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Diphenylvinylphosphine (DPVP) complexes containing the (η^5-MeC$_5$H$_4$)Ru(II) moiety: synthesis, characterization and reactions†

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The complex [(η^5-MeC$_5$H$_4$)Ru(DPVP)$_2$(CH$_3$CN)]PF$_6$ (**4**) (DPVP = Ph$_2$PCH=CH$_2$) loses CH$_3$CN under vacuum to produce the phosphaallyl complex [(η^5-MeC$_5$H$_4$)Ru(η^1-DPVP)(η^3-DPVP)]PF$_6$ (**6**) and reacts with Me$_3$SiC≡CH and PhC≡CH in CH$_2$Cl$_2$–CH$_3$OH solutions to form the methoxymethylcarbene [(η^5-MeC$_5$H$_4$)(DPVP)$_2$Ru=C(OCH$_3$)(CH$_3$)]PF$_6$ (**7**) and the carbonyl complex [(η^5-MeC$_5$H$_4$)Ru(DPVP)$_2$(CO)]PF$_6$ (**8**), respectively. In contrast [(η^5-MeC$_5$H$_4$)Ru(DPVP)(CO)(CH$_3$CN)]PF$_6$ (**15**) does not lose CH$_3$CN to form a phosphaallyl complex. The structures of the complexes described herein have been deduced from elemental analyses, infrared spectroscopy, ^{1}H, ^{13}C{^{1}H}, ^{1}H NOE, where appropriate by ^{31}P{^{1}H} NMR spectroscopy and in eight cases by X-ray crystallography.

Introduction

We have previously reported the synthesis and characterization of the only examples of ruthenium(II) complexes that contain diphenylvinylphosphine (DPVP) bound to the metal as a neutral four-electron donor phosphaallyl ligand. These complexes, [(η^5-C$_5$H$_5$)Ru(η^3-DPVP)(η^1-DPVP)]PF$_6$ (**A**)[1] and [(η^5-C$_5$Me$_5$)Ru(η^3-DPVP)(η^1-DPVP)]PF$_6$ (**B**)[2] are among a growing number of ruthenium complexes that contain hybrid hemilabile ligands.[3] Complexes of hemilabile ligands are of current interest because of their potential applications in molecular activation, homogeneous catalysis, functional materials, and small molecule sensing.

Synthesis of **A** entailed removing coordinated CH$_3$CN from the precursor [(η^5-C$_5$H$_5$)Ru(DPVP)$_2$(CH$_3$CN)]PF$_6$ by thermolysis under vacuum at 70–75 °C for 7 days. We reasoned that because the major stabilizing interaction in **A** is back donation from ruthenium into the π^* orbital of the vinyl group, the significantly better donor C$_5$Me$_5^-$ would cause **B** to be more easily formed and more stable than **A**. And in fact, we found that CH$_3$CN was removed from [(η^5-C$_5$Me$_5$)Ru(DPVP)$_2$(CH$_3$CN)]PF$_6$ on a rotary evaporator at ≈40 °C in 15 minutes.[2] Complexes **A** and **B** are novel compounds that can be considered to be latent stabilized coordinatively unsaturated species since the vinyl group is readily displaced by a variety of two-electron donor ligands.[1,2] We describe herein the synthesis, characterization, and reactions of an additional example of a phosphaallyl complex [(η^5-MeC$_5$H$_4$)Ru(η^3-DPVP)(η^1-DPVP)]PF$_6$ (**6**).

Results and discussion

[(η^5-MeC$_5$H$_4$)Ru(η^3-DPVP)(η^1-DPVP)]PF$_6$ (**6**) was prepared by the sequence of reactions illustrated in Scheme 1. The first three reactions are modeled after those employed in the syntheses of the C$_5$H$_5^-$ analogs.[4] Because the donor ability of MeC$_5$H$_4^-$ should lie between those of C$_5$H$_5^-$ and Me$_5$C$_5^-$, we expected that it would be easier to remove CH$_3$CN from **4** than from **A** and more difficult than from **B**. To our surprise, removal of CH$_3$CN from **4** was even more difficult than from **A** (10 days at 86–92 °C under vacuum *vs.* 7 days at 70–75 °C under vacuum).

Compounds **1**–**6** were characterized by elemental analyses, cyclic voltammetry, ^{1}H, ^{13}C{^{1}H}, and where appropriate ^{31}P{^{1}H} NMR spectroscopy. The structure of **6** was deduced from NMR spectroscopic data. The ^{31}P{^{1}H} NMR spectra of **4** and **6** are very different. For **4** two resonances at δ 39.95 (s, 2P, η^1-DPVP) and −145.00 (sept., ^1J(PF) = 712 Hz, 1P, PF$_6^-$) were observed. For **6** three resonances at δ 42.38 (d, ^2J(PP) = 45.0 Hz, 1P, η^1-DPVP), 24.12 (d, ^2J(PP) = 45.0 Hz, 1P, η^3-DPVP) and −145.00 (sept., ^1J(PF) = 713 Hz, 1P, PF$_6^-$) were observed. These data are similar to those reported for **A**[1] (δ 42.3, 24.2; ^2J(PP) = 43.9 Hz) and **B**[2] (δ 44.8, 14.3; ^2J(PP) = 48.5 Hz). It is interesting to note that while there is no clear trend in δ ^{31}P among these three complexes, ^2J(PP) increases of about 1 Hz for each additional CH$_3$ group added to the Cp ring. The ^{1}H NMR experiments illustrated in Fig. 1 were used to first make chemical shift assignments and then from the NOE experiment to assign the structure of **6**. The effects of phosphorus decoupling upon the line shapes of the vinyl proton resonances clearly established which phosphorus resonance was due to the η^1-DPVP and η^3-DPVP ligands. This is most evident in the proton resonances of the η^1-DPVP ligand which occur at δ 4.65, 5.09 and 5.61. Irradiation of the phosphorus resonance at δ 42.38 removes phosphorus coupling from these three resonances while irradiation of the phosphorus resonance at δ 24.12 does not. In contrast, all three protons of the η^3-DPVP ligand are coupled to both phosphorus nuclei.

A ^{13}C APT experiment established that the carbon resonance at δ 46.37 was due to a CH$_2$ group and that at δ 36.67 was due to a CH group of the phosphaallyl moiety. An HMQC experiment established that the CH$_2$ carbon resonance correlated with the proton resonances at δ 2.51 and 3.66 and the CH carbon resonance correlated with the proton resonance at δ 3.57. Hence, one of the two CH$_2$ protons (H$_{c'}$) resonates at δ 2.51.

The η^3-DPVP ligand is bound to ruthenium in the *exo* orientation in **A**[1] and **B**[2] in both the solution and solid states. The NOEs observed between the MeC$_5$H$_4$ – CH$_3$ protons and protons H$_{a'}$ and H$_{b'}$ (Fig. 1) of the η^3-DPVP ligand establish that these protons are proximate in space and that **6** also has the *exo* geometry in solution. Since **6**, like **A**[1] and **B**[2] is not dynamic in solution over the −90 to +60 °C temperature range in CDCl$_3$, it is most likely that **6** has the *exo* geometry in the solid state as well. The NOE observed between the CH$_3$ and H$_\alpha$ protons of the MeC$_5$H$_4$ ring allows assignment of the H$_\alpha$ and H$_\beta$ proton resonances. All aspects of the ^{1}H NMR spectral data for the η^3-DPVP protons of **6** are comparable to those of **A**[1] and **B**[2], and Table 1 summarizes selected ^{1}H NMR data for the three compounds.

Compounds **4**, **5**, and **6** all undergo quasireversible one-electron oxidations with $E_{1/2}$ values of 0.80, 0.90 and 0.89 V *vs.* Fc/Fc$^+$, respectively. It is somewhat surprising that **5** is not the easiest of the three compounds to oxidize as it possesses the

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† Dedicated to the late Professor Noel McAuliffe.

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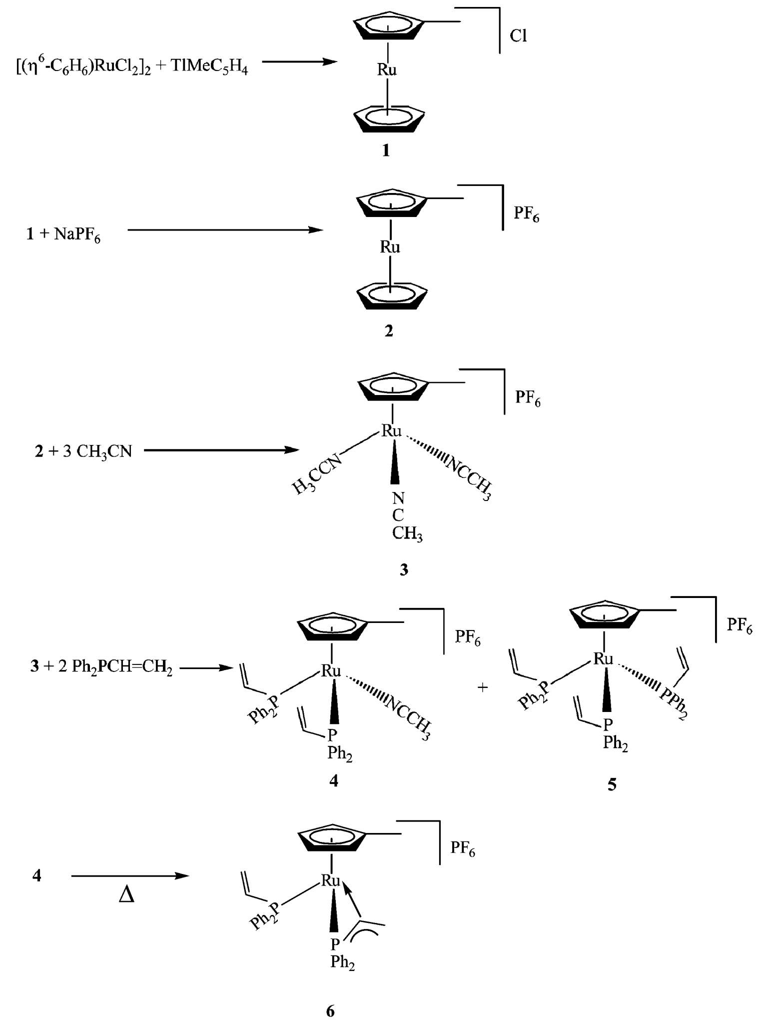
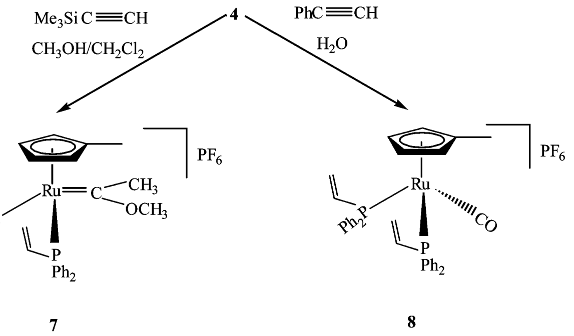


