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Phosphaallyl complexes of Ru(II) derived from dicyclohexylvinylphosphine (DCVP)

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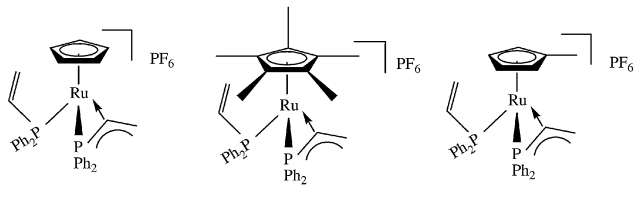
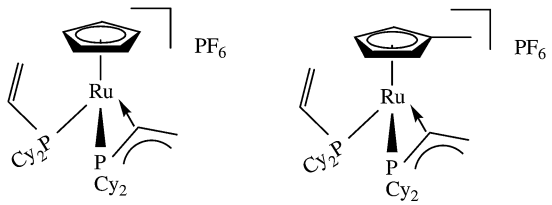
The complexes $[(\eta^5\text{-}RC_5H_4)Ru(CH_3CN)_3]PF_6$ (R = H, CH_3) react with DCVP (DCVP = $Cy_2PCH{=}CH_2$) at room temperature to produce the phosphaallyl complexes $[(\eta^5\text{-}C_5H_5)Ru(\eta^1\text{-DCVP})(\eta^3\text{-DCVP})]PF_6$ (**1**) and $[(\eta^5\text{-}MeC_5H_4)Ru(\eta^1\text{-DCVP})(\eta^3\text{-DCVP})]PF_6$ (**2**). Both compounds react with a variety of two-electron donor ligands displacing the coordinated vinyl moiety. In contrast, we failed to prepare the phosphaallyl complexes $[(\eta^5\text{-}C_5Me_5)Ru(\eta^1\text{-DCVP})(\eta^3\text{-DCVP})]PF_6$, $[(\eta^5\text{-}MeC_5H_4)Ru(CO)(\eta^3\text{-DCVP})]PF_6$ and $[(\eta^5\text{-}C_5Me_5)Ru(CO)(\eta^3\text{-DPVP})]PF_6$ (DPVP = $Ph_2PCH{=}CH_2$).The compounds $[(\eta^5\text{-}MeC_5H_4)Ru(CO)(CH_3CN)(DPVP)]PF_6$ and $[(\eta^5\text{-}C_5Me_5)Ru(CO)(CH_3CN)(DPVP)]PF_6$ (**12**) react with DMPP (3,4-dimethyl-1-phenylphosphole) to undergo [4 + 2] Diels–Alder cycloaddition reactions at elevated temperature. Attempts at ruthenium catalyzed hydration of phenylacetylene produced neither acetophenone nor phenylacetaldehyde but rather dimers and trimers of phenylacetylene. The structures of the complexes described herein have been deduced from elemental analyses, infrared spectroscopy, ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$ NMR spectroscopy and in several cases by X-ray crystallography.

Introduction

Hemilabile ligands contain at least two different types of chemical functionalities bound to metal centers.[1] One of these functionalities is substitutionally labile and "opens" during reactions, and the other group remains firmly bound to the metal. The presence of such ligands may enhance selectivity, influence reactivity, stabilize reactive intermediates and promote transformations that would not otherwise occur.[1,2] Complexes of hemilabile ligands are of current interest because of their potential applications in molecular activation, homogeneous catalysis, functional materials, and small molecular sensing. We have previously reported the synthesis and characterization of the only examples of ruthenium(II) complexes having diphenylvinylphosphine (DPVP) bound to the metal as a neutral, four-electron hemilabile phosphaallyl ligand; $[(\eta^5\text{-}C_5H_5)Ru(\eta^1\text{-DPVP})(\eta^3\text{-DPVP})]PF_6$ (**A**),[3] $[(\eta^5\text{-}C_5Me_5)Ru(\eta^1\text{-DPVP})(\eta^3\text{-DPVP})]PF_6$ (**B**)[4] and $[(\eta^5\text{-}MeC_5H_4)Ru(\eta^1\text{-DPVP})\text{-}(\eta^3\text{-DPVP})]PF_6$ (**C**)[5] (Scheme 1). We were interested in discerning whether similar phosphaallyl complexes with other olefinic phosphines such as dicyclohexylvinylphosphine (DCVP) could be prepared and if so in ascertaining their comparative stabilities. Accordingly, we prepared DCVP analogs of **A** and **C** namely; $[(\eta^5\text{-}C_5H_5)Ru(\eta^1\text{-DCVP})(\eta^3\text{-DCVP})]PF_6$ (**1**) and $[(\eta^5\text{-}MeC_5H_4)\text{-}Ru(\eta^1\text{-DCVP})(\eta^3\text{-DCVP})]PF_6$ (**2**) (Scheme 2), and probed their hemilabile character. As expected, the metal-bound vinyl group may be displaced by a variety of two-electron donor ligands such as CO, PhNC, HC≡CPh and HC≡CSiMe$_3$. Attempted preparation of a DCVP analog of **B** failed. Instead, the unexpected product **9** $[(C_6H_{11})_2P(\mu\text{-}CH_2CH_2)_2P(C_6H_{11})_2]PF_6$ was isolated and fully characterized. We failed also in attempts to prepare the carbonyl phosphaallyl complexes $[(\eta^5\text{-}MeC_5H_4)Ru(CO)(\eta^3\text{-DCVP})]PF_6$ and $[(\eta^5\text{-}C_5Me_5)Ru(CO)(\eta^3\text{-DPVP})]PF_6$. The complexes $[(\eta^5\text{-}MeC_5H_4)Ru(CO)(CH_3CN)(DPVP)]PF_6$[5] and $[(\eta^5\text{-}C_5Me_5)Ru(CO)(CH_3CN)(DPVP)]PF_6$ (**12**) react with DMPP (3,4-dimethyl-1-phenylphosphole) to undergo [4 + 2] Diels–Alder cycloadditions. Five new ruthenium compounds were tested as catalysts for the hydration of phenylacetylene but neither ketone nor aldehyde was obtained.



Scheme 1 Phosphaallyl complexes containing DPVP.



Scheme 2 New phosphaallyl complexes containing DCVP.

Results and discussion

Synthesis and characterization of phosphaallyl complexes

$[(\eta^5\text{-}C_5H_5)Ru(\eta^1\text{-DCVP})(\eta^3\text{-DCVP})]PF_6$ (**1**) and $[(\eta^5\text{-}MeC_5H_4)\text{-}Ru(\eta^1\text{-DCVP})(\eta^3\text{-DCVP})]PF_6$ (**2**) were prepared similarly to their DPVP analogs. The preparation of both **A** and **C** entailed removing coordinated CH_3CN from their precursors $[(\eta^5\text{-}RC_5H_4)Ru(CH_3CN)_3]PF_6$ (R = H, CH_3) by thermolysis under vacuum for several days at elevated temperature.[3,5] On the other hand, the syntheses of **1** and **2** did not require this step. Both phosphaallyl compounds were formed easily by simple addition of DCVP to $[(\eta^5\text{-}RC_5H_4)Ru(CH_3CN)_3]PF_6$ (R = H, CH_3), as shown in Scheme 3, and by stirring overnight at room temperature. This relative ease of formation may be attributed, in part, to the higher electron-donating ability of the bulky DCVP as compared to DPVP. Compounds **1** and **2** were characterized by elemental analyses, cyclic voltammetry, ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$ NMR spectroscopy, IR spectroscopy and X-ray crystallography. The $^{31}P\{^1H\}$ NMR spectra of **1** and **2** show two doublets corresponding to the two inequivalent phosphine groups at 41.80 ppm (η^1-DCVP) and 26.10 ppm (η^3-DCVP) with $^2J(PP) = 37.3$ Hz for **1**, and 38.49 ppm (η^1-DCVP) and 23.86 ppm (η^3-DCVP) with $^2J(PP) = 37.5$ Hz for **2**. The $^{31}P\{^1H\}$ spectrum of **2** also shows two additional doublet resonances at 38.56 and 23.28 ppm with $^2J(PP) = 37.6$ Hz. Those signals are attributed

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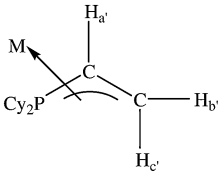
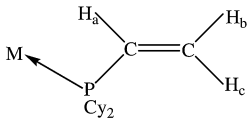
Table 1 Selected ^{1}H NMR data of **1** and **2** for the η^3- and the η^1-DCVP ligands



η^3-DCVP



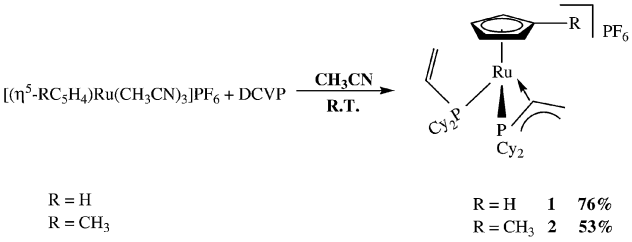
η^1-DCVP

		η^3-DCVP				η^1-DCVP		
		$H_{a'}$	$H_{b'}$	$H_{c'}$		H_a	H_b	H_c
1[a]	δ	3.91	3.30	1.57		5.81	5.64	5.97
	Multiplicity	apptdd	ddd	dddd		ddd	dd	dd
	^3J(PH)	10.8[c]	33.5	13.5	^3J(PH)	20.5[c]	13.5	30.0
	^3J(PH)	1.5[d]		8.5[e]				
	^3J(a′b′)[f]	8.8	8.8		^3J(ab)	18.5	18.5	
	^3J(a′c′)	10.8		10.8	^3J(ac)	13.0		13.0
	^2J(b′c′)		1.5	1.5	^2J(bc)			
2[b]	δ	3.20	2.84	2.2–1.0		5.81	5.98	5.67
	Multiplicity	appdtd	ddd	m		ddd	dd	dd
	^3J(PH)	9.0[c]	33.0		^3J(PH)	21.0[c]	30.0	13.5
	^3J(PH)	2.0[d]						
	^3J(a′b′)	9.0	9.0		^3J(ab)	13.0	13.0	
	^3J(a′c′)	10.5			^3J(ac)	18.8		18.8
	^2J(b′c′)		2.0		^2J(bc)			

[a] NMR spectra measured in $CDCl_3$, chemical shifts in ppm downfield from Me_4Si, coupling constants in Hz. [b] NMR spectra measured in CD_2Cl_2. [c] ^2J(PH). [d] ^4J(PH). [e] ^5J(PH). [f] 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.

to the presence of the *endo* isomer of **2**. The relative ratio of the *exo* and *endo* isomers was estimated as 7 : 1. The ^{1}H NMR spectrum of **1** shows three multiplets corresponding to the η^1-DCVP hydrogens at 5.97, 5.81 and 5.64 ppm for H_c, H_a and H_b protons, respectively. The η^3-DCVP phosphallyl hydrogens resonate at 3.91, 3.30 and 1.57 ppm for $H_{a'}$, $H_{b'}$, and $H_{c'}$, and appear as complex muliplets. Similarly, the ^{1}H NMR spectrum of **2** shows three multiplets at 5.98, 5.81 and 5.67 ppm for H_b, H_a, and H_c, respectively. The phosphaallyl hydrogens resonate at 3.20, 2.84 and 2.2–1.0 for $H_{a'}$, $H_{b'}$ and $H_{c'}$. Table 1 summarizes selected ^{1}H NMR data for **1** and **2** (major isomer). For **1** and the major isomer of **2** the η^3-DCVP ligand is bound in the *exo* orientation both in solution and in the solid state, as confirmed by 1D-NOE spectroscopy and X-ray crystallography. Views of the geometries of the cations of **1** and **2** are shown in Figs. 1 and 2, respectively. The analyses reveal that both compounds have a distorted octahedral geometry about ruthenium, the η^5-RC_5H_4 (R = H, CH_3) moiety occupies three coordination sites, with one η^1-DCVP and one η^3-DCVP completing the coordination sphere. The greater steric bulk of DCVP as compared to DPVP influences the bond distances and the bond angles. The C(14)–P(1)–P(8) angle (see Fig. 1) should be larger for **1** than for **A**, and the P(1)–C(6)–C(7) angle smaller for **1**. This trend is observed, the C(14)–P(1)–C(8) angle for **1** has a value of 113.23(22)° compared to 107.5(2)° for **A**.[3] The P(1)–C(6)–C(7) angle for **1** (117.33(17)°) is smaller than that for **A** (119.1(3)°).[3] Changes in bond distances should also be observed. The Ru(1)–P(1), Ru(1)–C(6) and Ru(1)–C(7) bond distances for **1** are expected to be shorter than those for **A**. But this trend is not observed here. The Ru(1)–P(1) and Ru(1)–C(7) bond distances for **1** are longer than analogous bonds for **A**, 2.2977(7) Å and 2.253(2) Å for **1** *vs.* 2.276(1) Å and 2.244(4) Å for **A**. The Ru(1)–C(6) bond distance is almost identical for both compounds, 2.171(2) Å for **1** and 2.176(3) Å for **A**. Unfortunately, we cannot compare these values for compounds **2** and **C** because the X-ray structure of **C** has not been reported.[5]

Compound **1** undergoes quasireversible one-electron oxidation with an $E_{1/2}$ value of 0.395 V.



