Monatshefte für Chemie 135, 1349–1357 (2004)
DOI 10.1007/s00706-004-0222-6

Monatshefte für Chemie
Chemical Monthly
Printed in Austria

Ruthenium Tris(pyrazolyl)borate Complexes. Part 20 [1]. Synthesis, Characterization, and Reactivity of Neutral Trispyrazolylborate Ruthenium Vinylidene Complexes

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Received April 26, 2004; accepted (revised) May 17, 2004
Published online August 13, 2004 © Springer-Verlag 2004

Summary. The reaction of Ru*Tp*(*COD*)Cl (**1**) with PPh_2Pr^i and terminal alkynes HC≡C*R* ($R = C_6H_5$, C_4H_3S, C_6H_4OMe, *Fc*, C_6H_4–*Fc*, C_6H_9) affords the neutral vinylidene complexes $RuTp(PPh_2Pr^i)(Cl)(=C=CHR)$ (**2a**–**2f**) in high yields. These complexes do not react with *Me*OH to give methoxy carbene complexes of the type $RuTp(PPh_2Pr^i)(Cl)(=C(OMe)CH_2R)$, but react with oxygen to yield the CO complex $RuTp(PPh_2R)(Cl)(CO)$ (**3**). The structures of **2b**, **2f**, and **3** have been determined by X-ray crystallography.

Keywords. Ruthenium; Hydridotrispyrazolylborate; Acetylenes; Vinylidene complexes; Structure analysis.

Introduction

The chemistry of vinylidene transition metal complexes has attracted increasing attention in recent years especially because of their appearance as key intermediates in stoichiometric and catalytic transformations of organic molecules [2]. Representative examples of ruthenium catalysis involving vinylidene complexes have been reported for the cyclization of dienylalkynes [3], the dimerization of HC≡CBu^t [4], the tandem cyclization-reconstructive addition of propargyl

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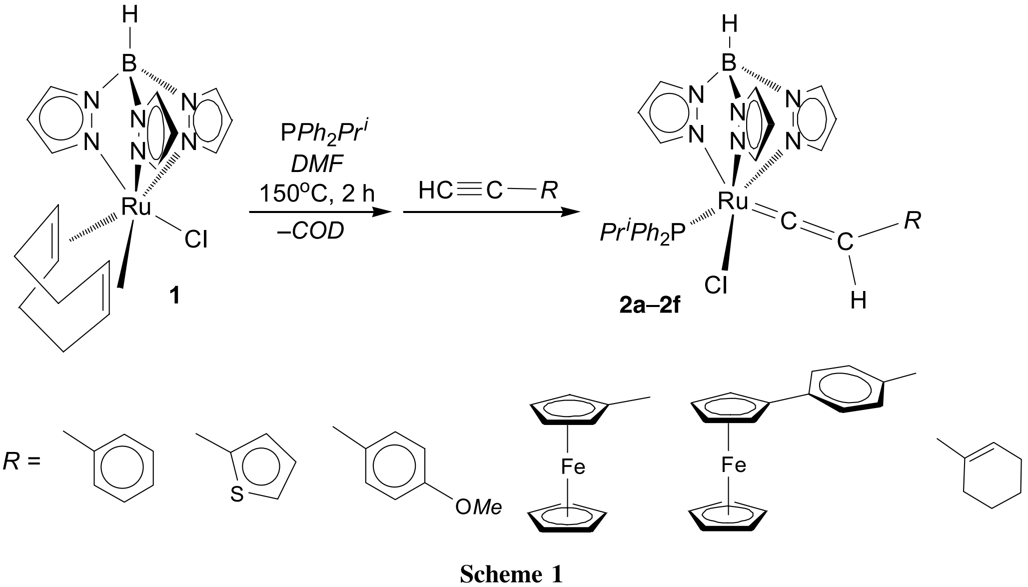
alcohols with allyl alcohols [5], and the reconstitute condensation of acetylenes and allyl alcohols [6]. In developing the chemistry of the tris(pyrazolyl)borate (*Tp*) ligand, we have recently shown [7] that also the neutral vinylidene complex Ru*Tp*(P*Ph*$_3$)(Cl)(=C=CH*Ph*) is an efficient catalyst precursor in the dimerization of terminal acetylenes to yield enynes.

In the present contribution we extend our studies on the chemistry of Ru*Tp* vinylidene complexes and report on the synthesis, characterization, and reactivity of some neutral Ru*Tp* vinylidene complexes. X-ray structures of representative complexes are presented.

Results and Discussion

The synthesis of Ru*Tp*(P*Ph*$_2$*Pr*^{i})(=C=CH*R*)Cl (*R* = C_6H_5, C_6H_4–O*Me*, C_4H_3S, *Fc* (*Fc* = ferrocenyl), C_6H_4–*Fc*, C_6H_9) was performed as a one-pot reaction with Ru*Tp*(*COD*)Cl (**1**) used as the starting material. This reaction proceeds via the highly reactive intermediate Ru*Tp*(P*Ph*$_2$*Pr*^{i})(Cl)(*DMF*). Though this latter complex could not be isolated in pure form, the P*Ph*$_3$ analog Ru*Tp*(P*Ph*$_3$)(Cl)(*DMF*) has recently been isolated and crystallographically characterized [8]. When **1** is refluxed in *DMF* in the presence of P*Ph*$_2$*Pr*^{i} ($\geq$1 equiv) and the resulting solid residue is exposed to HC≡C*R*, complexes **2a**–**2f** are, on workup, obtained in high yields (Scheme 1). It should be noted that even in the presence of P*Ph*$_2$*Pr*^{i} in excess there was no evidence of the formation of Ru*Tp*(P*Ph*$_2$*Pr*^{i})$_2$Cl, apparently for steric reasons. A similar observation has already been made in the case of Ru(η^5-C_5Me_5) complexes [6]. Complexes **2a**–**2f** are thermally robust orange to red solids which are stable to air in the solid state but rearrange in solution to give the respective CO complexes (vide infra). All compounds were characterized by ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy as well as by elemental analysis. In the ^{1}H and