Scheme 1

set of better electron donor ligands. An explanation may lie in the structures of these compounds. Complexes **4** and **5** were characterized by X-ray crystallography. Views of the structures of the cations are shown in Figs. 2 and 3, respectively. Selected bond distances and angles are given in the figure captions. Both complexes are three-legged piano stools with distorted octahedral structures. The three DPVP ligands in **5** are arranged with approximate C_3 symmetry minimizing interligand steric interactions. A comparison of the metrical parameters for the two compounds indicates that **5** is somewhat more sterically encumbered than **4**. This is evidenced by the slightly longer average Ru–P distances (2.356 *vs.* 2.315 Å) and Ru–C distances (2.238 *vs.* 2.212 Å) for **5** than **4**, respectively. Also, because of the small steric size of CH_3CN the P(1)–Ru(1)–P(2) angle (96.89(6)°) in **4** is larger than the average P–Ru–P angle (94.92(14)°) in **5**. Despite the steric crowding evidenced in **5**, it is formed by reaction of **3** with only two moles of DPVP per mole of **3**.

One of the reasons for preparing compounds **4** and **6** was to use them as precursors to vinylidene[5] and allenylidene[5] complexes that might be catalysts for the additions of nucleophiles to terminal alkynes.[6] Reaction of **4** with $Me_3SiC{\equiv}CH$ in CH_2Cl_2–CH_3OH solution gave the methoxymethylcarbene complex **7** (Scheme 2) by nucleophilic attack of CH_3OH on a vinylidene intermediate.[7] The formation of **7** was deduced by $^{13}C\{^1H\}$ NMR spectroscopy. In particular, the carbene carbon resonance is a triplet at δ 306.84 with $^2J(PC)$ = 12.3 Hz as typically found for such complexes.[8] The other ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR data (see Experimental section) are fully consistent with the assigned structure. The complex undergoes a quasireversible one-electron oxidation at 0.89 V *vs.* Fc/Fc$^+$, similar to **4**–**6**.



Scheme 2

The structure of **7** was confirmed by X-ray crystallography (Fig. 4). The complex is a three-legged piano stool with a distorted octahedral geometry. The Ru=C (carbene) bond length (1.921(10) Å) is on the low end of the range (1.90–2.02 Å) typically found for such complexes.[7–9] The Ru–P distances (2.311(3), 2.314(3) Å) and average Ru–C distance (2.262(13) Å) are in their expected ranges.[7–9] The dihedral angle measured between the $C(MeC_5H_4)$centroid–Ru–C(carbene) and CH_3–C(carbene)–OCH_3 planes, 29.6°, is small,[7–10] suggesting that this is the preferred geometry[7] and that the barrier to rotation about the Ru=C bond might be of the order of 6–12 kcal mol^{-1}.[10] Variable temperature ^1H, $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR studies in acetone-d$_6$ show that for this complex there is free rotation

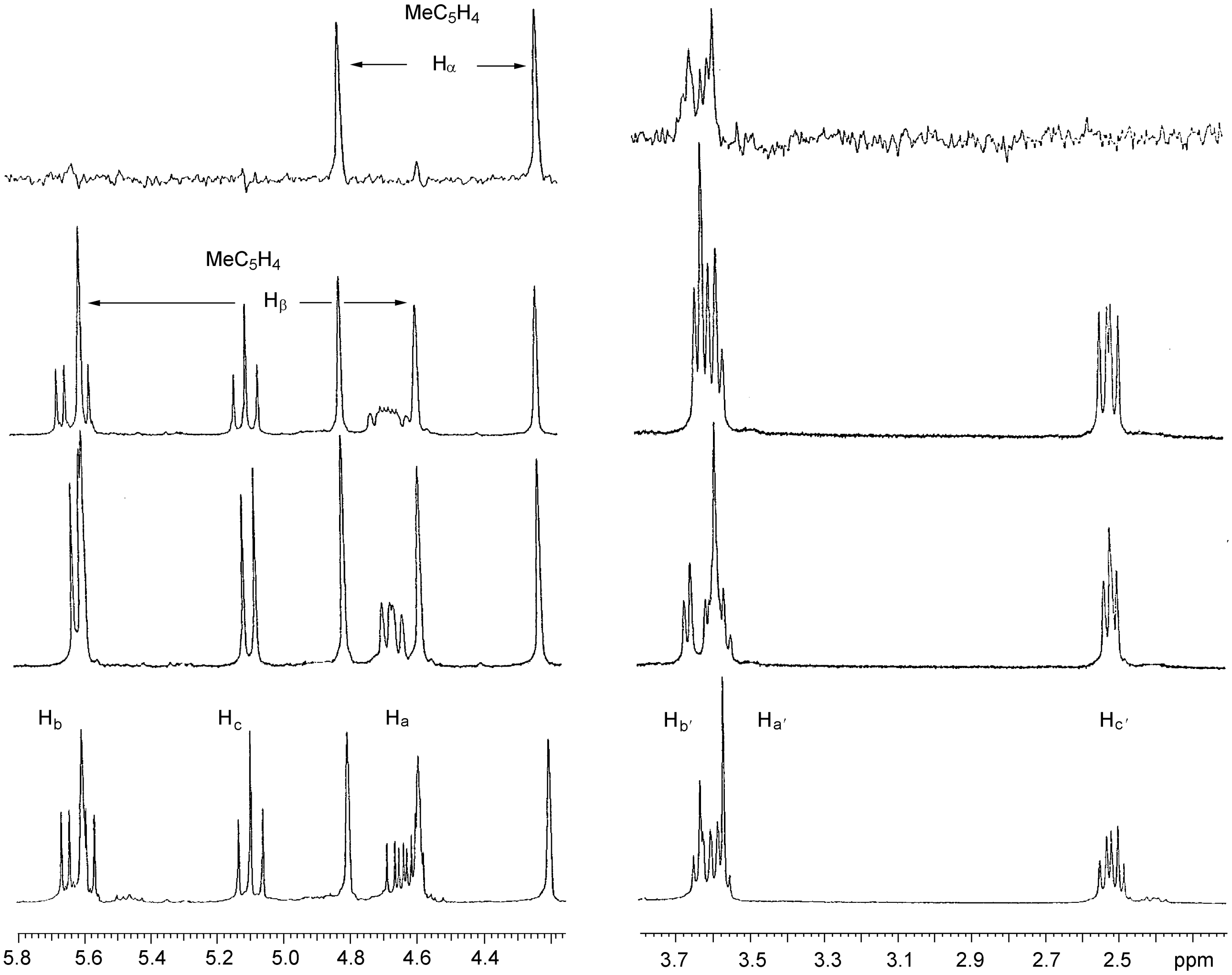


Fig. 1 Expansions of the 499.826 MHz ^{1}H NMR spectra for compound **6** (from bottom to top): normal spectrum; ^{1}H{^{31}P} decoupling of the vinylphosphine phosphorus; ^{1}H{^{31}P} decoupling of the phosphaallyl phosphorus; ^{1}H NOE difference spectrum with excitation of the MeC_5H_4–CH_3 resonance.

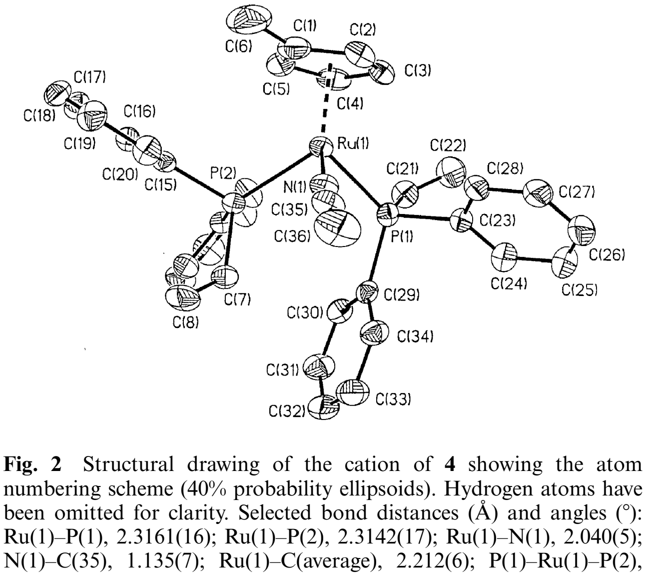


Fig. 2 Structural drawing of the cation of **4** showing the atom numbering scheme (40% probability ellipsoids). Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Ru(1)–P(1), 2.3161(16); Ru(1)–P(2), 2.3142(17); Ru(1)–N(1), 2.040(5); N(1)–C(35), 1.135(7); Ru(1)–C(average), 2.212(6); P(1)–Ru(1)–P(2), 96.89(6); P(1)–Ru(1)–N(1), 88.11(14); P(2)–Ru(1)–N(1), 91.72(15).

