,P}$ = 18.6 Hz, CH), 29.1 (CH$_2$), 27.4 (d, $J_{C,P}$ = 9.7 Hz, CH$_2$), 26.3 (CH$_2$), 3.9 (CH$_3$CN) ppm. ^{31}P{^{1}H} NMR (CD$_3$CN, 20 °C): δ = 38.8 ppm.

[RuTp(PPh$_3$)(py)Cl] (5). Method (a): Pyridine (63 µL, 0.75 mmol) and Zn powder (98 mg, 1.5 mmol) were added to a solution of **2a** (100 mg, 0.15 mmol) in toluene, and the reaction mixture was stirred at room temperature for 1 h. Insoluble materials were removed by filtration. The volume of the solution was then reduced to about 1 mL and the product was precipitated by addition of Et$_2$O and petroleum ether. The yellow residue was collected on a glass frit, washed with Et$_2$O and petroleum ether, and dried under vacuum. Yield: 102 mg (98%).

Method (b): A solution of **2a** (100 mg, 0.15 mmol) in pyridine (5 mL) was heated at reflux for 2 h. The volume of the solution was then reduced to about 1 mL and the product was precipitated by addition of Et$_2$O and petroleum ether. The yellow residue was collected on a glass frit, washed with petroleum ether, and dried under vacuum. Yield: 98 mg (95%). $C_{32}H_{30}BClN_7PRu$ (691.11): calcd. C 55.63, H 4.38, N 14.19; found C 55.70, H 4.48, N 14.23. ^{1}H NMR (CD$_2$Cl$_2$, 20 °C): δ = 8.78 (d, $J_{H,H}$ = 8.8 Hz, 2 H, py), 7.99 (t, $J_{H,H}$ = 7.7 Hz, 1 H, py), 7.89–6.73 (m, 22 H, Ph, Tp, py), 6.63 (d, $J_{H,H}$ = 1.7 Hz, 1 H, Tp), 6.18–6.12 (m, 1 H, Tp), 5.92 (dd, $^1J_{H,H}$ = 2.2, $^2J_{H,H}$ = 2.3 Hz, 1 H, Tp), 5.80 (dd, $^1J_{H,H}$ = 2.3, $^2J_{H,H}$ = 2.3 Hz, 1 H, Tp) ppm. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 20 °C): δ = 156.4 (py), 146.4 (Tp), 141.9 (Tp), 140.1 (Tp), 137.5–127.5 (Ph, Tp, py), 125.5 (py), 105.8 (Tp), 105.4 (Tp) ppm. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 20 °C): δ = 54.7 ppm.

X-ray Structure Determination: Crystals of **2a**, **2b**, **4b**·CH$_3$CN, and **5**·solv were obtained by diffusion of Et$_2$O or pentane into solutions in CH$_2$Cl$_2$ (**2a**, **2b**, **5**) or CH$_3$CN (**4b**). Crystals of **2d**·CH$_2$ClCH$_2$Cl were obtained by solvent evaporation. Crystal data and experimental details are given in Table 2. X-ray data were collected on a Bruker Smart CCD area detector diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) and 0.3° ω-scan frames covering either hemispheres or complete spheres of the reciprocal space. Corrections for absorption, λ/2 effects, and crystal decay were applied.[12] The structures were solved by direct methods using the program SHELXS-97.[13] Structure refinement on F^2 was carried out with the program SHELXL-97.[4] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were inserted in idealized positions and were refined as riding on the atoms to which they are bonded. Solvent disorder (**2d**·CH$_2$ClCH$_2$Cl, **4b**·CH$_3$CN) and anion disorder (**4b**·CH$_3$CN) was taken into account. The disordered solvent in **5**·solv (a mixture of CH$_2$Cl$_2$ and Et$_2$O) was squeezed with the program PARST.[14]

CCDC-609376 (for **2a**), -609377 (for **2b**), -609378 (for **2d**·CH$_2$ClCH$_2$Cl), -609379 (for **4b**·CH$_3$CN), and -609380 (for

Table 2. Details for the crystal structure determinations of complexes [RuTp(PPh$_3$)Cl$_2$] (**2a**), [RuTp(PPh$_2$*i*Pr)Cl$_2$] (**2b**), [RuTp(PCy$_3$)Cl$_2$]·CH$_2$ClCH$_2$Cl (**2d**·CH$_2$ClCH$_2$Cl), [RuTp(PPh$_2$*i*Pr)(CH$_3$CN)$_2$]$_2$[ZnCl$_4$]·CH$_3$CN (**4b**·CH$_3$CN), and [RuTp(PPh$_3$)(py)(Cl)]·solv (**5**·solv).