Scheme 3

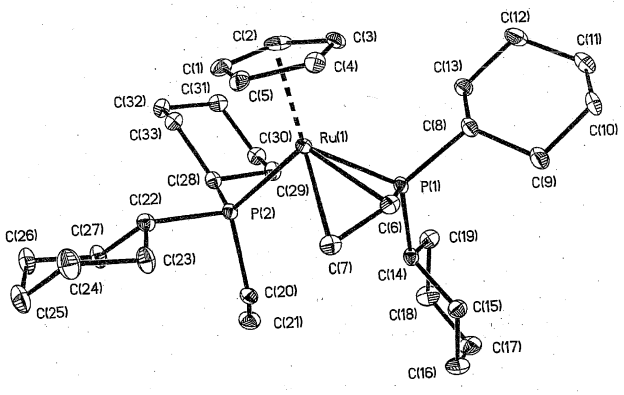


Fig. 1 Structural drawing of the cation of **1** showing the atom numbering scheme (40% probability ellipsoids). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ru(1)–P(1), 2.2977(7); Ru(1)–P(2), 2.3450(6); P(1)–C(6), 1.772(3); P(2)–C(20), 1.829(2); Ru(1)–C(average), 2.228(3); P(1)–Ru(1)–P(2), 99.58(2); P(1)–Ru(1)–C(6), 46.61(7); P(2)–C(20)–C(21), 128.5(2).

The addition of CD_3CN to compound **1** produces an equilibrium mixture of **1** and $[(\eta^5\text{-}C_5H_5)Ru(DCVP)_2(CD_3CN)]PF_6$ (Scheme 4). This equilibrium is evidenced by the two doublet $^{31}P\{^1H\}$ resonances for **1** diminishing in intensity as a singlet resonance for $[(\eta^5\text{-}C_5H_5)Ru\,(DCVP)_2(CD_3CN)]PF_6$ slowly appears.

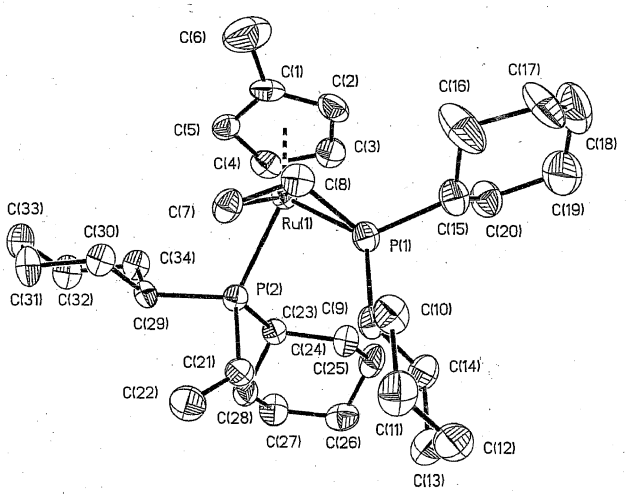


Fig. 2 Structural drawing of the cation of **2** showing the atom numbering scheme (40% probability ellipsoids). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ru(1)–P(1), 2.316(2); Ru(1)–P(2), 2.359(2); P(1)–C(8), 1.785(8); P(2)–C(21), 1.825(7); Ru(1)–C(average), 2.220(8); P(1)–Ru(1)–P(2), 99.41(7); P(1)–Ru(1)–C(8), 46.8(2); P(2)–C(21)–C(22), 128.4(7).

$$[(\eta^5\text{-}C_5H_5)Ru(\eta^1\text{-DCVP})(\eta^3\text{-DCVP})]PF_6 + CD_3CN \;\underset{}{\overset{K_{eq}}{\rightleftharpoons}}\; [(\eta^5\text{-}C_5H_5)Ru(DCVP)_2(CD_3CN)]PF_6$$

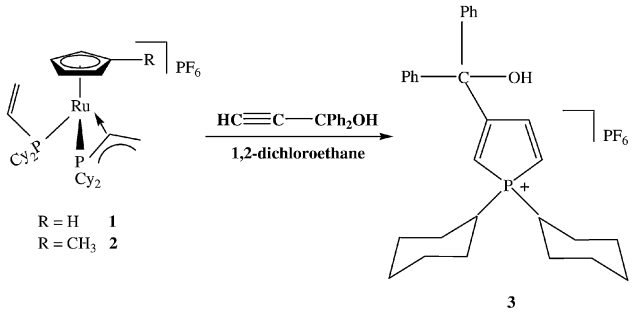
Scheme 4

The equilibrium constants in CD_3CN were evaluated as a function of temperature by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy and were determined to be 4.3×10^{-2} and 2.9×10^{-2} at 273 K and 303 K, respectively. Similarly the equilibrium constant for the addition of CH_3CN to **A** in $CDCl_3$ was found to be 4.8×10^2 at 303 K.[3] Thus, even in CD_3CN solution this equilibrium for **1** lies mostly on the left side. On the other hand, the equilibrium constant for the addition of CD_3CN to complex **2** was too small to measure by NMR spectroscopy. Thus, acetronitrile dissociates from **1** and **2** much more readily than from **A**.

Reactions of phosphaallyl complexes

One of the reasons for preparing compounds **1** and **2** was to use them as precursors to vinylidene[6] and allenylidene[6] complexes that might be catalysts for the addition of nucleophiles to terminal alkynes.[7] The reactions of propargyl alcohols $HC{\equiv}CC(OH)R_2$ with ruthenium complexes represent simple and convenient routes for the preparation of vinylidene and allenylidene complexes.[6] For example, treatment of complex **B** with propargyl alcohol ($HC{\equiv}CCH_2(OH)$) in chloroform resulted in the formation of the vinylidene species $[(\eta^5\text{-}C_5Me_5)Ru(DPVP)_2\{C{=}C(H)(CH_2OH)\}]PF_6$.[4] Refluxing a solution of this vinylidene compound in methanol over a period of several days resulted in the unexpected precipitation of the rose-colored solid $[(\eta^5\text{-}C_5Me_5)Ru(DPVP)_2\{C{=}\overline{C(CH_2)_2PPh_2CH_2}\}][PF_6]_2$.

This compound containes a heterocyclic, disubstituted vinylidene (C=CR~R′), where R~R′ is a P,P-diphenyltrihydrophospholonium ring. Formation of this unexpected product most probably resulted from the nucleophilic attack of DPVP on the C_γ carbon of an allenylidene intermediate. On the other hand, the reaction of **B** with 1,1-diphenylpropargyl alcohol ($HC{\equiv}CC(OH)Ph_2$) gave the diphenylallenylidene complex $[(\eta^5\text{-}C_5Me_5)(DPVP)_2Ru{=}C{=}C{=}CPh_2]PF_6$ *via* spontaneous dehydration of an intermediate vinylidene[6] complex with no competing reaction of DPVP with the allenylidene ligand.[8] The formation of this compound was confirmed by NMR spectroscopy of the product mixture (near complete conversion was achieved). But when we reacted compounds **1** and **2** with 1,1-diphenylpropargyl alcohol neither an allenylidene nor a vinylidene complex was obtained. The resulting purple reaction mixture was recrystallized from CH_2Cl_2/hexane and colorless crystals of phosphonium salt **3** were isolated (Scheme 5). Compound **3** was fully characterized by elemental analysis, ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy, and X-ray crystallography. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet resonance at 64.1 ppm for the cationic phosphorus and a septet resonance at −145.00 ppm for the PF_6^- group. Fig. 3 shows the geometry of cation **3**. Compound **3** was most likely formed by nucleophilic attack of DCVP on C_α of a vinylidene intermediate. $^{31}P\{^1H\}$ NMR spectroscopy of the crude reaction mixtures showed that the major phosphorus containing species is **3**. ^1H NMR spectroscpopy of the crude reaction mixtures showed that essentially all of the compounds **1** and **2** disappeared. Following separation of **3**, a brown gummy residue that defied purification and identification remained. The identity of the final ruthenium product/s of these reactions is unknown.



Scheme 5

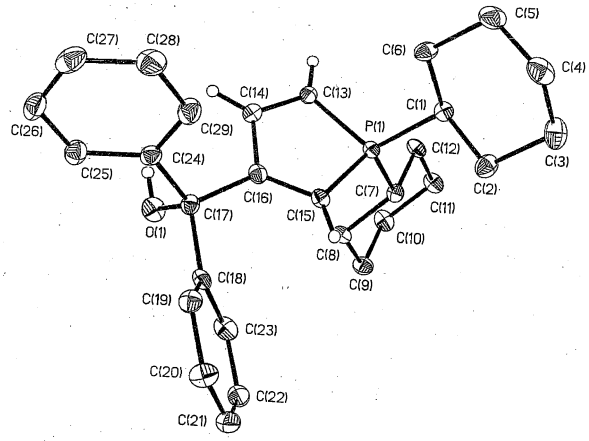
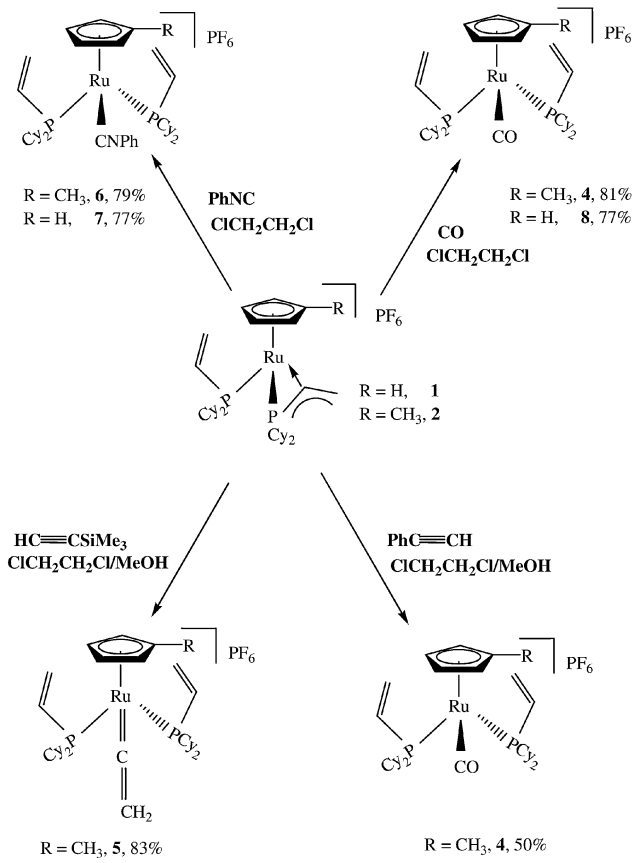


Fig. 3 Structural drawing of the cation of **3** showing the atom numbering scheme (50% probability ellipsoids). Included hydrogen atoms have an arbitrary radius of 0.1 Å. Selected bond lengths (Å) and angles (°): P(1)–C(1), 1.807(3); P(1)–C(7), 1.811(3); C(17)–O(1), 1.442(4); C(1)–P(1)–C(7), 110.26(14); C(24)–C(17)–O(1), 110.6(2).

Compound **2** reacts with $PhC{\equiv}CH$, $HC{\equiv}CSiMe_3$, CO and PhNC (Scheme 6) at the metal center displacing the coordinated vinyl moiety. This is evidenced by the disappearance of the two doublet resonances and appearance of a singlet resonance in the $^{31}P\{^1H\}$ spectra of the reaction mixtures. Compounds **4** were characterized by elemental analyses, ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$ NMR spectroscopy and IR spectroscopy. The product of the reaction of **2** with $PhC{\equiv}CH$ and adventitious water, the carbonyl



Scheme 6

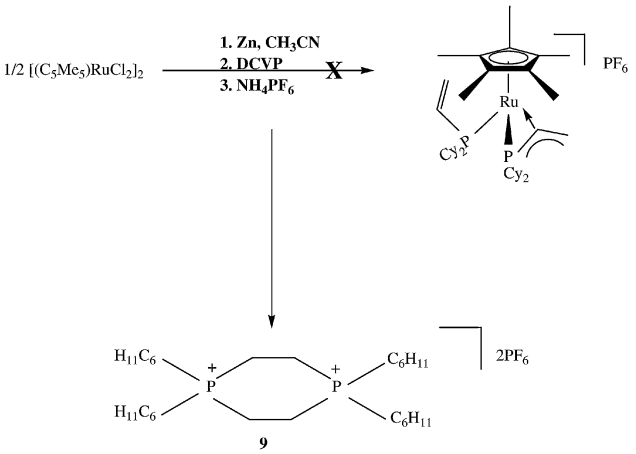
complex **4**, most probably resulted from nucleophilic attack of H_2O on a vinylidene intermediate according to a previously described mechanism.[9] In this reaction PhC≡CH dimers were also isolated and identified by GC/MS. Compound **4** was also obtained when a 1,2-dichloroethane solution of **2** was bubbled with CO for 5 days. Complex **4** exhibits ν_{CO} at 1966 cm^{-1} compared to ν_{CO} for its DPVP analog at 1983 cm^{-1}.[5] The low magnitude of ν_{CO} for **4** is a manifestation of the greater donor ability of DCVP compared to DPVP. The $^{31}P\{^1H\}$ NMR resonances for **4** and its DPVP analog occur at 37.75 and 36.60[5] ppm, respectively. The carbonyl carbon resonance in the $^{13}C\{^1H\}$ NMR spectra of both compounds is a triplet at 205.15 and 201.60[5] ppm with $^2J(PC) = 17.1$ Hz, and 17.3[5] Hz, respectively.

Reaction of **2** with $HC{\equiv}CSiMe_3$ in $ClCH_2CH_2Cl$–CH_3OH solution gave the reddish-brown vinylidene complex **5**. The formation of **5** was deduced from NMR and IR spectroscopy. The $^{13}C\{^1H\}$ NMR spectrum shows the characteristic $Ru{=}C_\alpha$ carbon resonance at 321.59 ppm, while the $^{31}P\{^1H\}$ NMR spectrum shows a singlet resonance at 40.68 ppm corresponding to two equivalent DCVP groups. The ^1H NMR spectrum shows the vinylidene hydrogens resonance as a singlet at 3.84 ppm. In the IR spectrum a strong band at 1621 cm^{-1} appears, a region typical for carbon–carbon double bonds.

Complex **2** reacts with PhNC in $ClCH_2CH_2Cl$ solution to afford compound **6**. The structure of **6** was deduced from NMR and IR data. The $^{13}C\{^1H\}$ NMR spectrum shows a triplet resonance at 164.37 ppm for the N≡C group with $^2J(PC) = 20.6$ Hz. The $^{31}P\{^1H\}$ NMR spectrum shows two singlet resonances at 39.56 and 39.27 ppm which indicates a lack of symmetry in the molecule caused by hindered rotation about the Ru–C bond. In the IR spectrum a strong band at 2091 cm^{-1} appears for the N≡C group.