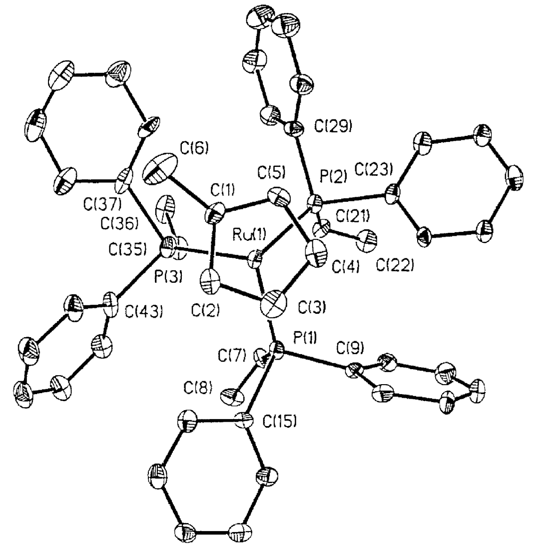
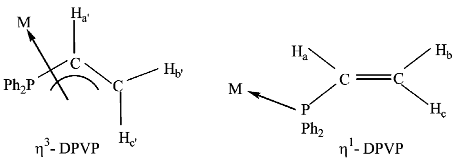


Fig. 3 Structural drawing of the cation of **5** showing the atom numbering scheme (20% probability ellipsoids). Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Ru(1)–P(1), 2.359(4); Ru(1)–P(2), 2.347(4); Ru(1)–P(3), 2.362(4); Ru(1)–C(average), 2.238(15); P(1)–Ru(1)–P(2), 94.33(13); P(1)–Ru(1)–P(3), 95.021(14); P(2)–Ru(1)–P(3), 95.41(13).

about the Ru=C bond between +50 and −90 °C. Experimentally, few ruthenium carbene complexes exhibit hindered rotation.[7]

Complex **4** reacts with PhC≡CH and adventitious H_2O to produce the carbonyl complex **8** (Scheme 2) by nucleophilic attack of H_2O on a vinylidene intermediate according to a previously described mechanism.[11] Complex **8** exhibits ν_{CO} at 1983 cm^{-1}. For [(η^5-C_5H_5)Ru(DPVP)$_2$(CO)]PF_6 (**9**)[1] and [(η^5-Me_5C_5)Ru(DPVP)$_2$(CO)]PF_6 (**10**)[2] ν_{CO} was observed at 1982

Table 1 Selected ^{1}H NMR data of **A**, **B** and **6** for the η^3- and η^1-DPVP ligands[a]



		η^3-DPVP				η^1-DPVP		
		H$_{a'}$	H$_{b'}$	H$_{c'}$		H$_a$	H$_b$	H$_c$
A	δ	4.08	4.06	2.41		4.54	5.61	5.12
	Multiplicity	m	m	m		ddd	ddd	ddd
	^3J(PH)	15.03[b]	22.24	21.94	^3J(PH)	25.24[b]	37.57	18.33
	^3J(PH)	10.52	4.51	10.52				
	^3J(a′b′)[c]	8.65	8.65		^3J(ab)	12.32	12.32	
	^3J(a′c′)	6.1		6.1	^3J(ac)	18.33		18.33
	^2J(b′c′)		2.96	2.96	^2J(bc)		0.90	0.90
B	δ	3.12	3.20	2.62		4.25	5.35	5.03
	Multiplicity	m	m	m		ddd	ddd	ddd
	^3J(PH)	13.22[b]	34.86	16.23	^3J(PH)	26.15[b]	36.06	17.43
	^3J(PH)	2.10	1.80	6.31				
	^3J(a′b′)	10.37	10.37		^3J(ab)	12.32	12.32	
	^3J(a′c′)	0.62		0.62	^3J(ac)	17.43		17.43
	^2J(b′c′)		9.91	9.91	^2J(bc)		0.60	0.60
6	δ	3.57	3.66	2.51		4.65	5.61	5.09
	Multiplicity	m	m	m		ddd	ddd	ddd
	^3J(PH)	18.5[b]	24.5	10.0	^3J(PH)	25.00[b]	37.50	18.00
	^3J(PH)	1.5	1.0	15.0				
	^3J(a′b′)	9.0	9.0		^3J(ab)	12.30	12.30	
	^3J(a′c′)	9.5		9.5	^3J(ac)	18.00		18.00
	^2J(b′c′)		2.0	2.0	^2J(bc)		<0.2	<0.2

[a] NMR spectra measured in $CDCl_3$, chemical shifts in ppm downfield from Me_4Si, coupling constants in Hz. [b] ^2J(PH). [c] J(HH) coupling where the symbols a′, b′, c′, and a, b, c represent H$_{a'}$, H$_{b'}$, H$_{c'}$, H$_a$, H$_b$, H$_c$, respectively.

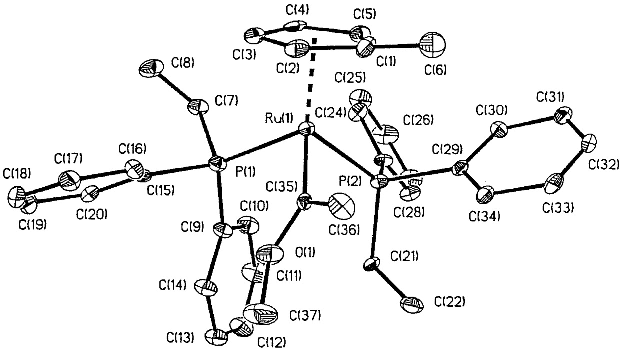


Fig. 4 Structural drawing of the cation of **7** showing the atom numbering scheme (10% probability ellipsoids). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ru(1)–P(1), 2.314(3); Ru(1)–P(2), 2.311(3); Ru(1)–C(35), 1.921(10); Ru(1)–C(average), 2.262(11); P(1)–Ru(1)–P(2), 96.86(11); P(1)–Ru(1)–C(35), 92.81(3); P(2)–Ru(1)–C(35), 88.2(3); C(36)–C(35)–O(1), 113.0 (9).

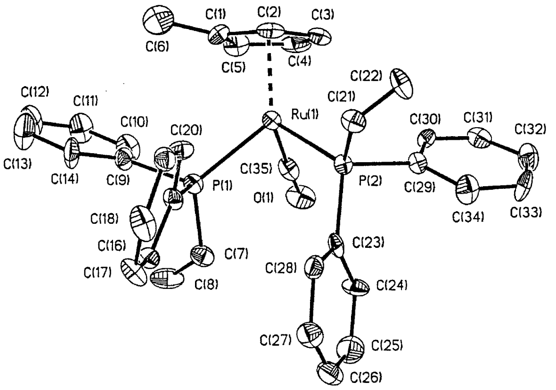
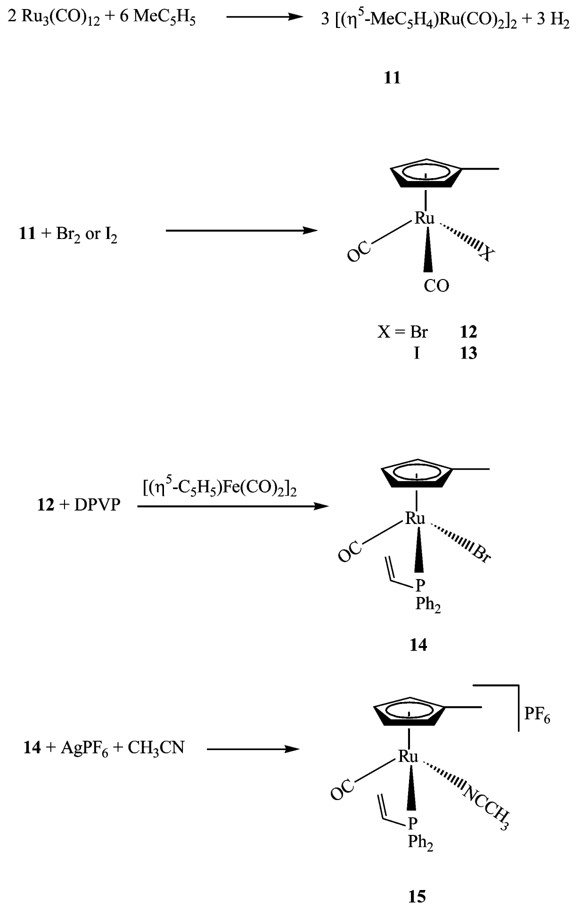


Fig. 5 Structural drawing of the cation of **8**·CH_2Cl_2 showing the atom numbering scheme (10% probability ellipsoids). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ru(1)–P(1), 2.332(4); Ru(1)–P(2), 2.320(4); Ru(1)–C(35), 1.87(2); C(35)–O(1), 1.172(19); Ru(1)–C(average), 2.247(16); P(1)–Ru–P(2), 95.76(13); P(1)–Ru(1)–C(35), 88.8(5); P(2)–Ru(1)–C(35), 91.9(5).

and 1969 cm^{-1}, respectively. The ^{31}P{^{1}H} NMR resonances for the DPVP ligands in **8**, **9**, and **10** occur at δ 36.60, 36.22 and 35.3, respectively. The carbonyl carbon resonances in the ^{13}C{^{1}H} NMR spectra of all three complexes is a triplet at δ 201.60, 202.68 and 204.25, with ^2J(PP) = 17.3, 17.34 and 17.2 Hz, respectively. Both **8** (Fig. 5) and **9**[1] have been characterized by X-ray crystallography. Both complexes are three-legged piano stools with distorted octahedral geometries. The metrical parameters for the two complexes are very similar. For **9** the Ru–P distances are 2.320(2) and 2.324(2) Å, the average Ru–C distance is 2.235(7) Å, and the Ru–CO, and C–O distances are 1.867(6) and 1.124(8) Å, respectively.[1]

Complex **B** reacts with $Me_3SiC{\equiv}CH$[12] and $PhC{\equiv}CH$[2] to form the vinylidene complexes [(η^5-Me_5C_5)(DPVP)$_2$Ru=C=CH_2]PF_6 and [(η^5-Me_5C_5)(DPVP)$_2$Ru=C=C(Ph)H]PF_6, respectively under conditions similar to those used for the syntheses of **7** and **8**. This suggests that the C$_α$ is less electrophilic in these vinylidene complexes than in the MeC_5H_4 analogs that are intermediates in the formation of **7** and **8**. Despite the formation of **8** by hydration of $PhC{\equiv}CH$, **4** is not a good catalyst for this hydration.

