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Hemilabile Properties of the η^3-Allyldiphenylphosphine (ADPP) Homophosphaallyl Ligand: Synthesis and Reactions of $[(\eta^5\text{-}C_5Me_5)Ru(\eta^3\text{-ADPP})(\eta^1\text{-ADPP})][PF_6]$

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Pentamethylcyclopentadienylruthenium(II) half-sandwich complexes containing the alkenyl phosphine ligand allyldiphenylphosphine (ADPP) are described. ADPP reacts with $[(\eta^5\text{-}C_5Me_5)RuCl_2]_2$ to give the disubstituted ruthenium(II) compound $[(\eta^5\text{-}C_5Me_5)Ru(\eta^3\text{-ADPP})(\eta^1\text{-ADPP})][PF_6]$ (**1**). The dynamic behavior of compound **1** has been studied by variable temperature ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. The hemilabile properties of the novel η^3-ADPP ligand, a neutral monometallic homophosphaallyl, are illustrated by reactions of compound **1** with sodium thiocyanate, carbon monoxide, and terminal alkynes. Compound **1** reacts with NaNCS, CO, $HC{\equiv}C(C_6H_5)$, $HC{\equiv}CCH_2OH$, and $HC{\equiv}CCH_2CH_2OH$ to form $[(\eta^5\text{-}C_5Me_5)Ru(\eta^1\text{-ADPP})_2(NCS)]$ (**2**), $[(\eta^5\text{-}C_5Me_5)Ru(\eta^1\text{-ADPP})_2(CO)][PF_6]$ (**3**), $[(\eta^5\text{-}C_5Me_5)Ru(\eta^1\text{-ADPP})_2\{C{=}C(H)(C_6H_5)\}][PF_6]$ (**4**), unstable $[(\eta^5\text{-}C_5Me_5)Ru(\eta^1\text{-ADPP})_2\{C{=}C(H)(CH_2OH)\}][PF_6]$ (**5**), and $[(\eta^5\text{-}C_5Me_5)Ru(\eta^3\text{-ADPP})\{\overline{C(CH_2)_3O}\}][PF_6]$ (**6**), respectively. Compound **6** is unusual because its formation is accompanied by the loss of one ADPP ligand, unlike the other substitution products **2**−**5**. Compound **6** is dynamic and readily epimerizes in solution. The characteristic ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopic features of all compounds are described. Crystal data for **6**: monoclinic space group $P2_1/n$, $a = 9.711(1)$ Å, $b = 12.418(2)$ Å, $c = 24.363(7)$ Å, $\beta = 99.60(2)°$, $V = 2896.9(10)$ $Å^3$, $Z = 4$, $D_c = 1.554$ g cm^{-3}, $R = 0.0336$.

Introduction

An expanding area of interest in organometallic chemistry is the use of "hybrid" ligands[1] in their transition metal complexes. Hybrid ligands contain two or more chemically different donor atoms. Hybrid ligands often contain functionalities that display hemilabile[2] properties. Hemilabile ligands can reversibly create or occupy a vacant coordination site on a transition metal. Consequently, hybrid hemilabile ligands may enhance selectivity in catalytic systems or stabilize reactive intermediates.[1−3] Ligands such as phosphino ethers, amines, and esters are known to exhibit hemilabile behavior.[2a−p] For example, Werner and co-workers have demonstrated the hemilabile properties of $Pr^i_2PCH_2CH_2OMe$ in the complex $[RuCl_2(\kappa\text{-}P,\kappa\text{-}O\text{-}Pr^i_2PCH_2CH_2OMe)_2]$ by displacement of the metal−O bond with CO and $HC{\equiv}C(C_6H_5)$.[2b] The $[(\eta^5\text{-}C_5Me_5)RuCl\{\kappa\text{-}P,\kappa\text{-}O\text{-}Pr^i_2PCH_2CO_2Me\}]$ compound behaved similarly.[2h] The $Pr^i_2PCH_2CH_2OMe$ and $Pr^i_2PCH_2CH_2NMe$ ligands, when bound to iridium catalyst precursors, exhibited hemilabile properties when used in the hydrogenation of phenylacetylene.[2d] Finally, Shell uses a nickel complex of a hybrid hemilabile phosphine in their large-scale commercial oligomerization of ethylene to linear α-olefins.[2i−k]

Our investigations with alkenyl phosphines as hybrid hemilabile ligands, specifically diphenylvinylphosphine (DPVP), resulted in the synthesis of compounds **A**, $[(\eta^5\text{-}C_5H_5)Ru(\eta^3\text{-DPVP})(\eta^1\text{-DPVP})][PF_6]$,[4] and **B**, $[(\eta^5\text{-}C_5Me_5)Ru(\eta^3\text{-DPVP})(\eta^1\text{-DPVP})][PF_6]$.[5] Compounds **A** and **B** contain the η^3-DPVP ligand which is a neutral, monometallic phosphaallyl ligand. The hemilabile character of the phosphaallyl ligand in **A** was illustrated by the reactions shown in Scheme 1. The hemilabile character of the phosphaallyl ligand in **B** was demonstrated by similar reactions.[5]