Compound **1** reacts with PhNC and CO to afford **7** and **8**, respectively (Scheme 6). Both complexes were fully characterized by elemental analyses, ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$ NMR spectroscopy and IR spectroscopy. Their structures were deduced from NMR and IR spectroscopies. For **7** the $^{13}C\{^1H\}$ NMR spectrum shows a triplet resonance for the N≡C group at 164.41 ppm with $^2J(PC) = 20.2$ Hz while the $^{31}P\{^1H\}$ NMR spectrum shows a singlet resonance at 39.70 ppm indicative of two equivalent DCVP groups. The absence of the CH_3 group on the C_5H_5 ring in this compound allows free rotation about the Ru–C bond. In the IR spectrum a strong band at 2096 cm^{-1} appears for the N≡C group. The $^{13}C\{^1H\}$ NMR spectrum of the DPVP analog of **7** also shows a triplet resonance for the N≡C group at 161.17 ppm with $^2J(PC) = 21.01$ Hz while the $^{31}P\{^1H\}$ spectrum shows a singlet resonance at 40.55 ppm.[3] For the DPVP analog of **7** a strong N≡C band was reported at 2130 cm^{-1}.[3] Complex **8** exhibits a strong carbonyl band, ν_{CO}, at 1962 cm^{-1} while for its DPVP analog this band occurs at 1982 cm^{-1}.[3] The carbonyl carbon resonances for **8** and its DPVP analog in their $^{13}C\{^1H\}$ spectra are triplets at 203.67 ppm with $^2J(PC) = 17.6$ Hz, and 202.68[3] Hz with $^2J(PC) = 17.3$[3] Hz, respectively. The $^{31}P\{^1H\}$ spectra of **8** and its DPVP analog show singlet resonances at 37.94 and 36.22[3] ppm, respectively, corresponding to equivalent phosphine groups. In general, the substitution reactions of **1** and **2** required higher temperatures and longer reaction times than for their DPVP analogs.

The $[(\eta^5\text{-}C_5Me_5)Ru(\eta^1\text{-DPVP})(\eta^3\text{-DPVP})]PF_6$ complex (**B**) was prepared by treating an acetonitrile solution of $[(\eta^5\text{-}C_5Me_5)RuCl_2]_2$ with excess Zn. After 2 hours of stirring at room temperature, the excess Zn was removed and DPVP was added. The stirring was continued for another 8 hours, and then the resulting solution was treated with $NaPF_6$ to produce the desired product in 72% yield.[4] We used the same procedure in an attempt to prepare the DCVP analog of **B** but instead of $[(\eta^5\text{-}C_5Me_5)Ru(\eta^1\text{-DCVP})(\eta^3\text{-DCVP})]PF_6$, the unexpected product, **9** was isolated (Scheme 7). $^{31}P\{^1H\}$ NMR spectroscopy showed two major resonances at 33.9 ppm, which we tentatively attributed to $[(\eta^5\text{-}C_5Me_5)Ru(\eta^1\text{-DCVP})_2(CH_3CN)]PF_6$, and 24.8 ppm attributed to **9**. Over time the former resonance disappeared as the latter augmented in intensity. Through repeated attempts at fractional crystallization and column chromatography on silica gel we were not able to isolate and identify the ruthenium containing material/s. Compound **9** was fully characterized by elemental analysis, ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy, IR spectroscopy and X-ray crystallography. Fig. 4 shows the geometry of cation **9**. The central ring, which sits on a crystallographic center of symmentry, is in the chair conformation. Each phosphorus ion has two cyclohexyl groups attached, one of which is equatorial and the other axial. As expected the C(1)–P(1)–C(7) angle is bigger for **9** than for its phenyl analog, 117.11(14)° and 111(1)°, respectively.[10] The value



unexpected product

Scheme 7

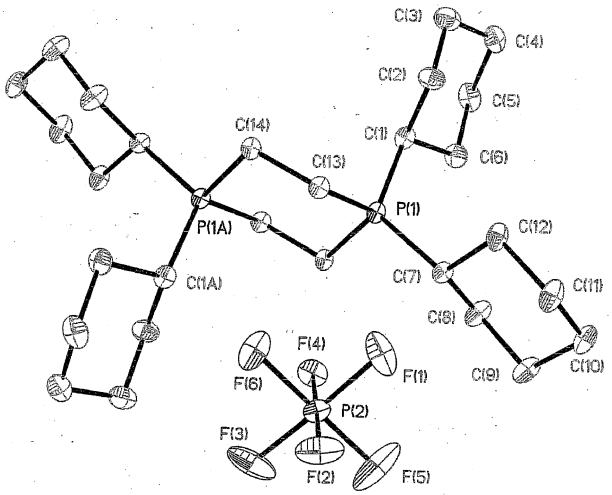
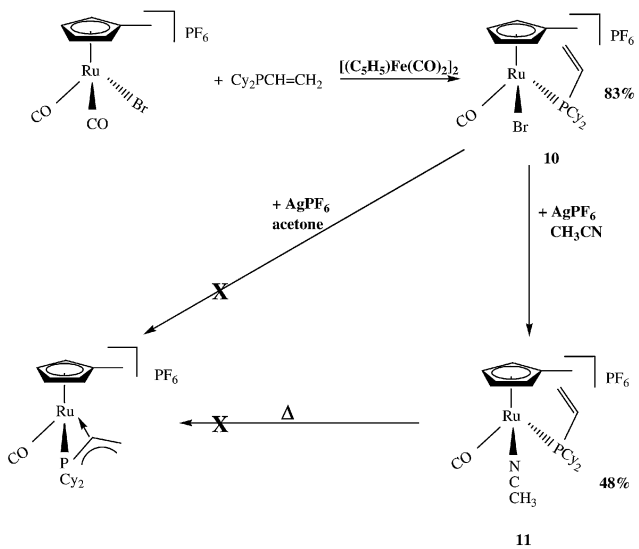


Fig. 4 Structural drawing of **9** showing the atom numbering scheme (40% probability ellipsoids). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): P(1)–C(13), 1.813(4); P(1)–C(1), 1.810(4); C(13)–P(1)–C(7), 106.51(18); C(14)–C(13)–P(1), 115.1(2).

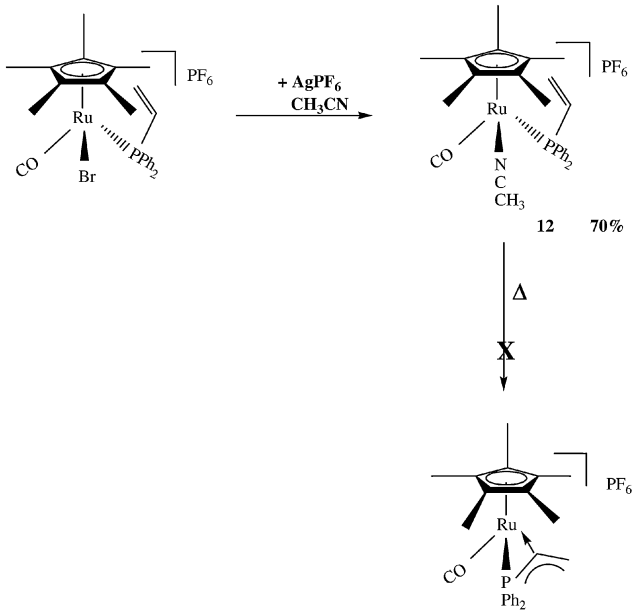
of the P(1)–C(13) bond distance (1.813(4) Å) is similar to the average P–C distance, 1.78(3) Å[10] for the phenyl analog.

We have previously shown[3] that $[(\eta^5\text{-}C_5H_5)Ru(CO)(\eta^3\text{-}DPVP)]PF_6$ has the *endo* geometry in contrast to **A**, **B**, **C** and **1** all of which have the *exo* geometry. As we mentioned before the phosphaallyl complex **2** was obtained as a 7 : 1 mixture of *exo* and *endo* isomers. Since this suggested that the ancillary ligands could control the geometry of the η^3-phosphaallyl ligand we tried to prepare other examples of such complexes. As we showed before attempts to prepare $[(\eta^5\text{-}MeC_5H_4)Ru(CO)(\eta^3\text{-}DPVP)]PF_6$ failed.[5] We set out to prepare $[(\eta^5\text{-}MeC_5H_4)Ru(CO)(\eta^3\text{-}DCVP)]PF_6$ by removal of bromide from **10** or CH_3CN from **11** (Scheme 8). Neither of these reactions were successful. Complexes **10** and **11** were characterized by elemental analyses, cyclic voltammetry, ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy, IR spectroscopy and X-ray crystallography. The crystals of **10** and **11** are of poor quality but confirmed the structures. Compound **10** undergoes a quasireversible one-electron oxidation with an $E_{1/2}$ value of 0.46 V compared with its DPVP analog for which $E_{1/2} = 0.53$ V.[5] Compound **10** is slightly easier to oxidize as it possesses the better electron donor ligand DCVP as compared to DPVP. It was also shown that when a dichloroetahane



Scheme 8

solution of $[(\eta^5\text{-}C_5Me_5)Ru(CO)(Br)DPVP)]$ was treated with AgOTf (AgOTf = silver trifuoromethanesulfonate) a mixture of starting material and $[(\eta^5\text{-}C_5Me_5)Ru(CO)(\eta^3\text{-}DPVP)]OTf$ was formed.[8] But these complexes have so far been inseparable and the η^3-phosphaallyl compound has not been characterized. We tried several different approaches in order to obtain a pure compound. First, we treated an acetonitrile solution of $[(\eta^5\text{-}C_5Me_5)Ru(CO)(Br)(DPVP)]$[8] with $AgPF_6$ to substitute bromide with CH_3CN. The isolated $[(\eta^5\text{-}C_5Me_5)Ru(CO)(CH_3CN)(DPVP)]PF_6$ (**12**) was then heated in a vacuum oven at 120 °C for several days. But this reaction also failed to produce the desired compound (Scheme 9). Complex **12** was characterized by elemental analysis, ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$ NMR spectroscopy, IR spectroscopy and X-ray crystallography. A view of the geometry of the cation of **12** is shown in Fig. 5. It is a three-legged piano stool with a distorted octahedral structure. Because CH_3CN could not be displaced by the vinyl group of DCVP in **11** or its DPVP analogue we wondered if other ligands would displace the CH_3CN from these complexes.



Scheme 9

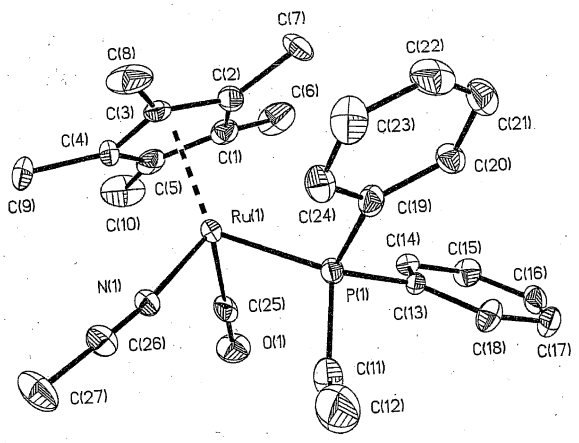
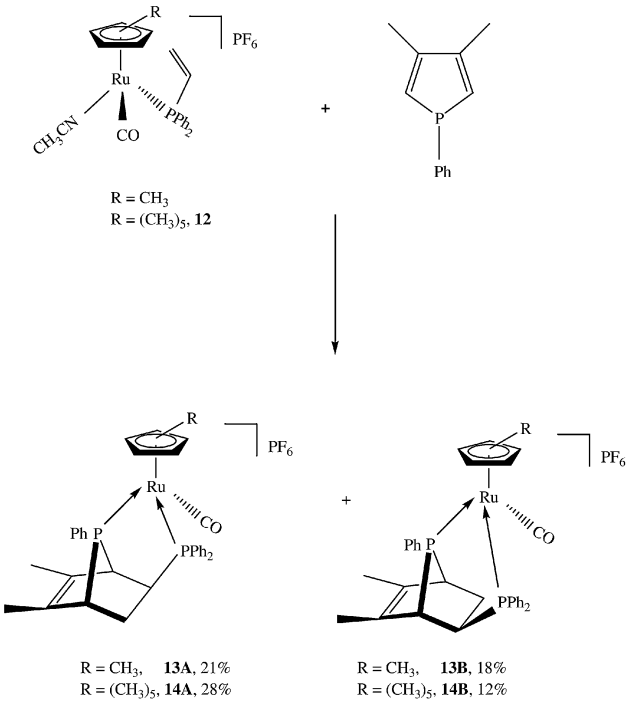


Fig. 5 Structural drawing of the cation of **12** showing the atom numbering scheme (20% probability ellipsoids). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ru(1)–P(1), 2.346(3); Ru(1)–N(1), 2.074(8); Ru(1)–C(25), 1.855(12); Ru(1)–C(average), 2.236(11); C(25)–O(1), 1.156(12); N(1)–C(26), 1.133(11), N(1)–Ru(1)–P(1), 88.1(2); C(25)–Ru(1)–P(1), 88.3(3); Ru(1)–P(1)–C(11), 112.5(4).