Scheme 1

$^{13}C\{^1H\}$ solution NMR spectra three distinct sets of pyrazol-1-yl resonances in a 1:1:1 ratio are observed. This points to three distinct pyrazol-1-yl rings differing by their trans ligand atoms. Characteristic features comprise, in the $^{13}C\{^1H\}$ NMR spectrum, a marked low-field resonance in the range of 365.3 to 368.6 ppm (d, $J_{CP} = 19$–20 Hz) assignable to the α-carbon of the vinylidene moiety. The C_β atom displays a doublet resonance in the range of 106 to 115 ppm, with J_{CP} coupling constants of about 1.5 Hz. Further, the C_β hydrogen atom of complexes **2a**–**2f** show a doublet centered at 5.19 ($J_{CP} = 3.5$ Hz), 5.53 ($J_{CP} = 3.9$ Hz), 5.14 ($J_{CP} = 3.8$ Hz), 4.94 ($J_{CP} = 3.5$ Hz), 5.17 ($J_{CP} = 3.5$ Hz), and 4.77 ppm ($J_{CP} = 3.2$ Hz). The $^{31}P\{^1H\}$ NMR resonances are observed at 42.3, 42.4, 41.6, 43.0, 41.1, and 40.7 ppm. Finally, the ^1H and $^{13}C\{^1H\}$ NMR resonances of *Tp* and the phosphine ligands are in the expected ranges.

Structural views of **2b** and **2f** are depicted in Figs. 1 and 2 with selected bond distances and angles given in the figure captions. The solid state structures of the two compounds are in principle isostructural with thiophene of **2b** replaced by a cyclohexene moiety in **2f**. The coordination geometry of both complexes is approximately octahedral with all angles at ruthenium between 83° and 97° and 168° and 178°. There are no structural features pointing to unusual deviations or distortions. The two Ru–N(*Tp*) bond lengths *cis* to vinylidene are significantly shorter than that *trans* to vinylidene. Clearly, vinylidene is a strongly π-accepting ligand giving rise to an appreciable *trans* influence. The Ru–C(25) bond distances in **2b** and **2f** are 1.812(3) and 1.827(4) Å, respectively, comparable to other neutral Ru*Tp* vinylidene complexes but somewhat shorter than in cationic Ru*Tp*

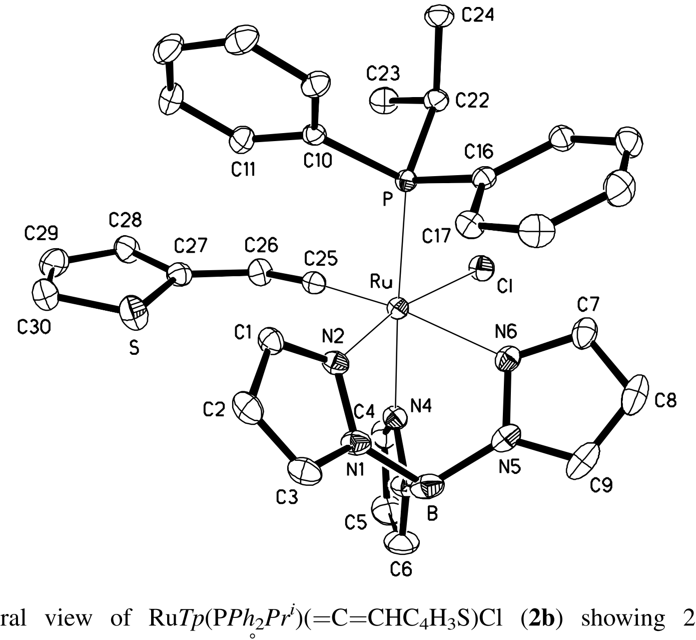


Fig. 1. Structural view of RuTp(PPh_2Pr^i)(=C=CHC_4H_3S)Cl (**2b**) showing 20% probability thermal ellipsoids; selected distances (Å) and angles (°): Ru–C(25) 1.812(3), Ru–N(2) 2.094(2), Ru–N(4) 2.136(2), Ru–N(6) 2.231(3), Ru–P 2.350(1), Ru–Cl 2.388(1), C(25)–C(26) 1.312(4), Ru–C(25)–C(26) 171.4(3)

