Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Organometallic Chemistry 682 (2003) 272–289
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Reactions of ruthenium(II) tris(pyrazolyl)borate and tris(pyrazolyl)methane complexes with diphenylvinylphosphine and 3,4-dimethyl-1-phenylphosphole

Dee C. Wilson, John H. Nelson *

Department of Chemistry/216, University of Nevada-Reno, Reno, NV 89557-0020, USA

Received 16 May 2003; received in revised form 28 July 2003; accepted 28 July 2003

Abstract

Several new ruthenium(II) tris(pyrazolyl)borate and tris(pyrazolyl)methane complexes containing diphenylvinylphosphine (DPVP), 3,4-dimethyl-1-phenylphosphole (DMPP) and 1,2-bis (diphenylphosphino) ethane (dppe), namely: (Tp)Ru (DPVP) (CH_3CN)Cl; (Tp)Ru (DPVP)$_2$Cl; (Tp)Ru (DPVP) (DMPP) [4+2]Cl; [(Tp)Ru (DPVP)$_2$ (CH_3CN)]PF_6; (Tp)Ru (DMPP)$_2$ [4+2]Cl; [(Tpm)Ru (DPVP)$_2$ Cl]PF_6; [(Tpm)Ru(dppe)Cl]PF_6; [(Tpm)Ru(DMPP)$_2$ [4+2]Cl]PF_6 and [(Tp)Ru (dppe) (Me_2CO)]PF_6 have been prepared, characterized and their reaction chemistry studied. Characterization includes infrared spectroscopy, ^{1}H-, ^{13}C{^{1}H}- and ^{31}P{^{1}H}-NMR spectroscopy and in several cases X-ray crystallography.
© 2003 Elsevier B.V. All rights reserved.

Keywords: Ruthenium; Tris(pyrazolyl)borate; Tris(pyrazolyl)methane; Phosphaallyl; [4+2] Diels–Alder cycloaddition

1. Introduction

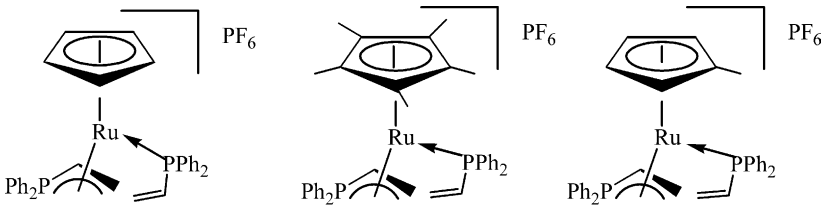
In the course of our investigations with transition metal complexes of olefinic phosphines we have found that diphenylvinylphosphine (DPVP) forms the unusual hemilabile phosphaallyl complexes [(η^5-C_5H_5)Ru(η^3-DPVP)(η^1-DPVP)]PF_6 (**A**) [1], [(η^5-C_5Me_5)Ru(η^3-DPVP)(η^1-DPVP)]PF_6 (**B**) [2], and [(η^5-C_5H_4Me)Ru(η^3-DPVP)(η^1-DPVP)]PF_6 (**C**) [3] (Scheme 1).

The phosphaallyl moiety in complexes **A**–**C** behaves as a hemilabile four-electron to two-electron donor ligand. The major stabilizing interaction in the η^3-four-electron donor bonding mode is back donation from the metal into the π^* orbital of the vinyl group. Consequently, both the thermodynamic stability and kinetic lability of these species is a strong function of the donor abilities of the ancillary ligands coordinated to ruthenium(II).

Complexes of hemilabile bifunctional phosphine ligands have proven to have novel and important applications in organometallic chemistry and in catalysis [4–17]. Complexes **A**–**C**, and other phosphine analogs, react with terminal alkynes to form vinylidene and allenylidene derivatives that react stoichiometrically and sometimes catalytically with a variety of nucleophiles [18–35]. The electrophilicity of the vinylidenes and allenylidenes is also a strong function of the electron density at ruthenium, which is moderated by the donor abilities of the ancillary ligands in the metal's coordination sphere. In order to gain additional information regarding these important areas we have prepared new ruthenium tris(pyrazolyl)borate and tris(pyrazolyl)methane complexes as these ligands are isoelectronic with cyclopentadiene ligands, but they possess quite different stereoelectronic properties [36–38].

* Corresponding author. Tel.: +1-775-784-6588; fax: +1-775-784-6804.
E-mail address: jhnelson@equinox.unr.edu (J.H. Nelson).

0022-328X/03/$ - see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2003.07.010



Scheme 1.

2. Results and discussion

2.1. Synthesis and characterization of *1–4*

The polymeric complexes $[Ru(COD)Cl_2]_n$ and $[Ru(NBD)Cl_2]_n$ [39] (COD = 1,5 cylooctadiene, NBD = norbonadiene) dissolve in refluxing CH_3CN to form compounds **1** and **2**, respectively. Compounds **1** and **2** react further in the presence of NH_4PF_6 to form **3** and **4** (Scheme 2).

All four complexes (**1**–**4**) were isolated in high yield as orange–brown crystals. Compounds **1** and **3** have been previously reported [40]. Both **1** and **2** could exist in isomeric forms with either the two chloride or two acetonitrile ligands in mutually *trans* positions. Since ^1H- and $^{13}C\{^1H\}$-NMR spectroscopy would reveal chemical shift equivalent CH_3CN molecules for both isomers, the structure of **2** was determined by X-ray crystallography (Fig. 1). Crystallographic data appear in Table 1. In the molecular structure, like that of the COD analog (**1**) [40], the two CH_3CN ligands occupy mutually *trans* positions. However, for both structures the N(1)–Ru(1)–N(2) bond angle is considerably less than 180° [167.7(2)° (**1**); 165.16(12)° (**2**)]. The smaller angle for **2** correlates with somewhat shorter Ru–C bond distances to the coordinated diolefin [2.437(1) Å (**1**); 2.4193(11) Å (ave. **2**)]. Collectively, these data suggest that NBD in sterically more bulky than COD and is bound more strongly to ruthenium. This latter conclusion is consistent with solution calorimetry measurments by Nolan and coworkers [41] with the $(\eta^5\text{-}C_5Me_5)RuCl$ moiety where they found a greater bond energy for NBD than COD.

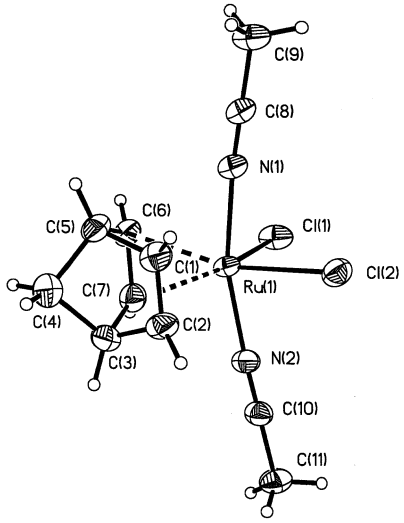


Fig. 1. Drawing of the molecular structure of **2** showing the atom-labeling scheme. Thermal ellipsoids enclose 40% of the electron density. Hydrogen atoms have an arbitrary radius of 0.1 Å. Selected bond distances (Å) and angles (°): Ru(1)–N(1), 2.045(3); Ru(1)–N(2), 2.053(3); Ru(1)–Cl(1), 2.4227(11); Ru(1)–Cl(2), 2.4159(11); Ru(1)–C(6), 2.183(4); Ru(1)–C(7), 2.193(4); Ru(1)–C(1), 2.208(4); Ru(1)–C(2), 2.201(4); N(1)–Ru(1)–N(2), 165.69(12); Cl(1)–Ru(1)–Cl(2), 92.92(4).

$$[Ru(COD)Cl_2]_n + 2\,CH_3CN \longrightarrow [Ru(COD)(CH_3CN)_2Cl_2]$$
1

$$[Ru(NBD)Cl_2]_n + 2\,CH_3CN \longrightarrow [Ru(NBD)(CH_3CN)_2Cl_2]$$
2

$$\mathbf{1} + CH_3CN + NH_4PF_6 \longrightarrow [Ru(COD)(CH_3CN)_3Cl]PF_6 + NH_4Cl$$
3

$$\mathbf{2} + CH_3CN + NH_4PF_6 \longrightarrow [Ru(NBD)(CH_3CN)_3Cl]PF_6 + NH_4Cl$$
4

Scheme 2.

Table 1
Crystallographic data for complexes **2** and **4**

Compound	**2**	**4**
Empirical formula	$C_{11}H_{14}Cl_2N_2Ru$	$C_{13}H_{17}ClF_6N_3PRu$
F_w	346.1	496.79
Crystal System	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions		
a (Å)	6.9282(8)	7.1058(18)
b (Å)	10.6617(18)	11.592(4)
c (Å)	12.6229(18)	11.986(3)
α (°)	72.329(9)	75.82(2)
β (°)	83.600(13)	87.74(2)
γ (°)	82.708(12)	84.39(3)
V (Å^3)	878.6(2)	952.5(5)
Z	2	2
ρ_{calc} (Mg m^{-3})	1.760	1.732
μ (mm^{-1})	1.643	1.104
Trans. Max/min	0.9668/0.8981	0.9042/0.8294
Data/restraints/parameters	3073/0/182	3346/0/212
GOF	1.029	1.016
$R_1(F^2)/wR_2(F^2)$	0.0325/0.0723	0.0448/0.1259

2.2. Synthesis and characterization of 5–8

Compounds **1** and **2** react cleanly with sodium or potassium tris(pyrazolyl)borate (NaTp, KTp) and **3** and **4** (Fig. 2) react with tris(pyrazolyl)methane (Tpm) to form **5**–**8** (Scheme 3).

Compounds **5** [42] and **7** [43] were previously prepared by other, and in our opinion, more difficult

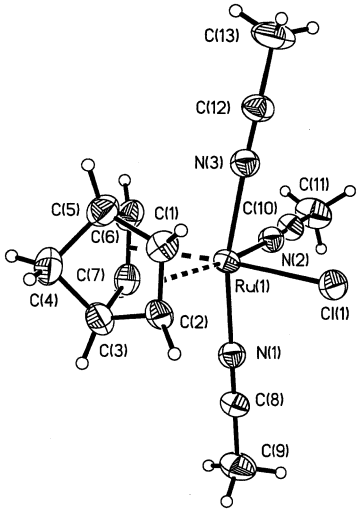
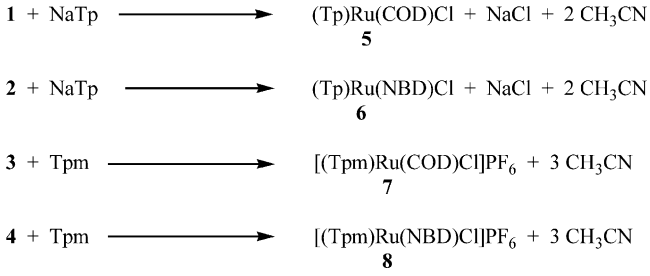


Fig. 2. Drawing of the structure of the cation of **4** showing the atom-labeling scheme. Thermal ellipsoids enclose 40% of the electron density. Hydrogen atoms have an arbitrary radius of 0.1 Å. Selected bond distances (Å) and angles (°): Ru(1)–N(3), 2.042 (5); Ru(1)–N(1), 2.043 (5); Ru(1)–N(2), 2.0179 (4); Ru(1)–Cl(1), 2.412 (16); Ru(1)–C(1), 2.191 (5); Ru(1)–C(2), 2.202 (5); Ru(1)–C(7), 2.203 (5); Ru(1)–C(6), 2.213 (16); N(3)–Ru(1)–N(1), 166.16 (17); N(3)–Ru(1)–N(2), 84.02 (17); N(1)–Ru(1)–N(2), 85.38 (17); N(3)–Ru(1)–N(1), 78.38 (19); N(3)–Ru(1)–Cl(1), 86.03 (13); N(1)–Ru(1)–Cl(1), 86.15 (13); N(2)–Ru(1)–Cl(1), 95.92 (13).



Scheme 3.

routes. The structures of **6** and **8** are shown in Figs. 3 and 4, respectively, and crystallographic data are given in Table 2. For the four compounds **5**–**8** the ruthenium coordination geometry is distorted octahedral. The Tp and Tpm ligands occupy three facial coordination sites, the diolefins two sites and the chloride the sixth site. For each structure one pyrazole ring and the Ru–Cl vector define an approximate mirror plane that relates the other two pyrazole rings and bisects the diolefin. The Ru–Cl bond lengths in the cations [2.413(2) Å (**5**); 2.416(6) Å (**6**)] are slightly shorter than those in the neutral complexes [2.4247(8) Å (**7**); 2.4393(17) Å (**8**)]. The ruthenium carbon bonds are shorter in the NBD complexes than in the COD complexes again implying stronger Ru–NBD bonding.

The proton and carbon-NMR chemical shifts for compounds **5**–**8** were assigned with the aid of COSY, HETCOR and ^{1}H NOE difference spectrscopies [44]. An example of the latter is shown in Fig. 5. The

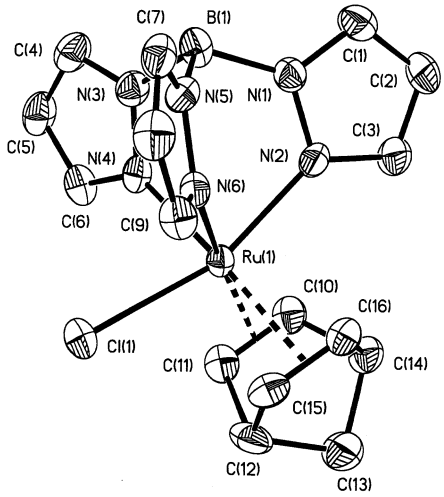


Fig. 3. Structural drawing of **6** showing the atom-labeling scheme. Thermal ellipsoids enclose 40% of the electron density. Selected bond distances (Å) and angles (°): Ru(1)–N(6), 2.100(5); Ru(1)–N(4), 2.113(5); Ru(1)–N(2), 2.144(6); Ru(1)–C(15), 2.189(6); Ru(1)–C(16), 2.213(6); Ru(1)–C(10), 2.208(6); Ru(1)–C(11), 2.204(7); Ru(1)–Cl(1), 2.4393(17); N(6)–Ru(1)–N(4), 88.3(2); N(6)–Ru(1)–N(2), 83.4(2); N(4)–Ru(1)–N(2), 83.4(2); N(6)–Ru(1)–Cl(1), 84.07(14); N(4)–Ru(1)–Cl(1), 83.06(15); N(2)–Ru(1)–Cl(1), 161.84(14).

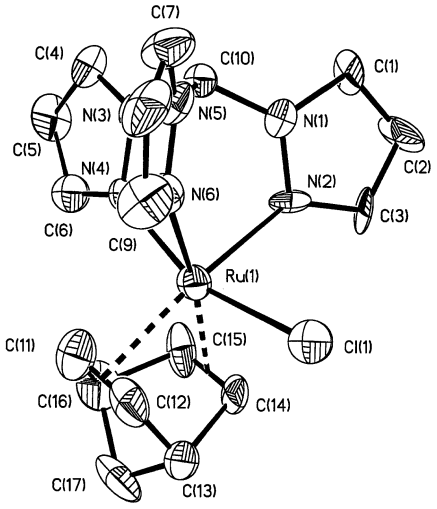


Fig. 4. Structural drawing of the cation of **8** showing the atom-labeling scheme. Thermal ellipsoids enclose 40% of the electron density. Selected bond distances (Å) and angles (°): Ru(1)–N(4), 2.12(2); Ru(1)–N(6), 2.14(2); Ru(1)–N(2), 2.140(16); Ru(1)–C(17), 2.19(2); Ru(1)–C(16), 2.15(2); Ru(1)–C(11), 2.19(2); Ru(1)–C(12), 2.22(3); Ru(1)–Cl(1), 2.416(6); N(4)–Ru(1)–N(6), 87.8(8); N(4)–Ru(1)–N(2), 80.8(7); N(6)–Ru(1)–N(2), 82.4(8).