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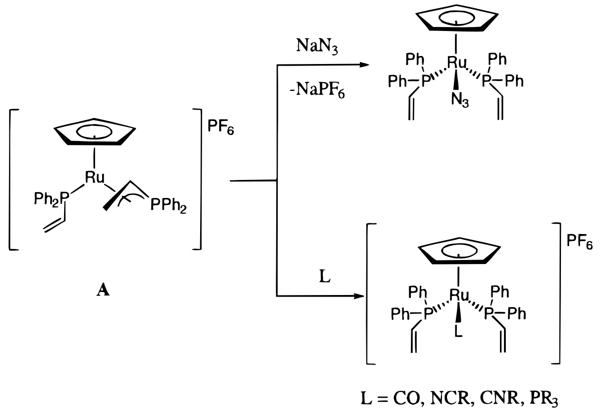
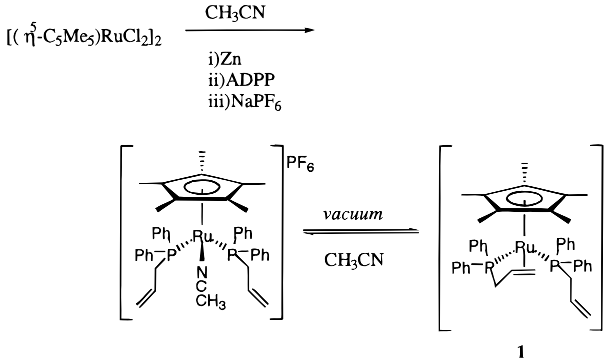
Scheme 1. Reactions of the Phosphaallyl Complex A[4]



Because of our interest in the hemilabile properties of the η^3-allyldiphenylphosphine (ADPP) ligand, we have prepared the ruthenium(II) compound $[(\eta^5\text{-}C_5Me_5)Ru(\eta^3\text{-ADPP})(\eta^1\text{-ADPP})][PF_6]$ (**1**), a close analog of **B**. Compound **1** contains the first example of the η^3-ADPP ligand, a neutral monometallic homophosphaallyl ligand. Herein we report the synthesis, characterization and preliminary reactivity studies of the novel compound **1**.

Results and Discussion

Synthesis and Properties of $[(\eta^5\text{-}C_5Me_5)Ru(\eta^3\text{-ADPP})(\eta^1\text{-ADPP})][PF_6]$ (1). Compound **1** is prepared *via* the same method as that used for **B**.[5] An acetonitrile solution of $[(\eta^5\text{-}C_5Me_5)RuCl_2]_2$ is treated with excess zinc, followed by addition of ADPP and then sodium hexafluorophosphate to give the desired product, **1**, in 67% isolated yield (eq 1). Compound **1** is bright yellow and air-stable as a solid but gradually decomposes in oxygenated solutions. Similar to what was observed for compound **B**,[5] compound **1** reversibly binds acetonitrile; however, all attempts to isolate the acetonitrile adduct of **1** resulted in decomposition of the complex. The reversible binding of acetonitrile as well as Me_2S has also been observed for cationic arene−ruthenium(II) complexes of the type, $[(\eta^6\text{-arene})Ru(\kappa\text{-}P,\kappa\text{-}O\text{-}Ph_2PCH_2C({=}O)OMe)(Cl)]^+$ (where arene = mesitylene, hexamethylbenzene), which contain the hemilabile $\kappa\text{-}P,\kappa\text{-}O\text{-}Ph_2PCH_2C({=}O)OMe$ ligand.[2o]



(1)

The $^{31}P\{^1H\}$ NMR spectrum of **1** in chloroform-*d* at ambient temperature shows two broad resonances for the inequivalent phosphines at 44 and −72 ppm. The breadth of these resonances ($\Delta\nu_{1/2}$ = 73 and 30 Hz, respectively) and the absence of P−P coupling suggest dynamic behavior. The spectrum of **1** contrasts with that of **B** which shows two doublets at 44 and 13 ppm. One explanation for the fluxional behavior in **1** is isomerization of the metal-coordinated alkene from the presumably preferred parallel position with respect to the η^5-C_5Me_5 ring to a perpendicular position (*vide infra*). Clark and Jones[6ab] have observed a similar phenomenon with the η^3-tribut-3-enylphosphine in the square planar complexes, $RhX\{P(CH_2CH_2CH{=}CH_2)_3\}$, where X = Cl,[6a] Br,[6a] I.[6b] The dynamic behavior of **1** was probed by variable temperature $^{31}P\{^1H\}$ NMR spectroscopy in chloroform-*d* from −60 to 50 °C as shown in Figure 1. The single broad resonance at 44 ppm separates into two resonances at 10 °C, while the resonance at −72 ppm begins to separate at −10 °C. At −20 °C two doublets are clearly visible which represent one compound with inequivalent phosphines. In addition, two broad resonances are also visible at 44 and −77 ppm at −20 °C. At −60 °C, three compounds are present as represented by three *sets* of doublets at 49.17 and −69.66 ppm ($^2J_{PP}$ = 42.9 Hz); 42.75 and −77.39 ppm ($^2J_{PP}$ = 43.9 Hz); and 39.57 and −59.88 ppm ($^2J_{PP}$ = 35.7 Hz), with an integrated intensity ratio of 4.4:2.9:1, respectively. The two major sets of doublets represent the two-diastereomeric conformations of the coordinated alkene, since the two faces of the alkene are diastereotopic when the ADPP ligand is bound in a bidentate manner. The minor resonances may represent a dimeric form of compound **1** (*vide infra*).