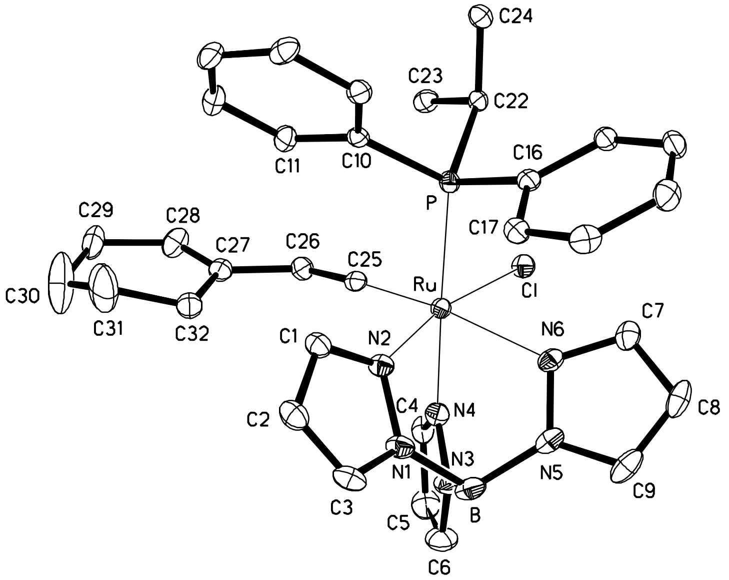
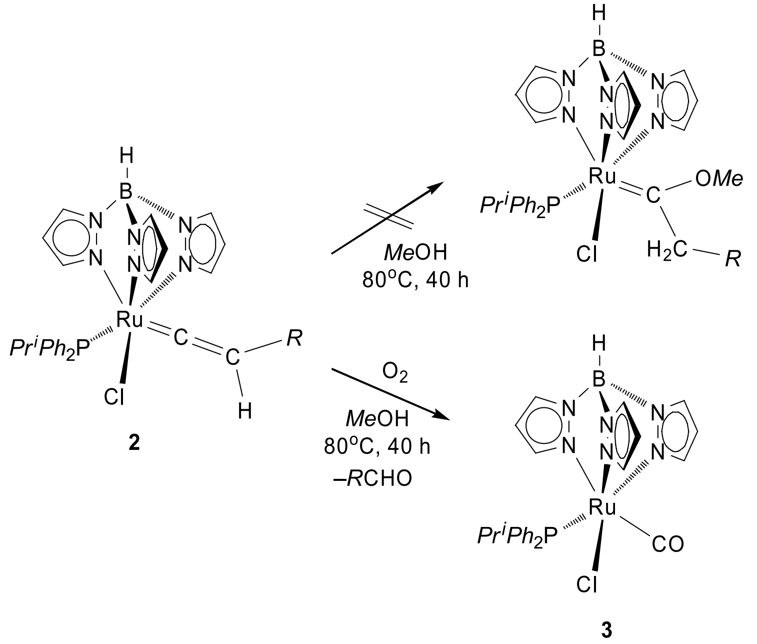


Fig. 2. Structural view of Ru*Tp*(P*Ph*$_2$*Pr*^{i})(=C=CHC$_6$H$_9$)Cl (**2f**) showing 30% probability thermal ellipsoids; selected distances (Å) and angles (°): Ru–C(25) 1.827(4), Ru–N(2) 2.089(3), Ru–N(4) 2.112(3), Ru–N(6) 2.217(3), Ru–P 2.343(1), Ru–Cl 2.383(1), C(25)–C(26) 1.291(6), Ru–C(25)–C(26) 172.1(3)

vinylidene complexes. For instance, in Ru*Tp*(P*Ph*$_3$)(=C=CH*Ph*)Cl and Ru*Tp*(κ^1(P)–*Ph*$_2$PCH$_2$ CH$_2$O*Me*)(=C=CH*Ph*)Cl the Ru–C bond distances are 1.801(4) and 1.810(3) Å, respectively [9], whereas in [Ru*Tp*(*Me*$_2$NCH$_2$CH$_2$N*Me*$_2$)(=C=CH*Ph*)]$^+$, [Ru*Tp* (*Ph*$_2$PCH$_2$CH$_2$N*Me*$_2$)(=C=CH*Ph*)]$^+$, and [Ru*Tp*(P*Et*$_3$)$_2$(=C=CH*Ph*)]$^+$ the Ru–C distances are 1.820(5), 1.821(5), and 1.81(1) Å, respectively [10, 11]. The Ru=C=C group is slightly bent with Ru–C(25)–C(26) angles of 171.4(3) and 172.1(3)°. The C(25)–C(26) bond distances are 1.312(4) and 1.291(6) Å corresponding to a bond order between two and three.

In contrast to Ru*Tp*(P*Cy*$_3$)(=C=CHSi*Me*$_3$) [12] which reacts with *Me*OH already at room temperature to afford the methoxycarbene complex Ru*Tp*(P*Cy*$_3$)(=C(O*Me*)*Me*), complexes **2** do not undergo such a reaction even under refluxing conditions for 40 h. However, when complexes **2** are treated with *Me*OH in the presence of air, the C=C bond is cleaved to afford the neutral complex Ru*Tp*(P*Ph*$_2$*Pr*^{i})(Cl)(CO) (**3**) adding to the known cases of the oxidation of Ru(II) vinylidene complexes by dioxygen as shown in Scheme 2 [2e]. The identity of **3** was proven by a combination of elemental analysis, ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy. In the ^{13}C{^{1}H} NMR spectrum the CO ligand exhibits a characteristic low-intensity doublet centered at 205.7 ppm (J_{CP} = 16.9 Hz). A structural view of **3** is depicted in Fig. 3 with selected structural data given in the caption. The overall octahedral structure of **3** is very similar to that of **2a**. While the Ru–N(4) and Ru–N(6) distances are relatively similar (2.139(1) and 2.117(1) Å), Ru–N(2) *trans* to chloride is significantly shorter with 2.093(1) Å. The Ru–P and Ru–Cl distances are 2.3495(4) and 2.3911(7) Å, respectively. The Ru–C(10) distance is 1.863(4) Å.