Table 2
Crystallographic data for complexes **6** and **8**

Compound	**6**	**8**
Empirical formula	$C_{16}H_{18}BClN_6Ru$	$C_{17}H_{18}ClF_6N_6PRu$
F_w	441.69	587.86
Crystal System	Triclinic	Orthorhombic
Space group	$P\bar{1}$	$P2_12_12_1$
Unit cell dimensions		
a (Å)	8.2716(12)	10.032(2)
b (Å)	8.9027(13)	14.336(4)
c (Å)	12.2674(16)	14.793(3)
α (°)	76.233(13)	90
β (°)	87.297(15)	90
γ (°)	78.921(17)	90
V (Å^3)	861.1(2)	2127.6 (8)
Z	2	4
ρ_{calc} (Mg m^{-3})	1.704	1.835
μ (mm^{-1})	1.077	1.008
Trans. Max/min	0.9909/0.8731	0.9485/0.9038
Data/restraints/paramerters	3032/0/226	2781/0/274
GOF	1.042	1.037
$R_1(F^2)$ [a]/$wR_2(F^2)$ [b]	0.0507/0.0945	0.0810/0.1010

[a] $R(F) = S([F_o]-[F_c])/S([F_o])$.
[b] $wR(F) = [S[\omega(F_o^2-F_c^2)^2]/S[\omega(F_o^2)^2]]^{0.5}$; $\omega = 1/\sigma^2$ (counts)$+(\rho I)^2$.

assignment of the pyrazole H_α and H_γ resonances for Tp complexes is often ambiguous. Based upon the magnitudes of the H–H internuclear separations measured by X-ray crystallography [H_2–H_α = 2.384 Å; H_1–H_α = 3.628 Å; H_1–$H_{\alpha'}$ = 2.726 Å; H_2–$H_{\alpha'}$ = 4.696 Å] one expects to observe NOE's between H_2 and both H_α and $H_{\alpha'}$, but only between H_1 and H_α. These NOE experiments (Fig. 5) allowed an unambiguous assign-

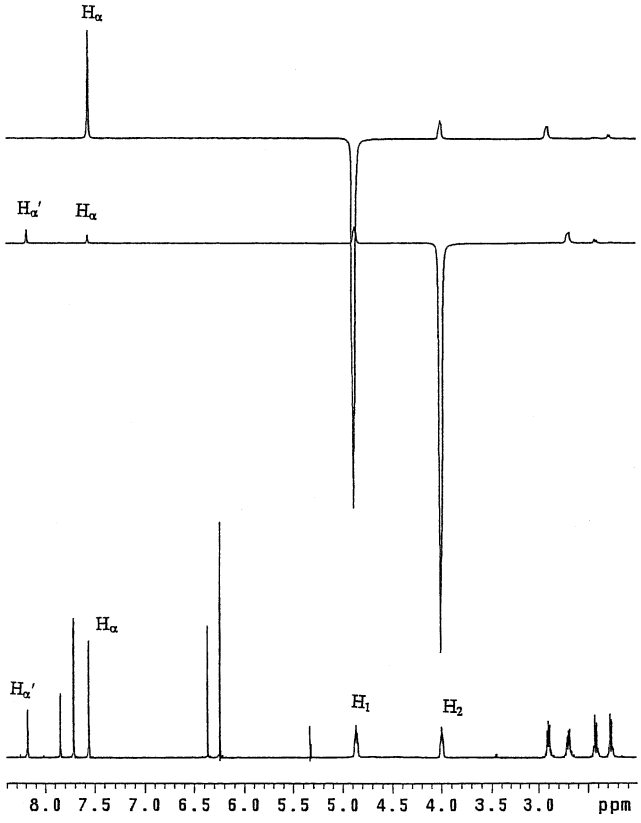


Fig. 5. 500 MHz 1H-NMR spectrum of **5** (bottom) compared with NOE difference spectra with irradiation of the two COD vinyl protons (top).

ment of the proton chemical shifts. The carbon chemical shifts were then assigned via HETCOR spectroscopy.

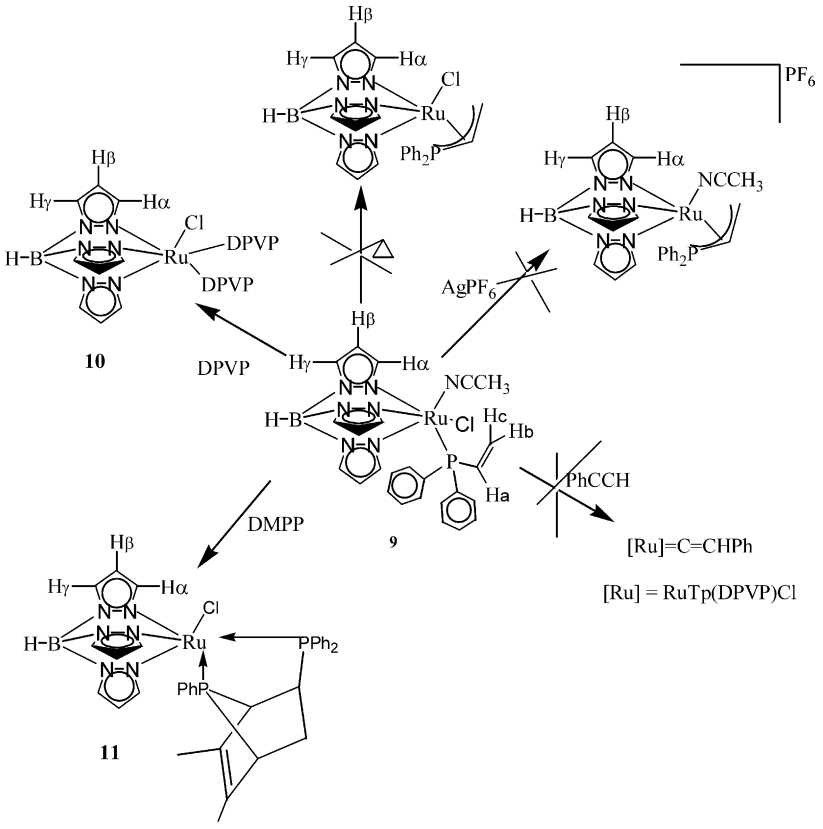
2.3. Synthesis and characterization of 9–11

Compound **9** was prepared according to reactions 1. The infrared spectrum for **9**

$$1 + KTp \xrightarrow[\Delta]{ClCH_2CH_2Cl} \underset{(87\%)}{(Tp)Ru(COD)Cl} + KCl$$

$$(Tp)Ru(COD)Cl + DPVP \xrightarrow[\Delta\ DMF/CH_3CN]{N_2} \underset{\mathbf{9}\ (80\%)}{(Tp)Ru(DPVP)(CH_3CN)Cl} \quad (1)$$

shows ν(B–H) at 2477 cm^{-1} and ν(CN) at 2279 cm^{-1}. The ^{1}H-NMR spectrum shows that all three pyrazole rings are inequivalent. The vinyl proton resonances for the coordinated DPVP ligand were clearly assigned with the aid of an $^1H\{^{31}P\}$ experiment. The ^{13}C chemical shifts were then assigned with the aid of APT and HETCOR spectra. Compound **9** was prepared for the purpose of studying its reactivity as illustrated in Scheme 4. It was hoped that, as in the synthesis of the phosphaallyl complexes **A**–**C** that heating **9** under



Scheme 4.

vacuum below its melting point would liberate CH_3CN and form a phosphaallyl complex. However, after heating this compound at 180 °C for 3 weeks under vacuum (1 mmHg), ^{1}H-NMR spectroscopy revealed that compound **9** remained unchanged. It was similarly hoped, on the basis of an analogous reaction of (η^6-Me_6C_6)Ru(DCVP)Cl_2 (DCVP = dicyclohexylvinylphosphine) with $AgPF_6$ [45] in acetone that **9** would form a phosphaallyl complex by chloride abstraction. Again **9** was recovered unchanged. Although the coordinated CH_3CN could not be displaced intramolecularly by the vinyl group of coordinated DPVP, complex **9** did react cleanly with DPVP and 3,4-dimethyl-1-phenylphosphole (DMPP) to produce **10** and **11**, respectively (Scheme 4). Both complexes were completely characterized by ^{1}H-, ^{13}C{^{1}H}- and ^{31}P{^{1}H}-NMR spectroscopy and by X-ray crystallography. The structures are shown in Figs. 6 and 7 and crystallographic data are given in Table 3.

For **10** the two Ru–P bond distances [Ru(1)–P(1), 2.340(3) Å; Ru(1)–P(2), 2.330(3) Å] are essentially the same and very similar to those observed [46] for (Tp)Ru(PPh_3)$_2$Cl [Ru(1)–P(1), 2.332(3) Å; Ru(1)–P(2), 2.349(3) Å]. The Ru–Cl bond distances [2.421(3) Å; 2.409(3) Å, respectively] are also quite similar. For **10** the Ru(1)–N(1) [2.138(9) Å] and Ru(1)–N(3) [2.153(10) Å] bonds are both longer than the Ru(1)–N(5) [2.072(9) Å] bond distance, because the former are *trans* to phosphorus and the latter are *trans* to chloride. Phos-

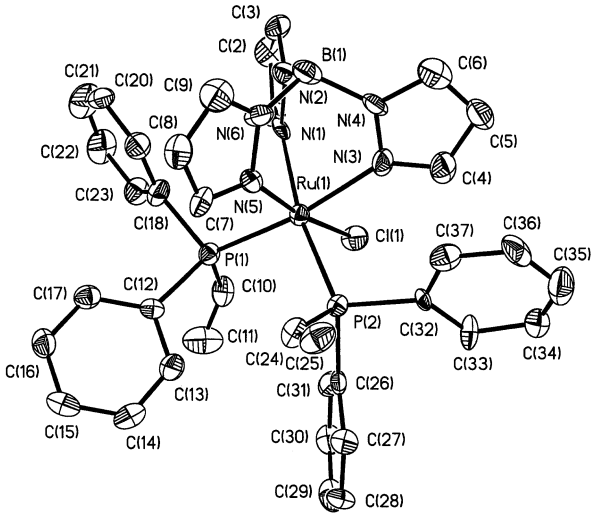


Fig. 6. Structural drawing of 10 showing the atom-labeling scheme. Thermal ellipsoids enclose 40% of the electron density. Selected bond distances (Å) and angles (°): Ru(1)–N(1), 2.138 (9); Ru(1)–N(3), 2.153 (10); Ru(1)–N(5), 2.072 (9); Ru(1)–P(1), 2.340 (3); Ru(1)–P(2), 2.330 (3); Ru(1)–Cl(1), 2.421 (3); N(5)–Ru(1)–N(1), 87.81 (3); N(5)–Ru(1)–N(3), 89.6 (4); N(1)–Ru(1)–N(3), 79.1 (3); N(5)–Ru(1)–P(2), 92.3 (2); N(3)–Ru(1)–P(2), 91.1 (2); N(5)–Ru(1)–P(1), 91.7 (2); N(1)–Ru(1)–P(1), 90.3 (2); P(2)–Ru(1)–P(1), 99.5 (10); P(2)–Ru(1)–Cl(1), 92.89 (11); P(1)–Ru(1)–Cl(1), 92.2 (11).

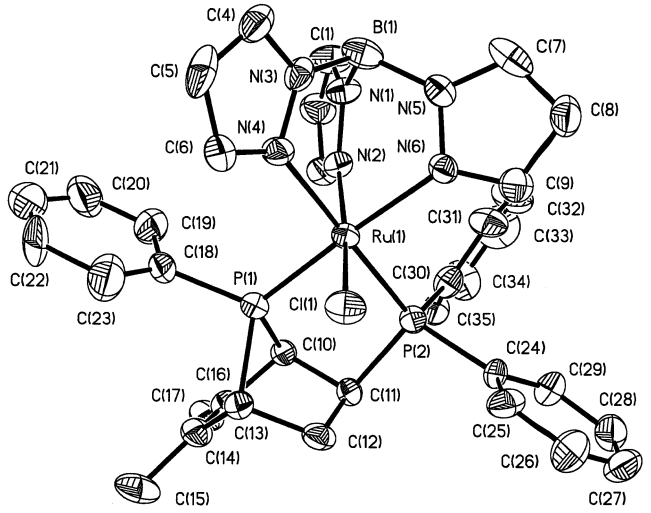


Fig. 7. Structural drawing of **11** showing the atom-labeling scheme. Thermal ellispoids enclose 40% of the electron density. Selected bond lengths (Å) and angles (°): Ru(1)–N(2), 2.158 (8); Ru(1)–N(4), 2.137 (7); Ru(1)–N(6), 2.117 (7); Ru(1)–P(1), 2.244 (2); Ru(1)–P(2), 2.295 (3); Ru(1)–Cl(1), 2.454 (2); C(14)–C(16), 1.343 (17); N(4)–Ru(1)–N(2), 84.9 (3); N(6)–Ru(1)–N(4), 84.5 (3); N(6)–Ru(1)–N(2), 86.2 (3); N(6)–Ru(1)–P(1), 94.1 (2); N(4)–Ru(1)–P(1), 96.7 (2); N(6)–Ru(1)–P(2), 93.3 (3); N(2)–Ru(1)–P(2), 97.1 (2); P(2)–Ru(1)–P(1), 81.32 (9); P(2)–Ru(1)–Cl(1), 96.83 (9); P(1)–Ru(1)–Cl(1), 90.76 (9).

phine ligands have a greater trans influence than chloride [47].

Compound **11** is not just a simple ligand substitution product, but rather a [4+2] Diels–Alder adduct of DMPP and DPVP. Such intramolecular transition-metal-promoted cycloadditions occur within the coordinatin spheres of a variety of metals [48]. Because of chelation the *syn*-exo 2-phosphino-7-phosphanorbornene is always formed, as in this case. Ruthenium becomes a stereocenter in this reaction. The $^{31}P\{^{1}H\}$-NMR spectrum exhibits only two doublets, so that this complex is more than 99% diastereomerically pure with the racemic $R_{Ru}R_{C}R_{P}/S_{Ru}S_{C}S_{P}$ absolute configuration. Thus, the cycloaddtion reaction, which is known to be quite sensitive to steric effects, is in this case very diastereoselective.

For **11** the Ru(1)–P(1) [2.244(2) Å] bond distance is shorter than the Ru(1)–P(2) [2.295(3) Å] distance because the 7-phosphaphosphorus is a better donor the 2-phosphinophosphorus in all complexes of this ligand.