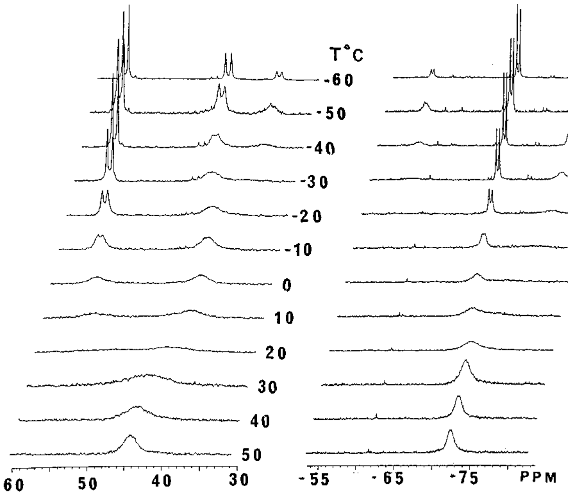


Figure 1. 121.65 MHz variable temperature $^{31}P\{^1H\}$ NMR spectra of **1** in $CDCl_3$ from −60 to 50 °C.

The ^1H NMR spectrum of **1** in chloroform-*d* at room temperature (Supporting Information) contains broad, featureless resonances for both the coordinated and uncoordinated alkene hydrogens. Broadening of the proton resonances of disubstituted metal−ADPP complexes is not unusual, since we have previously observed similar spectra for $[(\eta^5\text{-}C_5Me_5)Rh(\eta^1\text{-ADPP})_2(Cl)][PF_6]$ as a result of second-order effects from coupling to both phosphorus nuclei.[7] However, the ^1H NMR spectrum at −50 °C shows the same ratio of the two isomers of **1** as observed in the low-temperature $^{31}P\{^1H\}$ NMR spectrum. The ^1H and $^{31}P\{^1H\}$ NMR spectra at 60 °C indicate that some of the coordinated ADPP slowly dissociates and is subsequently oxidized to the phosphine oxide ($\delta^{31}P$ = 28.3 ppm) with a half-life of several hours.

Analysis of a framework molecular model suggests that the η^3-ADPP ligand cannot undergo a "CH_2-twitch" as described by Maitlis and co-workers for the η^5-$C_5Me_4CH_2CH_2CH{=}CH_2$ "bidentate" ligand in the $[(\eta^5\text{-}C_5Me_4CH_2CH_2CH{=}CH_2)IrCl_2]$

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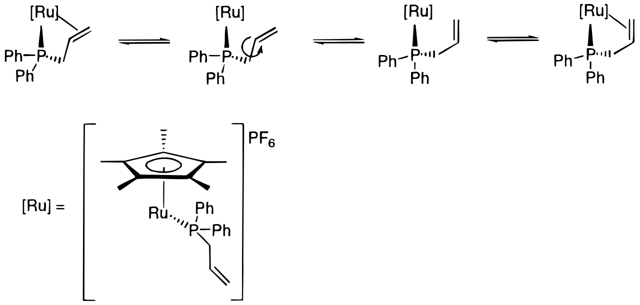
Scheme 2. Olefin Rotation of the η^3-ADPP Ligand



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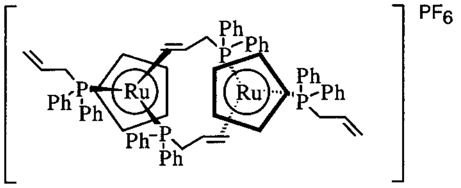
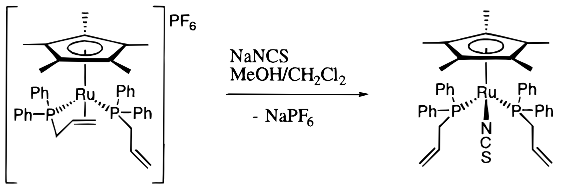
Scheme 3. Proposed Dimeric Intermediate for Olefin Exchange for Compound **1** in Solution[a]



[a] Top view of proposed dimeric structure is shown (methyl groups omitted for clarity).