We have previously shown[1] that [(η^5-C_5H_5)Ru(CO)(η^3-DPVP)]PF_6 has the *endo* geometry in contrast to **A**, **B**, and **6** all of which have the *exo* geometry. Since this suggested that the ancillary ligands could control the geometry of the η^3-phosphaallyl ligand we set out to prepare [(η^5-MeC_5H_4)Ru(CO)(η^3-DPVP)]PF_6 by the reactions illustrated in Scheme 3. Complex **11** exists in solution as an equilibrium mixture of *cis* and *trans*,



Scheme 3

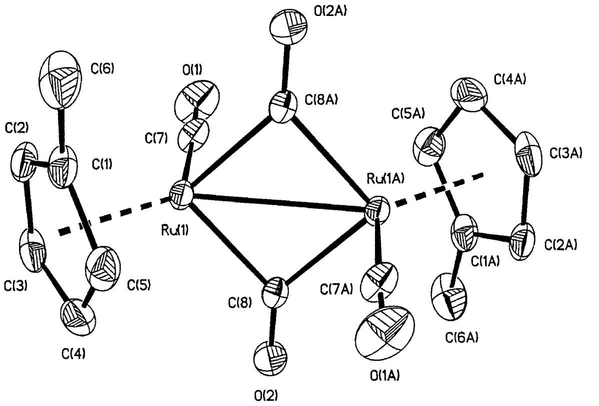


Fig. 6 Structural drawing of **11** showing the atom numbering scheme (30% probability ellipsoids). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ru(1)–C(7), 1.857(3); Ru(1)–C(8), 2.056(3); Ru(1)–Ru(1A), 2.7437(7); Ru(1)–C(average), 2.272(3); C(7)–O(1), 1.145(4); C(8)–O(2), 1.170(3); Ru(1)–C(8)–Ru(1A), 84.26(10); C(7)–Ru(1)–C(8), 92.19(12); C(8)–Ru(1)–C(8a), 95.74(10).

carbonyl bridged and nonbridged isomers.[13–15] Its solid state structure (Fig. 6) has not previously been reported. As can be seen in Fig. 6 it has the centrosymmetric *trans* structure in the solid state. The two compounds [(η^5-C_5H_5)M$(CO)_2]_2$ (M = Fe, Ru) also have centrosymmetric *trans* structures in the solid state.[16] There is very little difference in the metrical parameters of **11** and its C_5H_5 analog.

Compound **13** has been previously prepared[17] by oxidation of **11** with CH_3I. In our hands this procedure worked very poorly, whereas oxidation of **11** with I_2 to form **13** and with Br_2 to form **12** proceeded in good yield (see Scheme 3). Compound **14** was prepared by [(η^5-C_5H_5)Fe$(CO)_2]_2$ catalyzed[17] ligand substitution of **12**. Complex **15** was prepared by reaction of **14** with CH_3CN and $AgPF_6$. All complexes, except for **15** which is a low melting waxy solid, are air stable crystalline solids. They were characterized by elemental analyses, infrared spectroscopy, ^1H, $^{13}C\{^1H\}$, and for **14** and **15** by $^{31}P\{^1H\}$ NMR spectroscopy (see Experimental section). All spectroscopic data are consistent with the assigned structures and are unexceptional. Compounds **12**, **13**, and **14** were also characterized by X-ray crystallography. Structures are shown in Figs. 7 and 8. Compounds **12** and **13** are isostructural and for both the CH_3 and halide are eclipsed. Except for the Ru–X distances, the bond distances in the two compounds differ very little. All three compounds are three-legged piano stools with distorted octahedral structures. The Ru–Br distances in **12** and **14** are essentially the same. Neither **14** nor **15** could be converted to phosphaallyl complexes by removal of bromide from **14** or CH_3CN from **15**.

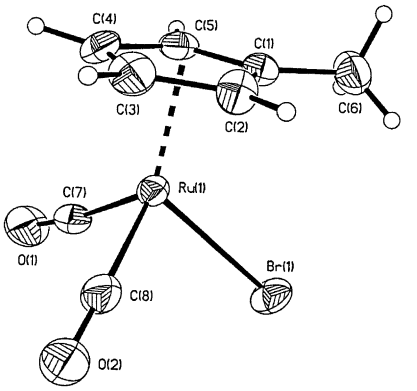


Fig. 7 Structural drawing of **12** showing the atom labelling scheme (30% probability ellipsoids). Hydrogen atoms have an arbitrary radius of 0.1 Å. Compound **13** is isostructural with **12**. Selected bond distances (Å) and angles (°): (**12**) Ru(1)–Br(1), 2.5349(16); Ru(1)–C(7), 1.885(6); Ru(1)–C(8), 1.881(6); C(7)–O(1), 1.127(7); C(8)–O(2), 1.131(8); Ru(1)–C(average), 2.232(6); C(7)–Ru(1)–Br(1), 92.64(19); C(7)–Ru(1)–C(8), 90.4(3); C(8)–Ru(1)–Br(1), 88.8(2). (**13**) Ru(1)–I(1), 2.7030(11); Ru(1)–C(7), 1.874(8); Ru(1)–C(8), 1.882(9); C(7)–O(1), 1.133(10); C(8)–O(2), 1.138(11); Ru(1)–C(average), 2.240(9); C(7)–Ru(1)–I(1), 91.6(3); C(7)–Ru(1)–C(8), 90.6(4); C(8)–Ru(1)–I(1), 88.2(3).

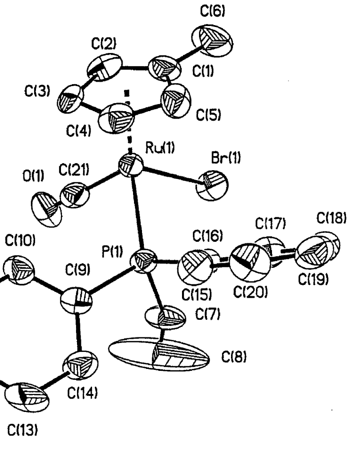


Fig. 8 Structural drawing of **14** showing the atom labelling scheme (30% probability ellipsoids). Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Ru(1)–P(1), 2.292(2); Ru(1)–Br(1), 2.5434(15); Ru(1)–C(21), 1.902(15); Ru(1)–C(average), 2.219(12); C(21)–O(1), 1.005(13); P(1)–Ru(1)–Br(1), 89.39(8); P(1)–Ru(1)–C(21), 91.3(3); Br(1)–Ru(1)–C(21), 92.5(4).

We have recently described the syntheses of tethered phosphinopropylcyclopentadiene[18] and phosphinopropylarene[19] compounds by hydroalkylation of coordinated DPVP. In an effort to extend the scope of the hydroalkylation reaction to the MeC_5H_4 ring system we reacted complex **14** with $KOBu^t$ in refluxing acetonitrile and with the radical initiator azobisisobutyronitrile (AIBN) in refluxing benzene. Both reactions failed to produce a tethered phosphinopropylcyclopentadienide complex. Decomposition occurred instead. With the weaker base, K_2CO_3, starting material was recovered.

Concluding remarks

We have synthesized and characterized nine new ruthenium complexes including the new phosphaallyl complex $[(\eta^5\text{-MeC}_5H_4)\text{Ru}(\eta^3\text{-DPVP})(\eta^1\text{-DPVP})]PF_6$ (**6**). It like its C_5H_5 (**A**) and C_5Me_5 (**B**) analogs contains the η^3-phosphaallyl ligand bound to ruthenium in the *exo* orientation. For all three phosphaallyl complexes the *exo* isomer does not interconvert with the *endo* isomer in solution. We have compared the reactivity of **4** with that of its Me_5C_5 analog toward terminal alkynes, and have shown that the Ru=C_α carbon of the vinylidenes derived from **4** is much more electrophilic than those derived from the Me_5C_5 analog. Attempted syntheses of the carbonylphosphaallyl complex $[(\eta^5\text{-MeC}_5H_4)\text{Ru}(\eta^3\text{-DPVP})(CO)]PF_6$ and a tethered phosphinopropylcyclopentadienide complex failed.

Experimental

Reagents and physical measurements

All chemicals were reagent grade and were used as received form commercial sources (Aldrich, Fisher Scientific, Acros Organics, GFS Chemicals, Strem Chemicals) or synthesized as described below. All syntheses were conducted under a nitrogen atmosphere. $[(C_6H_6)RuCl_2]_2$ was synthesized by the literature procedure.[20] Acetonitrile was distilled from CaH_2 prior to use. Melting points were obtained using a Mel-Temp melting point apparatus and are uncorrected. ^1H NMR spectra were recorded at 499.8 MHz on a Varian Unity Plus 500 FT-NMR spectrometer and at 300 MHz on a General Electric GN 300 FT-NMR spectrometer. $^{13}C\{^1H\}$ NMR spectra were recorded at 125.7 MHz on a Varian Unity Plus 500 FT-NMR spectrometer and at 75 MHz on a General Electric 300 FT-NMR spectrometer. $^{31}P\{^1H\}$ NMR spectra were recorded at 202.3 MHz on a Varian Unity Plus 500 FT-NMR spectrometer and at 121.65 MHz on a General Electric 300 FT-NMR spectrometer. Proton and carbon chemical shifts were referenced to residual solvent resonances; phosphorus chemical shifts were referenced to an external 85% aqueous solution of H_3PO_4. All shifts to low field, high frequency are positive. NOE experiments were performed with the pulse sequence reported by Shaka and co-workers.[21] IR spectra were recorded on a Perkin-Elmer Spectrum BX spectrometer. Cyclic voltammograms were obtained at 25 °C in freshly distilled CH_2Cl_2 containing 0.1 M tetrabutylammonium hexafluorophosphate using a BAS CV50-W voltammetric analyzer. A three-electrode system was used. The working electrode was glassy carbon, the auxiliary electrode was a platinum wire and the reference electrode was Ag/AgCl (aqueous) separated from the cell by a Luggin capillary. The Fc/Fc$^+$ couple occurred at 508 mV[22] under the same conditions. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Syntheses

$[(\eta^5\text{-MeC}_5H_4)\text{Ru}(\eta^6\text{-C}_6H_6)]Cl$ (1). *Method a.* A 100 mL, three-neck round-bottom flask was charged with 30 mL of absolute ethanol and purged with nitrogen for 30 min. Then 0.5 mL (5.0 mmol) of freshly cracked methylcyclopentadiene (MeC_5H_5) and 3.5 g (0.014 mol) of thallium ethoxide were added. The whole was stirred at ambient temperature for 30 min, giving a yellowish compound. $TlMeC_5H_4$ was isolated by filtration using a Schlenk line ($TlMeC_5H_4$-air sensitive) and immediately transferred to another round-bottom flask containing 0.5 g (1 mmol) of $[(C_6H_6)RuCl_2]_2$[22] suspended in 30 mL freshly distilled acetonitrile. The whole mixture was stirred at ambient temperature overnight. The resulting precipitate of TlCl was removed by filtration through Celite, and the filtrate evaporated. The dark-brown compound was dried under vacuum to give 0.30 g of pure product in 51% yield.