2.4. Reactions of (Tp)Ru(COD)Cl with DPVP and DMPP

Compound **10** can also be prepared directly from (Tp)Ru(COD)Cl (reaction 2).

$$(\mathrm{Tp})\mathrm{Ru}(\mathrm{COD})\mathrm{Cl} + 2\mathrm{DPVP} \xrightarrow[\Delta\ \mathrm{DMF/CH_3CN}]{\mathrm{N_2}} \underset{\mathbf{10}\ (75\%)}{(\mathrm{Tp})\mathrm{Ru}(\mathrm{DPVP})_2\mathrm{Cl}} + \mathrm{COD} \quad (2)$$

It reacts with NH_4PF_6 and CH_3CN to form 12 (reaction 3).

$$\mathbf{10} + \mathrm{NH_4PF_6} + \mathrm{CH_3CN} \xrightarrow[\Delta]{\mathrm{CH_2Cl_2}} \underset{\mathbf{12}\ (84\%)}{(\mathrm{Tp})\mathrm{Ru}(\mathrm{DPVP})_2(\mathrm{CH_3CN})\mathrm{PF_6}} + \mathrm{NH_4C} \quad (3)$$

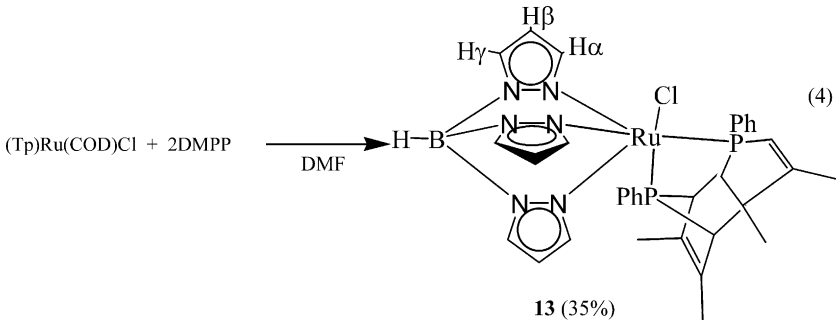
The infrared spectrum of **12** exhibits ν(BH) at 2486 cm^{-1} and ν(CN) at 2284 cm^{-1} similar to the values observed for $[(Tp)Ru(PPh_3)_2(CH_3CN)]PF_6$ (2487, 2279 cm^{-1}) [49] and $[(Tp)Ru(dppm)(CH_3CN)]CF_3SO_3$ (2490, 2284 cm^{-1}) [42]. In an attempt to form the phosphaallyl

Table 3
Crystallographic data for complexes **10**, **11** and **13**

Compound	**10**	**11**	**13**
Empirical formula	$C_{37}H_{36}BClN_6P_2Ru$	$C_{35}H_{37}BClN_6P_2Ru$	$C_{33}H_{36}BClN_6P_2Ru$
F_w	773.99	749.6	725.95
Crystal System	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
Unit cell dimensions			
a (Å)	12.561(5)	12.0074(13)	10.542(3)
b (Å)	15.659(3)	20.055(2)	18.053(3)
c (Å)	18.417(5)	17.123(2)	17.922(4)
α (°)	90	90	90
β (°)	105.57(3)	102.251(10)	97.82(3)
γ (°)	90	90	90
V (Å^3)	3489.5(17)	4029.4(8)	3379.1(12)
Z	4	4	4
ρ_{calc} (Mg m^{-3})	1.473	1.480	1.427
μ (mm^{-1})	0.655	0.708	0.671
Trans. Max/min	0.9133/0.7706	0.8944/0.7615	0.9350/0/0.8785
Data/restraints/paramerters	6132/0/437	7055/0/487	5958/0/402
GOF	1.038	1.008	1.031
$R_1(F^2)/wR_2(F^2)$	0.0847/0.1848	0.0803/0.1747	0.0369/0.0709

complex [(Tp)Ru(η^3-DPVP)(η^1-DPVP)]PF_6 from **12** this complex was heated in a vacuum oven (1 mmHg) for 3 weeks at 120 °C, just below the melting point of the complex. However, complex **12** remained unchanged.

Ruthenium(II) is known to promote the [2+2] and [4+2] and unusual [4+4] dimerizations of DMPP [50]. Thus, (Tp)Ru(COD)Cl was reacted (reaction 4) with DMPP in order to gain more information regarding the factors favoring each of these reaction pathways. The $^{31}P\{^1H\}$-NMR spectrum of **13** established that the product was the [4+2] dimer [δ 189.92 (d), 69.37 (d), $^2J(PP) = 36.6$ Hz] since the $^{31}P\{^1H\}$-NMR spectra of either the [2+2] or [4+4] products would exhibit singlets, because of symmetry equivalent phosphorus nuclei. The structure of **13** was confirmed by X-ray crystallography (Fig. 8). Crystallographic data are given in Table 3. The compound possesses a distorted octahedral geometry around ruthenium. The Ru–P distances [Ru(1)–P(1), 2.2456(10) Å; Ru(1)–P(2), 2.2619(11) Å] are not equal as is typically found for complexes of this ligand [50–52]. The Ru–N distances trans to phosphorus [Ru(1)–N(3), 2.151(3) Å; Ru(1)–N(5), 2.150(3) Å] are longer than that trans to chloride [Ru(1)–N(1), 2.097(3) Å] for reasons discussed previously.



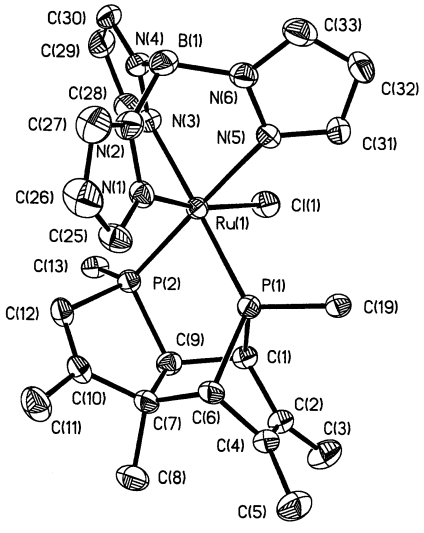


Fig. 8. Drawing of the molecular structure of **13** showing the atom numbering scheme. Phenyl carbons, except C_i, are omitted for clarity. Thermal ellipsoids enclose 40% of the electron density. Selected bond lengths (Å) and angles (°): Ru(1)–N(1), 2.097 (3); Ru(1)–N(5), 2.150 (3); Ru(1)–N(3), 2.151 (3); Ru(1)–P(1), 2.246 (10); Ru(1)–P(2), 2.262 (11); Ru(1)–Cl(1), 2.422 (10); C(2)–C(4), 1.330 (5); C(10)–C(12), 1.324 (5); N(1)–Ru(1)–N(5), 83.39 (11); N(1)–Ru(1)–N(3), 87.85 (11); N(5)–Ru(1)–N(3), 83.77 (11); N(1)–Ru(1)–P(1), 97.60 (8); N(5)–Ru(1)–P(1), 100.43 (8); N(1)–Ru(1)–P(2), 97.80 (8); N(3)–Ru(1)–P(2), 97.40 (8); P(2)–Ru(1)–P(1), 78.30 (4); N(5)–Ru(1)–Cl(1), 86.04 (8); N(3)–Ru(1)–Cl(1), 88.22 (8); P(2)–Ru(1)–Cl(1), 92.83 (4); P(1)–Ru(1)–Cl(1), 87.05 (4).

2.5. Reactions with phenylacetylene

Terminal alkynes react with a variety of ruthenium complexes to form vinylidene and allenylidene derivatives [19]. Transition-metal vinylidene complexes are known to be reactive intermediates in organic and organometallic synthesis [19] as well as in the oligomerization and polymerization of alkynes [20,28,29]. There have been several ruthenium tris(pyrazolyl)borate vinylidene complexes reported such as (Tp)Ru(PPh_3)Cl(=C=

Table 4
Reduction of acetophenone to 1-phenylethanol with complexes **10**, **13** and **17**

Entry	Substrate	Complex	t (h)	% Conversion
1	Acetophenone	10	48	12.4
2	Acetophenone	10	138	6.6
3	Acetophenone	13	48	43.2
4	Acetophenone	13	96	53.7
5	Acetophenone	13	138	55.0
6	Acetophenone	17	70	11.4

CPhH) [30,53], $[(Tp)Ru(PPh_3)_2(=C=CHR)]^+$ [26,54], $[(Tp)Ru(tmen)(=C=CPhH)]^+$ [31] (tmen = $(CH_3)_2NCH_2CH_2N(CH_3)_2$) and $[(Tp)Ru(dippe)(=C=CHR)]^+$ [55] (dippe = $(^iPr)_2PCH_2CH_2P(^iPr)_2$). Many of the TpRu–vinylidene complexes are used for the dimerization of terminal alkynes to form enynes [26,30,34,35].

We attempted the syntheses of vinylidene complexes by reacting complexes **10**, **11** and **13** with phenylacetylene under a variety of conditions but in each case only starting materials were obtained.

2.6. Catalytic hydrogenation of acetophenone

Ruthenium Tp complexes have been found to be hydrogenation catalysts. For example, $(Tp)Ru(PPh_3)(CH_3CN)H$ was found to catalyze the hydrogenation of CO_2 to formic acid [56]. Chaudret and coworkers [57] found that (Tp)Ru(COD)H is an effective hydrogenation catalyst for the reduction of ketones to alcohols. We investigated the reduction of acetophenone to 1-phenylethanol using Kirchner's [58] conditions (Table 4). These results show that compounds **10** and **13** are not very effective catalysts for the hydrogenation of ketones. Many ruthenium complexes are much better catalysts [17,59]. We thought that this might be due to the reluctance of these two compounds to convert to the hydride complexes. We reacted $(Tp)Ru(DMPP)_2[4+2]Cl$ (**13**) with Na_2CO_3 in isopropanol under catalytic conditions but only recovered starting material. However, when complex **11**, (Tp)Ru(DMPP)(DPVP)[4+2]Cl, was reacted with $NaBH_4$ in refluxing ethanol for 4 days a 91% conversion to (Tp)Ru(DMPP)(DPVP)[4+2]H occurred. The presence of a hydride was established by ^{1}H-NMR spectroscopy. The hydride resonance was observed as a doublet of doublets $\delta = -13.37$ ppm, $^2J(PH) = 33$, 26.5 Hz. Coupling to phosphorus was confirmed by $^1H\{^{31}P\}$-NMR experiments. The hydrogenation of acetophenone to 1-phenylethanol by (Tp)Ru(DMPP)(DPVP)[4+2]H was tested and found that only 11% conversion was obtained after 56 h at 82 °C.

2.7. Tris(pyrazolyl)methane complexes

Tris(pyrazolyl)methane complexes of ruthenium [60–70] have been less studied than analogous tris(pyrazolyl)borate complexes. We have prepared three representative tris(pyrazolyl)methane complexes in order to contrast and compare their properties with those of the tris(pyrazolyl)borate analogs. Accordingly, $[(Tpm)Ru(COD)Cl]PF_6$ (**7**) was reacted with DPVP, dppe, and DMPP (reactions 5). These three complexes were characterized by ^{1}H-, $^{13}C\{^1H\}$- and $^{31}P\{^1H\}$-NMR spectroscopy.

The latter was particularly informative. For **14** two

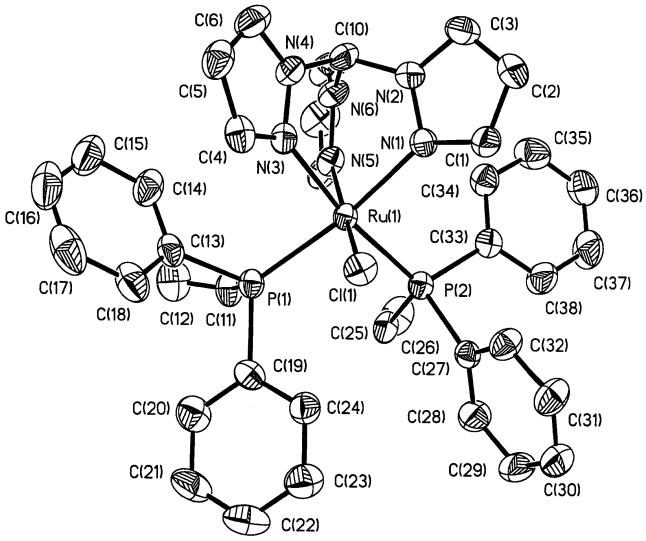
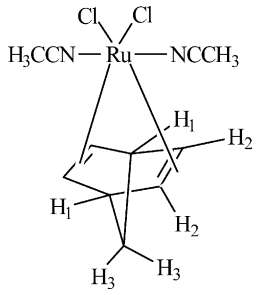


Fig. 9. Structural drawing of the cation of **14** showing the atom-labeling scheme. Thermal ellipsoids enclose 20% of the electron density. Selected bond lengths (Å) and angles (°): Ru(1)–N(5), 2.084(4); Ru(1)–N(3), 2.141(4); Ru(1)–N(1), 2.144(4); Ru(1)–P(2), 2.333(15); Ru(1)–P(1), 2.410(15); Ru(1)–Cl(1), 2.410(15); N(5)–Ru(1)–N(3), 86.14(18); N(5)–Ru(1)–N(1), 85.96(18); N(5)–Ru(1)–P(1), 92.93(14); N(5)–Ru(1)–P(2), 92.65(13); N(3)–Ru(1)–N(1), 78.96(17); N(3)–Ru(1)–P(1), 92.85(13); N(3)–Ru(1)–Cl(1), 84.37(13); N(1)–Ru(1)–P(2), 92.29(12); N(1)–Ru(1)–Cl(1), 88.26(13); P(2)–Ru(1)–P(1), 95.89(5); P(2)–Ru(1)–Cl(1), 96.12(5); P(1)–Ru(1)–Cl(1), 91.58(5).

phosphorus resonances were observed with a 2:1 integrated ratio; a singlet at 35.7 ppm and a septet at −142.09 ppm ($^1J(PF) = 708$ Hz). For **15** two resonances also in a 2:1 integrated ratio, a singlet at 70.40 ppm and a septet at −143.54 ppm ($^1J(PF) = 707$ Hz) were observed. For **16** three resonances in a 1:1:1 integrated ratio, a doublet at 187.38 ppm ($^2J(PP) = 37.2$ Hz, P_1), a doublet at 72.47 ppm ($^2J(PP) = 37.2$ Hz, P_2) and a septet at −143.58 ppm ($^1J(PF) = 708$ Hz) were observed. These latter data are consistent with **16** containing a [4+2] Diels–Alder dimer of DMPP as in the analog $(Tp)Ru(DMPP)_2[4+2]Cl$ (**13**).



The structure of **14** was determined by X-ray crystallography (Fig. 9). Crystallographic data are given in Table 5. As for **10** the Ru(1)–N(3) and Ru(1)–N(1)

Table 5
Crystallographic data for complexes **14**, **15** and **17**

Compound	**14**	**16**	**17**
Empirical formula	$C_{38}H_{36}ClF_6N_6P_3Ru$	$C_{36}H_{29}ClF_6N_6P_3Ru$	$C_{39}H_{41.5}BF_6N_6O_{1.5}P_3Ru$
F_w	919.2	888.6	937.07
Crystal System	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$C2/c$
Unit cell dimensions			
a (Å)	11.9453(12)	9.882(2)	34.344(7)
b (Å)	13.2256(13)	25.268(3)	12.720(3)
c (Å)	14.2944(12)	18.636(3)	20.482(6)
α (°)	99.993(9)	90	90
β (°)	101.794(9)	100.31(2)	96.50(3)
γ (°)	97.244(12)	90	90
V (Å^3)	2146.3	4578.1(13)	8890(4)
Z	2	4	8
ρ_{calc} (Mg m^{-3})	1.514	1.351	1.400
μ (mm^{-1})	0.606	0.565	0.524
Trans. Max/min	0.964/0.8808	0.9663/0.9133	–
Data/restraints/paramerters	7556/0/532	8057/0/254	5804/0/565
GOF	1.050	1.064	1.018
$R_1(F^2)$ [a]/$wR_2(F^2)$ [b]	0.0576/0.1254	0.0803/0.2079	0.0753/0/0.1659

[a] $R(F) = S([F_o]-[F_c])/S([F_o])$.
[b] $wR(F) = [S[\omega(F_o^2-F_c^2)^2]/S[\omega(F_o^2)^2]]^{0.5}$; $\omega = 1/\sigma^2$ (counts)$+(\rho I)^2$.

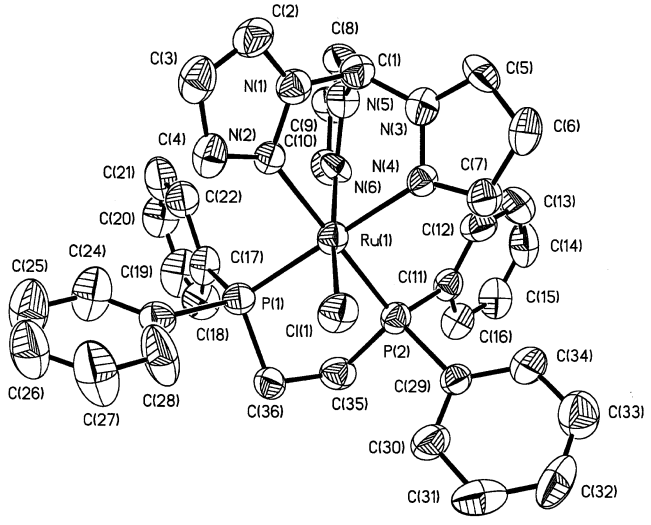


Fig. 10. Structural drawing of the cation of **15** showing the atom-labeling scheme. Thermal ellipsoids enclose 20% of the electron density. Selected bond distances (Å) and angles (°): Ru(1)–N(2), 2.141(8); Ru(1)–N(4), 2.124(8); Ru(1)–N(6), 2.090(8); Ru(1)–P(1), 2.313(3); Ru(1)–P(2), 2.287(3); N(2)–Ru(1)–N(4), 83.4(3); N(2)–Ru(1)–N(6), 85.7(3); N(4)–Ru(1)–N(6), 85.3(4); N(2)–Ru(1)–P(1), 95.9(2); N(4)–Ru(1)–P(2), 96.2(2); N(6)–Ru(1)–P(1), 96.7(2); N(6)–Ru(1)–P(2), 94.6(3); P(1)–Ru(1)–P(2), 84.46(11).