In their studies on the coordination modes of phospholes, Nelson and co-workers showed that coordinated 3,4-dimethyl-1-phenylphosphole (DMPP) is capable of undergoing [4 + 2] Diels–Alder reactions with a variety of dienophiles.[11] The coordination of the phosphole to a transition metal activates the cyclic diene towards [4 + 2] cycloaddition. Also, coordination of a dienophile, such as DPVP, activates the dienophile towards [4 + 2] cycloaddition.[11] Accordingly, we reacted $[(\eta^5\text{-}MeC_5H_4)Ru(CO)(CH_3CN)(DPVP)]PF_6$[5] and $[(\eta^5\text{-}C_5Me_5)Ru(CO)(CH_3CN)(DPVP)]PF_6$ (**12**) with DMPP, as shown in Scheme 10, and obtained [4 + 2] Diels–Alder adducts. The $^{31}P\{^1H\}$ NMR spectra of the reaction mixtures show four doublet resonances corresponding to two diastereomers in the ratios: **13A** : **13B**, 1.2 : 1 and **14A** : **14B**, 2 : 1. Recrystallization from nitromethane/diethyl ether allowed separation of these isomers. Isomers **13A** and **14A** were characterized by elemental analyses, ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy, IR spectroscopy and X-ray crystallography. The $^{31}P\{^1H\}$ NMR spectra show two doublet resonances at 141.06 and 69.81 ppm for **13A** and 142.88 and 72.67 for **14A**. IR spectra of those isomers show strong carbonyl bands ν_{CO} at 1982 cm^{-1} (**13A**) and 1969 cm^{-1} (**14A**). Views of the geometries of the cations of **13A** and **14A** are shown in Figs. 6 and 7, respectively. In the two structures, the geometry around the ruthenium center is pseudo-octahedral with the $\eta^5\text{-}C_5Me_5$ and $\eta^5\text{-}MeC_5H_4$ rings, the asymmetric bidenate phosphine and the CO group completing the coordination sphere.



Scheme 10

In principle, two regioisomeric adducts **A** and **B** could be formed in these reactions with one predominating, but in some cases only one regioisomeric adduct was formed.[11] The regioselectivity is mainly governed by the steric effects posed in the transition state between the emerging norbornene ligand and the CO ligand. Molecular models demonstrate that the intramolecular steric interactions in the transition states for the formation of the regioisomers **13A** and **14A** are smaller than for the formation of the regioisomers **13B** and **14B**; therefore regioisomers **13A** and **14A** should predominate in these [4 + 2] cycloaddition reactions. This assumption has been proved by X-ray crystallography. Because this regioselectivity is mainly affected by steric effects, the bigger the difference

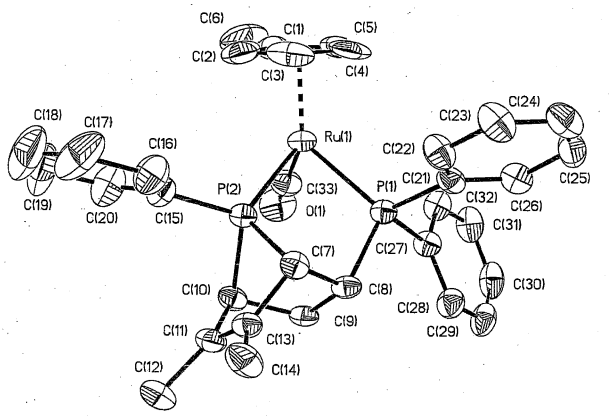


Fig. 6 Structural drawing of the cation of **13A** showing the atom numbering scheme (20% probability ellipsoids). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ru(1)–P(1), 2.313(2); Ru(1)–P(2), 2.2752(19); Ru(1)–C(33), 1.867(9); Ru(1)–C(average), 2.243(9); P(2)–C(10), 1.854(7); C(33)–O(1), 1.127(9); P(1)–Ru(1)–P(2), 80.80(7); P(1)–Ru(1)–C(33), 92.4(3); C(7)–P(2)–C(10), 81.1(3); Ru(1)–C(33)–O(1), 177.6(8).

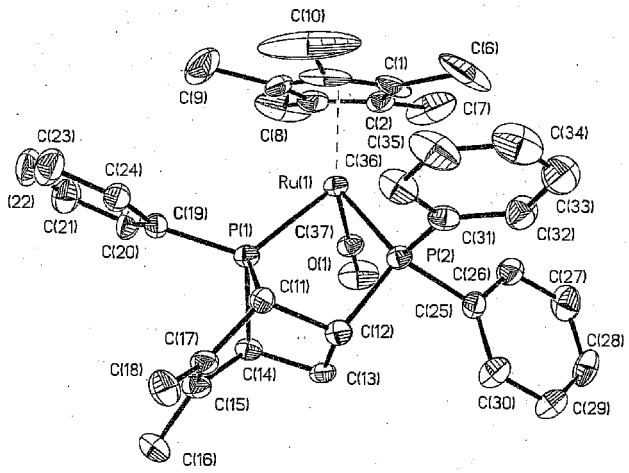
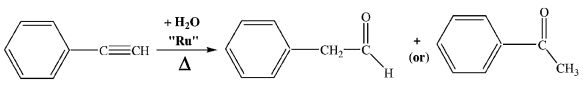


Fig. 7 Structural drawing of the cation of **14A** showing the atom numbering scheme (30% probability ellipsoids). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ru(1)–P(1), 2.302(2); Ru(1)–P(2), 2.322(2); Ru(1)–C(37), 1.865(8); Ru(1)–C(average), 2.254(8); P(1)–C(11), 1.848(7); C(37)–O(1), 1.137(8); P(1)–Ru(1)–P(2), 80.35(7); P(1)–Ru(1)–C(37), 90.1(2); C(11)–P(1)–C(14), 80.3(3); Ru(1)–C(37)–O(1), 174.2(7).

in the steric effects between two regioisomers the higher the diastereoselectivity.

Catalytic studies

Metal catalyzed hydration of alkynes is an important route to carbonyl compounds that are often precursors in many useful processes. The addition of water to terminal alkynes when following Markovnikov's rules produces ketones; the anti-Markovnikov addition yields aldehydes.[12] We have conducted tests with $[(\eta^5\text{-}MeC_5H_4)Ru(CO)(CH_3CN)(DPVP)]PF_6$[5], $[(\eta^5\text{-}C_5Me_5)Ru(CO)(CH_3CN)(DPVP)]PF_6$ (**12**), $[(\eta^5\text{-}C_5H_5)Ru(\eta^1\text{-}DCVP)(\eta^3\text{-}DCVP)]PF_6$ (**1**), $[(\eta^5\text{-}MeC_5H_4)Ru(\eta^1\text{-}DCVP)(\eta^3\text{-}DCVP)]PF_6$ (**2**) and $[(\eta^5\text{-}MeC_5H_4)Ru(\eta^1\text{-}DPVP)(\eta^3\text{-}DPVP)]PF_6$[5] as catalysts for the hydration of phenylacetylene (eqn. (1)).

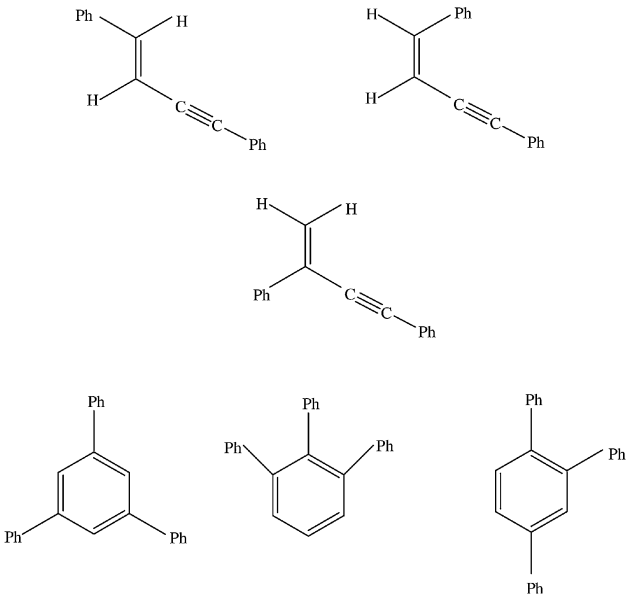


(1)

Table 2 Ruthenium catalyzed hydration of phenylacetylene

Catalyst	Method	% Dimers	% Trimers	Comments
$[(\eta^5\text{-}MeC_5H_4)Ru(CO)(CH_3CN)(DPVP)]PF_6$	A	trace	—	mostly starting material
$[(\eta^5\text{-}Me_5C_5)Ru(CO)(CH_3CN)(DPVP)]PF_6$	A	trace	—	mostly starting material
$[(\eta^5\text{-}C_5H_5)Ru(\eta^1\text{-}DCVP)(\eta^3\text{-}DCVP)]PF_6$	B	26.4	73.6	1 dimer 2 trimers
$[(\eta^5\text{-}MeC_5H_4)Ru(\eta^1\text{-}DCVP)(\eta^3\text{-}DCVP)]PF_6$	B	88.5	11.5	3 dimers 1 trimer
$[(\eta^5\text{-}MeC_5H_4)Ru(\eta^1\text{-}DPVP)(\eta^3\text{-}DPVP)]PF_6$	B	60.7	39.3	2 dimers 2 trimers

Neither acetophenone nor phenylacetaldehyde was detected. Instead phenylacetylene dimers and trimers were identified (Scheme 11) by GC/MS. We were unable to separate and fully characterize each of these compounds which have been noted before as products of similar reactions.[13] Table 2 shows the results of the catalytic reactions.



Scheme 11 Possible PhC≡CH dimers and trimers.

Concluding remarks

We have synthesized and characterized twelve new ruthenium complexes including the new phosphaallyl complexes $[(\eta^5\text{-}C_5H_5)Ru(\eta^1\text{-}DCVP)(\eta^3\text{-}DCVP)]PF_6$ (**1**) and $[(\eta^5\text{-}MeC_5H_4)Ru(\eta^1\text{-}DCVP)(\eta^3\text{-}DCVP)]PF_6$ (**2**). We have found that compounds **1** and **2** are much more stable than their DPVP analogs. The enhanced stability of these phospaallyl complexes is a result of the better donor ability of DCVP than DPVP and the greater steric bulk of the cyclohexyl than the phenyl group. Attempted syntheses of the $[(\eta^5\text{-}C_5Me_5)Ru(\eta^1\text{-}DCVP)(\eta^3\text{-}DCVP)]PF_6$ and the carbonylphosphaallyl complexes $[(\eta^5\text{-}MeC_5H_4)Ru(CO)(\eta^3\text{-}DCVP)]PF_6$ and $[(\eta^5\text{-}C_5Me_5)Ru(CO)(\eta^3\text{-}DPVP)]PF_6$ failed. The two compounds $[(\eta^5\text{-}MeC_5H_4)Ru(CO)(CH_3CN)(DPVP)]PF_6$[5] and $[(\eta^5\text{-}C_5Me_5)Ru(CO)(CH_3CN)(DPVP)]PF_6$ (**12**) undergo [4 + 2] Diels–Alder cycloaddition reactions with DMPP with only modest diastereoselectivity. The catalytic tests for the hydration of phenylacetylene failed to produce aldehyde or ketone but instead produced dimers and trimers of phenylacetylene with relatively poor selectivity.

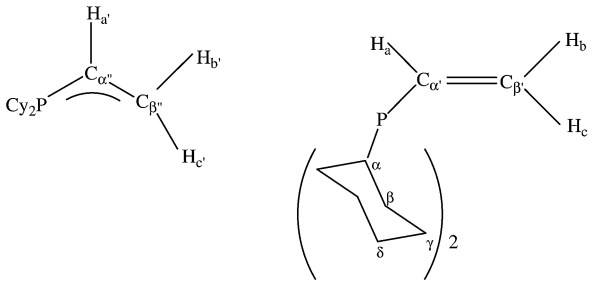
Experimental

A. Reagents and physical measurements

All chemicals were reagent grade and were used as received from commercial sources (Aldrich, Fisher Scientific, Acros Organics, GFS Chemicals, Strem Chemicals) or synthesized as described below. All syntheses were conducted under a nitrogen atmosphere. $[(\eta^5\text{-}Me_5C_5)Ru(CO)(Br)(DPVP)]$,[8] $[(\eta^5\text{-}MeC_5H_4)Ru(CO)_2Br]$,[5] $[(\eta^5\text{-}MeC_5H_4)Ru(CH_3CN)_3]PF_6$,[5] $[(\eta^5\text{-}C_5H_5)Ru(CH_3CN)_3]PF_6$,[14] $[(\eta^5\text{-}C_5Me_5)RuCl_2]_2PF_6$,[15] 3,4-dimethyl-1-phenylphosphole (DMPP),[16] phenylisocyanide PhNC[17] and dicyclohexylvinylphosphine (DCVP)[18] were synthesized by the literature procedure. Acetonitrile was distilled from CaH_2 prior to use. Melting points were obtained using a Mel-Temp melting point apparatus and are uncorrected. ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded at 499.8 MHz, 125.7 MHz, and 202.3 MHz on a Varian Unity Plus 500 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.[19] 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[20] under the same conditions. GC/MS analyses were performed on a Hewlet-Packard HP 5890 instrument. A HP-1 (cross linked methyl siloxane) column was used. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

B. Syntheses

Preparation of $[(\eta^5\text{-}C_5H_5)Ru(\eta^1\text{-}DCVP)(\eta^3\text{-}DCVP)]PF_6$ (1). A 250 mL, three-neck round-bottom flask was charged with 2.2 g (5.1 mmol) of $[(\eta^5\text{-}C_5H_5)Ru(CH_3CN)_3]PF_6$ and 120 mL of freshly distilled acetonitrile. The whole was stirred under a nitrogen atmosphere for 30 min. Then 2.4 mL (10.7 mmol) of DCVP was added and the mixture was stirred at room temperature overnight. Solvent was removed leaving a brown, oily residue. This residue 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–MeOH–diethyl ether gave 2.92 g (76% yield) of yellow crystals.Mp: 95–97 °C. Anal.