Method b. A 100 mL, three-neck round-bottom flask was charged with 2.5 mL (0.025 mol) of freshly cracked methylcyclopentadiene (MeC_5H_5) and 80 mL of freshly distilled hexane. The whole was purged with nitrogen for 30 min, and then cooled in ice. 20 mL (0.05 mol) of 2.5 M n-BuLi was added dropwise and the mixture was stirred for 2 hours, giving a yellowish precipitate. $LiMeC_5H_4$ was isolated by filtration using a Schlenk line ($LiMeC_5H_4$-air sensitive) and immediately transferred to another round-bottom flask containing 4 g (8 mmol) $[(C_6H_6)RuCl_2]_2$[22] suspended in 300 mL freshly distilled acetonitrile. The whole mixture was stirred at ambient temperature overnight. The resulting precipitate of LiCl was removed by filtration through Celite, and the filtrate evaporated. The dark-brown compound was dried under vacuum to give 1.34 g of pure product in 29% yield.

Anal. calc. for $C_{12}H_{13}ClRu$: C, 49.07; H, 4.46. Found: C, 49.12; H, 4.29%. ^1H NMR (acetone-d$_6$): δ 6.36 (s, 6H, C_6H_6), 5.58 (m, 2H, H_β), 5.43 (m, 2H, H_α), 2.11 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 100.70 (C_i), 87.34 (C_6H_6), 82.57 (C_β), 80.70 (C_α), 13.92 (CH_3).

$[(\eta^5\text{-MeC}_5H_4)\text{Ru}(\eta^6\text{-C}_6H_6)]PF_6$ (2). *Method a.* 0.25 g (0.9 mmol) of $[(\eta^5\text{-MeC}_5H_4)\text{Ru}(\eta^6\text{-C}_6H_6)]Cl$ (**1**) was dissolved in 30 mL distilled water, and the green–brown solution was filtered into a round-bottom flask. To this solution 0.5 g (3 mmol) of $NaPF_6$ was added. A precipitate of $[(\eta^5\text{-MeC}_5H_4)\text{Ru}(\eta^6\text{-C}_6H_6)]PF_6$ was immediately obtained. This compound was isolated by filtration, and dried in vacuum; 0.11 g of pure white solid was obtained in 32% yield.

Method b. An adaptation of the procedure of Trost and Older[23] was used. 50 mL of absolute ethanol was purged with nitrogen for 30 min. 1.95 g (14 mmol) of K_2CO_3 followed by 1.18 g (2.4 mmol) of $[(C_6H_6)RuCl_2]_2$[22] and 4.2 mL (0.042 mol) of freshly cracked methylcyclopentadiene (MeC_5H_5) were added. The resulting heterogeneous brown mixture was heated to 60 °C with rapid stirring and kept at this temperature overnight. The reaction mixture was cooled to room temperature and filtered through Celite. The brown filtrate was concentrated to about 20 mL, and then 1.61 g (9.8 mmol) of NH_4PF_6in 16 mL of water was added. The immediate formation of a brown precipitate was observed. The remaining ethanol was removed leaving a dark brown compound, which was dissolved in a minimum amount of acetone and passed through a short alumina column. The resulting yellow solution was concentrated, and an excess of ether was added; a white compound was formed immediately. The mixture was left in the freezer overnight. The white compound was separated by filtration, washed with ether and dried under vacuum for 4 hours. 0.45 g (24%) of pure compound was obtained.

Mp: 288–290 °C (decomp.). Anal. calc. for $C_{12}H_{13}F_6PRu$: C, 35.74; H, 3.25. Found: C, 35.61; H, 3.16%. ^1H NMR (acetone-d$_6$): δ 6.28 (s, 6H, C_6H_6), 5.52 (m, 2H, H_β), 5.38 (m, 2H, H_α), 2.08 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (acetone-d$_6$): δ 100.75 (C_i), 87.37 (C_6H_6), 82.51 (C_β), 80.62 (C_α), 13.71 (CH_3). $^{31}P\{^1H\}$ NMR (acetone-d$_6$): δ −142.06 (sept., ^1J(PF) = 706 Hz).

$[(\eta^5\text{-MeC}_5H_4)\text{Ru}(CH_3CN)_3]PF_6$ (3). A solution containing 0.45 g (1.12 mmol) of $[(\eta^5\text{-MeC}_5H_4)\text{Ru}(\eta^6\text{-C}_6H_6)]PF_6$ (**2**) in 150 mL of freshly distilled acetonitrile (yellowish solution) was irradiated in a quartz vessel with a medium pressure Hg lamp for 24 h. The solvent was removed from the golden-yellow solution on a rotary evaporator and the yellow solid residue was dried under vacuum. 0.45 g (90%) of pure compound was obtained. Mp: 67–70 °C. ^1H NMR (acetone-d$_6$): δ 4.23 (m, 2H, H_β), 3.99 (m, 2H, H_α), 2.45 (s, 9H, CH_3CN), 1.70 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (acetone-d$_6$): δ 126.16 (CN), 87.00 (C_i), 70.93 (C_β), 64.55 (C_α), 12.66 (CH_3), 3.06 (CH_3CN). $^{31}P\{^1H\}$ NMR (acetone-d_6): δ −142.3 (sept., ^1J(PF) = 705 Hz). IR (CN region, Nujol, cm^{-1}): 2324, 2283. IR (PF$_6$ region, acetone film, cm^{-1}): 842.

$[(\eta^5\text{-MeC}_5\text{H}_4)\text{Ru}(\text{CH}_3\text{CN})(\text{DPVP})_2]\text{PF}_6$ (4) and $[(\eta^5\text{-MeC}_5\text{H}_4)\text{Ru}(\text{DPVP})_3]\text{PF}_6$ (5). A 50 mL, three-neck round-bottom flask was charged with 0.45 g (1 mmol) of $[(\eta^5\text{-MeC}_5\text{H}_4)\text{Ru}(\text{CH}_3\text{CN})_3]\text{PF}_6$ (**3**) and 25 mL of freshly distilled acetonitrile. The whole was purged with nitrogen for 30 min. Then 0.5 mL (2.5 mmol) of DPVP ($\text{Ph}_2\text{PCH=CH}_2$) was added, and the mixture was stirred at room temperature overnight. Solvent was evaporated leaving a brown solid. This solid was dissolved in CH_2Cl_2 and passed through a silica gel column packed with hexane and eluted with CH_2Cl_2. Recrystallization from CH_2Cl_2–hexane gave 0.61 g (77% yield) of yellow crystalline **4**. Mp: 155–160 °C. Anal. calc. for $\text{C}_{36}\text{H}_{36}\text{F}_6\text{NP}_3\text{Ru}$: C, 54.69; H, 4.59. Found: C, 54.67; H, 4.81%. ^{1}H NMR (CDCl$_3$): δ 7.70 (m, 2H, H$_o$), 7.52 (m, 2H, H$_p$), 7.45 (m, 4H, H$_m$), 7.36 (m, 2H, H$_p$), 7.30 (m, 6H, H$_{o,m}$), 6.98 (m, 4H, H$_o$), 5.82 (m, 4H, H$_a$H$_b$), 5.11 (m, 2H, H$_c$), 4.40 (s, 2H, H$_{\beta'}$), 3.99 (s, 4H, H$_{\alpha'}$), 2.42 (s, 3H, CH$_3$CN), 2.01 (d, J(PH) = 1.0 Hz, 3H, CH$_3$). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 39.95 (s, 2P, DPVP), −145.00 (sept., ^1J(PF) = 712 Hz, 1P, PF$_6^-$). ^{13}C{^{1}H} NMR (CDCl$_3$):[24] δ 135.36 (m, $|^1J(\text{PC}) + {}^3J(\text{PC})|$ = 46.9 Hz, C$_i$), 133.87 (T, $|^2J(\text{PC}) + {}^4J(\text{PC})|$ = 11.3 Hz, C$_o$), 133.01 (m, $|^1J(\text{PC}) + {}^3J(\text{PC})|$ = 50.5 Hz, C$_i$), 132.29 (T, $|^2J(\text{PC}) + {}^4J(\text{PC})|$ = 10.1 Hz, C$_o$), 131.83 (m, $|^1J(\text{PC}) + {}^3J(\text{PC})|$ = 81.7 Hz, C$_\alpha$), 130.81 (s, C$_\text{p}$), 130.15 (s, C$_\text{p}$), 128.96 (s, C$_\beta$), 128.55 (T, $|^3J(\text{PC}) + {}^5J(\text{PC})|$ = 9.8 Hz, C$_m$), 128.40 (T, $|^3J(\text{PC}) + {}^5J(\text{PC})|$ = 9.8 Hz, C$_m$), 126.98 (s, CH$_3$CN), 107.12 (s, C$_i$Cp), 82.64 (s, C$_\beta$Cp), 80.30 (s, C$_\alpha$Cp), 12.48 (s, CH$_3$), 4.61 (s, CH$_3$CN). $E_{1/2}$ = 0.80 V *vs.* F$_c$/F$_c^+$.

When an excess of DPVP (for example a 1 : 3 molar ratio) is used, only $[(\eta^5\text{-MeC}_5\text{H}_4)\text{Ru}(\text{DPVP})_3]\text{PF}_6$ (**5**) is obtained in 65% yield. Mp: 188–189 °C. Anal. calc. for $\text{C}_{48}\text{H}_{46}\text{F}_6\text{P}_4\text{Ru}$: C, 59.94; H, 4.82. Found: C, 59.78; H, 4.63%. ^{1}H NMR (acetone-d_6): δ 7.44 (m, 6H, H$_p$), 7.32 (m, 12H, H$_m$), 7.15 (m, 6H, H$_o$), 7.15 (m, ^3J(H$_a$H$_c$) = 18.0 Hz, ^3J(H$_a$H$_b$) = 12.0 Hz, 3H, H$_a$), 6.08 (m, ^3J(H$_a$H$_b$) = 12.0 Hz, ^2J(H$_b$H$_c$) = 1.2 Hz, 3H, H$_b$), 5.17 ([AB]$_2$, $|^3J(\text{HH}) + {}^4J(\text{HH})|$ = 4.0 Hz, 2H, H$_\beta$Cp), 4.81 ([AB]$_2$, $|^3J(\text{HH}) + {}^4J(\text{HH})|$ = 4.0 Hz, 2H, H$_\alpha$Cp), 4.86 (m, ^3J(H$_a$H$_c$) = 18.0 Hz, ^2J(H$_b$H$_c$) = 1.2 Hz, 3H, H$_c$), 1.60 (s, 3H, CH$_3$). ^{31}P{^{1}H} NMR (acetone-d_6): δ 29.28 (s, 3P, DPVP), −145.96 (sept., ^1J(PF) = 707 Hz, 1P, PF$_6^-$). ^{13}C{^{1}H} NMR (acetone-d_6): δ 136.44 (m, C$_i$), 135.41 (m, C$_\alpha$), 134.58 (D, $|^2J(\text{PC}) + {}^4J(\text{PC})|$ = 6.5 Hz, C$_o$), 134.55 (D, $|^2J(\text{PC}) + {}^4J(\text{PC})|$ = 6.5 Hz, C$_o$), 131.23 (s, C$_\text{p}$), 130.91 (s, C$_\beta$), 129.12 (D, $|^3J(\text{PC}) + {}^5J(\text{PC})|$ = 6.3 Hz, C$_m$), 129.10 (D, $|^3J(\text{PC}) + {}^5J(\text{PC})|$ = 7.0 Hz, C$_m$), 104.08 (s, C$_i$Cp), 86.92 (q, J(PC) = 1.1 Hz, C$_\beta$Cp), 85.18 (q, J(PC) = 1.4 Hz, C$_\alpha$Cp), 13.29 (s, CH$_3$). $E_{1/2}$ = 0.90 V *vs.* F$_c$/F$_c^+$.