Scheme 2

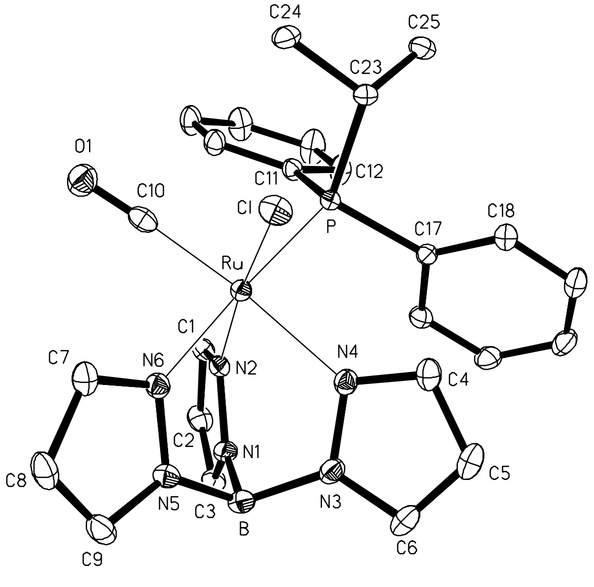


Fig. 3. Structural view of Ru*Tp*(P*Ph*$_2$*Pr*^{i})(CO)Cl · $(C_2H_5)_2O$ (**3** · $(C_2H_5)_2O$) showing 30% probability thermal ellipsoids (solvent molecule omitted for clarity); selected distances (Å) and angles (°): Ru–C(10) 1.863(4), Ru–N(2) 2.093(1), Ru–N(4) 2.139(1), Ru–N(6) 2.117(1), Ru–P 2.3495(4), Ru–Cl 2.3911(7), Ru–C(10)–O(1) 174.5(2)

Experimental

All manipulations were performed under an inert atmosphere of argon by using *Schlenk* techniques. All chemicals were standard reagent grade and used without further purification. The solvents were purified according to standard procedures [13]. The deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. Ru*Tp*(*COD*)Cl (**1**) was prepared according to the literature [14]. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AVANCE-250 spectrometer operating at 250.13, 62.86, and 101.26 MHz, respectively, and were referenced to $SiMe_4$ and H_3PO_4 (85%). Elemental analysis were found to agree favorably with the calculated values.

$RuTp(PPh_2Pr^i)(=C{=}CHPh)Cl$ (**2a**, $C_{32}H_{33}BClN_6PRu$)

A suspension of **1** (200 mg, 0.44 mmol) and PPh_2Pr^i (100.4 mg, 0.44 mmol) in *DMF* (4 cm^3) was heated for 2 h at reflux temperature. After removal of the solvent, the remaining residue was dissolved in CH_2Cl_2 and $HC\equiv CPh$ (145 mm^3, 1.32 mmol) was added and stirred for 24 h at room temperature. The volume of the solution was then reduced to about 1 cm^3 and the product was precipitated by addition of Et_2O and petroleum ether. The residue was collected on a glass frit, washed with *n*-hexane, and dried *in vacuo*. Yield 223 mg (74.3%); ^1H NMR ($CDCl_3$, 20°C): $\delta = 7.88$ (m, 2H, Ph), 7.79 (d, 1H, $J = 2.5$ Hz, Tp), 7.65 (d, 1H, $J = 2.5$ Hz, Tp) 7.51 (m, 2H, Tp), 7.43 (m, 1H, Ph), 7.33–7.03 (m, 13H), 6.55 (d, 1H, Tp), 6.10 (dd, 1H, $J_1 = J_2 = 2.7$ Hz, Tp), 5.88 (dd, 1H, $J_1 = J_2 = 2.5$ Hz, Tp), 5.82 (dd, 1H, $J_1 = J_2 = 2.2$ Hz, Tp), 5.19 (d, 1H, $^4J_{HP} = 3.5$ Hz, Ru=C=C*H*Ph), 3.52 (m, 1H), 1.65 (dd, 3H, $^3J_{PH} = 16.9$ Hz, $^3J_{HH} = 7$ Hz), 1.04 (dd, 3H, $^3J_{PH} = 13.7$ Hz, $^3J_{HH} = 7$ Hz) ppm; $^{13}C\ \{^1H\}$ NMR ($CDCl_3$, 20°C): $\delta = 366.0$ (d, $J_{PC} = 19$ Hz, Ru=*C*=CHPh), 144.7 (Tp), 143.4 (d, $J_{PC} = 1.5$ Hz, Tp), 142.9 (Tp), 136.7 (Tp), 134.3 (d, $J_{PC} = 3.2$ Hz, Tp), 134.2 (d, $^2J_{PC} = 8.0$ Hz, Ph), 133.9 (Tp), 133.3 (d, $^2J_{PC} = 7.2$ Hz, Ph), 131.4 (d, $^1J_{PC} = 37.8$ Hz, Ph), 130.9 (d, $J_{PC} = 2.3$ Hz, Ph), 130.3 (d, $^4J_{PC} = 2.4$ Hz, Ph), 129.7 (d, $^4J_{PC} = 2.4$ Hz, Ph), 128.9 (Ph), 128.3 (d, $^3J_{PC} = 8.8$ Hz, Ph), 128.1 (d, $^3J_{PC} = 8.8$ Hz, Ph), 126.2 (Ph), 125.2 (Ph), 112.9 (d, $^3J_{PC} = 1.6$ Hz, Ru=C=*C*HPh), 106.1 (d, $J_{PC} = 3.2$ Hz, Tp), 106.0 (Tp), 105.4 (Tp), 23.8 (d, $J_{PC} = 28.9$ Hz, CH), 19.2 (d, $J_{PC} = 1.6$ Hz, CH_3), 18.8 (d, $J_{PC} = 4.8$ Hz, CH_3) ppm; ^{31}P NMR ($CDCl_3$, 20°C): $\delta = 42.3$ ppm.