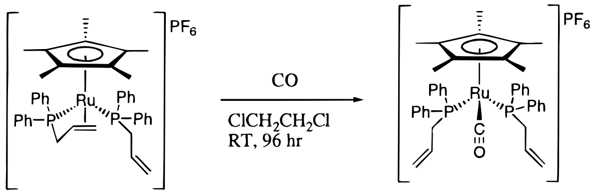
complex.[8] In this complex, the methylene linkages are fluxional while the iridium-bound alkene remains coordinated, but the alkene may coordinate in a parallel or perpendicular geometry with respect to the η^5-C$_5$Me$_4$R ring. For compound **1**, only one methylene group links the alkene moiety to the metal-bound phosphorus and such a "twitch" is not possible without breaking the metal−phosphorus bond. Analysis of the variable temperature ^{1}H NMR spectra for **1** shows that coalescence occurs at about 0 °C with $\Delta G^{\ddagger}_{273}$ of about 52.7 kJ mol^{-1}. Recent determinations of ruthenium−phosphorus bond enthalpies[9] toward the (η^5-C$_5$Me$_5$)RuCl moiety are in the 75.3−156.9 kJ mol^{-1} range, with that for the closest analog to ADPP, MePPh$_2$, being 123.0 kJ mol^{-1}. Therefore, the dynamic behavior of **1** likely involves metal−alkene bond dissociation followed by C−C rotation and re-coordination of the metal−alkene bond (Scheme 2). Such a process may also participate in the alkene exchange between ADPP ligands and/or the dimer shown in Scheme 3, which may be the minor species observed in the ^{31}P{^{1}H} NMR spectrum of **1** at −60 °C. In support of a μ-ADPP dimeric complex, the diphenylvinylphosphine (DPVP) ligand has been shown to bridge two metals in many complexes including bimetallic palladium,[10a] manganese,[10b] iron,[10c] molybdenum,[10d] osmium,[10e] and ruthenium[10e] cluster compounds. In the latter two examples, the metal abstracts a hydrogen from the vinyl moiety in forming the bridging ligand.[10c] A more limited number of complexes containing bridging ADPP ligands are known.[11] The dynamic behavior of compound **1** may also account for its increased sensitivity to oxygen in solution (compared to **B**) since complexes of the type [(η^5-C$_5$Me$_5$)RuP$_2$]$^+$ (where P = phosphines) form stable η^2-O$_2$ adducts.[2g,12]

Reaction Studies of 1 with Nucleophilic Ligands (L). Treatment of a dichloromethane/methanol solution of **1** with an excess of NaNCS at room temperature results in the formation of [(η^5-C$_5$Me$_5$)Ru(η^1-ADPP)$_2$(NCS)] (**2**) (eq 2). The ^{31}P{^{1}H} NMR spectrum of **2** in chloroform-*d* shows a singlet at 37.5 ppm, which confirms displacement of the η^2-ADPP alkene moiety and the formation of a symmetrical complex. The ^{1}H NMR spectrum shows the vinyl hydrogen resonances of the η^1-ADPP ligands as broadened, complex multiplets at 5.15, 4.29, and 4.65 ppm.[7] The diastereotopic hydrogens of the CH$_2$ groups appear as broad multiplets at 2.76 and 2.72 ppm. The η^5-C$_5$Me$_5$ methyl hydrogen resonance occurs as a triplet at 1.17 ppm ($^4J_{PH}$ = 1.5 Hz). The IR spectrum (Nujol) of **1** shows ν(N−CS) at 2100 cm^{-1} and ν(NC−S) at 805 cm^{-1}. The most notable feature of the ^{13}C{^{1}H} NMR spectrum in chloroform-*d* is the presence of the NCS carbon resonance as a triplet at 132.57 ppm ($^3J_{PC}$ = 5.41 Hz). Both the IR and ^{13}C{^{1}H} NMR data are characteristic of an N-bound NCS$^-$ moiety.[13]



1 **2** (2)

Treatment of **1** with CO in 1,2-dichloroethane at ambient temperature for 96 h results in the formation of [(η^5-C$_5$Me$_5$)Ru(η^1-ADPP)$_2$(CO)][PF$_6$] (**3**) (eq 3). The ^{31}P{^{1}H} NMR spectrum of **3** in chloroform-*d* shows a singlet at 34.6 ppm while in the ^{1}H NMR spectrum the typical complex pattern for two η^1-ADPP ligands appears. The ^{13}C{^{1}H} NMR spectrum shows a characteristic triplet at 206.39 ppm ($^2J_{PC}$ = 16.97 Hz) for the carbonyl carbon. The IR spectrum shows ν(CO) at 1954 cm^{-1}. Overall, the spectroscopic data for **3** are comparable with those of [(η^5-C$_5$Me$_5$)Ru(η^1-DPVP)$_2$(CO)][PF$_6$].[5] The substitution of CO onto compound **1** to form **3** is performed at room temperature in order to avoid the possible dissociation of one of the phosphine ligands. Even under the mild conditions shown in eq 3, the reaction goes to completion in a slightly shorter amount of time (96 h, room temperature) compared to the time required to produce [(η^5-C$_5$Me$_5$)Ru(η^1-DPVP)$_2$(CO)][PF$_6$] from **B** (116 h, reflux). In the case of compound **1**, the dynamic nature of the coordinated olefin probably facilitates ligand



1 **3** (3)

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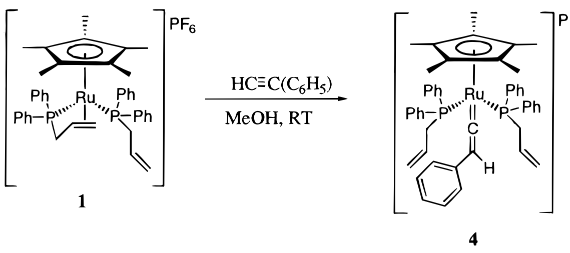
substitution. Similar to the reaction of **B** with CO, displacement of the metal−olefin bond in **1** illustrates the hemilabile properties of the η^3-ADPP ligand.