$[(\eta^5\text{-MeC}_5\text{H}_4)\text{Ru}(\eta^1\text{-DPVP})(\eta^3\text{-DPVP})]\text{PF}_6$ (6). 0.51 g (0.6 mmol) of $[(\eta^5\text{-MeC}_5\text{H}_4)\text{Ru}(\text{CH}_3\text{CN})(\text{DPVP})_2]\text{PF}_6$ (**4**) was heated under vacuum at 86–92 °C for 10 days. Recrystallization from CH_2Cl_2–MeOH–hexane gave 0.19 g (40%) of a yellow product. Mp: 212–220 °C. Anal. calc. for $\text{C}_{34}\text{H}_{33}\text{F}_6\text{P}_3\text{Ru}$: C, 54.31; H, 4.74. Found: C, 54.01; H, 4.43%. ^{1}H NMR (CDCl$_3$): δ 7.82 (m, 2H, H$_o$), 7.56 (m, 8H, H$_{o,m}$), 7.44 (m, 3H, H$_p$), 7.31 (m, 3H, H$_{m,p}$), 7.04 (m, 2H, H$_m$), 6.91 (m, 2H, H$_o$), 5.61 (dd, ^3J(PH) = 37.5 Hz, ^3J(H$_a$H$_b$) = 12.3 Hz, 1H, H$_b$), 5.60 (bs, 1H, MeCpH$_\beta$), 5.09 (apparent t, ^3J(PH) = ^3J(H$_a$H$_c$) = 18.0 Hz, 1H, H$_c$), 4.81 (bs, 1H, MeCpH$_\alpha$), 4.65 (ddd, ^2J(PH) = 25.0 Hz, ^3J(H$_a$H$_c$) = 18.0 Hz, ^3J(H$_a$H$_b$) = 12.3 Hz, 1H, H$_a$), 4.57 (bs, 1H, MeCpH$_\beta$), 4.21 (bs, 1H, MeCpH$_\alpha$), 3.66 (ABMX, ^3J(PH) = 24.5 Hz, ^3J(H$_{a'}$H$_{b'}$) = 9.0 Hz, ^2J(H$_{b'}$H$_{c'}$) = 2.0 Hz, ^3J(PH) = 1.0 Hz, 1H, H$_{b'}$), 3.57 (ABMX, ^3J(PH) = 18.5 Hz, ^3J(H$_{a'}$H$_{c'}$) = 9.5 Hz, ^3J(H$_{a'}$H$_{b'}$) = 9.0 Hz, ^3J(PH) = 1.5 Hz, 1H, H$_{a'}$), 2.51 (dddd, ^3J(PH) = 15.0 Hz, ^3J(PH) = 10.0 Hz, ^3J(H$_{a'}$H$_{c'}$) = 9.5 Hz, ^2J(H$_{b'}$H$_{c'}$) = 2.0 Hz, 1H, H$_{c'}$), 1.45 (s, 3H, CH$_3$). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 42.38 (d, ^2J(PP) = 45.0 Hz, 1P, η^1-DPVP), 24.12 (d, ^2J(PP) = 45.0 Hz, 1P, η^3-DPVP), −145.00 (sept., ^1J(PF) = 713 Hz, 1P, PF$_6^-$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 135.11 (d, ^2J(PC) = 11.3 Hz, C$_o$), 134.45 (dd, ^1J(PC) = 48.0 Hz, ^3J(PC) = 2.6 Hz, C$_i$), 133.00 (d, ^2J(PC) = 12.6 Hz, C$_o$), 132.57 (d, ^2J(PC) = 11.3 Hz, 2C$_o$), 132.41 (d, ^4J(PC) = 2.4 Hz, C$_p$), 131.79 (d, ^4J(PC) = 2.1 Hz, C$_p$), 131.61 (d, ^4J(PC) = 2.0 Hz, C$_p$), 131.51 (dd, ^1J(PC) = 52.3 Hz, ^3J(PC) = 4.0 Hz, C$_i$), 130.57 (C$_\beta$C$_p$), 129.78 (d, ^1J(PC) = 43.5 Hz, C$_\alpha$), 129.59 (d, ^3J(PC) = 12.2 Hz, C$_m$), 129.42 (d, ^3J(PC) = 11.9 Hz, C$_m$), 128.76 (d, ^3J(PC) = 10.4 Hz, C$_m$), 128.54 (d, ^3J(PC) = 10.2 Hz, C$_m$), 125.34 (dd, ^1J(PC) = 52.7 Hz, ^3J(PC) = 5.0 Hz, C$_i$), 102.68 (C$_i$MeCp), 86.46 (C$_\beta$MeCp), 85.09 (d, J(PC) = 4.9 Hz, C$_\alpha$MeCp), 84.88 (C$_\alpha$MeCp), 83.31 (C$_\beta$MeCp), 46.37 (d, ^2J(PC) = 4.8 Hz, C$_{\beta'}$), 36.67 (d, ^1J(PC) = 32.2 Hz, C$_{\alpha'}$), 11.06 (CH$_3$).

$[(\eta^5\text{-MeC}_5\text{H}_4)(\text{DPVP})_2\text{Ru=C(OCH}_3)(\text{CH}_3)]\text{PF}_6$ (7). A 50 mL, three-neck round-bottom flask was charged with 0.40 g (0.5 mmol) of $[(\eta^5\text{-MeC}_5\text{H}_4)\text{Ru}(\text{CH}_3\text{CN})(\text{DPVP})_2]\text{PF}_6$ (**4**) and 30 mL of a 1 : 1 CH_2Cl_2–MeOH mixture. The whole was purged with nitrogen for 30 min. Then 0.25 mL (1.8 mmol) of HC≡CSiMe$_3$was added, and the mixture was heated at reflux for 3 days (color turned dark). The solution was placed in a freezer and the formation of a yellow precipitate was observed. This precipitate was separated by filtration and analyzed. It appeared to be starting material (0.014 g). Solvent from the filtrate was evaporated and the residue was recrystallized from CH_2Cl_2–hexane to give 0.12 g of pure product in 29% yield. Mp: 221–225 °C. Anal. calc. for $\text{C}_{37}\text{H}_{39}\text{F}_6\text{OP}_3\text{Ru}$: C, 55.02; H, 4.89. Found: C, 54.93; H, 5.10%. ^{1}H NMR (CDCl$_3$): δ 7.52 (m, 2H, H$_p$), 7.45 (m, 4H, H$_m$), 7.36 (m, 2H, H$_p$), 7.29 (m, 4H, H$_m$), 7.18 (m, 4H, H$_o$), 6.96 (m, 4H, H$_o$), 6.14 (m, $|^2J(\text{PH}) + {}^4J(\text{PH})|$ = 24.5 Hz, ^3J(H$_a$H$_c$) = 18.0 Hz, ^3J(H$_a$H$_b$) = 12.3 Hz, 2H, H$_a$), 5.78 (m, $|^3J(\text{PH}) + {}^5J(\text{PH})|$ = 36.0 Hz, ^3J(H$_a$H$_b$) = 12.3 Hz, 2H, H$_b$), 4.89 (m, $|^3J(\text{PH}) + {}^5J(\text{PH})|$ = 18.0 Hz, ^3J(H$_a$H$_c$) = 18.0 Hz, 2H, H$_c$), 4.73 (m, $|^3J(\text{HH}) + {}^4J(\text{HH})|$ = 3.5 Hz, 2H, H$_\beta$), 4.68 (m, $|^3J(\text{HH}) + {}^4J(\text{HH})|$ = 3.5 Hz, 2H, H$_\alpha$), 3.73 (s, 3H, OCH$_3$), 3.01 (s, 3H, CH$_3$), 1.60 (s, 3H, CH$_3$). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 45.17 (s, 2P), −145.00 (sept., ^1J(PF) = 713 Hz, 1P, PF$_6^-$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 306.84 (t, ^2J(PC) = 12.3 Hz, Ru=C), 134.50 (AXX′, 5L, ^2J(PP) = 34.5 Hz, ^1J(PC) = 48.5 Hz, ^3J(PC) = 2.3 Hz, C$_i$), 133.73 (T, $|^2J(\text{PC}) + {}^4J(\text{PC})|$ = 10.9 Hz, C$_o$), 133.39 (AXX′, 5L, ^2J(PP) = 34.5 Hz, ^1J(PC) = 42.7 Hz, ^3J(PC) = 2.0 Hz, C$_\alpha$), 132.80 (T, $|^2J(\text{PC}) + {}^4J(\text{PC})|$ = 9.7 Hz, C$_o$), 132.62 (AXX′, 5L, ^2J(PP) = 34.5 Hz, ^1J(PC) = 46.1 Hz, ^3J(PC) = 2.2 Hz, C$_i$), 130.89 (s, Cp), 130.27 (s, Cp), 128.48 (T, $|^3J(\text{PC}) + {}^5J(\text{PC})|$ = 9.9 Hz, C$_m$), 128.23 (T, $|^3J(\text{PC}) + {}^5J(\text{PC})|$ = 9.7 Hz, C$_m$), 127.72 (s, C$_\beta$), 110.42 (s, C$_q$Cp), 89.95 (s, C$_{\alpha'}$), 89.57 (s, C$_{\beta'}$), 61.26 (s, OCH$_3$), 45.25 (s, CH$_3$), 12.43 (s, CH$_3$). $E_{1/2}$ = 0.89 V *vs.* F$_c$/F$_c^+$.