	2a	**2b**	**2d**·CH$_2$ClCH$_2$Cl	**4b**·CH$_3$CN	**5**·solv[a]
Formula	$C_{27}H_{25}BCl_2N_6PRu$	$C_{24}H_{27}BCl_2N_6PRu$	$C_{29}H_{47}BCl_4N_6PRu$	$C_{58}H_{69}B_2Cl_4N_{17}P_2Ru_2Zn$	$C_{32}H_{30}BClN_7PRu$
Fw	647.28	613.27	764.38	1497.17	690.93
Crystal size [mm]	0.58 × 0.31 × 0.21	0.33 × 0.32 × 0.14	0.24 × 0.12 × 0.06	0.40 × 0.30 × 0.25	0.45 × 0.18 × 0.08
Space group	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)	$C2/c$ (no. 15)	$P2_1/n$ (no. 14)
a [Å]	10.3997(4)	9.2269(5)	17.9316(10)	24.7471(12)	10.892(3)
b [Å]	19.9941(9)	29.8909(17)	8.8672(5)	18.9497(9)	30.243(7)
c [Å]	13.2929(6)	10.0220(6)	23.4699(13)	18.7346(9)	11.008(3)
β [°]	93.397(1)	104.133(1)	111.056(1)	129.629(1)	99.425(5)
V [Å^3]	2759.2(2)	2680.4(3)	3482.6(3)	6766.6(6)	3577.3(15)
Z	4	4	4	4	4
$\rho_{calcd.}$ [g cm^{-3}]	1.558	1.520	1.458	1.470	1.283
T [K]	173(2)	297(2)	173(2)	173(2)	173(2)
μ [mm^{-1}] (Mo-K_α)	0.849	0.869	0.833	1.048	0.588
F(000)	1308	1244	1580	3048	1408
θ_{max} [deg]	30	27	27	30	25
Reflections measd.	27878	24434	37555	34395	11091
Unique reflections	8034	5830	7579	9766	5517
Refl. with $I > 2\sigma(I)$	6739	4951	5554	8010	3657
Parameters	344	316	386	433	388
R_1 [$I > 2\sigma(I)$][b]	0.0390	0.0363	0.0396	0.0322	0.0829
R_1 (all data)	0.0510	0.0462	0.0664	0.0430	0.1250
wR_2 (all data)	0.0848	0.0787	0.0844	0.0871	0.1912
Diff. Fourier peaks, min./max. [e Å^{-3}]	–1.10/0.62	–0.35/0.28	–0.58/0.66	–0.53/0.77	–1.08/1.32

[a] Disordered solvent (CH$_2$Cl$_2$/Et$_2$O) squeezed with program PARST. Chemical formula and derived quantities given without solvent content. [b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{1/2}$.

5·solv) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Electrochemical Studies: Cyclic voltammograms were measured in a three-electrode cell using a 0.2-mm-diameter glassy carbon working electrode, a platinum auxiliary electrode, and a Ag|Ag$^+$ reference electrode containing 0.1 M AgNO$_3$, the potential of which was corrected using an internal standard redox couple of ferrocenium/ferrocene. Measurements were performed at room temperature using an EG & G PARC 273A potentiostat/galvanostat. Deaeration of solutions was accomplished by passing a stream of argon through the solution for 5 min prior to the measurement and then maintaining a blanket atmosphere of argon over the solution during the measurement. The potentials were measured in 0.15 M [nBu$_4$N][BF$_4$]/CH$_3$CN, using FeCp$_2$ ($E_{1/2}$ = +0.69 V vs. NHE) as internal standard and are quoted relative to NHE.

Magnetic Measurements: For the determination of the magnetic susceptibility, the powdered complex was pressed into pellets. VT magnetic susceptibility measurements of the complex were performed with a superconductivity interferometer device (SQUID) in external fields of up to 3 T, within the temperature range 4.2–300 K.

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