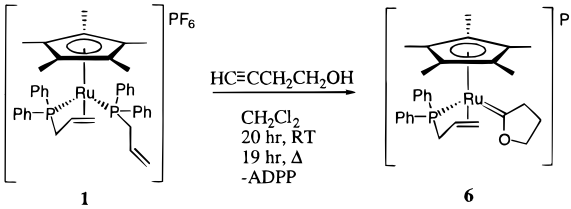
Methanol solutions of **1** react with phenylacetylene at room temperature to form the vinylidene complex $[(\eta^5\text{-}C_5Me_5)Ru(\eta^1\text{-ADPP})_2\{C{=}C(H)(C_6H_5)\}][PF_6]$ (**4**) (eq 4). The $^{31}P\{^1H\}$ NMR spectrum in chloroform-*d* exhibits a singlet at 36.7 ppm while in the ^1H NMR spectrum the unique vinylidene hydrogen resonance appears as a triplet at 5.34 ppm ($^2J_{PH}$ = 1.5 Hz). The η^5-C_5Me_5 methyl hydrogen resonance occurs as a triplet at 1.50 ppm ($^4J_{PH}$ = 1.7 Hz). The $^{13}C\{^1H\}$ NMR spectrum shows a characteristic $Ru{=}C_\alpha$ carbon resonance as a triplet at 351.98 ppm ($^2J_{PC}$ = 15.4 Hz). The spectroscopic data for **4** are comparable with those of $[(\eta^5\text{-}C_5Me_5)Ru(\eta^1\text{-DPVP})_2\{C{=}C(H)(C_6H_5)\}][PF_6]$.[5]



(4)

Treatment of a solution of **1** at ambient temperature with propargyl alcohol in dichloromethane gives a new compound after stirring for 24 h. The $^{31}P\{^1H\}$ NMR spectrum of this solution shows a singlet at 37.4 ppm. By analogy with the reaction of **B** with propargyl alcohol[5] and the reaction of **1** with phenylacetylene, the NMR data suggest that the vinylidene product, $[(\eta^5\text{-}C_5Me_5)Ru(\eta^1\text{-ADPP})_2\{C{=}C(H)(CH_2OH)\}][PF_6]$ (**5**), is the first product formed. Unfortunately, solutions containing this product slowly decomposed and tractable products were not isolated. In addition to the primary product **5**, another minor compound is spectroscopically observed in the reaction mixtures. The $^{31}P\{^1H\}$ NMR spectra of reaction mixtures contains two doublets at 93.0 and 43.5 ppm with a *cis*-phosphorus coupling constant of $^2J_{PP}$ = 35.8 Hz. The ^{31}P NMR data suggest the presence of a ruthenium complex with two nonequivalent phosphine ligands. The structure of the minor compound remains unknown.

Treatment of **1** with 3-butyn-1-ol in dichloromethane for 20 h, followed by 19 h of refluxing results in the unexpected formation of the monosubstituted η^3-ADPP cyclic carbene complex $[(\eta^5\text{-}C_5Me_5)Ru(\eta^3\text{-ADPP})\{\overline{C(CH_2)_3O}\}][PF_6]$ (**6**) (eq 5).



(5)

The $^{31}P\{^1H\}$ NMR spectrum of **6** in chloroform-*d* shows a broad resonance at 46.1 ppm. Compound **6** exhibits the same type of dynamic properties as observed for **1**. Variable temperature ^1H NMR spectroscopy shows that coalescence occurs at about 10 °C with $\Delta G^{\ddagger}_{283}$ of about 53.1 kJ mol^{-1}. The dynamic behavior of **6** results in epimerization at the ruthenium stereocenter. This could arise by dissociation−re-coordination of the alkene moiety, rotation about the Ru=C bond of the carbene, or both. Because the barrier to rotation about the Ru=C bond is expected to be about 12 kJ mol^{-1}, we believe that the most likely mechanism for epimerization involves dissociation−recoordination of the alkene moiety.[14] The most distinguishable feature in the $^{13}C\{^1H\}$ NMR spectrum (chloroform-*d*) is the $Ru{=}C_\alpha$ resonance which appears as a doublet at 299.43 ppm ($^2J_{PC}$ = 13.6 Hz). The loss of one ADPP ligand in the formation of **6** by refluxing the reaction mixture is consistent with the observations in the high-temperature ^1H NMR spectrum of **1** (*vide supra*). Compound **6** is unstable in oxygenated solvents and slowly decomposes to the phosphine oxide and unidentified ruthenium species.