$[(\eta^5\text{-MeC}_5\text{H}_4)\text{Ru}(\text{DPVP})_2(\text{CO})]\text{PF}_6$ (8). A 50 mL, three-neck round-bottom flask was charged with 0.40 g (0.5 mmol) of $[(\eta^5\text{-MeC}_5\text{H}_4)\text{Ru}(\text{CH}_3\text{CN})(\text{DPVP})_2]\text{PF}_6$ (**4**) and 30 mL of a 1 : 1 CH_2Cl_2–MeOH mixture. The whole was purged with nitrogen for 30 min. Then 0.3 mL (2.7 mmol) of HC≡CPh was added, and the mixture was heated at reflux overnight (change of color was noticed: yellow to orange to red). The solution was placed in a freezer and the formation of a yellow precipitate was observed. This precipitate was collected by filtration and analyzed. It appeared to be starting material (0.017 g). Solvent from the filtrate was evaporated and the residue was recrystallized from CH_2Cl_2–MeOH–ether to give 0.10 g of pure product in 26% yield. Mp: 95–98 °C. Anal. calc. for $\text{C}_{35}\text{H}_{33}\text{F}_6\text{OP}_3\text{Ru}$: C, 54.06; H, 4.28. Found: C, 53.95; H, 4.34%. ^{1}H NMR (CDCl$_3$): δ 7.60 (m, 6H, H$_{o,p}$), 7.38 (m, 6H, H$_{m,p}$), 7.29 (m, 4H, H$_m$), 6.91 (m, 4H, H$_o$), 5.93 (dd, ^3J(H$_a$H$_b$) = 12.3 Hz, ^3J(PH) = 39.5 Hz, 2H, H$_b$), 5.78 (ddd, ^2J(PH) = 29.5 Hz,^3J(H$_a$H$_c$) = 18.0 Hz, ^3J(H$_a$H$_b$) = 12.3 Hz, 2H, H$_a$), 5.16 (apparent t, ^3J(PH) = ^3J(H$_a$H$_c$) = 18.0 Hz, 2H, H$_c$), 5.00 (s, 2H, Cp$_\beta$), 4.86 (s, 2H, Cp$_\alpha$), 2.01 (s, 3H, CH$_3$). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 36.60 (s, 2P, DPVP), −145.00 (sept., ^1J(PF) = 713 Hz, 1P, PF$_6^-$). ^{13}C{^{1}H}

NMR ($\mathrm{CDCl_3}$): δ 201.60 (t, ^2J(PC) = 17.3 Hz, CO), 134.08 (T, $|^2J$(PC) + ^4J(PC)$|$ = 11.7 Hz, C_o), 133.75 (AXX′, ^1J(PC) = 49.4 Hz, ^2J(PP) = 30.7 Hz, ^3J(PC)$|$ = 5.1 Hz, C_i), 132. 04 (s, C_p), 131.91 (T, $|^2J$(PC) + ^4J(PC)$|$ = 10.3 Hz, C_o), 130.96 (s, Cp), 130.77 (s, C_β), 130.60 (D, $|^1J$(PC) + ^3J(PC)$|$ = 45.2 Hz, C_α), 130.09 (AXX′, ^1J(PC) = 49.5 Hz, ^2J(PP) = 30.7 Hz, ^3J(PC) = 5.0 Hz, C_i), 129.26 (T, $|^3J$(PC) + ^5J(PC)$|$ = 10.8 Hz, C_m), 128.76 (T, $|^3J$(PC) + ^5J(PC)$|$ = 10.6 Hz, C_m), 110. 34 (t, J(PC) = 2.0 Hz, $\mathrm{Cp_q}$), 91.36 (s, $\mathrm{Cp_\beta}$), 66.74 (s, $\mathrm{Cp_\alpha}$), 13.19 (s, $\mathrm{CH_3}$). IR (CO region, $\mathrm{CH_2Cl_2}$, $\mathrm{cm^{-1}}$): 1983.

[(η^5-$\mathrm{MeC_5H_4}$)Ru(CO)$_2$]$_2$ (11). A 500 mL, three-neck round-bottom flask was charged with 4.0 g (6.3 mmol) of $\mathrm{Ru_3(CO)_{12}}$ and 280 mL freshly distilled heptane (2,2,4-trimethylpentane may be used as well). This solution was then heated to reflux under a nitrogen atmosphere. When all $\mathrm{Ru_3(CO)_{12}}$ had dissolved, 7.0 mL (0.070 mol) of freshly cracked methylcyclopentadiene ($\mathrm{MeC_5H_5}$) was added *via* syringe, and the whole was heated at reflux for 2 days. The resulting orange–brown solution was stirred magnetically at ambient temperature for another 2 days. Solvent was removed, leaving a brown, oily compound, which was washed with pentane. This compound was dissolved in $\mathrm{CH_2Cl_2}$ and passed through a silica gel column wetted with hexane and eluted with $\mathrm{CH_2Cl_2}$. Recrystallization from $\mathrm{CH_2Cl_2}$–hexane gave 3.11 g of orange crystals in 70% yield. Mp: 135–137 °C. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 5.18 ([AB]$_2$, $|^3J$(HH) + ^4J(HH)$|$ = 4.5 Hz, 4H, $\mathrm{H_\beta}$), 5.01 ([AB]$_2$, $|^3J$(HH) + ^4J(HH)$|$ = 4.5 Hz, 4H, $\mathrm{H_\alpha}$), 2.02 (s, 6H, 2$\mathrm{CH_3}$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$): δ 222.87 (CO), 109.45 (C_i), 89.40 (C_β), 88.57 (C_α), 12.85 ($\mathrm{CH_3}$). IR (CO region, $\mathrm{CH_2Cl_2}$, $\mathrm{cm^{-1}}$): 2044, 1992, 1766, 1964 (sh).

[(η^5-$\mathrm{MeC_5H_4}$)Ru(CO)$_2$(Br)] (12). A solution of 0.7 g (4.4 mmol) of bromine in 30 mL $\mathrm{CH_2Cl_2}$ was added dropwise to a solution of 2.03 g (4.3 mmol) of [(η^5-$\mathrm{MeC_5H_4}$)Ru(CO)$_2$]$_2$ (**11**) in 40 mL $\mathrm{CH_2Cl_2}$ at −20 °C ($\mathrm{CCl_4}$ with dry ice) under a nitrogen atmosphere. The dark red solution was then stirred for 2 hours at ambient temperature. Solvent was removed. The brown residue was dissolved in $\mathrm{CH_2Cl_2}$ and passed through a silica gel column wetted with hexane and eluted with $\mathrm{CH_2Cl_2}$. Recrystallization from $\mathrm{CH_2Cl_2}$–hexane gave 1.52 g of pure product in 56% yield. Mp: 48–53 °C. Anal. calc. for $\mathrm{C_8H_7BrO_2Ru}$: C, 30.40; H, 2.23; Br, 25.28. Found: C, 30.24; H, 2.19; Br, 25.31%. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 5.11 ([AB]$_2$, $|^3J$(HH) + ^4J(HH)$|$ = 4.0 Hz, 2H, $\mathrm{H_\beta}$), 5.09 ([AB]$_2$, $|^3J$(HH) + ^4J(HH)$|$ = 4.0 Hz, 2H, $\mathrm{H_\alpha}$), 1.99 (s, 3H, $\mathrm{CH_3}$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$): δ 195.75 (CO), 115.48 (s, C_i), 83.93 (s, C_β), 83.85 (s, C_α), 13.39 (s, $\mathrm{CH_3}$). IR (CO region, $\mathrm{CH_2Cl_2}$, $\mathrm{cm^{-1}}$): 2049, 1997.

[(η^5-$\mathrm{MeC_5H_4}$)Ru(CO)$_2$(I)] (13). A solution of 0.8 g (3.1 mmol) of iodine in 30 mL $\mathrm{CH_2Cl_2}$ was added dropwise to a solution of 1.48 g (3.1 mmol) of [(η^5-$\mathrm{MeC_5H_4}$)Ru(CO)$_2$]$_2$ (**11**) in 35 mL $\mathrm{CH_2Cl_2}$ at −20 °C ($\mathrm{CCl_4}$ with dry ice) under a nitrogen atmosphere. The dark purple solution was then stirred for 2 hours at ambient temperature. Solvent was removed. The brown residue was dissolved in $\mathrm{CH_2Cl_2}$ and passed through a silica gel column wetted with hexane and eluted with $\mathrm{CH_2Cl_2}$. The first fraction (purple) contained iodine, and the second (orange) the product. Recrystallization from ether–hexane gave 1.97 g of pure product in 86% yield. Mp: 43–45 °C. Anal. calc. for $\mathrm{C_8H_7IO_2Ru}$: C, 26.46; H, 1.94; I, 34.95. Found: C, 26.22; H, 1.69; I, 35.02%. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 5.28 ([AB]$_2$, $|^3J$(HH) + ^4J(HH)$|$ = 4.0 Hz, 2H, $\mathrm{H_\beta}$), 5.19 ([AB]$_2$, $|^3J$(HH) + ^4J(HH)$|$ = 4.0 Hz, 2H, $\mathrm{H_\alpha}$), 2.24 (s, 3H, $\mathrm{CH_3}$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$): δ 195.61 (CO), 111.47 ($\mathrm{C_i}$), 85.32 (C_β), 85.01 (C_α), 14.54 ($\mathrm{CH_3}$). IR (CO region, $\mathrm{CH_2Cl_2}$, $\mathrm{cm^{-1}}$): 2044, 1994.