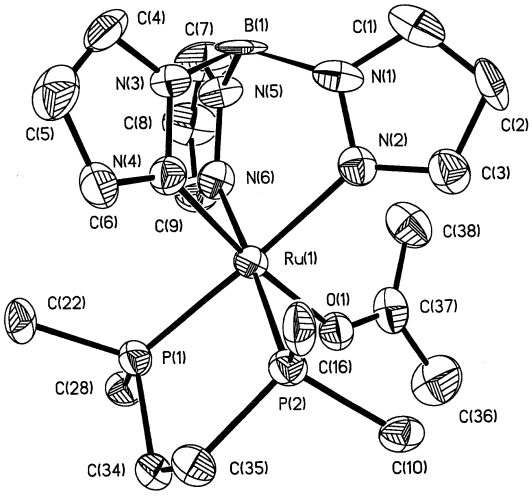


Fig. 11. Structural drawing of the cation of **17** showing the atom-labeling scheme. All phenyl carbons, except C_i, are omitted for clarity. Thermal ellipsoids enclose 40% of the electron density. Selected bond distances (Å) and angles (°): Ru(1)–N(2), 2.141(9); Ru(1)–N(4), 2.064(9); Ru(1)–N(6), 2.137(9); Ru(1)–P(1), 2.302(3); Ru(1)–P(2), 2.300(3); N(2)–Ru(1)–N(4), 84.2(4); N(2)–Ru(1)–N(6), 86.5(3); N(4)–Ru(1)–N(6), 86.9(4); N(2)–Ru(1)–P(2), 96.0(3); N(4)–Ru(1)–P(1), 94.5(3); N(4)–Ru(1)–P(2), 93.8(3); N(6)–Ru(1)–P(1), 92.2(3); P(1)–Ru(1)–P(2), 85.2(11).

bond distances are longer than the Ru(1)–N(5) distances due to the trans influence of the phosphine ligands trans to N(1) and N(3). The Ru–P and Ru–Cl distances differ very little between the two compounds. However, the P(2)–Ru(1)–P(1) bond angles [95.89(5)°, **14**; 99.51(10)°, **10**], P(2)–Ru(1)–Cl(1) angles [96.15(5)°, **14**; 92.89(11)°, **10**] and P(1)–Ru(1)–Cl(1) [91.58(5)°, **14**; 92.2(11)°, **10**] differ considerably suggesting that the steric bulk of the Tp and Tpm ligands is quite different. A measure of the steric bulk of a ligand is the Tolman cone angle [71]. The cone angles calculated from the crystal structures of **10** and **14** are: Tp(180°), Tpm

(170°). This shows that tris(pyrazolyl)borate is sterically larger than tris(pyrazolyl)methane.

The crystal structure of **15** (Fig. 10) was also determined in order to compare the structure of $[(Tpm)Ru(dppe)Cl]PF_6$ (**15**) with that of an analogous Tp containing cation, $[(Tp)Ru(dppe)(Me_2CO)]PF_6$ (**17**) (Fig. 11) that we prepared according to reactions (6).

$$(Tp)Ru(COD)Cl + dppe \xrightarrow[\Delta]{DMF} \underset{(52\%)}{(Tp)Ru(dppe)Cl} + COD$$

$$(Tp)Ru(dppe)Cl + AgPF_6 \xrightarrow{Me_2CO} \underset{\mathbf{17}\ (70\%)}{[(Tp)Ru(dppe)(Me_2CO)]PF_6} + AgCl \quad (6)$$

Crystallographic data are given in Table 5. The Ru–P and Ru–N distances in the two compounds are nearly the same. The Ru–N distances trans to chloride in **16** [2.090(8) Å] and *trans* to oxygen in **17** [2.064(9) Å] are nearly equal and shorter than all the Ru–N distances to nitrogens *trans* to phosphorus.

3. Concluding remarks

Several new ruthenium(II) tris(pyrazolyl)borate and tris(pyrazolyl)methane complexes containing DPVP and DMPP have been prepared and completely characterized. Attempts at forming phosphaallyl derivatives from various DPVP complexes were all unsuccessful. This could be due to an insufficient electron donor ability for both Tp and Tpm, as we have shown that electron rich ruthenium(II) centers are necessary to stabilize the η^3-DPVP phosphaallyl bonding mode by π-back donation into the vinyl π* orbital. It has been demonstrated that toward ruthenium(II) the Tp ligand is less electron donating than Cp [38]. This has been argued on the basis of comparative values of ν(CO) in ruthenium carbonyl complexes. For example, $(Tp)Ru(PPh_3)(CO)Cl$ has ν(CO) at 1965 cm^{-1} while $(Cp)Ru(PPh_3)(CO)Cl$ has ν(CO) at 1958 cm^{-1} [72]. The inability to remove CH_3CN thermally or to be displaced by terminal alkynes in these complexes is consistent with the stabilities of other ruthenium tris(pyrazolyl)borate acetonitrile complexes. For example, the stability of the complexes $[(Tp)Ru(tmeda)L]^+$ (tmeda = $Me_2NCH_2CH_2NMe_2$) was found to increase with L in the order $L = THF < CF_3SO_3 < acetone < CH_3CN \approx DMF$ [73]. These workers also found that the CH_3CN exchange rate is more than eight orders of magnitude slower for $[(Tp)Ru(CH_3CN)_3]^+$ than for $[(Cp)Ru(CH_3CN)_3]^+$ [74,75].

4. Experimental

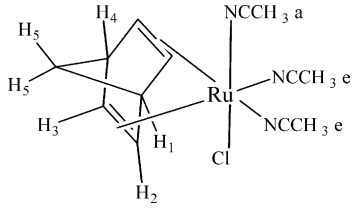
4.1. Reagents and physical measurements

All Chemicals were reagent grade and were used as received or synthesized as described below. NaTp [36], KTp [36], Tpm [76], DPVP [77], DMPP [78], $[Ru(COD)Cl_2]_n$ [39], $[Ru(NBD)Cl_2]_n$ [39], $[Ru(COD)(CH_3CN)_2Cl_2]$ [40] and $[Ru(COD)(CH_3CN)_3Cl]PF_6$ [40] were synthesized by literature procedures. Solvents were dried by standard procedures [79]. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Melting points were obtained using a Mel-Temp apparatus and are uncorrected. NMR spectra were recorded on a Varian Unity Plus 500 FT-NMR spectrometer operating at 499.8 MHz for ^1H, 125.7 MHz for $^{13}C\{^1H\}$ and 202.3 MHz for $^{31}P\{^1H\}$. Proton and carbon chemical shifts are relative to internal Me_4Si, while phosphorus chemical shifts are relative to external 85% H_3PO_4 (aq) with positive values being downfield of the respective reference. FT-IR spectra were obtained as thin films or Nujol mulls on NaCl windows on a Perkin–Elmer 2000 Ft-IR spectrometer. Gas chromatography mass-spectra, GCMS, were recorded on a Hewlett–Packard 59970 gas chromatograph; 20% DC 200 Chromosorb P (10.16, 0.64 cm) or HP-1 (cross linked methyl siloxane) columns (2.5 m, 0.11 m) were used.

4.2. Synthesis

4.2.1. $Ru(NBD)(CH_3CN)_2Cl_2$ (**2**)

CH_3CN (215 ml) was added to $\{RuCl_2(NBD)\}_n$ (7.575g, 28.68 mmol). In order to suppress the formation of $RuCl_2(NCCH_3)_4$, norbornadiene (4.6 ml, 42.64 mmol) was added. The mixture was heated at reflux for 5 h. The mixture was then filtered hot to remove unreacted $\{RuCl_2(NBD)_n\}$. The volume of the filtrate was concentrated to 100 ml, and the mixture was placed in a freezer overnight to yield orange–brown crystals.



Yield 4.399 g (44.3%). X-ray quality crystals were grown by slow recrystallization from acetonitrile. IR (Nujol): 2320 cm^{-1} ν(CN). M.p. = 150 °C dec without melting. Anal. Calc. for $C_{11}H_{14}Cl_2N_2Ru$: C, 38.16; H, 4.08; Cl, 20.48. Found: C, 37.95; H, 4.16; Cl, 20.34%. ^1H-NMR

(499.8 MHz, 25°C, $CDCl_3$): δ 4.78 (s, 4H, H_2), 3.85 (s, 2H, H_1), 2.72 (s, 6H, CH_3CN), 1.53 (s, 2H, H_3). $^{13}C\{^1H\}$-NMR (125.7 MHz, 25 °C, $CDCl_3$): δ 126.94 (s, 2C, CH_3CN), 72.36 (s, 4C, C=C, C_2), 61.18 (s, 2C, C_1), 49.23 (s, 1C, C3), 6.66 (s, 2C, CH_3CN).

4.2.2. [Ru(NBD)(CH$_3$CN)$_3$Cl]PF$_6$ (4)

An acetonitrile solution (50 ml) containing $Ru(NBD)(CH_3CN)_2Cl_2$ (1.886 g, 5.45 mmol) and NH_4PF_6 (1.923 g, 11.80 mmol) was heated at reflux for 15 min. The solution was then cooled to room temperature (r.t.), and the insolubles were removed by filtration. The volume of the filtrate was concentrated to one half the original volume, and absolute ethanol (50 ml) and ether (100 ml) were added. The solution was then cooled in a freezer overnight during which time yellow-needle crystals precipitated out and were isolated by filtration. Yield 1.803 g (67%). M.p. = 171 °C dec. Anal. Calc. for $C_{13}H_{17}ClF_6N_3PRu$: C, 31.43; H, 3.45; Cl, 7.14. Found: C, 31.29; H, 3.51; Cl, 7.20%. IR (Nujol): 2335 cm^{-1} ν(CN). ^{1}H-NMR (499.8 MHz, 25 °C, CD_3NO_2): δ 5.12 (m, 2H, H_2), 4.97 (m, 2H, H_3), 3.94 (m, 2H, $H_{1,4}$), 2.74 (s, 6H, 2CH_3CN e), 2.43 (s, 3H, CH_3CN a), 1.54 (t, ^3J(HH) = 1.5 Hz), 2H, H_5). $^{13}C\{^1H\}$-NMR (125.7 MHz, 25 °C, CD_3NO_2): δ 129.52 (s, 2C, CH_3CN e), 125.34 (s, 1C, CH_3CN a), 79.89 (s, 2C, C_2), 75.55 (s, 2C, C_3), 61.65 (s, 1C, C_5), 49.63 (s, 2C, $C_{1,4}$), 3.06 (s, 2C, CH_3CN e), 1.99 (s, 1C, CH_3CN a).

4.2.3. (Tp)Ru(COD)Cl (5)

A mixture of $Ru(COD)(CH_3CN)_2Cl_2$ (0.817 g, 2.26 mmol) and KTp (0.574 g, 2.28 mmol) in 50 ml of 1,2-dichloroethane was heated at reflux overnight. The solution was then cooled and the solid KCl was removed by filtration over Celite. The solvents were removed by rotary evaporation to obtain an orange solid. Yield 0.901 g (86.6%). X-ray quality crystals were obtained from CH_2Cl_2–hexane. ^{1}H-NMR (499.8 MHz, δ, CD_2Cl_2, 25 °C): 8.18 (d, $^3J(H_{\alpha'}H_{\beta'}) = 2.50$ Hz, 1H, $H_{\alpha'}$), 7.84 (dd, $^3J(H_{\beta',\gamma'}) = 2.0$ Hz, $4J(H_{\gamma,\alpha'}) = 0.50$ Hz, 1H, $H_{\gamma'}$), 7.71 (dd, $^3J(H_{\gamma,\beta}) = 2.5$ Hz, $^4J(H_{\gamma,\alpha}) = 0.50$ Hz, 2H, H_γ), 7.56 (d, $^3J(H_{\alpha,\beta}) = 2.0$ Hz, 2H, H_α), 6.36 (apparent t, $^3J(H_{\beta,\gamma'}) = 2.5$ Hz, $^3J(H_{\beta,\alpha'}) = 2.0$ Hz, 1H, $H_{\beta'}$), 6.24 (apparent t, $^3J(H_{\beta,\gamma}) = 2.5$ Hz, $^3J(H_{\beta,\alpha}) = 2.0$ Hz, 2H, H_β), 4.85 (m, 2H, H_1), 4.00 (m, 2H, H_2), 2.90 (m, 2H, H_3), 2.70 (m, 2H, H_5), 2.43 (m, 2H, H_6), 2.27 (m, 2H, H_4). $^{13}C\{^1H\}$-NMR (125.7 MHz, δ, CD_2Cl_2, 25 °C): 145.80 (s, 1C, $C_{\alpha'}$), 142.37 (s, 2C, C_α), 138.17 (s, 1C, $C_{\gamma'}$), 135.39 (s, 2C, C_γ), 106.76 (s, 1C, $C_{\beta'}$), 106.35 (s, 2C, C_β), 94.92 (s, 2C, C_1), 87.42 (s, 2C, C_2), 30.83 (s, 2C, C_4), 30.27 (s, 2C, C_3). IR (Nujol, cm^{-1}): 2502 (ν_{B-H}), m.p.: 195 °C dec.

4.2.4. (Tp)Ru(NBD)Cl (6)

A mixture containing $Ru(NBD)(CH_3CN)_2Cl_2$ (2.06 g, 5.95 mmol) and NaTp (1.72 g, 7.29 mmol) was heated at reflux in 1,2-dichloroethane (50 ml) for 3 h. The solvent was removed by rotary evaporation to leave a brown–orange solid. The solid was washed with acetone and the orange solid was isolated by filtration. Yield: 1.861 g (70.8%). X-ray quality crystals were obtained from CH_2Cl_2–Et_2O. M.p: 227 °C dec. Anal. Calc. for $C_{16}H_{18}BClN_6Ru$: C, 43.51; H, 4.11; Cl, 8.03. Found: C, 43.36; H, 4.23; Cl, 7.89%. IR (Nujol) 2481 cm^{-1} ν(BH). ^{1}H-NMR (499.8 MHz, 25 °C, $CDCl_3$): δ 8.43 (d, $^3J(H_{\alpha'}H_{\beta'}) = 2.0$ Hz, 1H, $H_{\alpha'}$), 7.76 (d, $^3J(H_{\gamma'}H_{\beta'}) = 2.5$ Hz, 1H, $H_{\gamma'}$), 7.64 (d, $^3J(H_\gamma H_\beta) = 2.0$ Hz, 2H, H_γ), 7.30 (d, $^3J(H_\alpha H_\beta) = 2.0$ Hz, 2H, H_α), 6.33 (apparent t, $^3J(H_{\beta'}H_{\gamma'}) = 2.5$ Hz., $^3J(H_{\beta'}H_{\alpha'}) = 2.0$ Hz, 1H, $H_{\beta'}$), 6.16 (apparent t, $^3J(H_\beta H_\gamma) = {}^3J(H_\beta H_\alpha) = 2.0$ Hz, 2H, H_β), 5.28 (apparent t, $^3J(H_3H_2) = {}^3J(H_3H_4) = 5.0$ Hz, 2H, H_3), 4.44 (apparent t, $^3J(H_2H_3) = {}^3J(H_2H_1) = 4.5$ Hz, 2H, H_2), 4.25 (mult., 2H, H $_{1,4}$), 1.70 (apparent t, $^3J(H_5H_1) = {}^3J(H_5H_4) = 1.5$ Hz, 2H, H_5). $^{13}C\{^1H\}$-NMR (125.7 MHz, 25 °C, CDCl3): δ 144.90 (s, 1C, $C_{\alpha'}$), 140.95 (s, 2C, C_α), 137.05 (s, 1C, $C^{\gamma\prime}$), 134.60 (s, 2C, C_γ), 106.24 (s, 1C, $C_{\beta'}$), 105.80 (s, 2C, C_β), 80.21 (s, 2C, C_3), 70.27 (s, 2C, C_2), 60.21 (s, 1C, C_5), 52.52 (s, 1C, C_1), 51.25 (s, 1C, C_4).