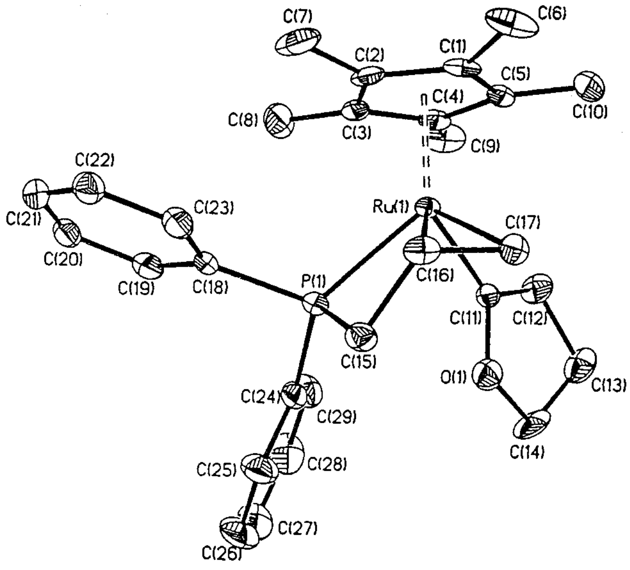


Figure 2. Structural drawing of the cation of $[(\eta^5\text{-}C_5Me_5)Ru(\eta^3\text{-ADPP})\{\overline{C(CH_2)_3O}\}][PF_6]$ (**6**) showing the atom numbering scheme (50% probability ellipsoids). Hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Distances (Å) and Angles (deg) for $[(\eta^5\text{-}C_5Me_5)Ru(\eta^3\text{-ADPP})\{\overline{C(CH_2)_3O}\}][PF_6]$ (**6**)

Bond Distances (Å)			
Ru(1)−P(1)	2.304(1)	P(1)−C(15)	1.819(4)
Ru(1)−C(11)	1.956(4)	C(15)−C(16)	1.529(5)
Ru(1)−C(16)	2.215(4)	C(16)−C(17)	1.392(6)
Ru(1)−C(17)	2.222(4)	Ru(1)−C(1)	2.257(4)
O(1)−C(11)	1.322(5)	Ru(1)−C(2)	2.273(4)
O(1)−C(14)	1.476(5)	Ru(1)−C(3)	2.256(4)
C(13)−C(14)	1.506(7)	Ru(1)−C(4)	2.267(4)
C(12)−C(13)	1.519(6)	Ru(1)−C(5)	2.267(4)
C(11)−C(12)	1.502(6)	Ru(1)−Cp*	1.913[a]
Bond Angles (deg)			
C(11)−Ru(1)−P(1)	88.8(1)	C(15)−P(1)−Ru(1)	91.3(1)
C(11)−Ru(1)−C(17)	81.1(2)	C(11)−O(1)−C(14)	113.0(3)
C(11)−Ru(1)−C(16)	103.2(2)	O(1)−C(14)−C(13)	105.0(3)
C(16)−Ru(1)−C(17)	36.6(2)	C(14)−C(13)−C(12)	102.3(3)
C(16)−Ru(1)−P(1)	65.71(10)	C(11)−C(12)−C(13)	106.7(4)
C(16)−C(15)−P(1)	93.8(2)	O(1)−C(11)−C(12)	107.6(3)

[a] Cp* denotes the centroid of the C(1−5) ring.

An X-ray crystallographic analysis confirmed the structure of **6**. A view of the molecular geometry of the cation of **6** is shown in Figure 2. Selected bond distances and angles are listed in Table 1. The analysis reveals a distorted octahedral coordination geometry at ruthenium with one η^5-C_5Me_5 ligand, one η^3-ADPP ligand, and the cyclic carbene moiety completing the coordination sphere. The Ru(1)−C(11) carbene bond distance

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(14) Nakatsuji, H.; Ushio, J.; Han, S.; Yonezawa, T. *J. Am. Chem. Soc.* **1983**, *105*, 426.

is 1.956(4) Å and the C(1)−O(1) bond distance is 1.322(5) Å, consistent with partial double-bond character. These metrical parameters are comparable with the analogous distances found for [(η^5-C_5Me_5)Ru(η^1-DPVP)$_2${$\overline{C(CH_2)_3O}$}][PF_6].[5] The remaining distances around the carbene ring are also comparable with those of this compound and warrant no further discussion. The Ru(1)−P(1) bond distance in **6** is 2.3038(11) Å, which is only slightly shorter than the Ru−P bond distance of 2.355(5) Å for the η^1-DPVP ligand in **B**. The P(1)−C(15) and C(15)−C(16) bond lengths for **6** are 1.819(4) and 1.529(5) Å, respectively, and are very similar to the analogous bonds in [(η^5-C_5Me_5)Rh(η^1-ADPP)$_2$(Cl)][PF_6], which average 1.838(7) and 1.506(10) Å, respectively.[7] The coordinated alkene is oriented parallel to the plane of the η^5-C_5Me_5 ring, which is presumed to be the favored orientation[8] and is the observed orientation in the cobalt(I) complex, [(η^5-$C_5Me_4CH_2CH_2CH{=}CH_2$)Co(L)].[3c] As expected, the metal-coordinated alkene bond distance, C(16)−C(17), of 1.392(6) Å is longer than that of the uncoordinated alkene bond distance for the η^1-ADPP ligand. The rhodium compound mentioned above has an average η^1-ADPP alkene bond distance of 1.275(10) Å. The C(16)−C(17) bond distance in **6** is also very similar to the average metal-coordinated alkene bond distance of 1.374(14) Å in the rhodium complex, RhCl{$P(CH_2CH_2CH{=}CH_2)_3$}.[6a] For compound **6**, the carbene ring adopts an envelope conformation and the deviations from the mean plane of the carbene ring defined by Ru(1), C(11), C(12), O(1) are Ru(1), −0.0018 Å; C(11), 0.0059 Å; C(12), −0.0020 Å; C(13), −0.3382 Å; C(14), 0.0322 Å; and O(1), −0.0021 Å. Similar deviations are observed for [(η^5-C_5Me_5)Ru(η^1-DPVP)$_2$-{$\overline{C(CH_2)_3O}$}][PF_6].[5]