$RuTp(PPh_2Pr^i)(=C{=}CHC_4H_3S)Cl$ (**2b**, $C_{30}H_{31}BClN_6PSRu$)

This complex has been prepared analogously to **2a** using **1** (200 mg, 0.44 mmol), PPh_2Pr^i (117.3 mg, 0.44 mmol), and 2-ethynylthiophene (76.8 mm^3, 0.66 mmol) as starting materials. Yield 249 mg (71%); ^1H NMR ($CDCl_3$, 20°C): $\delta = 7.85$ (m, 3H), 7.65 (d, 1H, $J = 2.2$ Hz, Tp), 7.51–6.93 (m, 11H), 6.77 (d, 1H, $J = 3.0$ Hz, Tp), 6.59 (d, 1H, $J = 1.7$ Hz, Tp), 6.12 (dd, 1H, $J_1 = 2.0$ Hz, $J_2 = 2.8$ Hz, Tp), 5.87 (dd, 1H, $J_1 = J_2 = 2.4$ Hz, Tp), 5.81 (dd, 1H, $J_1 = J_2 = 2.2$ Hz, Tp), 5.53 (d, 1H, $J = 3.9$ Hz, $^4J_{PH} = 3.9$ Hz, Ru=C=C*H*Ph), 3.50 (m, 1H), 1.64 (dd, 3H, $^3J_{PH} = 16.4$ Hz, $^3J_{HH} = 7$ Hz), 1.03 (dd, 3H, $^3J_{PH} = 13.4$ Hz, $^3J_{HH} = 7$ Hz) ppm; $^{13}C\ \{^1H\}$ NMR ($CDCl_3$, 20°C): $\delta = 365.3$ (d, $J_{PC} = 19.9$ Hz, Ru=*C*=CHC_4H_3S), 144.8 (Tp), 143.0 (Tp), 142.6 (Tp), 136.5 (Tp), 134.1 (d, $J_{PC} = 3.1$ Hz, Tp), 133.9 (d, $^2J_{PC} = 7.7$ Hz, Ph), 133.8 (Tp), 133.0 (d, $^2J_{PC} = 7.7$ Hz, Ph), 130.9 (d, $^1J_{PC} = 37.6$ Hz, Ph), 130.3 (d, $^1J_{PC} = 38.3$ Hz, Ph), 130.1 (d, $^4J_{PC} = 2.3$ Hz, Ph), 129.5 (d, $^4J_{PC} = 2.3$ Hz, Ph), 128.2 (d, $^3J_{PC} = 8.4$ Hz, Ph), 127.9 (d, $J_{PC} = 4.3$ Hz, C_4H_3S), 127.9 (d, $^3J_{PC} = 8.4$ Hz, Ph), 127.2 (C_4H_3S), 122.6 (C_4H_3S), 121.74 (C_4H_3S), 106.5 (d, $^3J_{PC} = 1.5$ Hz, Ru=C=*C*HPh), 105.8 (d, $J_{PC} = 3.1$ Hz, Tp), 105.7 (Tp), 105.2 (Tp), 23.8 (d, $J_{PC} = 28.4$ Hz, CH), 19.0 (d, $J_{PC} = 1.5$ Hz, CH_3), 18.5 (d, $J_{PC} = 4.6$ Hz, CH_3) ppm; ^{31}P NMR ($CDCl_3$, 20°C): $\delta = 42.4$ ppm.

$RuTp(PPh_2Pr^i)(=C{=}CHC_6H_4OMe)Cl$ (**2c**, $C_{33}H_{35}BClN_6OPRu$)

This complex has been prepared analogously to **2a** using **1** (150 mg, 0.33 mmol), PPh_2Pr^i (75.3 mg, 0.33 mmol), and 1-ethynyl-4-methoxybenzene (87.2 mg, 0.66 mmol) as starting materials. Yield 186 mg (81%); ^1H NMR ($CDCl_3$, 20°C): $\delta = 7.91$–7.77 (m, 2H), 7.73 (d, 1H, $J = 1.9$ Hz, Tp), 7.61 (d, 1H, $J = 1.9$ Hz, Tp) 7.55–6.75 (m, 15H), 6.48 (d, 1H, $J = 1.9$ Hz, Tp), 6.10 (d, 1H, $J = 1.9$ Hz, Tp), 5.83 (dd, 1H, $J_1 = J_2 = 2.1$ Hz, Tp), 5.78 (dd, 1H, $J_1 = J_2 = 2.0$ Hz, Tp), 5.14 (d, 1H, $^4J_{PH} = 3.8$ Hz, Ru=C=C*H*Ph), 3.79 (3H, –O*Me*), 3.61–3.35 (m, 1H), 1.61 (dd, 3H, $^{3}J_{PH} = 16.8$ Hz, $^{3}J_{HH} = 6.9$ Hz), 1.0 (dd, 3H, $^{3}J_{PH} = 13.4$ Hz, $^{3}J_{HH} = 6.8$ Hz) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 20°C): $\delta = 368.6$ (d, $J_{PC} = 19.2$ Hz, Ru=*C*=CHPh), 157.3 (C_6H_4OMe, C^1), 144.5 (Tp), 143.1 (d, $J_{PC} = 1.5$ Hz, Tp), 142.7 (Tp), 136.5 (Tp), 134.1 (d, $J_{PC} = 3.1$ Hz, Tp), 133.9 (d, $^{2}J_{PC} = 8.4$ Hz, Ph), 133.7 (Tp), 133.0 (d, $^{2}J_{PC} = 7.7$ Hz, Ph), 131.3 (d, $^{1}J_{PC} = 37.6$ Hz, Ph), 130.5 (d, $^{1}J_{PC} = 38.3$ Hz, Ph), 130.1 (d, $^{4}J_{PC} = 2.3$ Hz, Ph), 129.4 (d, $^{4}J_{PC} = 2.3$ Hz, Ph), 128.1 (d, $^{3}J_{PC} = 9.2$ Hz, Ph), 127.8 (d, $^{3}J_{PC} = 8.4$ Hz, Ph), 127.1 (C_6H_4OMe, $C^{3,5}$), 121.6 (d, $J_{PC} = 2.3$ Hz, C_6H_4OMe, C^4), 114.3 (C_6H_4OMe, $C^{2,6}$), 112.0 (d, $^{3}J_{PC} = 1.5$ Hz, Ru=C=*C*HPh), 105.8 (d, $J_{PC} = 3.1$ Hz, Tp), 105.7 (Tp), 105.2 (Tp), 55.3 (OMe), 23.5 (d, $^{1}J_{PC} = 28.4$ Hz, CH), 18.9 (d, $^{2}J_{PC} = 2.3$ Hz, CH_3), 18.5 (d, $^{2}J_{PC} = 4.6$ Hz, CH_3) ppm; ^{31}P NMR ($CDCl_3$, 20°C): $\delta = 41.6$ ppm.