4.2.5. [(Tpm)Ru(COD)Cl]PF$_6$ (7)

A solution of $[Ru(COD)(CH_3CN)_3Cl]PF_6$ (3.52 g, 6.87 mmol) and Tpm (1.47 g, 6.87 mmol) in 1,2-dichloroethane (35.0 ml) was heated at reflux for 3 h. During this time an orange solid formed which was isolated by filtration to obtain **7**. Yield: 2.03 g (49%). X-ray quality crystals were obtained from acetone–Et_2O. ^{1}H-NMR (499.8 MHz, δ, acetone, 25 °C): 9.68 (s, 1H, HCN_3), 8.73 (d, $^3J(H_{\alpha,\beta'}) = 2.5$ Hz, 1H, $H_{\alpha'}$), 8.68 (dd, $^3J(H_{\gamma,\beta'}) = 3.0$ Hz, $^4J(H_{\gamma,\alpha'}) = 0.50$ Hz, 1H, $H_{\gamma'}$), 8.50 (dd, $^3J(H_{\gamma,\beta}) = 2.5$ Hz, $^4J(H_{\gamma,\alpha}) = 0.50$ Hz, 2H, H_γ), 8.01 (apparent dt, $^5J(H_{\alpha,HCN}) = 1.0$ Hz, $^3J(H_{\alpha,\beta}) = 2.0$ Hz, $^4J(H_{\alpha,\gamma}) = 0.50$ Hz, 2H, H_α), 6.82 (dd, $^3J(H_{\beta\gamma'}) = 2.5$ Hz, $^3J(H_{\beta\alpha'}) = 2.5$ Hz, 1H, $H_{\beta'}$), 6.65 (dd, $^3J(H_{\beta,\gamma}) = 2.6$ Hz, $^3J(H_{\beta,\alpha}) = 3.0$ Hz, 2H, H_β), 5.06 (m, 2H, H_1), 4.29 (m, 2H, H_2), 2.85 (m, 2H, H_3), 2.50 (m, 2H, H_5), 2.36 (m, 2H, H_6), 2.21 (m, 2H, H_4). $^{13}C\{^1H\}$-NMR (125.7 MHz, δ, acetone-d_6, 25 °C): 150.62 (s, 1C, $C_{\alpha'}$), 146.94 (s, 2c, C_α), 138.34 (s, 1C, $C_{\gamma'}$), 135.07 (s, 2C, C_γ), 110.40 (s, 1C, $C_{\beta'}$), 109.65 (s, 2C, C_β), 96.63 (s, 2C, C_1), 89.69 (s, 2C, C_2), 77.23 (s, 1C, HCN), 29.99 (CH_2's). $^{31}P\{^1H\}$ (202.3 MHz, δ, acetone, 25 °C): −142.96 (septet, ^1J(PF) = 706 Hz, PF_6). M.p. = 222 °C dec.

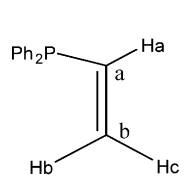
4.2.6. [(Tpm)Ru(NBD)Cl]PF_6 (**8**)

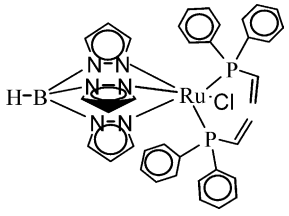
A mixture containing [Ru(NBD)$(CH_3CN)_3$Cl]PF_6 (0.715 g, 1.51 mmol) and Tpm (0.383 g, 1.79 mmol) was heated at reflux in 1,2-dichloroethane (15 ml) for 3 h. The resulting orange solid was isolated by filtration. The orange solid was extracted with acetone, and the insolubles were removed by filtration. The solvent was then removed by rotary evaporation. Recrystallization from nitromethane–ether afforded orange crystals. Yield 0.376 g (42%). Anal. Calc. for $C_{17}H_{18}ClF_6N_6PRu$: C, 34.73; H, 3.09; Cl, 6.03. Found: C, 34.65; H, 3.18; Cl, 6.12%. ^{1}H-NMR (499.8 MHz, 25 °C, CD_3NO_2): δ 9.05 (s, 1H, HCN_3), 8.88 (d, $^3J(H_\alpha'H_\beta') = 2.0$ Hz, 1H, H_α'), 8.45 (d, $^3J(H_\gamma'H_\beta') = 2.5$ Hz, 1H, H_γ'), 8.31 (d, $^3J(H_\gamma H_\beta) = 2.5$ Hz, $^4J(H_\gamma H_\alpha) = 1.0$ Hz, 2H, H_γ), 7.68 (d, $^3J(H_\alpha H_\beta) = 2.5$ Hz, 2H, H_α), 6.75 (apparent t, $^3J(H_\beta'H_\gamma') = 2.5$ Hz $= {}^3J(H_\beta'H_\alpha') = 2.5$ Hz, 1H, H_β'), 6.56 (apparent t, $^3J(H_\beta H_\gamma) = 2.5$ Hz, $^3J(H_\beta H_\alpha) = 2.0$ Hz, 2H, H_β), 5.50 (apparent t, $^3J(H_3H_2) = 4.0$ Hz, $^3J(H_3H_4) = 3.5$ Hz, 2H, H_3), 4.91 (apparent t, $^3J(H_2H_3) = 4.0$ Hz, $^3J(H_2H_1) = 3.0$ Hz, 2H, H_2), 4.45 (mult., 1H, H_1), 4.16 (m, 1H, H_4), 1.79 (apparent t, $^3J(H_5H_1) = {}^3J(H_5H_4) = 1.5$ Hz, 2H, H_5). ^{13}C{^{1}H}-NMR (125.7 MHz, 25 °C, CD_3NO_2): δ 149.54 (s, 1C, C_α'), 145.46 (s, 2C, C_α), 136.26 (s, 1C, $C^{\gamma\prime}$), 133.49 (s, 2C, C_γ), 109.03 (s, 1C, C_β'), 108.518 (s, 2C, C_β), 82.05 (s, 2C, C_3), 76.55 (s, 1C, HCN_3), 72.83 (s, 2C, C_2), 60.71 (s, 1C, C_5), 52.43 (s, 1C, C_1), 50.98 (s, 1C, C_4).

4.2.7. (Tp)Ru(DPVP)(CH_3CN)Cl (**9**)

A solution containing (Tp)Ru(COD)Cl (1.00g, 2.18 mmol) and DPVP (0.6 ml, 3.02 mmol) in CH_3CN (15 ml) and DMF (20 ml) was heated at reflux for 24 h under an atmosphere of nitrogen. The solvent was then removed be vacuum distillation to obtain a yellow residue. The residue was dissolved in a miminum amount of CH_2Cl_2. Hexane was added and the resulting yellow solid was isolated by filtration. Yield: 0.423 g (33%). M.p. = 215 °C. Anal. Calc. for $C_{25}H_{26}BClN_7PRu$: C, 49.81; H, 4.35; N, 16.26. Found: C, 49.57; H, 4.60; N, 16.13. ^{1}H-NMR (499.8 MHz, CD_2Cl_2, 25 °C): δ 7.97 (dd, $^3J(H_\gamma H_\beta) = 2.0$ Hz, 1H, $H_{\gamma a}$), 7.83 (ddd, $^2J(PH) = 24.0$ Hz, $^3J(H_aH_c) = 18.3$ Hz, $^3J(H_aH_b) = 12.0$ Hz, 1H, H_a), 7.80 (dd, $^3J(H_\gamma H_\beta) = 2.0$ Hz, $^4J(H_\gamma H_\alpha) = 0.5$ Hz, 1H, $H_{\gamma b}$), 7.75 (dd, $^3J(H_\gamma H_\beta) = 2.5$ Hz, $^4J(H_\gamma H_\alpha) = 0.5$ Hz, 1H, $H_{\gamma c}$), 7.74 (app dt, $^3J(H_\beta H_\alpha) = 2.5$ Hz, $^4J(H_\gamma H_\alpha) = {}^4J(PH) = 0.5$ Hz, 1H, $H_{\alpha a}$), 7.66 (dd, $^3J(H_\beta H_\alpha) = 2.0$ Hz, $^4J(H_\gamma H_\alpha) = 0.5$ Hz, 1H, $H_{\alpha b}$), 7.63 (m, 2H, H_o), 7.49 (m, 2H, H_m), 7.46 (m, 1H, H_p), 7.01 (m, 2H, H_m), 6.91 (d, $^3J(H_\beta H_\alpha) = 2.0$ Hz, 1H, $H_{\alpha c}$), 6.59 (m, 2H, H_o), 6.28 (ddd, $^3J(H_\beta H_\alpha) = 2.5$ Hz, $^3J(H_\gamma H_\beta) = 2.0$ Hz, $^5J(PH) = 1.0$ Hz, $H_{\beta a}$), 6.06 (dd, $^3J(H_\beta H_\alpha) = 2.5$ Hz, $^3J(H_\gamma H_\beta) = 2.0$ Hz, 1H, $H_{\beta b}$), 6.00 (ddd, $^3J(PH) = 32.5$ Hz, $^3J(H_aH_b) = 12.0$ Hz, $^2J(H_bH_c) = 2.0$ Hz, 1H, H_b), 5.94 (dd, $^3J(H_\beta H_\alpha) = 2.5$ Hz, $^3J(H_\gamma H_\beta) = 2.0$ Hz, 1H, $H_{\beta c}$), 4.97 (ddd, $^3J(H_aH_c) = 18.3$ Hz, $^3J(PH) = 16.5$ Hz, $^2J(H_bH_c) = 2.0$ Hz, 1H, H_c), 1.94 (s, 3H, CH_3). ^{31}P{^{1}H}-NMR (202.3 MHz, CD_2Cl_2, 25 °C): δ 46.78. ^{13}C{^{1}H}-NMR (125.7 MHz, CD_2Cl_2, 25 °C): δ 145.57 (d, $^3J(PC) = 1.0$ Hz, C_α), 145.54 (d, $^3J(PC) = 1.4$ Hz, C_α), 142.51 (s, C_α), 136.68 (d, $^1J(PC) = 41.7$ Hz, C_i), 136.54 (d, $^1J(PC) = 30.9$ Hz, C_α'), 136.36 (2C, C_γ), 135.70 (d, $^2J(PC) = 10.3$ Hz, C_o), 134.99 (d, $^4J(PC) = 2.0$ Hz, C_γ), 132.41 (d, $^2J(PC) = 8.5$ Hz, C_o), 130.26 (d, $^4J(PC) = 2.1$ Hz, C_p), 129.68 (d, $^1J(PC) = 40.5$ Hz, C_i), 129.07 (d, $^4J(PC) = 2.0$ Hz, C_p), 128.68 (d, $^3J(PC) = 8.5$ Hz, C_m), 128.03 (d, $^3J(PC) = 9.2$ Hz, C_m), 127.04 (d, $^2J(PC) = 3.8$ Hz, C_β'), 121.50 (s, CH_3CN), 106.32 (s, C_β), 105.99 (s, C_β), 105.98 (s, C_β), 4.00 (CH_3CN). IR (Nujol, cm^{-1}): 2477 (m, ν(BH)), 2279 (m, ν(CN)).

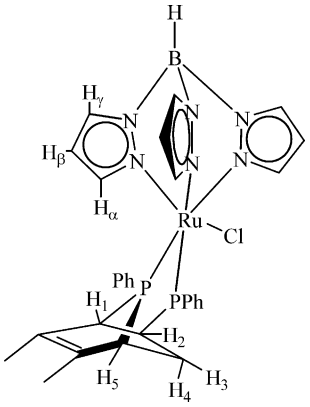
4.2.8. (Tp)Ru(DPVP)$_2$Cl (**10**)





A suspension of (Tp)Ru(COD)Cl (286 mg, 0.624 mmol) and diphenylvinylphosphine, DPVP, (213 mg, 1.01 mmol) was heated at reflux for 20 h in a 1:1 DMF–CH_3CN (12 ml) mixture. After removal of the solvents in vacuo a bright yellow solid was obtained. Yield 360 mg (74.6%). X-ray quality crystals were obtained after recrystallization from CH_2Cl_2/–$C_2H_5)_2O$. Anal. Calc. for $C_{37}H_{36}BClN_6P_2Ru$: C, 57.27; H, 4.68. Found: C, 57.01; H, 4.81%. ^{1}H-NMR (499.8 MHz δ, CD_2Cl_2, 25 °C): 7.92 (d, $^3J(H_\gamma'H_\beta') = 2.5$ Hz, 1H, H_γ'), 7.64 (d, $^3J(H_\gamma H_\beta) = 2.5$ Hz, 2H, H_γ), 7.39 (m, 2H, H_p), 7.35 (m, 4H, H_m), 7.24 (m, 4H, H_o), 7.16 (m, 2H, H_p), 7.14 (d, $^3J(H_\alpha'H_\beta') = 2.0$ Hz,1H, H_α'), 6.96 (m, 6H, $H_m + H_\alpha$), 6.59 (m, 4H, H_o), 6.50 (m, 2H, H_a), 5.92 (t, $^3J(H_\alpha'H_\beta') = 2.0$ Hz, $^3J(H_\gamma'H_\beta') = 2.5$ Hz, 1H, H_β'), 5.80 (t, $^3J(H_\alpha H_\beta) = 2.0$ Hz, $^3J(H_\gamma H_\beta) = 2.5$ Hz, 2H, H_β), 5.76 (m, 2H, H_b), 4.91 (m, 2H, H_c). ^{31}P{^{1}H} (δ, CD_2Cl_2, 202.3 MHz, 25 °C): 22.32 (s, 2P, DPV*P*). ^{13}C{^{1}H} (125.7 MHz δ, CD_2Cl_2, 25 °C): 149.36 (s, C_α'), 145.04 (s, C_α), 137.37 (s, C_b), 136.26 (m, $[^2J(PC_o) + {}^4J(PC_o] + C_\gamma' + C_i)$, 136.20 (d, $^1J(PC_\alpha) = 235.5$ Hz, C_a), 135.14 (s, C_γ), 133.49 (s, C_o), 132.67 (d, $[^1J(PC_i) + {}^3J(PC_i)] = 40.2$ Hz, C_i), 130.01 (s, C_p'), 129.11 (s, C_p), 128.07 (t, $[^3J(PC_m) + {}^5J(PC_m)] = 14.5$ Hz, C_m), 127.77 (t, $[^3J(PC_m) + {}^5J(PC_m)] = 16.0$ Hz, C_m), 105.74 (s, C_β'), 105.50 (s, C_β). IR (Nujol, cm^{-1}): 2476 (m, ν_{B-H}). MP: 145 °C.