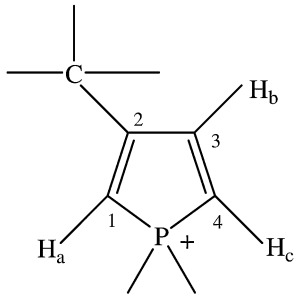


calc. for $C_{33}H_{55}F_6P_3Ru$: C, 52.12; H, 7.24. Found: C, 51.98; H, 7.11%. ^1H NMR ($CDCl_3$): δ 5.97 (dd, $^3J(PH) = 30.0$ Hz, $^3J(H_aH_c) = 13.0$ Hz, 1H, H_c), 5.81 (ddd, $^2J(PH) = 20.5$ Hz, $^3J(H_aH_b) = 18.5$ Hz, $^3J(H_aH_c) = 13.0$ Hz, 1H, H_a), 5.64 (dd, $^3J(H_aH_b) = 18.5$ Hz, $^3J(PH) = 13.5$ Hz, 1H, H_b), 5.10 (s, 5H, Cp), 3.91 (app tdd, $^2J(PH) = {}^3J(H_{a'}H_{c'}) = 10.8$ Hz, $^3J(H_{a'}H_{b'}) = 8.8$ Hz, $^4J(PH) = 1.5$ Hz, 1H, $H_{a'}$), 3.30 (ddd, $^3J(PH) = 33.5$ Hz,

$^3J(H_{a'}H_{b'}) = 8.8$ Hz, $^2J(H_{b'}H_{c'}) = 1.5$ Hz, 1H, $H_{b'}$), 2.2–1.0 (m, 44H, 4 × C_6H_{11}), 1.57(dddd, $^3J(PH) = 13.5$ Hz, $^3J(H_{a'}H_{c'}) = 10.8$ Hz,$^5J(PH) = 8.5$ Hz, $^2J(H_{b'}H_{c'}) = 1.5$ Hz, 1H, $H_{c'}$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 41.80 (d, $^2J(PP) = 37.3$ Hz, 1P, η^1-DCVP), 26.10 (d, $^2J(PP) = 37.3$ Hz, 1P, η^3-DCVP), −145.00 (sept., $^1J(PF) = 714$ Hz, 1P, PF_6^-). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 130.61 (d, $|^1J(PC) = 31.8$ Hz, $C_{\alpha'}$), 129.02 (d,$^2J(PC)| = 6.0$ Hz, $C_{\beta'}$), 81.55 (app t, $J(PC)| = 1.1$ Hz, Cp), 39.67 (dd, $|^1J(PC) = 26.1$ Hz, $|^3J(PC) = 2.4$ Hz, C_α), 37.06 (d, $|^1J(PC) = 25.4$ Hz, C_α), 36.69 (app t, $^2J(PC) = |^4J(PC) = 3.9$ Hz, $C_{\beta''}$), 35.39 (d, $^1J(PC) = 26.9$ Hz, C_α), 34.32 (d, $^2J(PC) = 9.4$ Hz, C_β), 33.20 (s, C_β), 32.56 (d, $^1J(PC) = 20.7$ Hz, $C_{\alpha''}$), 32.22 (dd, $|^1J(PC) = 14.6$ Hz, $|^3J(PC) = 3.0$ Hz, C_α), 30.38 (s, C_β), 29.43 (s, C_β), 29.40 (s, C_β), 29.20 (s, C_β), 29.04 (s, C_β), 28.98 (s, C_β), 27.56 (d, $|^3J(PC) = 12.1$ Hz, C_γ), 27.28 (d, $^3J(PC) = 12.1$ Hz, C_γ), 27.24 (s, C_δ), 26.96 (d, $^3J(PC) = 8.7$ Hz, C_γ), 26.75 (d, $^3J(PC) = 12.4$ Hz, C_γ), 26.60 (d, $^3J(PC) = 10.2$ Hz, C_γ), 26.50 (d, $^3J(PC) = 14.3$ Hz, C_γ), 26.38 (d, $^3J(PC) = 10.8$ Hz, C_γ), 26.23 (d, $^3J(PC) = 11.2$ Hz, C_γ), 26.15 (s, C_δ), 25.57 (s, C_δ), 25.33 (s, C_δ). IR (PF_6 region, Nujol, cm^{-1}): 840. $E_{1/2} = 0.395$ V *vs.* F_c/F_c^+.

Preparation of [(η^5-MeC_5H_4)Ru(η^1-DCVP)(η^3-DCVP)]PF_6·CH_2Cl_2 (2). A 250 mL, three-neck round-bottom flask was charged with 2.6 g (5.8 mmol) of [(η^5-MeC_5H_4)Ru(CH_3CN)$_3$]PF_6 and 120 mL of freshly distilled acetonitrile. The whole was stirred under a nitrogen atmosphere for 30 min. Then 2.8 mL (12.5 mmol) of DCVP was added and the mixture was stirred at room temperature overnight. Solvent was evaporated leaving a brown, oily residue. This residue 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 2.65 g (53% yield) of yellow crystals. Mp: 228–230 °C. Anal. calc. for $C_{35}H_{59}Cl_2F_6P_3Ru$: C, 48.91; H, 6.87. Found: C, 48.76; H, 6.80%. For the *exo* isomer only: ^1H NMR (CD_2Cl_2): δ 5.98 (dd, $^3J(PH) = 30.0$ Hz, $^3J(H_aH_b) = 13.0$ Hz, 1H, H_b), 5.81 (ddd, $^2J(PH) = 21.0$ Hz, $^3J(H_aH_c) = 18.8$ Hz, $^3J(H_aH_b) = 13.0$ Hz, 1H, H_a), 5.67 (dd, $^3J(H_aH_c) = 18.8$ Hz,$^3J(PH) = 13.5$ Hz, 1H, H_c), 3.20 (app dtd, $^3J(H_{a'}H_{c'}) = 10.5$ Hz, $^2J(PH) = {}^3J(H_{a'}H_{b'}) = 9.0$ Hz, $^4J(PH) = 2.0$ Hz, 1H, $H_{a'}$), 2.84 (ddd, $^3J(PH) = 33.0$ Hz, $^3J(H_{a'}H_{b'}) = 9.0$ Hz, $^2J(H_{b'}H_{c'}) = 2.0$ Hz, 1H, $H_{b'}$), 2.2–1.0 (m, 45H, 4·C_6H_{11}, $H_{c'}$), 1.61 (s, 3H, CH_3Cp). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 38.49 (d, $^2J(PP) = 37.5$ Hz, 1P, η^1-DCVP), 23.86 (d, $^2J(PP) = 37.5$ Hz, 1P, η^3-DCVP), −148.11 (sept., $^1J(PF) = 711$ Hz, 1P, PF_6^-). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 130.95 (d, $|^1J(PC) = 32.1$ Hz, $C_{\alpha'}$), 129.78 (d,$^2J(PC)| = 6.0$ Hz, $C_{\beta'}$), 99.94 (app t, $J(PC)| = 1.8$ Hz, Cp_q), 84.14 (Cp), 82.31 (d, $J(PC) = 4.8$ Hz, Cp), 80.42 (d, $J(PC) = 5.3$ Hz, Cp), 79.42 (Cp), 40.13 (dd, $|^1J(PC) = 26.0$ Hz, $|^3J(PC) = 2.4$ Hz, C_α), 39.74 (app t, $^2J(PC) = |^4J(PC) = 4.3$ Hz, $C_{\beta''}$), 36.99 (d, $^1J(PC) = 25.0$ Hz, C_α), 36.79 (d, $^1J(PC) = 19.9$ Hz, C_α), 36.02 (d, $^1J(PC) = 27.0$ Hz, $C_{\alpha''}$), 34.81 (C_β), 34.74 (C_β), 33.81 (C_β), 33.14 (dd, $|^1J(PC) = 14.6$ Hz, $^3J(PC) = 3.4$ Hz, C_α), 30.87 (C_β), 30.03 (C_β), 30.00 (C_β), 29.90 (C_β), 29.62 (C_β), 29.60 (C_β), 28.07 (d, $^3J(PC) = 11.9$ Hz, C_γ), 27.91 (d, $^3J(PC) = 12.1$ Hz, C_γ), 27.61 (C_δ), 27.47 (d, $^3J(PC) = 18.4$ Hz, C_γ), 27.24 (d, $^3J(PC) = 15.6$ Hz, C_γ), 27.21 (d, $^3J(PC) = 14.3$ Hz, C_γ), 27.10 (d, $^3J(PC) = 19.1$ Hz, C_γ), 27.02 (d, $^3J(PC) = 19.9$ Hz, C_γ), 26.81 (C_δ), 26.75 (d, $^3J(PC) = 14.8$ Hz, C_γ), 26.11 (C_δ), 25.92 (d, $^4J(PC) = 1.4$ Hz, C_δ), 11.46 (CH_3Cp). IR (PF_6 region, Nujol, cm^{-1}): 839.

Attempted preparation of [(η^5-MeC_5H_4)$(DCVP)_2$Ru=C=C=CPh_2)]PF_6; Formation of (3). A 100 mL, three-neck round-bottom flask was charged with 0.31 g (0.4 mmol) of [(η^5-MeC_5H_4)Ru(η^1-DCVP)(η^3-DCVP)]PF_6·CH_2Cl_2 and 50 mL of 1,2-dichloroethane. The whole was stirred under a nitrogen atmosphere for 30 min. Then 0.19 g (0.9 mmol) of HC≡C–C(OH)Ph_2 was added and the mixture was refluxed for 9 days (change of color was observed: yellow to orange to red to purple). Recrystallization from CH_2Cl_2–hexane gave 0.1 g of colorless crystals of the phosphonium salt.The same product was isolated in the raction of [(η^5-C_5H_5)Ru(η^1-DCVP)(η^3-DCVP)]PF_6 with HC≡C–C(OH)Ph_2. Anal. calc. for $C_{29}H_{36}F_6OP_2$: C, 60.42; H, 6.24. Found: C, 60.22; H, 6.17. ^1H NMR (acetone-d_6): δ 7.45 (ddd, $^2J(PH) = 40.5$ Hz, $^4J(H_aH_b) = 8.0$ Hz, $^4J(H_aH_c) = 1.5$ Hz, 1H, H_a), 7.40 (m, 10H, Ph), 6.95 (ddd, $^2J(PH) = 32.5$ Hz, $^4J(H_aH_b) = 8.0$ Hz, $^3J(H_bH_c) = 2.0$ Hz, 1H, H_b), 6.62 (ddd, $^3J(PH) = 32.5$ Hz, $^3J(H_bH_c) = 2.0$ Hz, $^4J(H_aH_c) = 1.5$ Hz, 1H, H_c), 5.98 (1H, OH), 3.10 (m, 1H, H_α), 2.82 (m, 1H, H_α), 2.10 (m, 2H, H_γ), 1.83 (m, 4H, H_γ), 1.71 (m, 2H, H_γ), 1.45 (m, 8H, H_β), 1.28 (m, 4H, H_δ). $^{31}P\{^1H\}$ NMR (acetone-d_6): δ 64.1 (s, 1P), −145.00 (sept., $^1J(PF) = 708$ Hz, 1P, PF_6^-). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 172.70 (d, $|^2J(PC) = 14.7$ Hz, C_2), 153.77 (d, $|^2J(PC) = 10.4$ Hz, C_3), 143.64 (s, C_i), 129.39 (s, C_m), 129.11 (s, C_p), 128.46 (s, C_o), 117.97 (d, $|^1J(PC) = 67.6$ Hz, C_1), 110.29 (d, $|^1J(PC) = 71.6$ Hz, C_4), 31.20 (d, $|^1J(PC) = 43.1$ Hz, C_α), 30.33 (d, $|^1J(PC) = 40.1$ Hz, C_α), 27.09 (d, $|^3J(PC) = 3.0$ Hz, C_γ), 27.02 (d, $|^3J(PC) = 3.1$ Hz, C_γ), 26.75 (s, C_β), 26.64 (s, C_β), 25.88 (s, C_δ), 25.86 (s, C_δ).



Preparation of [(η^5-MeC_5H_4)Ru$(DCVP)_2$(CO)]PF_6 (4).

Method A. A 100 mL, three-neck round-bottom flask was charged with 0.28 g (0.3 mmol) of [(η^5-MeC_5H_4)Ru(η^1-DCVP)-(η^3-DCVP)]PF_6·CH_2Cl_2 and 50 mL of 1,2-dichloroethane. The solution was brought to reflux and bubbled with CO for 5 days. Solvent was removed *in vacuo* leaving 0.21 g (81%) of yellow product.

Method B. A 100 mL, three-neck round-bottom flask was charged with 0.43 g (0.5 mmol) of [(η^5-MeC_5H_4)Ru(η^1-DCVP)(η^3-DCVP)]PF_6·CH_2Cl_2 and 40 mL of a 1 : 1 $ClCH_2CH_2$-Cl/MeOH mixture. The whole was stirred under a nitrogen atmosphere for 30 min. Then 0.2 mL (1.8 mmol) of PhC≡CH was added and the whole was heated under reflux for 4 days (change of color was observed: yellow to orange to red). Solvents were removed leaving a reddish brown, oily residue. This residue was dissolved in CH_2Cl_2 and passed through a silica gel column packed with hexane and eluted with CH_2Cl_2. The first yellow fraction contained mostly PhC≡CH dimers, and the second orange fraction 0.20 g of carbonyl compound (50% yield). Mp: 90–92 °C. Anal. calc. for $C_{35}H_{57}F_6OP_3Ru$: C, 52.43; H, 7.12. Found: C, 52.24; H, 7.01%. ^1H NMR ($CDCl_3$): δ 6.01 (m, 4H, $H_{a,b}$), 5.61 (m, 2H, H_c), 5.26 (app t, $|^3J(HH) + {}^4J(HH)| = 3.5$ Hz, 2H, Cp), 5.04 (app t, $|^3J(HH) + {}^4J(HH)| = 3.0$ Hz, 2H, Cp), 2.09 (s, 3H, CH_3Cp), 1.80 (m, 12H, Cy), 1.25 (m, 10H, Cy). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 37.75 (s, 2P, DCVP), −145.00 (sept., $^1J(PF) = 712$ Hz, 1P, PF_6^-). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 205.15 (t, $|^2J(PC) = 17.1$ Hz, CO), 130.62 (AXX′, $|^1J(PC)| = 35.1$ Hz, $|^2J(PP) = 25.6$ Hz, $|^3J(PC) = 2.3$ Hz, $C_{\alpha'}$), 129.16 (s, $C_{\beta'}$), 106.36 (t, $J(PC) = 1.9$ Hz, Cp_q), 87.11 (Cp), 86.29 (Cp), 40.25 (AXX′, $^2J(PP) = |25.6$ Hz, $^1J(PC) = 24.0$ Hz, $^3J(PC) = 5.0$ Hz, C_α), 38.08 (AXX′, $^2J(PP) = |25.6$ Hz, $^1J(PC) = 24.1$ Hz, $^3J(PC) = 0.8$ Hz, C_α), 29.30 (C_β), 28.88 (C_β), 28.46 (C_β), 28.21 (C_β), 26.91 (app T, $|^3J(PC) + {}^5J(PC)| = 11.8$ Hz, C_γ), 26.86 (app T, $|^3J(PC) + {}^5J(PC)| = 12.8$ Hz, C_γ), 26.77 (app T, $|^3J(PC) + {}^5J(PC)| = 10.1$ Hz, C_γ), 26.30 (app T, $|^3J(PC) + {}^5J(PC)| = 10.6$ Hz, C_γ), 25.81 (C_δ), 22.47 (C_δ), 13.19 (CH_3Cp). IR (CO region, CH_2Cl_2, cm^{-1}): 1966, IR (PF_6 region, Nujol, cm^{-1}): 831.