RuTp(PPh$_2$Pr^i)(=C=CHFc)Cl (**2d**, $C_{36}H_{37}BClFeN_6PRu$)

This complex has been prepared analogously to **2a** using **1** (150 mg, 0.33 mmol), P*Ph$_2$Pr^i* (75.3 mg, 0.33 mmol), and 1-ethynylferrocene (75.7 mg, 0.36 mmol) as starting materials. Yield 115 mg (45%); ^{1}H NMR ($CDCl_3$, 20°C): $\delta = 8.13$–6.87 (m, 15H), 6.55 (1H, Tp), 6.15 (1H, Tp), 5.86 (1H, Tp), 5.77 (1H, Tp), 4.94 (d, 1H, $^{4}J_{PH} = 3.5$ Hz, Ru=C=C*H*Ph), 4.19–4.08 (m, 3H, Fc), 4.05 (s, 5H, Fc), 4.01–3.94 (m, 1H, Fc), 3.58–3.34 (m, 1H), 1.65 (dd, 3H, $^{3}J_{PH} = 16.9$ Hz, $^{3}J_{HH} = 6.8$ Hz), 0.97 (dd, 3H, $^{3}J_{PH} = 13.3$ Hz, $^{3}J_{HH} = 6.5$ Hz) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 20°C): $\delta = 366.3$ (d, $J_{PC} = 19.9$ Hz, Ru=*C*=CHPh), 144.7 (Tp), 142.9 (Tp), 142.6 (Tp), 136.5 (Tp), 134.2 (Tp), 134.1 (d, $^{2}J_{PC} = 8.4$ Hz, Ph), 133.7 (Tp), 132.9 (d, $^{2}J_{PC} = 7.7$ Hz, Ph), 131.4 (d, $^{1}J_{PC} = 37.6$ Hz, Ph), 130.7 (d, $^{1}J_{PC} = 38.3$ Hz, Ph), 130.1 (d, $^{4}J_{PC} = 2.3$ Hz, Ph), 129.4 (d, $^{4}J_{PC} = 2.3$ Hz, Ph), 128.1 (d, $^{3}J_{PC} = 9.2$ Hz, Ph), 127.9 (d, $^{3}J_{PC} = 8.4$ Hz, Ph), 106.8 (Ru=C=*C*HPh), 105.7 (d, $J_{PC} = 3.1$ Hz, Tp), 105.6 (Tp), 105.1 (Tp), 75.3 (d, $J_{PC} = 2.3$ Hz, Fc), 69.2 (5C, Fc), 67.6 (Fc), 67.4 (Fc), 66.8 (Fc), 66.1 (Fc), 23.6 (d, $^{1}J_{PC} = 29.1$ Hz, CH), 19.2 (d, $^{2}J_{PC} = 1.5$ Hz, CH_3), 18.5 (d, $J_{PC} = 4.6$ Hz, CH_3) ppm; ^{31}P NMR ($CDCl_3$, 20°C): $\delta = 43.0$ ppm.

RuTp(PPh$_2$Pr^i)(=C=CHC$_6$H$_4$Fc)Cl (**2e**, $C_{42}H_{41}BClFeN_6PRu$)