[(η^5-$\mathrm{MeC_5H_4}$)Ru(CO)(DPVP)(Br)] (14). A 100 mL, three-neck round-bottom flask was charged with 1.4 g (4.4 mmol) of [(η^5-$\mathrm{MeC_5H_4}$)Ru(CO)$_2$(Br)] (**12**), 20 mL of benzene and 0.9 mL (4.5 mmol) of DPVP ($\mathrm{Ph_2PCH{=}CH_2}$). This solution was then brought to reflux under a nitrogen atmosphere. A tenth-molar amount of the catalyst (17 mg) [(η^5-$\mathrm{C_5H_5}$)Fe(CO)$_2$]$_2$, was added to the refluxing mixture. The reaction progress was monitored by IR spectroscopy in the CO region. After 3 hours at reflux the reaction was complete (band at 2057 $\mathrm{cm^{-1}}$ disappeared). Solvent was removed leaving a brown, oily compound. This compound was dissolved in $\mathrm{CH_2Cl_2}$ and passed through a silica gel column packed with hexane and eluted with $\mathrm{CH_2Cl_2}$. Recrystallization from $\mathrm{CH_2Cl_2}$–hexane gave 1.17 g of pure product in 53% yield. Mp: 130–131 °C. Anal. calc. for $\mathrm{C_{21}H_{20}BrOPRu}$: C, 50.41; H, 4.03; Br, 15.97. Found: C, 50.26; H, 3.95; Br, 15.62%. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 7.06 (m, 4H, H_m), 6.89 (m, 6H, $\mathrm{H}_{o,p}$), 6.26 (apparent td, ^2J(PH) = $^3J(\mathrm{H_aH_c})$ = 19.3 Hz, $^3J(\mathrm{H_aH_b})$ = 11.8 Hz, 1H, $\mathrm{H_a}$), 5.50 (dd, ^3J(PH) = 39.5 Hz, $^2J(\mathrm{H_aH_b})$ = 11.8 Hz, 1H, $\mathrm{H_b}$), 5.01 (apparent t, ^3J(PH) = $^3J(\mathrm{H_aH_c})$ = 19.3 Hz, 1H, $\mathrm{H_c}$), 4.26 (s, 1H, Cp), 4.12 (s, 1H, Cp), 4.06 (s, 1H, Cp), 3.90 (s, 1H, Cp), 1.43 (s, 3H, $\mathrm{CH_3}$). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$): δ 42.14 (s). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$): δ 202.80 (d, ^2J(PC) = 20.5 Hz, CO), 134.64 (d, ^1J(PC) = 29.9 Hz, C_i), 134.61 (d, ^1J(PC) = 45.5 Hz, C_α), 134.25 (d, ^1J(PC) = 31.0 Hz, C_i), 133.22 (d, ^2J(PC) = 10.8 Hz, C_o), 132.70 (d, ^2J(PC) = 10.6 Hz, C_o), 130.50 (s, C_β), 130.25 (d, ^4J(PC) = 2.4 Hz, C_p), 130.04 (d, ^4J(PC) = 2.4 Hz, C_p), 128.20 (d, ^3J(PC) = 8.8 Hz, C_m), 128.11 (d, ^3J(PC) = 8.8 Hz, C_m), 110.10 (d, J(PC) = 2.0 Hz, $\mathrm{C}_{i'}$), 86.29 (d, J(PC) = 1.5 Hz, Cp), 84.10 (s, Cp), 80.97 (d, J(PC) = 5.7 Hz, Cp), 79.65 (s, Cp), 13.31 (s, $\mathrm{CH_3}$). IR (CO region, $\mathrm{CH_2Cl_2}$, $\mathrm{cm^{-1}}$): 1955. $E_{1/2}$ = 0.53 V *vs.* $\mathrm{F_c/F_c^+}$.

[(η^5-$\mathrm{MeC_5H_4}$)Ru(DPVP)($\mathrm{CH_3CN}$)(CO)]$\mathrm{PF_6}$ (15). A 250 mL, three-neck round-bottom flask was charged with 2.05 g (4.1 mmol) of [(η^5-$\mathrm{MeC_5H_4}$)Ru(CO)(DPVP)(Br)] (**14**), and 100 mL freshly distilled acetonitrile. The whole was stirred under a nitrogen atmosphere for 30 min. The flask was wrapped with aluminium foil and then 1.14 g (4.5 mmol) of $\mathrm{AgPF_6}$ was added. The solution was heated at reflux overnight. AgBr was separated by filtration through Celite and the solvent was evaporated. The green–brown residue was dissolved in $\mathrm{CH_2Cl_2}$ and passed through a silica gel column packed with hexane and eluted with $\mathrm{CH_2Cl_2}$. Solvent was removed *in vacuo* leaving 1.06 g (43% yield) of waxy product. Anal. calc. for $\mathrm{C_{23}H_{23}NOF_6P_2Ru}$: C, 45.55; H, 3.82. Found: C, 45.49; H, 3.84%. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 7.45 (m, 6H, $\mathrm{H}_{m,p}$), 7.33 (m, 4H, H_o), 6.78 (ddd, ^2J(PH) = 30.0 Hz, $^3J(\mathrm{H_aH_c})$ = 18.0 Hz, $^3J(\mathrm{H_aH_b})$ = 12.0 Hz, 1H, $\mathrm{H_a}$), 6.15 (dd, ^3J(PH) = 41.5 Hz, $^3J(\mathrm{H_aH_b})$ = 12.0 Hz, 1H, $\mathrm{H_b}$), 5.40 (dd, ^3J(PH) = 20.5 Hz, $^3J(\mathrm{H_aH_c})$ = 18.0 Hz, 1H, $\mathrm{H_c}$), 4.96 (s, 1H, Cp), 4.94 (s, 1H, Cp), 4.80 (s, 2H, Cp), 2.09 (s, 3H, $\mathrm{CH_3CN}$), 1.87 (s, 3H, $\mathrm{CpCH_3}$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$): δ 200.02 (d, ^2J(PC) = 18.2 Hz, CO), 132.81 (d, ^2J(PC) = 11.3 Hz, C_o), 132.14 (d, ^2J(PC) = 10.6 Hz, C_o), 132.03 (d, ^1J(PC) = 46.0 Hz, C_α), 131.9 (s, C_β), 131.49 (d, ^1J(PC) = 52.4 Hz, C_i), 131.15 (d, ^4J(PC) = 2.4 Hz, C_p), 130.95 (d, ^4J(PC) = 2.5 Hz, C_p), 130.81 (d, ^1J(PC) = 52.0 Hz, C_i), 128.88 (d, ^3J(PC) = 10.4 Hz, C_m), 128.85 (d, ^3J(PC) = 10.6 Hz, C_m), 127.98 (s, $\mathrm{CH_3CN}$), 111.84 (d, J(PC) = 2.5 Hz, $\mathrm{Cp_q}$), 86.61 (s, Cp), 85.12 (s, Cp), 81.10 (s, Cp), 80.51 (d, J(PC) = 4.0 Hz, Cp), 12.48 (s, $\mathrm{CpCH_3}$), 3.16 (s, $\mathrm{CH_3CN}$). IR (CO region, $\mathrm{CH_2Cl_2}$, $\mathrm{cm^{-1}}$): 1988, IR (CN region, $\mathrm{CH_2Cl_2}$, $\mathrm{cm^{-1}}$): 2306.

X-Ray crystallographic studies

Single crystals of **4**, **5**, **7**, **8**·$\mathrm{CH_2Cl_2}$, **11**, **12**, **13**, and **14** were obtained as follows: slow diffusion of hexane into a $\mathrm{CH_2Cl_2}$ solution (**4**, **11**, **12**, and **14**), slow diffusion of ether into a $\mathrm{CH_2Cl_2}$ solution (**7** and **8**), slow diffusion of ether into a $\mathrm{CHCl_3}$ solution (**5**), and slow diffusion of hexane into an ether solution (**13**). The crystals were mounted on glass fibers, coated with epoxy, and placed on a Siemens P4 diffractometer. Intensity data were taken in the ω mode with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). Three check reflections, monitored every 100 reflections, showed random (<2%)

Table 2 Crystallographic data

	4	**5**	**7**	**8**·CH_2Cl_2	**11**	**12**	**13**	**14**
Empirical formula	$C_{36}H_{36}F_6NP_3Ru$	$C_{48}H_{47}F_6P_4Ru$	$C_{37}H_{39}F_6OP_3Ru$	$C_{36}H_{35}Cl_2F_6OP_3Ru$	$C_8H_7O_2Ru$	$C_8H_7BrO_2Ru$	$C_8H_7IO_2Ru$	$C_{21}H_{17}BrOPRu$
FW	790.64	962.81	807.66	862.52	236.21	316.12	363.11	497.30
Crystal system	Monoclinic	Monoclinic	Tetragonal	Triclinic	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P4_12_12$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a/Å	13.5787(10)	15.716(4)	13.6771(19)	9.464(20)	8.0001(12)	6.959(5)	7.0680(17)	9.665(2)
b/Å	13.166(4)	13.605(2)	13.6771(19)	10.951(4)	11.9948(14)	7.662(3)	7.538(2)	14.513(4)
c/Å	20.392(2)	20.704(5)	39.271(8)	18.964(7)	8.2434(14)	9.871(4)	10.2386(14)	14.740(3)
a/°	90	90	90	90.68(4)	90	91.84(3)	92.931(18)	90
β/°	97.630(8)	97.081(19)	90	103.09(3)	100.329(16)	93.86(5)	96.106(13)	104.747(18)
γ/°	90	90	90	101.30(3)	90	112.85(4)	109.316(19)	90
V/Å^3	3613.4(12)	4392.9(17)	7346(2)	1874.1(11)	778.2(2)	483.0(5)	509.7(2)	1999.4(8)
Z	4	4	8	2	4	2	2	4
d_c/g cm^{-3}	1.453	1.456	1.461	1.528	2.016	2.174	2.366	1.652
μ/mm^{-1}	0.624	0.562	0.617	0.747	1.954	5.715	4.525	2.868
$R1(F)$/ $wR2(F^2)$ [a]	0.0562/ 0.1262	0.0859/ 0.1913	0.0598/ 0.1089	0.1040/ 0.2298	0.0308/ 0.0782	0.0446/ 0.1085	0.0845/ 0.2023	0.0605/ 0.1504

[a] Final R indices have $I > 2\sigma(I)$. $R1(F) = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; $wR2(F^2) = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma w(|F_o^2|)^2]^{½}$.

variation during the data collections. The data were corrected for Lorentz, polarization effects, and absorption (using an empirical model derived from azimuthal data collections). Crystals of **8** were of poor quality and did not diffract well. For **14** the vinyl group is disordered over two sites. Scattering factors and corrections for anomalous dispersion were taken from a standard source.[25] Calculations were performed within the Siemens SHELXTL Plus (version 5.10) software package on a PC. The structures were solved by direct methods (**4**, **8**, and **11**) or Patterson methods (**5**, **7**, **12**, **13**, and **14**). 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. The data were refined by the method of full matrix least-squares on F^2. Final cycles of refinement converged to the $R1$(F) and $wR2(F^2)$ values given in Table 2, where $w^{-1} = \sigma^2(F) + 0.001F^2$.

CCDC reference numbers 195526–195533.

See http://www.rsc.org/suppdata/dt/b2/b210492j/ for crystallographic data in CIF or other electronic format.

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