Preparation of [(η^5-MeC_5H_4)Ru$(DCVP)_2$(C=CH_2)]PF_6 (5). A 100 mL, three-neck round-bottom flask was charged

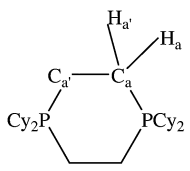
with 0.32 g (0.4 mmol) of $[(\eta^5\text{-}MeC_5H_4)Ru(\eta^1\text{-}DCVP)(\eta^3\text{-}DCVP)]PF_6{\cdot}CH_2Cl_2$ and 40 mL of a 1 : 1 $ClCH_2CH_2Cl/MeOH$ mixture. The whole was stirred under a nitrogen atmosphere for 30 min. Then 0.2 mL (1.4 mmol) of $HC{\equiv}CSiMe_3$ was added *via* syringe and the whole was heated under reflux for 5 days. Solvents were removed leaving a brown-green oily residue. This residue was dissolved in CH_2Cl_2 and passed through a silica gel column packed with hexane and eluted with CH_2Cl_2. Recrystallization from acetone–diethyl ether gave 0.25 g of reddish-brown product in 83% yield. Mp: 70–72 °C. Anal. calc. for $C_{36}H_{59}F_6P_3Ru$: C, 54.07; H, 7.38. Found: C, 53.92; H, 7.29%. ^1H NMR ($CDCl_3$): δ 6.22 (ddd, $^2J(PH) = 21.0$ Hz, $^3J(H_aH_c) = 18.8$ Hz, $^3J(H_aH_b) = 12.8$ Hz, 2H, H_a), 6.00 (dd, $^3J(PH) = 33.5$ Hz, $^3J(H_aH_b) = 12.8$ Hz, 2H, H_b), 5.61 (dd, $^3J(H_aH_c) = 18.8$ Hz, $^3J(PH) = 15.5$ Hz, 2H, H_c), 5.91 (app t, $|^3J(HH) + {}^4J(HH)| = 3.0$ Hz, 2H, Cp), 5.03 (app t, $|^3J(HH) + {}^4J(HH)| = 3.0$ Hz, 2H, Cp), 3.84 (s, 2H, $C{=}CH_2$), 2.12 (s, 3H, CH_3Cp), 1.75 (m, 12H, Cy), 1.18 (m, 10H, Cy). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 40.68 (s, 2P, DCVP), −145.00 (sept., $^1J(PF) = 714$ Hz, 1P, PF_6^-). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 321.59 (Ru=C), 207.25 (C=*C*H2), 129.46 (AXX′, $^1J(PC)| = 35.9$ Hz, $|^2J(PP) = 23.5$ Hz, $|^3J(PC) = 2.6$ Hz, $C_{\alpha'}$), 128.91 (s, $C_{\beta'}$), 108.96 (t, $J(PC) = 2.5$ Hz, Cp_q), 89.96 (Cp), 88.45 (Cp), 41.63 (AXX′, $^1J(PC) = 41.1$ Hz, $^2J(PP) = 23.5$ Hz, $^3J(PC) = -10.8$ Hz, C_α), 37.44 (app T, $|^1J(PC) + {}^3J(PC)| = 25.1$ Hz, C_α), 29.38 (C_β), 28.93 (C_β), 28.51 (C_β), 27.85 (C_β), 26.93 (app T, $|^3J(PC) + {}^5J(PC)| = 12.4$ Hz, C_γ), 26.91 (app T, $|^3J(PC) + {}^5J(PC)| = 11.1$ Hz, C_γ), 26.71 (app T, $|^3J(PC) + {}^5J(PC)| = 10.4$ Hz, C_γ), 26.06 (app T, $|^3J(PC) + {}^5J(PC)| = 10.7$ Hz, C_γ), 25.81 (C_δ), 25.68 (C_δ), 12.23 (CH_3Cp). IR (C=C region, CH_2Cl_2, cm^{-1}): 1621, IR (PF_6 region, Nujol, cm^{-1}): 832.

Preparation of $[(\eta^5\text{-}MeC_5H_4)Ru(DCVP)_2(PhNC)]PF_6$ (6). A 100 mL, three-neck round-bottom flask was charged with 0.32 g (0.4 mmol) of $[(\eta^5\text{-}MeC_5H_4)Ru(\eta^1\text{-}DCVP)(\eta^3\text{-}DCVP)]PF_6{\cdot}CH_2Cl_2$ and 40 mL of 1,2-dichloroethane. The whole was stirred under a nitrogen atmosphere and then 0.5 mL (4.8 mmol) of PhNC was added. The mixture was heated under reflux for 9 days. Solvent was removed leaving a brown oily residue. This residue was dissolved in CH_2Cl_2 and passed through a silica gel column packed with hexane and eluted with CH_2Cl_2. Solvents were evaporated leaving 0.26 g (79%) of yellow product. Mp: 85–87 °C. Anal. calc. for $C_{41}H_{62}F_6NP_3Ru$: C, 56.16; H, 7.08. Found: C, 56.02; H, 6.93%. ^1H NMR ($CDCl_3$): δ 7.45 (m, 1H, H_m), 7.43 (m, 1H, H_m), 7.36 (m, 1H, H_p), 7.20 (m, 1H, H_o), 7.17 (m, 1H, H_o), 6.04 (m, 4H, $H_{a,b}$), 5.88 (m, 2H, H_c), 5.17 (s, 2H, Cp), 4.91 (s, 2H, Cp), 2.11 (s, 3H, CH_3Cp), 1.84 (m, 24H, Cy), 1.28 (m, 20H, Cy). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 39.56 (s, 1P, DCVP), 39.27 (s, 1P, DCVP), −144.94 (sept., $^1J(PF) = 714$ Hz, 1P, PF_6^-). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 164.37 (t, $|^2J(PC) = 20.6$ Hz, CN), 132.03 (AXX′, $^1J(PC)| = 28.0$ Hz, $|^2J(PP) = 26.2$ Hz, $|^3J(PC) = 4.4$ Hz, $C_{\alpha'}$), 131.77 (AXX′, $^1J(PC)| = 29.3$ Hz, $|^2J(PP) = 26.2$ Hz, $|^3J(PC) = 3.3$ Hz, $C_{\alpha'}$), 129.94 (C_m), 129.80 (C_m), 129.25 (C_i), 128.23 (C_p), 128.11 ($C_{\beta'}$), 127.87 ($C_{\beta'}$), 124.80 (C_o), 124.55 (C_o), 104. 22 (Cp_q), 83.54 (Cp), 83.50 (Cp), 83.13 (Cp), 81.81 (Cp), 40.44 (AXX′, $^1J(PC)| = 25.9$ Hz, $|^2J(PP) = 26.2$ Hz, $|^3J(PC) = 2.7$ Hz, C_α), 38.06 (AXX′, $^1J(PC)| = 24.3$ Hz, $|^2J(PP) = 26.2$ Hz, $|^3J(PC) = 0.2$ Hz, C_α), 37.84 (AXX′, $^1J(PC)| = 24.3$ Hz, $|^2J(PP) = 26.2$ Hz, $|^3J(PC) = 1.6$ Hz, C_α), 29.47 (C_β), 29.40 (C_β), 28.96 (C_β), 28.86 (C_β), 28.46 (C_β), 28.36 (C_β), 28.16 (C_β), 28.07 (C_β), 27.07 (AXX′, $|^3J(PC)| + {}^5J(PC)| = 10.2$ Hz, C_γ), 26.92 (AXX′, $|^3J(PC)| + {}^5J(PC)| = 10.9$ Hz, C_γ), 26.87 (AXX′, $|^3J(PC)| + {}^5J(PC)| = 7.5$ Hz, C_γ), 26.43 (AXX′, $|^3J(PC)| + {}^5J(PC)| = 10.6$ Hz, C_γ), 25.86 (C_δ), 25.82 (C_δ), 15.04 (CH_3Cp). IR (NC region, CH_2Cl_2, cm^{-1}): 2091, IR (PF_6 region, CH_2Cl_2 film, cm^{-1}): 844.

Preparation of $[(\eta^5\text{-}C_5H_5)Ru(DCVP)_2(PhNC)]PF_6$ (7). A 100 mL, three-neck round-bottom flask was charged with 0.27 g (0.4 mmol) of $[(\eta^5\text{-}C_5H_5)Ru(\eta^1\text{-}DCVP)(\eta^3\text{-}DCVP)]PF_6$ and 40 mL of 1,2-dichloroethane. The whole was stirred under a nitrogen atmosphere and then 0.5 mL (4.8 mmol) of PhNC was added. The mixture was heated under reflux for 9 days. Solvent was removed leaving a brown oily residue. This residue was dissolved in CH_2Cl_2 and passed through a silica gel column packed with hexane and eluted with CH_2Cl_2. Solvent was evaporated leaving 0.24 g (77% yield) of brown microcrystals. Mp: 80–82 °C. Anal. calc. for $C_{40}H_{60}F_6NP_3Ru$: C, 55.68; H, 6.96. Found: C, 55.54; H, 6.83%. ^1H NMR ($CDCl_3$): δ 7.43 (m, 2H, H_m), 7.34 (m, 1H, H_p), 7.19 (m, 2H, H_o), 6.03 (m, 4H, $H_{a,b}$), 5.58 (m, 2H, H_c), 5.23 (s, 5H, Cp), 1.85 (m, 24H, Cy), 1.25 (m, 20H, Cy). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 39.70 (s, 2P, DCVP), −144.76 (sept., $^1J(PF) = 713$ Hz, 1P, PF_6^-). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 164.41 (t, $|^2J(PC) = 20.2$ Hz, CN), 131.86 (AXX′, $^1J(PC)| = 34.4$ Hz, $|^2J(PP) = 25.7$ Hz, $|^3J(PC) = 1.2$ Hz, $C_{\alpha'}$), 129.87 (C_m), 129.23 (C_i), 128.26 (C_p), 128.15 ($C_{\beta'}$), 124.84 (C_o), 83.58 (t, $J(PC) = 2.6$ Hz, Cp), 40.51 (AXX′, $^1J(PC)| = 23.9$ Hz, $|^2J(PP) = 25.7$ Hz, $|^3J(PC) = 5.3$ Hz, C_α), 37.91 (AXX′, $^1J(PC)| = 25.4$ Hz, $|^2J(PP) = 25.7$ Hz, $|^3J(PC) = -1.1$ Hz, C_α), 29.53 (C_β), 29.03 (C_β), 28.52 (C_β), 28.14 (C_β), 27.14 (AXX′, $|^2J(PC)| + {}^4J(PC)| = 10.9$ Hz, C_γ), 26.97 (AXX′, $|^2J(PC)| + {}^4J(PC)| = 12.8$ Hz, C_γ), 29.63 (AXX′, $|^2J(PC)| + {}^4J(PC)| = 12.8$ Hz, C_γ), 26.57 (AXX′, $|^2J(PC)| + {}^4J(PC)| = 10.2$ Hz, C_γ), 25.91 (C_δ), 25.86 (C_δ). IR (NC region, CH_2Cl_2, cm^{-1}): 2096, IR (PF_6 region, CH_2Cl_2 film, cm^{-1}): 840.

Preparation of $[(\eta^5\text{-}C_5H_5)Ru(DCVP)_2(CO)]PF_6$ (8). A 100 mL, three-neck round-bottom flask was charged with 0.21 g (0.3 mmol) of $[(\eta^5\text{-}C_5H_5)Ru(\eta^1\text{-}DCVP)(\eta^3\text{-}DCVP)]PF_6$ and 50 mL of 1,2-dichloroethane. The solution was brought to reflux and bubbled with CO for 3 days. Solvent was removed *in vacuo* leaving 0.17 g (77% yield) of yellow microcrystalline product. Mp: 100–102 °C. Anal. calc. for $C_{34}H_{55}F_6OP_3Ru$: C, 51.84; H, 6.99. Found: C, 51.67; H, 6.82%. ^1H NMR ($CDCl_3$): δ 6.0 (m, 4H, $H_{a,b}$), 5.59 (m, 2H, H_c), 5.31 (s, 5H, Cp), 2.0–0.8 (m, 44H, $4{\cdot}C_6H_{11}$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 37.94 (s, 2P, DCVP), −145.00 (sept., $^1J(PF) = 713$ Hz, 1P, PF_6^-). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 203.67 (t, $|^2J(PC) = 17.6$ Hz, CO), 130.46 (AXX′, $^2J(PP)| = 22.3$ Hz, $|^1J(PC) = 37.4$ Hz, $|^3J(PC) = 0.5$ Hz, $C_{\alpha'}$), 129.46 (s, $C_{\beta'}$), 86.33 (s, Cp), 40.28 (AXX′, $^2J(PP)| = 22.3$ Hz, $|^1J(PC) = 29.4$ Hz, $|^3J(PC) = 0.05$ Hz, C_α), 38.04 (AXX′, $^2J(PP)| = 22.3$ Hz, $|^1J(PC) = 23.7$ Hz, $|^3J(PC) = 1.3$ Hz, C_α), 29.99 (s, $2C_\beta$), 29.34 (s, C_β), 28.96 (s, C_β), 28.45 (AXX′, $|^2J(PC)| + {}^4J(PC)| = 10.4$ Hz, C_γ), 26.91 (m, C_γ), 26.85 (m, C_γ), 26.71 (s, C_δ), 26.36 (AXX′, $|^2J(PC)| + {}^4J(PC)| = 10.4$ Hz, C_γ), 25.79 (s, C_δ). IR (CO region, CH_2Cl_2 film, cm^{-1}): 2051, 1962, IR (PF_6 region, CH_2Cl_2 film, cm^{-1}): 841.