This complex has been prepared analogously to **2a** using **1** (110.6 mg, 0.24 mmol), P*Ph$_2$Pr^i* (55.8 mg, 0.24 mmol), and 1-ethynyl-4-ferrocenylbenzene (84.0 mg, 0.29 mmol) as starting materials. Yield 96 mg (60.4%); ^{1}H NMR ($CDCl_3$, 20°C): $\delta = 8.17$–6.69 (m, 19H), 6.46 (1H, Tp), 6.02 (1H, Tp), 5.83 (1H, Tp), 5.78 (1H, Tp), 5.17 (d, 1H, $^{4}J_{PH} = 3.5$ Hz, Ru=C=C*H*Ph), 4.86–4.73 (m, 2H, Fc), 4.33–4.18 (m, 2H, Fc), 4.04 (s, 5H, Fc), 3.67–3.49 (m, 1H), 1.68 (dd, 3H, $^{3}J_{PH} = 17.1$ Hz, $^{3}J_{HH} = 6.6$ Hz), 1.00 (dd, 3H, $^{3}J_{PH} = 13.0$ Hz, $^{3}J_{HH} = 6.1$ Hz) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 20°C): $\delta = 366.7$ (d, $J_{PC} = 19.9$ Hz, Ru=*C*=CHPh), 144.3 (Tp), 143.5 (Tp), 142.7 (Tp), 139.8 (C_6H_4–Fc), 136.5 (Tp), 134.1 (Tp), 134.0 (d, $^{2}J_{PC} = 8.4$ Hz, Ph), 133.7 (Tp), 133.0 (d, $^{2}J_{PC} = 6.9$ Hz, Ph), 131.6 (C_6H_4–Fc), 131.2 (d, $^{1}J_{PC} = 43.7$ Hz, Ph), 130.3 (d, $^{1}J_{PC} = 38.3$ Hz, Ph), 130.1 (d, $^{4}J_{PC} = 3.1$ Hz, Ph), 129.5 (d, $^{4}J_{PC} = 3.0$ Hz, Ph), 128.5 (C_6H_4–Fc), 128.1 (d, $^{3}J_{PC} = 9.2$ Hz, Ph), 127.9 (d, $^{3}J_{PC} = 8.4$ Hz, Ph), 124.9 (C_6H_4–Fc), 122.5 (C_6H_4–Fc), 121.8 (C_6H_4–Fc), 113.1 (Ru=C=*C*HPh), 105.9 (Tp), 105.8 (Tp), 105.3 (Tp), 84.8 (Fc), 69.6 (5C, Fc), 68.9 (Fc), 68.8 (Fc), 66.8 (Fc), 66.3 (Fc), 23.5 (d, $^{1}J_{PC} = 29.0$ Hz, CH), 19.0 (d, $^{2}J_{PC} = 1.8$ Hz, CH_3), 18.5 (d, $J_{PC} = 4.6$ Hz, CH_3) ppm; ^{31}P NMR ($CDCl_3$, 20°C): $\delta = 41.1$ ppm.

RuTp(PPh$_2$Pr^i)(=C=CHC$_6$H$_9$)Cl (**2f**, $C_{32}H_{37}BClN_6PRu$)

This complex has been prepared analogously to **2a** using **1** (100 mg, 0.22 mmol), P*Ph$_2$Pr^i* (50.2 mg, 0.22 mmol), and 1-ethynylcyclohexene (49.2 mg, 0.33 mmol) as starting materials. Yield 103 mg (69%). ^{1}H NMR (CD_2Cl_2, 20°C): $\delta = 8.05$–6.89 (m, 15H), 6.52–6.36 (m, 1H, Tp), 6.31–6.10 (m, 1H, Tp), 5.96–5.73 (m, 2H, Tp), 5.26–5.16 (m, 1H), 4.77 (d, 1H, $^{4}J_{HP} = 3.2$ Hz, Ru=C=C*H*C_6H_9), 3.54–3.29 (m, 1H), 2.36–2.16 (m, 2H), 2.10–1.82 (m, 2H), 1.74–1.56 (m, 4H), 1.50 (dd, 3H, $^3J_{PH}=16.1$ Hz, $^3J_{HH}=6.8$ Hz), 1.11 (dd, 3H, $^3J_{PH}=13.9$ Hz, $^3J_{HH}=6.5$ Hz) ppm; ^{13}C {^{1}H} NMR (CD_2Cl_2, 20°C): $\delta=369.2$ (d, $J_{PC}=19.2$ Hz, Ru=*C*=CHC_6H_9), 144.5 (Tp), 142.7 (Tp), 142.5 (d, $J_{PC}=1.5$ Hz, Tp), 136.3 (Tp), 134.3 (d, $J_{PC}=3.1$ Hz, Tp), 134.0 (Tp), 133.9 (d, $^2J_{PC}=7.7$ Hz, Ph), 133.3 (d, $^2J_{PC}=7.7$ Hz, Ph), 131.4 (d, $^1J_{PC}=37.6$ Hz, Ph), 130.5 (d, $^1J_{PC}=37.6$ Hz, Ph), 129.9 (d, $^4J_{PC}=2.3$ Hz, Ph), 129.5 (d, $^4J_{PC}=2.3$ Hz, Ph), 128.0 (d, $^3J_{PC}=8.4$ Hz, Ph), 127.8 (d, $^3J_{PC}=8.4$ Hz, Ph), 126.1 (C_6H_9), 116.8 (C_6H_9), 115.0 (d, $^3J_{PC}=1.5$ Hz, Ru=C=*C*HC_6H_9), 105.5 (Tp), 105.3 (d, $J_{PC}=3.1$ Hz, Tp), 104.9 (Tp), 29.7 (C_6H_9), 25.6 (C_6H_9), 23.9 (d, $J_{PC}=28.4$ Hz, –CH), 23.1 (C_6H_9), 22.4 (C_6H_9), 18.7 (CH_3), 18.4 (d, $J_{PC}=3.8$ Hz, CH_3) ppm; ^{31}P NMR (CD_2Cl_2, 20°C): $\delta=40.7$ ppm.