Compound **6** represents a new starting point from which derivatives can be prepared in order to probe the hemilabile properties of the η^3-ADPP ligand in a sterically less demanding environment than that found in compound **1**, [(η^5-C_5Me_5)Ru(η^3-ADPP)(η^1-ADPP)][PF_6], and its derivatives discussed herein. Studies to address this issue are in progress.

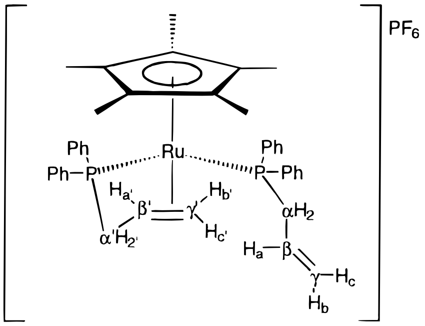
Summary

The synthesis, characterization, and properties of the homophosphaallyl compound **1** are presented for the first time. Compound **1** contains the bidentate, alkenylphosphine ligand (η^3-ADPP) that displays hemilabile properties as illustrated by displacement of the coordinated alkene moiety with CO and terminal alkynes. Compound **6** represents a potentially new starting point for continued investigations into the hemilabile properties of the ADPP ligand in complexes of the type [(η^5-C_5R_5)Ru(η^3-ADPP)L][PF_6], (where R = H, Me, L = neutral, 2e$^-$ donor).

Experimental Section

A. Reagents and Physical Measurements. All chemicals were reagent grade and were used as received from commercial sources (Aldrich or Fisher Scientific) or synthesized as described below. Allyldiphenylphosphine was purchased from Organometallics, Inc., and used as received. Solvents were dried by standard procedures and stored over Linde type 4 Å molecular sieves. All syntheses were conducted in Schlenk glassware under a nitrogen atmosphere. HC_5Me_5[15] and [(η^5-C_5Me_5)$RuCl_2$]$_2$[16] were synthesized by literature procedures. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Melting points were obtained using a Mel-Temp melting point apparatus and are uncorrected. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded at 499.86 and 125.7 MHz, respectively, on a Varian Unity Plus 500 FT-NMR spectrometer. Proton and carbon chemical shifts are relative to internal Me_4Si or solvent resonances. ^{31}P{^{1}H} NMR spectra were recorded at 121.65 MHz on a General Electric GN 300 FT-NMR spectrometer. Phosphorus chemical shifts are relative to external 85% H_3PO_4(aq) with positive values being downfield of the reference. Unless otherwise stated, all chromatography was performed using the following general procedure: A 60 mL sintered glass fritted funnel was used as the column and attached to a 1000 mL Erlenmeyer flask equipped with a sidearm. A 2.5 cm layer of silica gel (grade 12, 28−300 mesh, Aldrich) was covered with Celite (Aldrich, 0.5 cm layer) and firmly packed with a spatula and suction. The crude reaction product was dissolved in a minimal amount of a volatile solvent, (usually CH_2Cl_2), loaded onto the column, and the solvent was removed with suction. All subsequent solvents were eluted with suction.