4.2.9. (Tp)Ru(DPVP)(DMPP)[4+2]Cl (**11**)

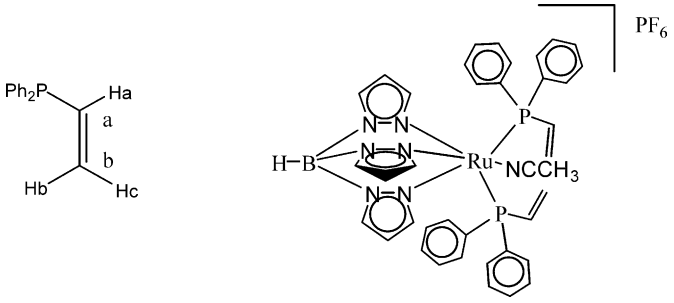


A solution containing (Tp)Ru(DPVP)(CH_3CN)Cl (0.239 g, 0.397 mmol) and DMPP (0.1 ml, 0.53 mmol) was heated at reflux in 1,2-dichloroethane (100 ml) under an atmosphere of nitrogen for 20 h. The solvent was then removed to obtain a red residue. The residue was dissolved in a minimum amount of CH_2Cl_2. Hexane was added to the CH_2Cl_2 solution and the resulting yellow solid was isolated by filtration to obtain **11**. Yield 0.214 g (69.6%). Anal. Calc. for $C_{35}H_{36}BClN_6P_2Ru$: C, 56.05; H, 4.84. Found: C, 55.92; H, 4.93%. X-ray quality crystals were obtained by recrystallization from CH_2Cl_2/Et_2O. ^{1}H-NMR(499.8 MHz, $CDCl_3$, 25 °C): δ 8.44 (m, 2H, H_o), 8.17 (d, ^3J(HH) = 2.0 Hz, 1H, $H_{\alpha1}$), 7.78 (d, ^3J(HH) = 2.5 Hz, 1H, $H_{\gamma1}$), 7.53 (d, ^3J(HH) = 2.5 Hz, 1H, $H_{\gamma3}$), 7.49 (d, ^3J(HH) = 2.5 Hz, 1H, $H_{\gamma2}$), 7.42 (m, 4H, H_m), 7.32 (d, ^3J(HH) = 2.5 Hz, 1H, $H_{\alpha2}$), 7.22 (m, 1H, H), 7.19 (m, 2H, H), 7.03 (m, 6H, $H_{o,m}$), 6.55 (d, ^3J(HH) = 2.0 Hz, 1H, $H_{\alpha3}$), 6.21 (dd, ^3J(HH) = 2.5, 2.0 Hz, 1H, $H_{\beta1}$), 5.83 (dd, ^3J(HH) = 2.5, 2.0 Hz, 1H, $H_{\beta2}$), 5.61 (dd, ^3J(HH) = 2.5, 2.0 Hz, 1H, $H_{\beta3}$), 3.57 (bs, 1H, H_5), 3.41 (bs, 1H, H_1), 3.29 (ddd, ^3J(PH) = 20.5 Hz, $^2J(H_3H_4)$ = 12.5 Hz, $^3J(H_3H_5)$ = 2.0 Hz, 1H, H_3), 3.13 (app dt, ^3J(PH) = 27.0 Hz, ^2J(PH) = $^3J(H_2H_4)$ = 8.8 Hz, 1H, H_2), 1.82 (s, 3H, CH_3), 1.72 (s, 3H, CH^3), 1.49 (dddd, ^3J(PH) = 29.0 Hz, ^3J(PH) = 12.8 Hz, $^2J(H_3H_4)$ = 12.5 Hz, $^3J(H_2H_4)$ = 8.8 Hz, 1H, H_4). ^{31}P{^{1}H}-NMR (202.3 MHz, $CDCl_3$, 25 °C): δ 168.01 (d, ^2J(PP) = 35.0 Hz, 1P, P_1), 50.40 (d, ^2J(PP) = 35.0 Hz, 1P, P_2). ^{13}C{^{1}H}-NMR (125.7 MHz, $CDCl_3$, 25 °C): δ 146.11 (s, $C_{\alpha3}$), 144.54 (s, $C_{\alpha1}$), 143.68 (s, $C_{\alpha2}$), 138.78 (d, ^2J(PC) = 1.9 Hz, C_6), 135.88 (d, ^1J(PC) = 33.3 Hz, C_i), 135.26 (s, $C_{\gamma2}$), 135.43 (d, ^1J(PC) = 32.7 Hz, C_i), 135.30 (s, C_5), 135.02 (d, ^2J(PC) = 9.3 Hz, C_o), 135.02 (s, $C_{\gamma1}$), 134.46 (s, $C_{\gamma3}$), 133.32 (d, ^4J(PC) = 2.0 Hz, C_p), 132.05 (d, ^1J(PC) = 25.9 Hz, C_i), 131.64 (d, ^2J(PC) = 8.3 Hz, C_o), 129.43 (d, ^4J(PC) = 2.0 Hz, C_p), 128.80 (d, ^3J(PC) = 11.3 Hz, C_m), 128.34 (d, ^1J(PC) = 14.1 Hz, C_o), 127.97 (d, ^3J(PC) = 8.9 Hz, C_m), 127.38 (d, ^3J(PC) = 8.0 Hz, C_m), 105.47 (s, $C_{\beta1}$), 104.48 (s, ^5J(PC) = $C_{\beta2}$), 104.15 (s, $C_{\beta3}$), 56.23 (dd, ^1J(PC) = 30.3 Hz, ^2J(PC) = 10.8 Hz, C_1), 47.44 (d, ^1J(PC) = 31.2 Hz, C_4), 36.76 (dd, ^1J(PC) = 35.4 Hz, ^2J(PC) = 29.9 Hz, C_2), 29.29 (dd, ^2J(PC) = 12.9 Hz, ^2J(PC) = 5.7 Hz, C_3), 15.27 (s, $CH_{3(5)}$), 13.90 (d, ^3J(PC) = 1.9 Hz, $CH_{3(6)}$).

4.2.10. (Tp)Ru(DPVP)(DMPP)[4+2]H

An ethanol solution containing RuTp(DPVP)(DMPP)[4+2]Cl (0.200 g, 0.267 mmol) and $NaBH_4$ (0.0947, 2.5 mmol) was heated at reflux for 4 days. The solution was cooled to r.t. and the insolubles were removed by filtration. The solvent was removed by rotary evaporation to obtain a light colored solid. Yield 0.1238 g (65%). ^{1}H-NMR (499.8 MHz, 25 °C, C_6D_6): δ 8.54 (app t, $^3J(H_oP)$ = 8.0 Hz, ^3J (H_oH_m) = 5.0 Hz, 2H, H_o), 8.01 (d, $^3J(H_\alpha H_\beta)$ = 1.5 Hz, 1H, H_α), 7.57 (d, $^3J(H_\gamma H_\beta)$ = 2.5 Hz, 1H, H_γ), 7.49 (d, $^3J(H_\gamma H_\beta)$ = 2.0 Hz, 1H, H_γ), 7.38 (d, $^3J(H_\alpha H_\beta)$ = 2.5 Hz, 1H, H_α), 7.32 (m, 4H, H_m), 6.96 (m, 3H, H_p), 6.86 (d, $^3J(H_\alpha H_\beta)$ = 2.0 Hz, 1H, H_α), 6.78 (m, 6H, $H_{o,m}$), 5.83 (appt t, $^3J(H_\beta H_\gamma) = {}^3J(H_\beta H_\alpha)$ = 2.5, Hz, 1H, H_β), 5.76 (app t, $^3J(H_\beta H_\gamma) = {}^3J(H_\beta H_\alpha)$ = 2.0 Hz, 1H, H_β), 5.61 (app t, $^3J(H_\beta H_\gamma) = {}^3J(H_\beta H_\alpha)$ = 2.5 Hz, 1H, H_β), 3.09 (bs, 1H, H_5), 2.09 (s, 1H, H_1), 2.65 (m, 1H, H_3), 2.56 (bs, 1H, H_2), 1.57 (s, 3H, CH_3), 1.40 (s, 3H, CH_3), 1.09 (m, 1H, H_4), −13.37 (dd, ^2J(HP) = 32 Hz, ^2J(HP) = 26.5 Hz, 1H, H_H). ^{31}P{^{1}H}-NMR (202.3 MHz, C_6D_6, 25 °C): δ 172.90 (d, ^2J(PP) = 41.4 Hz, 1P, P_1), 79.25 (d, ^2J(PP) = 41.4 Hz, 1P, P_2). The NMR data shows a 10:1 ratio of RuTp(DPVP)(DMPP)[4+2]H to RuTp(DPVP)(DMPP)[4+2]Cl. IR (Nujol, cm^{-1}): 2468 (w, ν(BH)). M.p.: 280 °C dec.

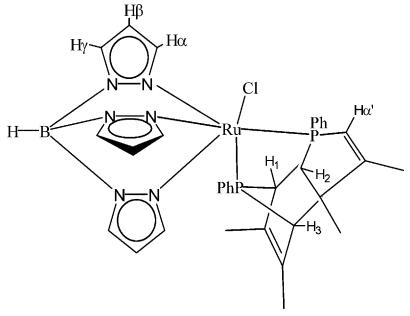
4.2.11. [(Tp)Ru(DPVP)$_2$(CH_3CN)]PF_6 (**12**)



(Tp)Ru(DPVP)$_2$Cl, 10, (510 mg, 0.659 mmol) and NH_4PF_6 (122 mg, 0.749 mmol) were dissolved in CH_2Cl_2 (15 ml) and acetonitrile was added (10 ml). The mixture was heated at reflux under nitrogen overnight. The resulting precipitate (NH_4Cl) was removed by filtration. Ether was added to the filtrate, which caused the product to precipitate. This was collected on a glass frit, washed with ether, and dried in vacuum. Yield: 351.0 mg (83.7%). Anal. Calc. for $C_{39}H_{39}BF_6N_7P_3Ru$: C, 50.50; H, 4.24. Found: C,

50.23; H, 4.17. ^{1}H-NMR (499.8 MHz δ, $CDCl_3$, 25 °C): 8.02 (d, 1H, J = 2.5 Hz, $H_{\gamma'}$), 7.68 (d, 2H, J = 2.5 Hz, H_{γ}), 7.49 (m, 7H, $H_{\alpha'}+H_m+H_p$), 7.21 (m, 6H, H_o+H_p), 6.99 (d, 2H, J = 2.5 Hz, H_{α}), 6.97 (m, 4H, H_m), 6.76 (m, 2H, H_a), 6.39 (apparent t, 4H, J = 9.0 Hz, H_o), 6.15 (apparent t, 1H, J = 2.5 Hz, $H_{\beta'}$), 6.03 (m, 2H, H_b), 5.89 (apparent t, 2H, J = 2.0 Hz, H_{β}), 4.94 (m, 2H, H_c), 1.75 (s, 3H, NC*CH*$_3$). ^{31}P{^{1}H}-NMR (202.3 MHz δ, $CDCl_3$, 25 °C): 35.31 (s, 2P, DPV*P*), −145.21 (septet, ^1J(PF) = 710 Hz, 1P, PF_6^-). ^{13}C{^{1}H}-NMR (125.7 MHz δ, $CDCl_3$, 25 °C): 147.02 (s, $C_{\alpha'}$), 143.32 (s, C_{α}), 137.74 (s, $C_{\gamma'}$), 135.70 (s, C_{γ}), 133.46 (d, $^1J(PC_a)$ = 37.7 Hz), 133.43 (dd, $[^2J(PC_o)+{}^4J(PC_o)]$ = 17.5 Hz, C_o), 132.65 (apparent t, $[^2J(PC_o)+{}^4J(PC_o)]$ = 4.0 Hz, C_o), 131.68 (dd, $[^1J(PC_i)+{}^3J(PC_i)]$ = 44 Hz, C_i), 130.27 (s, C_p), 129.94 (s, C_p), 129.34 (dd, $[^1J(PC_i)+{}^3J(PC_i)]$ = 46 Hz, C_i), 128.58 (apparent t, $[^3J(PC_m)+{}^5J(PC_m)]$ = 15.0 Hz, C_m), 127.83 (apparent t, $[^3J(PC_m)+{}^5J(PC_m)]$ = 16.5 Hz, C_m), 124.35 (s, C_{β}), 106.59 (s, $C_{\beta'}$), 106.43 (s, C_{β}), 3.07 (m, ^4J(PC), NC*CH*$_3$). IR (Nujol, cm^{-1}): 2486 (m, ν_{B-H}), 2281 (w, ν_{CN}). M.p.: 137 °C.

4.2.12. (Tp)Ru(DMPP)$_2$[4+2]Cl (**13**)



DMPP (0.2 ml, 1.06 mmol) was added to a solution of RuTp(COD)Cl (0.30 g, 0.65 mmol) in DMF (22 ml) and the orange solution was heated to reflux. As the solution refluxed it turned from orange to dark red in a period of 5 h at which time the solvent was removed by vacuum distillation. The reddish-foamy residue was dissolved in CH_2Cl_2 and the insolubles were removed by filtration. Hexane was added to the filtrate and the solution was concentrated until a reddish–orange solid precipitated. The precipitate was isolated by filtration and placed in a vacuum oven to dry. Yield 0.1630 g (35%). Anal. Calc. for $C_{33}H_{36}BClN_6P_2Ru$: C, 54.45; H, 4.98. Found: C, 54.18: H, 4.79%. ^{1}H-NMR(499.8 MHz δ, CD_2Cl_2, 25 °C): 7.87 (m, 4H, H_o), 7.71 (dd, $^3J(H_{\gamma}H_{\beta})$ = 2.5 Hz, $^4J(H_{\alpha}H_{\gamma})$ = 1.0 Hz, 1H, H_{γ}), 7.63 (d, $^3J(H_{\gamma}H_{\beta})$ = 2.0 Hz, 1H, H_{γ}), 7.46 (m, 7H, H_m, H_p, H_{γ}), 7.19 (d, $^3J(H_{\beta}H_{\alpha})$ = 1.5 Hz, 1H, H_{α}), 6.62 (d, $^3J(H_{\beta}H_{\alpha})$ = 2.0 Hz, 1H, H_{α}), 6.37 (d, $^3J(H_{\beta}H_{\alpha})$ = 2.0 Hz, 1H, H_{α}), 6.15 (dd, $^3J(H_{\gamma}H_{\beta})$ = 2.5 Hz, $^3J(H_{\beta}H_{\alpha})$ = 2.0 Hz, 1H, H_{β}), 5.91 (dq, ^2J(PH) = 28.5 Hz, ^4J(HH) = 1.5 Hz, 1H, $H_{\alpha'}$), 5.89 (apparent t, $^3J(H_{\gamma}H_{\beta})=^3J(H_{\beta}H_{\alpha})$ = 2.0 Hz, 1H, H_{β}), 5.70 (td, $^3J(H_{\gamma}H_{\beta})=^3J(H_{\beta}H_{\alpha})$ = 2.0 Hz, ^5J(PH) = 1.0 Hz, 1H, H_{β}), 4.39 (apparent dt, ^2J(PH) = $^3J(H_1H_2)$ = 3.0 Hz, $^4J(H_1H_3)$ = 2.2 Hz, 1H, H_1), 2.86 (dd, ^2J(PH) = 7.0 Hz, $^4J(H_1H_3)$ = 2.2 Hz, 1H, H_3), 2.78 (ddd, ^3J(PH) = 43.5 Hz, ^2J(PH) = 5.0Hz, $^3J(H_1H_2)$ = 3.0 Hz, 1H H_2), 2.09 (apparent t, ^4J(PH) = ^4J(HH) = 1.5 Hz, 3H, $CH_{3(a)}$), 1.81 (s, 3H, $CH_{3(b)}$), 1.47 (d, ^4J(PH) = 1.0 Hz, 3H, $CH_{3(c)}$), 1.19 (s, 3H, $CH_{3(d)}$). ^{31}P{^{1}H}-NMR (202.3 MHz δ, CD_2Cl_2, 25 °C): 189.92 (d, ^2J(PP) = 36.6 Hz, 1P,P_1), 69.31 (d, ^2J(PP) = 36.6 Hz, 1P, P_2). ^{13}C{^{1}H}-NMR (125.7 MHz δ, CD_2Cl_2, 25 °C): 152.09 (d, ^2J(PC) = 12.8 Hz, C=C), 146.62 (d, ^3J(PC) = 2.1 Hz, C_{α}), 143.77 (s, C_{α}), 142.78 (s, C_{α}), 137.94 (s, C=C), 137.32 (s, C_{γ}), 135.87 (dd, ^1J(PC) = 27.4 Hz, ^3J(PC) = 3.5 Hz, C_i), 135.57 (d, ^1J(PC) = 29.3 Hz, C_i), 134.78 (s, C_{γ}), 134.42 (s, C=C), 134.33 (s, C_{γ}), 132.34 (d, ^2J(PC) = 8.5 Hz, C_o), 131.00 (d, ^2J(PC) = 8.5 Hz, C_o), 130.12 (d, ^4J(PC) = 2.5 Hz, C_p), 128.99 (s, C_{β}), 128.77 (d, ^3J(PC) = 9.2 Hz, C_m), 128.59 (d, ^3J(PC) = 6.4 Hz, C_m), 124.90 (d, ^1J(PC) = 47.0 Hz, C_3), 105.19 (s, C_{β}), 104.66 (d, J(PC) = 2.1 Hz, C_{β}), 62.08 (dd, ^3J(PC) = 13.2 Hz, ^2J(PC) = 5.4 Hz, C_5), 55.05 (dd, ^1J(PC) = 38.5 Hz, ^2J(PC) = 11.3 Hz, C_1), 53.02 (dd, ^1J(PC) = 21.4 Hz, ^3J(PC) = 5.4 Hz, C_6), 52.55 (dd, ^1J(PC) = 32.1 Hz, ^2J(PC) = 28.8 Hz, C_2), 27.14 (d, ^3J(PC) = 4.3 Hz, $CH_{3\ (a)}$), 18.62 (d, ^3J(PC) = 13.2 Hz, $CH_{3(d)}$), 17.61 (s, $CH_{3(c)}$), 15.99 (s, $CH_{3(b)}$). IR (Nujol, cm^{-1}): 2478 (m, ν_{B-H}). M.p.: dec. 275 °C.