RuTp(PPh$_2$Pr^i)(CO)Cl (**3**, $C_{25}H_{27}BClN_6OPRu$)

A suspension of **2a** (50 mg, 0.07 mmol) in *Me*OH (3 cm^3) was heated to 80°C for 40 h in the presence of air. After the volume of solution was reduced to about 0.5 cm^3, the product was precipitated with *Et*$_2$O (10 cm^3) and petroleum ether (10 cm^3). The product was collected on a glass frit, washed with *Et*$_2$O, and dried under vacuum. Yield 34 mg (77%); ^{1}H NMR ($CDCl_3$, 20°C): $\delta=8.02$ (m, 1H, Tp), 7.62–7.09 (m, 14H), 6.75 (d, 1H, $J=1.7$ Hz, Tp), 6.17 (dd, 1H, $J_1=J_2=2.5$ Hz, Tp), 5.88 (dd, 1H, $J_1=J_2=2.2$ Hz, Tp), 5.74 (dd, 1H, $J_1=J_2=2.2$ Hz, Tp), 3.28 (m, 1H), 1.62 (dd, 3H, $^3J_{PH}=16.8$ Hz, $^3J_{HH}=7$ Hz), 1.23 (dd, 3H, $^3J_{PH}=14.2$ Hz, $^3J_{HH}=6.8$ Hz) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 20°C): $\delta=205.7$ (d, $^2J_{CP}=16.9$ Hz, Ru–CO), 144.2 (Tp), 143.7 (Tp), 136.9 (Tp), 134.9 (d, $^2J_{PC}=8.8$ Hz, Ph), 134.0 (d, $^2J_{PC}=8.0$ Hz, Ph), 132.5 (d, $^1J_{PC}=38.6$ Hz, Ph), 131.8 (d, $^1J_{PC}=37.8$ Hz, Ph), 131.7 (Tp), 130.45 (Ph), 130.0 (Ph), 128.7 (d, $^3J_{PC}=8.8$ Hz, Ph), 128.4 (d, $^3J_{PC}=8.8$ Hz, Ph), 128.4 (Tp), 124.70 (Tp), 106.0 (Tp), 105.7 (Tp), 105.4 (Tp), 26.9 (d, $J_{PC}=31.3$ Hz, CH), 19.5 (d, 15.3 Hz, CH_3) ppm; ^{31}P {^{1}H} NMR ($CDCl_3$, 20°C): $\delta=56.2$ ppm.

X-Ray Structure Determination

Crystals of Ru*Tp*(P*Ph*$_2$*Pr*^{i})Cl(=C=CHC_4H_3S) (**2b**), Ru*Tp*(P*Ph*$_2$*Pr*^{i})Cl(=C=CHC_6H_9) (**2f**), and Ru*Tp*(P*Ph*$_2$*Pr*^{i})Cl(CO) · $(C_2H_5)_2O$ (**3** · $(C_2H_5)_2O$) were obtained by diffusion of diethyl ether into acetone solutions (**2b**, **3** · $(C_2H_5)_2O$) or by evaporation of a CH_2Cl_2 solution (**2f**). X-Ray data were collected on a Bruker Smart APEX CCD area detector diffractometer (graphite monochromated Mo$K\alpha$ radiation, $\lambda=0.71073$ Å, 0.3° ω-scan frames covering complete spheres of the reciprocal space) [15]. Corrections for crystal decay and for absorption were applied. The structures were solved with direct methods using the program SHELXS97 [16]. Structure refinements on F^2 were carried out with program SHELXL97 [16]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were inserted in idealized positions and were refined riding with the atoms to which they were bound. Complete structure data have been deposited [17]. Salient crystal data are: **2b**: $C_{30}H_{31}BClN_6PRuS$, $M_r=685.97$, monoclinic, space group $C2/c$ (No. 15), $T=295(2)$ K, $a=16.390(4)$ Å, $b=14.601(3)$ Å, $c=26.726(6)$ Å, $\beta=99.24(2)°$, $V=6313(2)$ Å^3, $Z=8$, $\mu=0.728$ mm^{-1}. Of 32051 reflections collected up to $\theta=25°$, 5529 were independent, $R_{int}=0.046$; final R indices: $R_1=0.033$ (all data), $wR_2=0.070$ (all data). **2f**: $C_{32}H_{37}BClN_6PRu$, $M_r=683.98$, monoclinic, space group $C2/c$ (No. 15), $T=123(2)$ K, $a=16.3374(6)$ Å, $b=14.8021(5)$ Å, $c=26.755(1)$ Å, $\beta=99.205(1)°$, $V=6386.9(4)$ Å^3, $Z=8$, $\mu=0.657$ mm^{-1}. Of 45821 reflections collected up to $\theta=25°$, 29073 were independent, $R_{int}=0.064$; final R indices: $R_1=0.063$ (all data), $wR_2=0.099$ (all data); this solid state structure is isostructural with **2b** (thiophene of **2b** replaced by a cyclohexene moiety in **2f**, all other features of molecular and crystal structures in good agreement, as shown in Figs. 1 and 2). **3**: $C_{28}H_{37}BClN_6O_2PRu$, $M_r=667.94$, triclinic, space group $P\bar{1}$ (No. 2), $T=173(2)$ K, $a=9.1350(5)$ Å, $b=12.8201(7)$ Å, $c=13.8500(7)$ Å, $\alpha=73.134(2)°$, $\beta=84.399(2)°$, $\gamma=88.404(2)°$, $V=1544.8(1)$ Å^3, $Z=2$, $\mu=0.681$ mm^{-1}. Of 23348 reflections collected up to $\theta=30°$, 8922 were independent, $R_{int}=0.022$; final R indices: $R_1=0.033$ (all data), $wR_2=0.073$ (all data).

Acknowledgements

Financial support by the "Fonds zur Förderung der wissenschaftlichen Forschung" (Project No. P16600-N11) is gratefully acknowledged.

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