Attempted preparation of $[(\eta^5\text{-}C_5Me_5)Ru(\eta^1\text{-}DCVP)(\eta^3\text{-}DCVP)]PF_6$ by reaction of $[(\eta^5\text{-}Me_5C_5)RuCl_2]_2$ with Zn, DCVP and NH_4PF_6 (9). A 100 mL, three-neck round-bottom flask was charged with 1.0 g (1.6 mmol) of $[(\eta^5\text{-}Me_5C_5)RuCl_2]_2$, 2.6 g (40 mmol) of Zn dust and 30 mL of freshly distilled acetonitrile. The whole was stirred vigorously under a nitrogen atmosphere for 2 hours (a change of color was observed: brown to green to red). The excess Zn was removed by filtration and then 1.5 mL (6.7 mmol) of DCVP was added. The mixture was stirred at room temperature overnight and then 0.8 g (4.9 mmol) of NH_4PF_6 in 10 mL of MeOH was added. Solvents were removed. Recrystallization from acetone–diethyl ether–hexane gave 0.2 g of colorless crystals in 8% yield.Mp: 355–357 °C. Anal. calc.



for $C_{28}H_{52}F_{12}P_4$: C, 45.37; H, 7.02. Found: C, 45.25; H, 6.94. ^1H NMR (acetone-d_6): δ 3.13 (m, $|^2J(PH)| + |^3J(PH)| = 5$ Hz, 8H, $H_{a,a'}$), 2.90 (app qt, $^2J(PH)| = {}^3J(H_\alpha H_\beta)| = 12.0$ Hz, $^3J(H_\alpha H_\beta)| = 3.0$ Hz, 4H, H_α), 2.17 (m, 8H, H_β)|, 1.88 (m, 8H, H_γ)|, 1.73 (m, 12H, $H_{\beta,\gamma}$|)|, 1.45 (m, 4H, H_γ)|, 1.37 (m, 8H, H_δ)|. $^{31}P\{^1H\}$ NMR

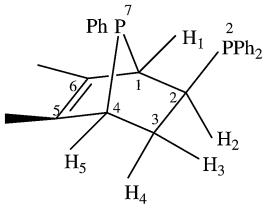
(acetone-d_6): δ 24.80 (s, 2P, P^+), −145.00 (sept., ^1J(PF) = 709 Hz, 2P, PF_6^-). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 31.11 (AXX′, ^1J(PC)| = 40.7 Hz, |^3J(PP) = 16.2 Hz, |^4J(PC) = 0.2 Hz, C_α), 26.70 (AXX′, ^3J(PP)| = 16.2 Hz, |^3J(PC) = 12.6 Hz, |^6J(PC) = 0.9 Hz, C_γ), 26.32 (AXX′, |^2J(PC)| + |^5J(PC)| = 3.5 Hz, C_β), 25.62 (AXX′, |^4J(PC)| + ^7J(PC)| = 1.8 Hz, C_δ), 9.43 (AXX′, ^1J(PC)| = 44.6 Hz, |^3J(PP) = 16.2 Hz, |^2J(PC) = −4.6 Hz, $C_{a,a'}$). IR (PF_6 region, Nujol, cm^{-1}): 840.

Preparation of [(η^5-MeC_5H_4)Ru(CO)(Br)(DCVP)] (10). A 100 mL, three-neck round-bottom flask was charged with 1.0 g (3.2 mmol) of [(η^5-MeC_5H_4)Ru(CO)$_2$Br], 40 mL of benzene and 1 mL (4.5 mmol) of DCVP. This solution was then brought to reflux under a nitrogen atmosphere. A tenth-molar amount (40 mg) of the catalyst [(η^5-C_5H_5)Fe(CO)$_2$]$_2$[21] was added to the refluxing mixture. The reaction progress was monitored by IR spectroscopy in the CO region. After 2 hours of reflux the reaction was complete (bands at 1996 cm^{-1} and 2045 cm^{-1} disappeared). Solvent was removed leaving a brown, oily residue. This residue was dissolved in CH_2Cl_2 and passed through a silica gel column packed with hexane and eluted with CH_2Cl_2. Recrystallization from hot isopropanol gave 1.35 g of red crystals in 83% yield. Mp: 103–105 °C. Anal. calc. for $C_{21}H_{31}BrOPRu$: C, 49.28; H, 6.06. Found: C, 49.13; H, 6.00%. ^1H NMR (CD_2Cl_2): δ 6.37 (ddd, $^3J(H_aH_c)$ = 18.5 Hz, $^3J(H_aH_b)$ = 12.5 Hz, ^2J(PH) = 15.0 Hz, 1H, H_a), 5.99 (ddd, ^3J(PH) = 35.0 Hz, $^3J(H_aH_b)$ = 12.5 Hz, $^2J(H_bH_c)$ = 1.5 Hz, 1H, H_b), 5.80 (ddd, $^3J(H_aH_c)$ = 18.5 Hz, ^3J(PH) = 16.5 Hz, $^2J(H_bH_c)$ = 1.5 Hz, 1H, H_c), 5.01 (m, 1H, H_2Cp), 4.85 (m, 2H, H_2Cp), 4.71 (m, 1H, H_1Cp), 2.09 (m, 2H, H_α), 2.02 (d, J(PH) = 1.0 Hz, 3H, CH_3Cp), 1.85 (m, 8H, H_β), 1.29 (m, 12H, $H_{\gamma,\delta}$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 31.35 (s, 1P, DCVP). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 205.44 (d, |^2J(PC) = 19.9 Hz, CO), 132.66 (d, ^1J(PC)| = 18.0 Hz, $C_{\alpha'}$), 131.57 (s, $C_{\beta'}$), 110.04 (d, J(PC)| = 2.6 Hz, Cp_q), 86.32 (d, J(PC) = 1.5 Hz, C_1Cp), 82.57 (s, C_2Cp), 80.40 (d, J(PC) = 5.4 Hz, C_1Cp), 77.77 (s, C_2Cp), 37.94 (d, ^1J(PC) = 25.3 Hz, C_α), 37.67 (d, ^1J(PC) = 28.3 Hz, C_α), 29.41 (s, C_β), 29.21 (d, ^3J(PC) = 2.0 Hz, C_γ), 29.09 (s, C_β), 28.79 (s, C_β), 27.82 (d, ^3J(PC) = 2.0 Hz, C_γ), 27.73 (s, C_β), 27.64 (d, ^3J(PC) = 11.8 Hz, C_γ), 27.49 (d, ^3J(PC) = 11.3 Hz, C_γ), 26.95 (d, ^4J(PC) = 1.3 Hz, C_δ), 26.83 (d, ^4J(PC) = 1.4 Hz, C_δ), 13.89 (d, J(PC) = 0.6 Hz, CH_3Cp). IR (CO region, CH_2Cl_2, cm^{-1}): 1948. $E_{1/2}$ = 0.46 V *vs.* F_c/F_c^+.

Preparation of [(η^5-MeC_5H_4)Ru(CO)(CH_3CN)(DCVP)]PF_6 (11). A 250 mL, three-neck round-bottom flask was charged with 1.25 g (2.4 mmol) of [(η^5-MeC_5H_4)Ru(CO)(Br)(DCVP)] 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 0.7 g (2.8 mmol) of $AgPF_6$ was added. The solution was heated at reflux overnight. AgBr was separated by filtration through Celite and the solvent was evaporated. The green-yellow residue 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 0.72 g of yellow crystals in 48% yield. Mp: 142–145 °C. Anal. calc. for $C_{23}H_{31}F_6NOP_2Ru$: C, 44.91; H, 5.04. Found: C, 44.76; H, 4.96%. ^1H NMR (CD_2Cl_2): δ 6.18 (m, 2H, $H_{a,b}$), 5.81 (m, 1H, H_c), 5.29 (m, 1H, Cp), 5.15 (m, 1H, Cp), 5.05 (bs, 1H, Cp), 4.85 (m, 1H, Cp), 2.36 (d, ^5J(PH) = 1.0 Hz, 3H, CH_3CN), 2.08 (m, 2H, H_α), 1.97 (d, J(PH) = 1.5 Hz, CH_3Cp), 1.84 (m, 8H, H_β), 1.30 (m, 12H, $H_{\gamma,\delta}$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 202.03 (d, |^2J(PC) = 17.2 Hz, CO), 134.49 (d, ^2J(PC)| = 1.5 Hz, $C_{\beta'}$), 129.53 (s, CN), 128.99 (d, ^1J(PC) = 38.3 Hz, $C_{\alpha'}$), 110.34 (d, J(PC) = 2.5 Hz, Cp), 85.61 (s, Cp), 85.25 (s, Cp), 80.62 (d, J(PC) = 3.6 Hz, Cp), 79.13 (s, Cp), 38.06 (d, ^1J(PC) = |25.9 Hz, C_α), 37.65 (d, ^1J(PC) = 29.5 Hz, C_α), 28.80 (d, ^2J(PC) = 2.0 Hz, C_β), 28.66 (s, C_β), 28.49 (d, ^2J(PC) = 2.5 Hz, C_β), 28.39 (s, C_β), 27.36 (d, ^3J(PC) = 2.8 Hz, C_γ), 27.26 (d, ^3J(PC) = 2.9 Hz, C_γ), 27.17 (d, ^3J(PC) = 2.4 Hz, C_γ), 26.48 (d, ^4J(PC) = 1.3 Hz, C_δ), 26.44 (d, ^4J(PC) = 1.5 Hz, C_δ), 13.12 (d, J(PC) = 0.6 Hz, CH_3Cp), 4.30 (s, CH_3CN). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 48.53 (s, 1P, DCVP), −145.0 (sept., ^1J(PF) = 711 Hz, 1P, PF_6^-). IR (CO region, CH_2Cl_2, cm^{-1}): 1984, IR (CN region, CH_2Cl_2, cm^{-1}): 2360, 2342.

Preparation of [(η^5-C_5Me_5)Ru(CO)(CH_3CN)(DPVP)]PF_6 (12). A 250 mL, three-neck round-bottom flask was charged with 2.19 g (3.9 mmol) of [(η^5-Me_5C_5)Ru(CO)(Br)(DPVP)] 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 1.20 g (4.7 mmol) of $AgPF_6$ was added. The solution was heated at reflux overnight. AgBr was separated by filtration through Celite and the solvent was evaporated. The green-yellow residue 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 1.82 g of pure product in 70% yield. Mp: 185–190 °C. Anal. calc. for $C_{27}H_{31}F_6NOP_2Ru$: C, 48.90; H, 4.68. Found: C, 48.56; H, 4.39%. ^1H NMR ($CDCl_3$): δ 7.46 (m, 8H, Ph), 7.36 (m, 2H, H_o), 6.22 (ddd, ^2J(PH) = 22.0 Hz, $^3J(H_aH_c)$ = 18.0 Hz, $^3J(H_aH_b)$ = 12.0 Hz, 1H, H_a), 6.20 (dd, ^3J(PH) = 40.0 Hz, $^3J(H_aH_b)$ = 12.0 Hz, 1H, H_b), 5.49 (dd, ^3J(PH) = 20.0 Hz, $^3J(H_aH_c)$ = 18.0 Hz, 1H, H_c), 2.20 (s, 3H, CH_3CN), 1.65 (d, J(PH) = 1.5 Hz, 15H, $5CH_3Cp^*$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 202.83 (d, |^2J(PC) = 18.6 Hz, CO), 133.04 (d, ^2J(PC)| = 10.9 Hz, C_o), 132.55 (d, ^2J(PC) = 10.7 Hz, C_o), 131.66 (s, $C_{\beta'}$), 131.27 (d, ^1J(PC) = 48.1 Hz, $C_{\alpha'}$), 131.10 (s, C_p), 131.07 (s, C_p), 130.80 (d, ^1J(PC)| = 48.9 Hz, C_i), 130.10 (d, ^1J(PC) = 48.6 Hz, C_i), 129.00 (d, ^3J(PC) = 10.9 Hz, C_m), 128.91 (d, ^3J(PC) = 10.7 Hz, C_m), 127.89 (s, CN), 97.48 (d, J(PC) = 1.6 Hz, Cp*), 9.40 (s, $5CH_3Cp^*$), 3.57 (s, CH_3CN). $^{31}P\{^1H\}$ NMR (acetone-d_6): δ 39.20 (s, 1P, DPVP), −145.0 (sept., ^1J(PF) = 707 Hz, 1P, PF_6^-). IR (CO region, CH_2Cl_2, cm^{-1}): 1970, IR (CN region, Nujol, cm^{-1}): 2319, 2284.