4.2.13. Reactions with phenylacetylene

Solutions of **10** in CH_3OH containing an excess of phenylacetylene were heated for 24 h at reflux in the presence and absence of a stoichiometric quantity of NH_4PF_6. In both cases **10** was recovered unchanged. A solution of **12** in CH_2Cl_2–CH_3OH containing an excess of phenylacetylene was heated at 40 °C overnight, and **12** was recovered unchanged. Solutions of **13** in CH_3OH containing an excess of phenylacetylene and NH_4PF_6 or $AgPF_6$ were heated at reflux overnight and **13** was recovered unchanged.

4.2.14. Transfer hydrogenation of acetophenone

The catalyst (0.08 mmol) and 2-propanol (85 ml) were heated at reflux until dissolved. Then acetophenone (8.5 mmol) and Na^{i}OPr (0.14 mmol) were introduced into the solution. The reaction mixture was heated at reflux for the required time. Once the reaction was complete (monitored by ^{1}H-NMR spectroscopy) the solvent was removed by rotary evaporation. The remaining liquids were distilled under reduced pressure.

4.2.15. [(Tpm(Ru(DPVP)$_2$Cl]PF$_6$ (**14**)

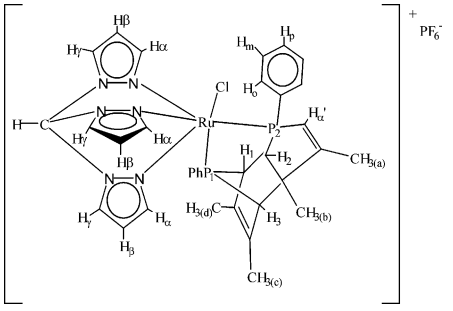
A mixture containing [(Tpm)Ru(COD)Cl]PF_6 (0.301g, 0.500 mmol) and diphenylvinylphosphine, DPVP, (0.20ml, 1.00 mmol) in DMF (25 ml) was heated at reflux under an atmosphere of nitrogen overnight.

The solvent was removed in vacuo leaving a yellow solid of **14**. Yield 0.1723g (35%). Anal. Calc. for $C_{38}H_{36}ClF_6N_6P_3Ru$: C, 54.59; H, 4.34. Found: C, 54.36; H, 4.51%. X-ray quality crystals were obtained by the diffusion of ether into an acetone solution of 14. ^{1}H-NMR (499.8 MHz, δ, acetone-d_6, 25 °C): 9.45 (s, 1H, HCN_3), 8.66 (d, $^3J(H_\gamma'H_\beta') = 2.5$ Hz, 1H, H_γ'), 8.42 (d, $^3J(H_\gamma H_\beta) = 2.5$ Hz, 2H, H_γ), 7.68 (m,4H, H_o), 7.50 (m, 2H, H_p), 7.35 (m, 4H, H_m), 7.34 (d, $^3J(H_\alpha H_\beta) = 2.0$ Hz, 2H, H_α), 7.30 (m, 2H, H_p), 7.23 (d, $^3J(H_\alpha'H_\beta') = 2.0$ Hz, 1H, H_α'), 7.09 (m, 4H, H_m), 6.91 (ddd, $^2J(H_aP) = 26$ Hz, $^3J(H_aH_b) = 12$ Hz, $^3J(H_aH_c) = 16.2$ Hz, 2H, H_a), 6.77 (m, 4H, H_o), 6.35 (apparent t, $^3J(H_\beta'H_\gamma') = 2.5$ Hz, $^3J(H_\beta'H_\alpha') = 3.0$ Hz, 1H, H_β'), 6.22 (apparent t, $^3J(H_\beta H_\gamma) = 2.5$ Hz, $^3J(H_\beta H\alpha) = 2.5$ Hz, 2H, H_β), 6.04 (ddd, $^3J(H_bP) = 33.5$ Hz, $^3J(H_bH_a) = 12.5$ Hz, $^2J(H_bH_c) = 1.5$ Hz, 2H, H_b), 5.19 (ddd, $^3J(H_cP) = 18.0$ Hz, $^3J(H_cH_a) = 17.5$ Hz, $^2J(H_cH_b) = 1.0$ Hz, 2H, H_c). ^{13}C {^{1}H}-NMR (125.7 MHz, δ, acetone-d_6, 25 °C): 151.58 (s, 1C, C_α') 148.33 (s, 2C, C_α), 132.25 (s, 1C, C_γ'), 135.99 (t, $[^2J(PC)+{}^4J(PC)] = 8.9$ Hz, 4H, C_o), 135.12 (s, 2C, C_γ), 134.97 (5 lines AXX′, $^1J(PC_a) = 28.6$ Hz, $^3J(PC) = -5.8$ Hz, $^2J(PP) = 32.1$ Hz, C_a), 134.11 (t, $[^2J(PC)+{}^4J(PC)] = 8.9$ Hz, 4H, C_o), 133.26 (5 lines AXX', $^1J(PC) = 43.9$ Hz, $^3J(PC) = -.8$ Hz, $^2J(PP) = 32.1$ Hz, 2C, C_i), 132.30 (5 lines AXX', $^1J(PC) = 49.7$ Hz, $^3J(PC) = -5.5$ Hz, $^2J(PP) = 32.1$ Hz, 2C, C_i), 131.23 (s, 1C, C_p), 130.69 (s, 1C, C_p), 130.65 (s, 2C, C_β), 129.02 (t, $[^3J(PC)+{}^5J(PC)] = 9.2$ Hz, C_m), 128.85 (t, $[^3J(PC)+{}^5J(PC)] = 9.4$ Hz, C_m), 109.02 (s, C_2), 108.99 (s, C_2'), 76.51 (s, HCN_3). ^{31}P{^{1}H}-NMR (202.3 MHz, acetone-d_6, 25 °C): δ 35.7 (s, 2P, DPVP), −145.0 (sept, $^1J(PF) = 708$ Hz, 1P, PF_6^-).

4.2.16. [(Tpm)Ru(dppe)Cl]PF$_6$ (**15**)

A solution containing [(Tpm)Ru(COD)Cl]PF$_6$ (0.204 g, 0.337 mmol) and 1,2-bis(diphenylphosphino)ethane, dppe, (0.144 g, 0.361 mmol) in DMF (15 ml) was heated at reflux overnight. The yellow homogeneous solution turned to a dark brown during the course of the reaction. The solvent was removed by vacuum distillation to obtain a green residue. The residue was dissolved in a minimum amount of CH_2Cl_2 and run through a silica gel/celite column with CH_2Cl_2. Ether was added to the yellow eluate and the resulting yellow solid was isolated by filtration to obtain **15**. X-ray quality crystals were obtained by the slow diffusion of ether into an acetone solution of **15**. Yield: 0.969 g (30.9%). Anal. Calc. for $C_{36}H_{34}ClF_6N_6P_3Ru$: C, 50.36; H, 3.99. Found: C, 50.19; H, 4.08%. ^{1}H-NMR (499.8 MHz, acetone-d_6, 25 °C): δ 9.64 (s, 1H, HCN_3), 8.53 (d, $^3J(H_\gamma H_\beta) = 2.5$ Hz, 2H, H_γ), 8.33 (dd, $^3J(H_\gamma'H_\beta') = 3.0$ Hz, $^4J(H_\gamma'H_\alpha') = 0.5$ Hz, 1H, H_γ'), 7.67 (m, 4H, H_o), 7.50 (d, $^3J(H_\alpha H_\beta) = 2.5$ Hz, 2H, H_α), 7.45 (m, 2H, H_p), 7.40 (m, 4H, H_m), 7.30 (m, 2H, H_p), 7.13 (m, 4H, H_m), 6.93 (m, 4H, H_o), 6.53 (apparent t, $^3J(H_\beta H_\gamma) = {}^3J(H_\beta H_\alpha) =$ 2.5 Hz, 2H, H_β), 5.67 (dd, $^3J(H_\beta'H_\gamma') = 3.0$ Hz, $^3J(H_\beta'H_\alpha') = 2.0$ Hz, 1H, H_β'), 5.47 (d, $3J(H_\alpha'H_\beta') =$ 2.0 Hz, 1H, H_α'), 3.24 M (4H, $2CH_2$). ^{13}C{^{1}H}-NMR (125.7 MHz, acetone-d_6, 25 °C): δ 151.25 (s, 2C, C_α), 147.08 (s, 1C, C_α'), 136.47 (AXX′, $^2J(PP) = 19.9$ Hz, $^1J(PC) = -1.74$ Hz, $^3J(PC) = 39.9$ Hz, 2C, C_i), 135.79 (s, 1C, C_γ'), 135.06 (s, 2C, C_γ), 133.91 (t, $[^2J(PC)+{}^4J(PC)] = 8.3$ Hz, 4C, C_o), 133.12 (t, $[^2J(PC)+{}^4J(PC) = 8.5$ Hz, 4C, C_o), 131.51 (AXX′, $^2J(PP) = 19.9$ Hz, $^1J(PC) = 43.4$ Hz, $^3J(PC) = -2.1$ Hz, 2C, C_i), 131.13 (s, 2C, C_p), 130.53 (s, 2C, C_p), 129.52 (t, $[^3J(PC)+{}^5J(PC)] = 8.9$ Hz, 4C, C_m), 128.74 (t, $[^3J(PC)+{}^5J(PC)] = 9.2$ Hz, 4C, C_m), 109.27 (s, 1C, C_β'), 108.02 (s, 2C, C_β), 77.70 (s, 1C, HCN_3), 29.92 (m, $[^1J(PC)+{}^3J(PC)] = 43.7$ Hz, 2C, CH_2). ^{31}P{^{1}H}-NMR (202.3 MHz, acetone-d_6, 25 °C): δ 70.40 (s, 2P, dppe), −143.54 (sept, $^1J(PF) = 708$ Hz, 1P, PF_6^-).

4.2.17. [(Tpm)Ru(DMPP)$_2$[4+2]Cl]PF$_6$ (**16**)



A solution containing [(Tpm)Ru(COD)Cl]PF$_6$ (0.651 g, 1.08 mmol) and 3,4-dimethyl-1-phenylphosphole, DMPP, (0.3 ml, 1.60 mmol) in DMF (35 ml) was heated at reflux under nitrogen for 27 h. The solvent was removed in vacuo to leave an orange glassy residue. The residue was dissolved in a minimum amount of CH_2Cl_2 and the insolubles were removed by filtration. Ether was added to the filtrate and the resulting yellow solid was isolated by filtration to obtain **16**. Yield 0.405g (43.1%). Anal. Calc. for $C_{34}H_{36}ClF_6N_6P_3Ru$: C, 46.82; H, 4.16. Found: C, 46.91; H, 4.35%.^{1}H-NMR (499.8 MHz, acetone-d_6, 25 °C): δ 9.48 (s, 1H, HCN_3), 8.48 (d, $^3J(H_\gamma H_\beta) = 2.0$ Hz, 1H, H_γ), 8.39 (d, $^3J(H_\gamma H_\beta) = 2.0$ Hz, 1H, H_γ), 8.23 (d, $^3J(H_\gamma H_\beta) = 2.0$ Hz, 1H, H_γ), 7.97 (m, 4H, H_o), 7.67 (d, $3J(H_\alpha H_\beta) = 2.0$ Hz, 1H, H_α), 7.59 (m, 2H, H_p), 7.52 (m, 4H, H_m), 6.83 (d, $^3J(H_\alpha H_\beta) = 2.0$ Hz, 1H, H_α), 6.59 (t, $^3J(H_\beta H_\gamma) = {}^3J(H_\beta H_\alpha) = 2.0$ Hz, 1H, H_β), 6.52 (d, $^3J(H_\alpha H_\beta) = 2.0$ Hz, 1H, H_α), 6.33 (t, $^3J(H_\beta H_\gamma) = {}^3J(H_\beta H_\alpha) = 2.0$ Hz, 1H, H_β), 6.19 (dq, $^2J(PH) = 29.5$ Hz, $^4J(HH) = 1.5$ Hz, 1H, H_α'), 6.11 (t, $^3J(H_\beta H_\gamma) = {}^3J(H_\beta H_\alpha) = 2.0$ Hz, 1H, H_β), 4.38 (app dt, $^2J(PH) = {}^3J(H_1H_2) = 3.5$ Hz, $^4J(H_1H_3) = 2.2$ Hz, 1H, H_1), 3.45 (app t, $^2J(PH) = {}^4J(H_1H_3) = 2.2$ Hz, 1H, H_3), 2.94 (ddd, $^3J(PH) = 44.0$ Hz, $^2J(PH) = 5.5$ Hz, $^3J(H_1H_2) = 3.5$ Hz, 1H, H_2), 2.24 (app t,

$^4J(PH) = {}^4J(HH) = 1.5$ Hz, 3H, CH_3(b)), 1.83 (s, 3H, CH_3(c)), 1.55 (s, 3H, CH_3(d)), 1.28 (s, CH_3(a)). $^{13}C\{^1H\}$-NMR (125.8 MHz, acetone-d_6), 25 °C): δ 154.72 (d, $^2J(PC) = 13.3$ Hz, C=C), 150.38 (s, 1C, C_α), 146.41 (s, 1C, C_α), 145.50 (s, 1C, C_α), 138.91 (d, $^2J(PC) = 1.3$ Hz, C=C), 137.12 (s, 1C, C_γ), 134.91 (dd, $^1J(PC) = 32.9$ Hz, $^3J(PC) = 2.9$ Hz, 1C, C_i), 134.58 (d, $^1J(PC) = 14.8$ Hz, 1C, C_i), 134.32 (s, 1C, C_γ), 133.96 (s, 1C, C=C), 133.69 (s, 1C, C_γ), 132.84 (d, $^2J(PC) = 8.9$ Hz, 2C, C_o), 131.40 (d, $^2J(PC) = 8.8$ Hz, 2C, C_o), 131.34 (d, $^4J(PC) = 2.6$ Hz, 1C, C_p), 130.27 (d, $^4J(PC) = 1.1$ Hz, 1C, C_β), 129.47 (d, $^3J(PC) = 9.7$ Hz, 2C, C_m), 129.29 (d, $^3J(PC) = 8.5$ Hz, 2C, C_m), 123.77 (d, $^1J(PC) = 50.3$ Hz, C_3), 108.66 (d, $^4J(PC) = 1.1$ Hz, 1C, C_β), 108.15 (d, $^4J(PC) = 2.4$ Hz, 1C, C_β), 77.47 (s, 1C, H*C*N_3), 62.59 (dd, $^2J(PC) = 13.4$ Hz, $^2J(PC) = 5.9$ Hz, 1C, C_5), 55.42 (dd, $^1J(PC) = 39.8$ Hz, $^2J(PC) = 10.8$ Hz, 1C, C_1), 52.42 (dd, $^1J(PC) = 24.0$ Hz, $^3J(PC) = 5.2$ Hz, 1C, C_6), 52.11 (dd, $^1J(PC) = 32.8$ Hz, $^2J(PC) = 29.2$ Hz, 1C, C_2), 26.94 (d, $^3J(PC) = 5.0$ Hz, 1C, CH_3(a)), 18.42 (d, $^2J(PC) = 13.8$ Hz, 1C, CH_3(b)), 17.49 (d, $^3J(PC) = 1.4$ Hz, 1C, CH_3(c)), 15.70 (s, 1C, CH_3(d)). $^{31}P\{^1H\}$-NMR (202.3 MHz, acetone-d_6, 25 °C): δ 187.38 (d, $^2J(PP) = 37.2$ Hz, 1P, P_1), 72.47 (d, $^2J(PP) = 37.2$ Hz, 1P, P_2), −143.58 (sept, $^1J(PF) = 708$ Hz), 1P, PF_6^-).

4.2.18. [(Tp)Ru(dppe)(Me_2CO)]PF_6 (17)

A heterogeneous yellow suspension of (Tp)Ru(dppe)Cl (0.394 g, 0.527 mmol) and $AgPF_6$ (0.170g, 0.672 mmol) in acetone (30 ml) was heated to a gentle reflux overnight. The solution was then cooled to r.t. and filtered over Celite to remove AgCl and excess $AgPF_6$. The solvent was removed from the filtrate and a yellow solid remained. Yield 0.346 g (70.1%). X-ray quality crystals were obtained by slow diffusion of ether into an acetone solution of the product. The crystals were red in color. Anal. Calc. for $C_{38}H_{40}BF_6N_6OP_3Ru$: C, 49.85; H, 4.40. Found: C, 49.57; H, 4.12%. ^{1}H-NMR (499.8 MHz δ, CD_3NO_2, 25 °C): 8.05 (d, $^3J(H_\gamma H_\beta) = 2.0$ Hz, 2H, H_γ), 8.80 (d, $^3J(H_\gamma' H_\beta') = 2.0$ Hz, 1H, H_γ'), 7.47 (m, 8H, $H_o + H_m$), 7.31 (m, 2H, H_p), 7.10 (m, 4H, H_m), 6.98 (d, $^3J(H_\beta H_\alpha) = 2.0$ Hz, 2H, H_α), 6.95 (d, $^3J(H_\alpha H_\beta) = 2.0$ Hz, 1H, H_α') 6.85 (m, 2H, H_p), 6.81 (m, 4H, H_o), 6.25 (t, $^3J(H_\gamma H_\beta) = 2.0$ Hz, 2H, H_β), 6.21 (apparent t, $^3J(H_\gamma' H_\beta') = {}^3J(H_\beta' H_\alpha') = 2.0$ Hz, H_β'), 3.43 (m, 4H, 2 CH_2), 2.07 (s, 6H, 2 CH_3). $^{31}P\{^1H\}$-NMR (202.3 MHz δ, CD_3NO_2, 25 °C): 72.81 (2p, dppe), −145.0 (septet, $^1J(PF) = 707$ Hz, 1P, PF_6^-). $^{13}C\{^1H\}$-NMR (125.7 MHz δ, CD_3NO_2, 25 °C): 143.71 (s, C_α'), 136.46 (s, C_α), 136.03 (s, C_γ'), 132.74 (T, $[^2J(PC) + {}^4J(PC)] = 9.4$ Hz, C_o), 131.60 (T, $[^2J(PC) + {}^4J(PC)] = 9.0$ Hz, C_o), 130.63 (s, C_p), 130.30 (s, C_p), 129.03 (T, $[^3J(PC) + {}^5J(PC)] = 8.7$ Hz, C_m), 128.40 (T, $[^3J(PC) + {}^5J(PC)] = 9.8$ Hz, C_m), 106.18 (s, C_β'), 105.76 (C_β'), 29.38 (s, $OC(CH_3)_2$), 29.18 (AXX′, $[^1J(PC) + {}^2J(PC)] = 10.2$ Hz, CH_2). IR (Nujol, cm^{-1}): 2479 (m, ν(B–H)), 1652 (m, ν(CO)). M.p.: 172 °C, dec.

4.3. X-ray data collection and processing

Crystals of **2** and **4** (acetonitrile); **6**, **10**, **11** and **13** (CH_2Cl_2–ether); **8** (CH_3NO_2–ether); **14**, **15** and **17** (acetone–ether) were mounted on glass fibers, coated with epoxy, and placed on a Siemens P4 diffractometer. Intensity data were taken in the ω-mode at 298 K with Mo–K_α graphite monochromated radiation (λ = 0.71073 Å). Three check reflections monitored every 100 reflections showed random (< 2%) variation during the data collections. The data were corrected for Lorentz, polarization effects and absorption using an emperical model derived from azimuthal data collections. Scattering factors and corrections for anomalous dispersion were taken from a standard source [80]. Calculations were performed with the SHELXTL plus version 5.10 software package on a personal computer. The structures were solved by Patterson methods. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. Hydrogen atoms were refined at calculated positions with a riding model in which the C–H vector was fixed at 0.96 Å.

5. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 210294–210303 for compounds **2**, **4**, **6**, **8**, **10**, **11**, **13**, **14**, **15** and **17**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

This research was supported by an award from the Research Corporation and by the donors of the Petroleum Research Fund Administered by the American Chemical Society. We are grateful for this support.

References

[1] H.-L. Ji, J.H. Nelson, A. DeCian, J. Fischer, L. Solujić, E.B. Milosavljević, Organometallics 11 (1992) 401.
[2] L.P. Barthel-Rosa, K. Maitra, J. Fischer, J.H. Nelson, Organometallics 16 (1997) 1714.
[3] D. Duraczynska, J.H. Nelson, J. Chem. Soc. Dalton Trans. (2003) 449.
[4] J.C. Jeffrey, T.B. Rauchfuss, Inorg. Chem. 18 (1979) 2658.

[5] W. Keim, Angew. Chem. Int. Ed. Engl. 29 (1990) 235.
[6] G.W. Parshall, S.D. Ittel, Homogeneous Catalysis: the Application and Chemistry of Catalysis by Soluble Transition Metal Complexes, 2nd ed., Wiley–Interscience, New York, 1992, pp. 70–72.
[7] E. Lindner, B. Keppler, P. Wegner, Inorg. Chim. Acta 258 (1997) 97.
[8] J. Pietsch, P. Braunstein, Y. Chauvin, New J. Chem. (1998) 467.
[9] A. Lightfoot, P. Schnider, A.P. Faltz, Angew. Chem. Int. Ed. Engl. 37 (1998) 2897.
[10] P. Espinet, K. Soulantica, Coord. Chem. Rev. 193-195 (1999) 499.
[11] E. Lindner, T. Schneller, F. Auer, H.A. Mayer, Angew. Chem. Int. Ed. Engl. 38 (1999) 2154.
[12] C.S. Slone, D.A. Weinberger, C.A. Mirkin, Prog. Inorg. Chem. 48 (1999) 233.
[13] J. Holt, R. Kadyrov, S. Borns, D. Heller, A. Börner, J. Organomet. Chem. 603 (2000) 61.
[14] P. Braunstein, F. Naud, Angew. Chem. Int. Ed. Engl. 40 (2001) 680.
[15] V.V. Grushin, Organometallics 20 (2001) 3950.
[16] B. Demerseman, D. Reonard, R. Lelagadec, M. Gonzalez, P. Crochet, P.H. Dixneuf, J. Organomet. Chem. 471 (1994) 229.
[17] C. Thoumazet, M. Melaimi, C. Ricard, F. Mathey, P. LeFloch, Organometallics 22 (2003) 1580.
[18] T.P. Gill, K.R. Mann, Organometallics 1 (1982) 485.
[19] (a) M.I. Bruce, Chem. Rev. 98 (1998) 2797;
(b) M.I. Bruce, Chem. Rev. 91 (1991) 197.
[20] C. Bruneau, P.H. Dixneuf, Acc. Chem. Res. 32 (1999) 311.
[21] B.M. Trost, F.D. Toste, A.B. Pinkerton, Chem. Rev. 101 (2001) 2067.
[22] V. Guerchais, Eur. J. Inorg. Chem. (2002) 783.
[23] V. Cadierno, M.P. Gamasa, J. Gimeno, Eur. J. Inorg. Chem. (2001) 571.
[24] H.D. Hansen, J.H. Nelson, Organometallics 19 (2000) 4740 (and references therein).
[25] C. Slugovc, P. Wiede, K. Mereiter, R. Schmid, K. Kirchner, Organometallics 19 (1997) 2768.
[26] M.A.J. Tenorio, M.J. Tenorio, M.C. Puerta, P. Valerga, Organometallics 19 (2000) 1333.
[27] C. Slugovc, K. Mereiter, R. Schmid, K. Kirchner, Organometallics 17 (1998) 827.
[28] H.G. Alt, H.E. Engelhardt, M.D. Rausch, L.B. Kool, J. Organomet. Chem. 329 (1987) 61.
[29] S.J. Landon, P.M. Shulman, G.L. Geoffroy, J. Am. Chem. Soc. 107 (1985) 6739.
[30] C. Slugovc, V.N. Sapunov, P. Wiede, K. Mereiter, R. Schmid, K. Kirchner, J. Chem. Soc. Dalton Trans. (1997) 4209.
[31] C. Gemel, P. Wiede, K. Mereiter, V.N. Sapunov, R. Schmid, K. Kirchner, J. Chem. Soc. Dalton Trans. (1996) 4071.
[32] B. Buriez, I.D. Burns, A.F. Hill, A.J.P. White, D.J. Williams, J.D.E.T. Wilton-Ely, Organometallics 18 (1999) 1504.
[33] M.A.J. Tenorio, M.J. Tenorio, M.C. Puerta, P. Valerga, Organometallics 16 (1997) 5528.
[34] S. Pavlik, C. Gemel, C. Slugovc, K. Mereiter, R. Schmid, K. Kirchner, J. Organomet. Chem. 617–618 (2001) 301.
[35] C. Slugovc, D. Doberer, C. Gemel, R. Schmid, K. Kirchner, B. Winkler, F. Stelzer, Monatsch. Chem. 129 (1998) 221.
[36] S. Trofimenko, Scorpionates the Coordination Chemistry of Polypyrazolylborate Ligands, Imperial College Press, London, 1999.
[37] S. Trofimenko, Chem. Rev. 93 (1993) 943.
[38] D.M. Tellers, S.J. Skoog, R. Bergman, T.B. Gunnoe, W.D. Harman, Organometallics 19 (2000) 2428.
[39] M.A. Bennett, G. Wilkinson, Chem. Ind. (Lond.) (1959) 1516.
[40] T.V. Ashworth, D.C. Liles, D.J. Robinson, E. Singleton, N.J. Coville, E. Darling, A.J. Markwell, S. Afr. J. Chem. 40 (1987) 183.
[41] L. Luo, S.P. Nolan, P.J. Fagan, Organometallics 12 (1993) 4305.
[42] C. Gemel, G. Trimmel, C. Slugovc, S. Kremel, K. Mereiter, R. Schmid, K. Kirchner, Organometallics 15 (1996) 3998.
[43] M. Fajardo, A. de la Hoz, E. Diez-Barra, F.A. Jalon, A. Ortero, A. Rodriguez, A. Tajeda, D. Belletti, M. Lanfranchi, M. Pellinghelli, J. Chem. Soc. Dalton Trans. (1993) 1935.
[44] J.H. Nelson, Nuclear Magnetic Resonance Spectroscopy, Prentice-Hall, Upper Saddle River, NJ, 2003.
[45] J.H. Nelson, K.Y. Ghebreyessus, Syn. React. Inorg. Met.-Org. Chem. 33 (2003) 1329.
[46] N.W. Alcock, I.D. Burns, K.S. Claire, A.F. Hill, Inorg. Chem. 31 (1992) 2906.
[47] T.G. Appleton, H.C. Clark, L.E. Manzer, Coord. Chem. Rev. 10 (1973) 335.
[48] K.D. Redwine, J.H. Nelson, J. Organomet. Chem. 613 (2000) 177 (and references therein).
[49] W.-C. Chan, C.-P. Lau, Y.-Z. Chen, Y.-Q. Fang, S.-M. Ng, Organometallics 16 (1997) 34.
[50] K.D. Redwine, J.H. Nelson, Organometallics 19 (2000) 3054.
[51] W.L. Wilson, J.A. Rahn, N.W. Alcock, J. Fischer, J. Frederick, J.H. Nelson, Inorg. Chem. 33 (1994) 109.
[52] C.C. Santini, J. Fischer, F. Mathey, A. Mitschler, J. Am. Chem. Soc. 102 (1980) 5809.
[53] C. Slugovc, K. Mereiter, E. Zobetz, R. Schmid, K. Kirchner, Organometallics 15 (1996) 5275.
[54] B. Buriez, I.D. Burns, A.F. Hill, A.J.P. White, D.J. Williams, J.D.E.T. Wilton-Ely, Organometallics 18 (1999) 1504.
[55] M.A.J. Tenorio, M.J. Tenorio, M.C. Puerta, P. Valerga, Organometallics 16 (1997) 5528.
[56] C. Yin, Z. Xu, S.-Y. Yang, S.M. Ng, K.Y. Wong, Z. Lin, C.P. Lau, Organometallics 20 (2001) 1216.
[57] C. Vicente, G.B. Shul'pin, B. Moreno, S. Sabo-Etienne, B. Chaudret, J. Mol. Catal. A: Chemical 98 (1995) L5.
[58] C. Standfest-Hauser, C. Slugovc, K. Mereiter, R. Schmid, K. Kirchner, L. Xiao, W. Weissensteiner, J. Chem. Soc. Dalton Trans. (2001) 2989.
[59] K. Ghebreyessus, J.H. Nelson, J. Organomet. Chem. 669 (2003) 48.
[60] A. Llobet, P. Doppelt, T. Meyer, Inorg. Chem. 27 (1988) 514.
[61] L.D. Field, B.A. Messerle, L. Soler, I.E. Buys, T.W. Hambley, J. Chem. Soc. Dalton Trans. (2001) 1959.
[62] M. Fajardo, A. de la Hoz, E. Diez-Barra, F.A. Jalon, A. Otero, A. Rodriguez, J. Tejeda, D. Belletti,. M. Lanffranchi, M.A. Pellinghelli, J. Chem. Soc. Dalton Trans. (1993) 1935.
[63] M. Yamaguchi, T. Iida, T. Yamagishi, Inorg. Chem. Commun. 1 (1998) 299.
[64] E. Wayne, J. Jones, C.A. Bignozzi, C.P. Chen., T.J. Meyer, Inorg. Chem. 32 (1993) 1167.
[65] H.S. Chu, Z. Xu, X. Ng, M. Lau, C.P. Lin, Eur. J. Inorg. Chem. (2000) 993.
[66] A. Llobet, D. Hodgson, T.J. Meyer, Inorg. Chem. 29 (1990) 3760.
[67] S. Bhambri, D.A. Tocher, J. Chem. Soc. Dalton Trans. (1997) 3367.
[68] F. Laurent, E. Plantalech, B. Domnadieu, A. Jimenez, F. Hernandez, M. Martinez-Ripoll, M. Biner, A. Llobet, Polyhedron 18 (1999) 3321.
[69] S. Bhambri, D. Tocher, Polyhedron 15 (1996) 2763.
[70] A. Macchioni, G. Bellachioma, G. Cardaci, G. Cruciani, E. Foresti, P. Sabatino, C. Zuccaccia, Organometallics 17 (1998) 5549.
[71] C.A. Tolman, Chem. Rev. 77 (1977) 313.
[72] N.-Y. Sun, S.J. Simpson, J. Organomet. Chem. 434 (1992) 341.
[73] G. Trimmel, C. Slugovc, P. Wiede, K. Mereiter, V.N. Sapunov, R. Schmid, K. Kirchner, Inorg. Chem. 36 (1997) 1076.
[74] E. Ruba, W. Simanko, K. Mereiter, R. Schmid, K. Kirchner, Inorg. Chem. 39 (2000) 382.

[75] C. Gemel, R. John, C. Slugovc, K. Mereiter, R. Schmid, K. Kirchner, J. Chem. Soc. Dalton Trans. (2000) 2607.
[76] D. Reger, T. Grattan, K. Brown, C. Little, J. Lambda, A. Rheingold, R. Sommer, J. Organomet. Chem. 607 (2000) 120.
[77] J.R. Laucer, J. Scwarz, J.D. Park., J. Org. Chem. 26 (1961) 983.
[78] A. Breque, F. Mathey, P. Savignac, Synthesis (1981) 983.
[79] D. Perrin, W. Armarego, D. Perrin, Purification of Laboratory Chemicals, Pergamon Press, Oxford, 1980.
[80] International Tables for X-ray Crystallography, vol. C., D. Reidel, Boston, MA, 1992.