Preparation of [(η^5-MeC_5H_4)Ru(CO)(DMPP)(DPVP)]PF_6 Diels–Alder adduct (13). A 100 mL, three-neck round-bottom flask was charged with 0.43 g (0.7 mmol) of [(η^5-MeC_5H_4)Ru(CH_3CN)(CO)(DPVP)]PF_6 and 50 mL of 1,2-dichloroethane. The whole was stirred under a nitrogen atmosphere for 40 min., and then 0.2 mL (1.1 mmol) of DMPP was added *via* syringe. The mixture was refluxed for 3 days (change of color was noticed: yellow to orange). Recrystallization from CH_2Cl_2–hexane gave 0.22 g of yellow crystals (diastereoisomers **13A** and **13B** in 1.2 : 1 ratio) in 39% yield. Recrystallization from CH_3NO_2–diethyl ether resulted in formation of 0.12 g of diastereomer **13A** in 21% yield.Mp: 180 °C (decomp.). Anal.



calc. for $C_{35}H_{33}F_6O_{1.5}P_3Ru$: C, 53.46; H, 4.20. Found: C, 53.51; H, 4.06%. ^1H NMR (CD_3NO_2): δ 7.96 (m, 2H, H_o), 7.72 (m, 2H, H_o), 7.67 (m, 3H, $H_{m,p}$), 7.58 (m, 3H, $H_{m,p}$), 7.50 (m, 3H, $H_{m,p}$), 7.44 (m, 2H, H_o), 5.41 (m, 1H, Cp), 4.84 (m, 2H, Cp), 4.77 (m, 1H, Cp), 3.79 (dd, $^3J(H_1H_2)$ = 2.0 Hz, $^4J(H_1H_5)$ = 2.0 Hz, 1H, H_1), 3.42 (ddddd, ^3J(PH) = 41.0 Hz, $^3J(H_2H_4)$ = 8.5 Hz, ^2J(PH) = 6.5 Hz, $^3J(H_2H_3)$ = 2.0 Hz, $^3J(H_1H_2)$ = 2.0 Hz, 1H, H_2), 3.19 (dd, $^4J(H_1H_5)$ = 2.0 Hz, $^3J(H_3H_5)$ = 1.5 Hz, 1H, H_5), 1.97 (m, 2H, $H_{3,4}$), 1.84 (s, 3H, CH_3), 1.78 (s, 3H, CH_3), 1.58 (s, 3H, CH_3). $^{31}P\{^1H\}$ NMR (CD_3NO_2): δ 141.06 (d, ^2J(PP) = 37.0 Hz, 1P, P_7), 69.81 (d, ^2J(PP) = 37.0 Hz, 1P, P_2), −145.0 (sept., ^1J(PF) = 707 Hz, 1P, PF_6^-). $^{13}C\{^1H\}$ NMR (CD_3NO_2): δ 201.95 (dd, |^2J(PC) = 16.5 Hz, |^2J(PC) = 13.2 Hz, CO), 138.36 (d, |^2J(PC) = 2.3 Hz, C_5), 134.73 (d, |^1J(PC) = 40.9 Hz, C_i), 134.13 (d, |^2J(PC) = 11.4 Hz, C_o), 131.78 (d, |^4J(PC) = 2.4 Hz, C_p), 131.70 (d, |^3J(PC) = 3.6 Hz, C_6), 131.44 (d, |^2J(PC) = 10.6 Hz, C_o), 131.30 (d, |^1J(PC) = 10.6 Hz, C_i),

131.04 (d, $|^2J(PC) = 9.8$ Hz, C_o), 131.03 (d, $|^4J(PC) = 2.4$ Hz, C_p), 130.97 (d, $|^4J(PC) = 2.8$ Hz, C_p), 130.73 (dd, $|^1J(PC) = 16.1$ Hz, $|^3J(PC) = 1.4$ Hz, C_i), 129.17 (d, $|^3J(PC) = 10.9$ Hz, C_m), 128.95 (d, $|^3J(PC) = 10.2$ Hz, C_m), 128.91 (d, $|^3J(PC) = 10.3$ Hz, C_m), 107.07 (d, $J(PC) = 1.1$ Hz, Cp_q), 89.27 (s, Cp), 87.35 (d, $J(PC) = 3.3$ Hz, Cp), 87.15 (s, Cp), 85.90 (d, $J(PC) = 3.0$ Hz, Cp), 56.65 (dd, $|^1J(PC) = 35.3$ Hz, $^2J(PC) = 13.7$ Hz, C_1), 49.60 (dd, $|^1J(PC) = 33.1$ Hz, $^3J(PC) = 1.4$ Hz, C_4), 32.51 (dd, $|^1J(PC) = 37.1$ Hz, $^2J(PC) = 31.8$ Hz, C_2), 31.11 (dd, $|^2J(PC) = 17.3$ Hz, $^2J(PC) = 2.9$ Hz, C_3), 13.59 (dd, $|^2J(PC) = 2.8$ Hz, $^4J(PC) = 1.6$ Hz, $CH_{3(6)}$), 13.37 (d, $|^2J(PC) = 3.5$ Hz, $CH_{3(5)}$), 11.81 (s, CH_3Cp). IR (CO region, CH_2Cl_2, cm^{-1}): 1982.

Preparation of [(η^5-C_5Me_5)Ru(CO)(DMPP)(DPVP)]PF_6 Diels–Alder adduct (14). A 250 mL, three-neck round-bottom flask was charged with 0.88 g (1.3 mmol) of [(η^5-C_5Me_5)Ru(CH_3CN)(CO)(DPVP)]PF_6 and 100 mL of 1,2-dichloroethane. The whole was stirred under a nitrogen atmosphere for 40 min., and then 0.4 mL (2.1 mmol) of DMPP was added *via* syringe. The mixture was refluxed for 3 days (change of color was noticed: yellow to orange). Recrystallization from CH_2Cl_2–hexane gave 0.43 g of yellow crystals (diastereoisomers **14A** and **14B** in 2 : 1 ratio) in 40% yield. Recrystallization from CH_3NO_2–diethyl ether resulted in formation of 0.30 g of diastereomer **14A** in 28% yield. Mp: 275 °C (decomp.). Anal. calc. for $C_{37}H_{41}F_6OP_3Ru$: C, 54.84; H, 5.06. Found: C, 54.66; H, 4.91%. ^{1}H NMR (acetone-d_6): δ 7.90 (m, 2H, H_o), 7.74 (m, 4H, H_m), 7.61 (m, 3H, H_p), 7.53 (m, 4H, $H_{o,m}$), 7.32 (m, 2H, H_o), 4.17 (dd, $^3J(H_1H_2) = 2.1$ Hz, $^4J(H_1H_5) = 2.0$ Hz, 1H, H_1), 3.45 (ddddd, $^3J(PH) = 40.0$ Hz, $^3J(H_2H_4) = 8.0$ Hz, $^2J(PH) = 6.5$Hz, $^3J(H_1H_2) = 2.1$ Hz, $^3J(H_2H_3) = 1.5$ Hz, 1H, H_2), 3.06 (dddd, $^4J(H_1H_5) = 2.0$ Hz, $^3J(H_3H_5) = 4.0$ Hz, $^2J(PH) = 0.8$ Hz, $^3J(H_4H_5) = 0.5$ Hz,1H, H_5), 1.86 (app tdd, $^2J(H_3H_4) = {}^3J(PH) = 14.0$ Hz, $^3J(H_3H_5) = 4.0$ Hz, $^3J(H_2H_3) = 1.5$ Hz, 1H, H_3), 1.80 (m, H_4), 1.75 (s, 3H, CH_3), 1.54 (s, 15H, $5CH_3Cp^*$), 1.45 (d, $^4J(PH) = 0.5$ Hz, 3H, CH_3). $^{31}P\{^1H\}$ NMR (acetone-d_6): δ 142.88 (d, $^2J(PP) = 35.1$ Hz, 1P, P_7), 72.67 (d, $^2J(PP) = 35.1$ Hz, 1P, P_2), −144.77 (sept., $^1J(PF) = 707$ Hz, 1P, PF_6^-). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 205.44 (dd, $|^2J(PC) = 16.8$ Hz, $|^2J(PC) = 12.6$ Hz, CO), 139.90 (d, $|^2J(PC) = 2.4$ Hz, C_5), 135.44 (d, $|^2J(PC) = 11.2$ Hz, C_o), 133.60 (d, $|^2J(PC) = 10.1$ Hz, C_o), 133.05 (s, C_6), 132.90 (d, $|^2J(PC) = 9.4$ Hz, C_o), 132.20 (d, $|^1J(PC) = 42.5$ Hz, C_i), 132.19 (d, $|^1J(PC) = 41.9$ Hz, C_i), 132.12 (d, $|^4J(PC) = 2.5$ Hz, C_1), 131.91 (d, $|^4J(PC) = 2.3$ Hz, C_p), 130.30 (d, $|^3J(PC) = 10.7$ Hz, C_m), 129.85 (d, $|^3J(PC) = 9.9$ Hz, C_m), 129.70 (d, $|^3J(PC) = 9.4$ Hz, C_m), 128.91 (dd, $|^1J(PC) = 40.7$ Hz, $|^3J(PC) = 2.8$ Hz, C_i), 100.42 (app t, $J(PC) = 1.1$ Hz, Cp*), 57.38 (dd, $|^1J(PC) = 32.5$ Hz, $|^2J(PC) = 13.8$ Hz, C_1), 51.68 (dd, $|^1J(PC) = 33.2$ Hz, $|^3J(PC) = 1.3$ Hz, C_4), 35.15 (dd, $|^2J(PC) = 37.2$ Hz, $|^2J(PC) = 29.5$ Hz, C_3), 33.04 (dd, $|^1J(PC) = 12.8$ Hz, $|^2J(PC) = 2.9$ Hz, C_2), 15.11 (app t, $|^3J(PC) = |^4J(PC) = 2.5$ Hz, C_6), 13.68 (d, $^3J(PC) = 3.3$ Hz, C_5), 9.86 (s, $5CH_3Cp^*$). IR (CO region, CH_2Cl_2, cm^{-1}): 1969.

C. Ruthenium catalyzed hydration of phenylacetylene

Method A. A solution containing 2.5 mol% of the catalyst and 2 mL of phenylacetylene in 10 mL of 95% ethanol was heated at reflux overnight. Then the solution was cooled to room temperature and dried over anhydrous magnesium sulfate. After filtration, the remaining mixture was analyzed by GC/MS.

Method B. A solution containing 1.4 mol% of the catalyst and 1 mL of phenylacetylene in 15 mL of isopropanol and 3 mL of water was heated at reflux overnight. Then the solution was cooled to room temperature and dried over anhydrous magnesium sulfate. After filtration, the remaining mixture was analyzed by GC/MS.

The results are given in Table 2.

Table 3 Crystallographic data

	1	2·CH_2Cl_2	3	9	12	13A	14A
Empirical formula	$C_{33}H_{55}F_6P_3Ru$	$C_{35}H_{59}Cl_2F_6P_3Ru$	$C_{29}H_{36}F_6OP_2$	$C_{28}H_{52}F_{12}P_4$	$C_{27}H_{31}F_6NOP_2Ru$	$C_{35.5}H_{33}F_6O_{1.5}P_3Ru$	$C_{37}H_{41}F_6OP_3Ru$
FW	759.75	858.70	576.52	740.58	662.54	791.60	809.68
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a/Å	9.6206(4)	10.1094(14)	9.6199(6)	7.934(7)	13.309(4)	10.8398(18)	11.119(2)
b/Å	23.1706(10)	12.8338(14)	12.0564(8)	12.17(2)	14.461(4)	19.6539(18)	27.564(5)
c/Å	15.5767(7)	17.610(2)	13.1906(8)	17.83(4)	15.945(5)	16.9986(15)	12.1072(19)
α/°	90	101.606(11)	72.1230(10)	90	90	90	90
β/°	95.2030(10)	100.011(14)	75.2560(10)	100.60(14)	108.71(4)	104.883(9)	94.171(15)
γ/°	90	113.171(11)	69.1020(10)	90	90	90	90
V/Å^3	3458.0(3)	1974.7(4)	1342.01(15)	1692(5)	2906.6(16)	3500.0(7)	3700.7(11)
Z	4	2	2	2	4	4	4
d_{calcd} /g cm^{-3}	1.459	1.444	1.427	1.453	1.514	1.502	1.453
μ/mm^{-1}	0.647	0.706	0.226	0.309	0.709	0.646	0.612
$R1(F)/\omega R2(F^2)^a$	0.0547/0.1602	0.0721/0.1488	0.0657/0.1885	0.0588/0.1455	0.0757/0.1428	0.0665/0.1565	0.0684/0.1325

^{a} Final R indices have $I > 2\sigma(I)$. $R1(F) = \Sigma(||F_o|| - ||F_c||)/\Sigma||F_o||$; $wR2(F^2) = [\Sigma w(||F_o^2|| - ||F_c^2||)^2/\Sigma w(||F_o^2||^2]^{1/2}$.

D. X-Ray crystallographic studies

Single crystals of **1**, **2**, **3**, **9**, **10**, **11**, **12**, **13B** and **14B** were obtained as follows: slow diffusion of hexane into a CH_2Cl_2 solution (**2**, **3**, **11** and **12**), slow diffusion of diethyl ether into a CH_2Cl_2–MeOH solution (**1**), slow diffusion of diethyl ether–hexane into an acetone solution (**9**), slow diffusion of diethyl ether into a nitromethane solution (**13A** and **14A**) and slow crystallization from hot isopropanol (**10**). Compound **13A** is a disordered hemi etherate and solvent hydrogens were not included. The crystals of **2**, **12**, **13A** and **14A** 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-K_α radiation ($\lambda = 0.71073$ 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 empirical model derived from azimuthal data collections). Scattering factors and corrections for anomalous dispersion were taken from a standard source.[22] For **1**, **3** and **9** data collection was carried out on a Bruker SMART diffractometer with the crystal mounted in a nitrogen stream at 100 K. The structures were solved by direct methods and refined by full-matrix least-squares on F^2. Calculations were performed within the Siemens SHELXTL Plus[23] software package on a PC. The structures were solved by direct or 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. 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 $\omega R2(F^2)$ values given in Table 3, where $\omega^{-1} = \sigma^2(F) + 0.001F^2$.

CCDC reference numbers 248575–248583.

See http://www.rsc.org/suppdata/dt/b4/b413446j/ for crystallographic data in CIF or other electronic format.

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