B. Syntheses. Preparation of [(η^5-C_5Me_5)Ru(η^3-ADPP)(η^1-ADPP)][PF_6] (1). A 250 mL, three-neck round bottom flask was fitted with a septum, gas inlet adapter, and a U-tube adapter. A glass frit funnel was attached to both the U-tube and a second 250 mL round bottom flask equipped with two necks. The entire apparatus was flame-dried under vacuum and flushed with nitrogen. The first flask was charged with [(η^5-C_5Me_5)$RuCl_2$]$_2$ (2.5 g, 4.1 mmol), powdered zinc (6.6 g, 101 mmol), and 100 mL of freshly distilled CH_3CN. The dark red mixture was stirred vigorously for 2 h and gradually turned from red to green to yellow/brown. The excess zinc was removed by filtration under nitrogen and washed with 2 × 5 mL portions of CH_3CN. The yellow/brown filtrate was charged with allyldiphenylphosphine (3.95 mL, 18.3 mmol), and the solution was stirred at room temperature for 8 h. To this mixture was added a solution of $NaPF_6$ (1.7 g, 10.1 mmol) in 35 mL of MeOH. A precipitate formed upon addition of the salt solution. The reaction mixture was stirred for 45 min, after which all solvents were removed *in vacuo*. The resulting brown residue was dissolved in a minimal amount of CH_2Cl_2 and filtered, and the solvent was removed *in vacuo*. The yellow/brown residue was flash chromatographed over Celite/silica gel with 1250 mL of CH_2Cl_2 to give a yellow solution. The solvent was removed *in vacuo*, and the yellow amorphous solid was dried under high vacuum for 24 h to give 4.6 g (67%) of **1** as a bright yellow powder, which slowly decomposes over a period of several months in air. Mp: 140 °C dec. Anal. Calcd for $C_{40}H_{45}F_6P_3Ru$: C, 57.62; H, 5.13. Found: C, 57.54; H, 4.97. ^{1}H NMR ($CDCl_3$, 25 °C): δ 7.0−7.7 (m, 20H, Ph), 5.51 (m, 1H, H_a), 4.91 (m, 1H, H_b), 4.6 (m, 1H, H_c), 4.3 (m, 1H, $H_{a'}$), 3.5 (m, 1H, $H_{b'}$), 3.1 (m, 2H, CH_2), 1.95 (m, 3H, $CH_{2'}$, $H_{c'}$), 1.3 (m, 15H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): δ 136−127.8 (m, Ph, C_γ), 120.40 (d, $^2J_{PC}$ = 8.9 Hz, C_β), 96.5 (s, C_5Me$_5$), 49.17 (br, CH_2), 46.59 (br, $CH_{2'}$), 37.47 (br, $C_{\beta'}$ or $C_{\gamma'}$), 32.09 (br, $C_{\beta'}$ or $C_{\gamma'}$), 9.02 (s, CH_3). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 44 (br s, 1P, η^3-ADPP), −72 (br s, 1P, η^1-ADPP), −145.1 (septet, $^1J_{PF}$ = 712.6 Hz, PF_6^-). ^{1}H NMR ($CDCl_3$, −50 °C), *major conformer*: δ 6.8−7.8 (m, 20H, Ph), 5.71 (ddt, $^3J_{H_aH_c}$ = 17.5 Hz, $^3J_{H_aH_b}$ = 9.5 Hz, $^3J_{H_aCH_2}$ = 8.0 Hz, 1H, H_a), 5.09 (d, $^3J_{H_aH_b}$ = 9.5 Hz, 1H, H_b), 4.92 (d, $^3J_{H_aH_c}$ = 17.5 Hz, 1H, H_c), 3.9 (m, 1H, $H_{a'}$), 3.7 (m, 1H, $H_{b'}$), 3.5 (m, 1H, CH_2), 2.9 (m, 1H, CH_2), 2.04 (m, 1H, $H_{c'}$), 2.0 (m, 2H, $CH_{2'}$), 1.5 (s, 15H, CH_3). *Minor conformer*: δ 6.8−7.8 (m, 20H, Ph), 5.3 (m, 1H, H_a), 4.74 (m, 1H, H_b), 4.67 (m, 1H, H_c), 3.85 (m, 1H, $H_{a'}$), 3.33 (m, 1H, $H_{b'}$), 3.18 (m,



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1H, CH_2), 2.91 (m, 1H, CH_2), 1.54 (m, 1H, $H_{c'}$), 1.0 (s, 15H, CH_3). The ratio of major to minor conformer is 1.5:1.

Preparation of $[(\eta^5\text{-}C_5Me_5)Ru(\eta^1\text{-}ADPP)_2(NCS)]$ (2). A 25 mL Schlenk flask was charged with **1** (0.5 g, 0.6 mmol), 30 mL of CH_2Cl_2, and a solution of NaNCS (0.49 g, 6.0 mmol) in 30 mL of MeOH. The solution was stirred vigorously for 20 h and gradually turned from yellow to red. The solvents were removed *in vacuo*, and the residue was dissolved in a minimal amount of CH_2Cl_2 and filtered. The filtrate was evaporated, and the product was extracted with 8 × 20 mL of Et_2O. The Et_2O washings were combined, evaporated to dryness, and dried to give 0.45 g (98%) of **2** as a red powder. Mp: 124−126 °C. Anal. Calcd for $C_{41}H_{45}NP_2RuS$: C, 65.93; H, 6.07. Found: C, 65.78; H, 6.00. ^1H NMR ($CDCl_3$): δ 7.04−7.32 (m, 20H, Ph), 5.15 (m, 2H, H_a), 4.29 (m, 2H, H_c), 4.65 (m, 2H, H_b), 2.76 (m, 2H, CH_{2a}), 2.72 (m, 2H, CH_{2b}), 1.17 (t, $^4J_{PH}$ = 1.5 Hz, 15H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 135.31 (m, C_i), 135.12 (m, C_i), 132.95 (apparent t, $|^2J_{PC} + {}^4J_{PC}| = 10.68$ Hz, C_o), 132.57 (t, $^3J_{PC} = 5.41$ Hz, NCS), 132.56 (apparent t, $|^2J_{PC} + {}^4J_{PC}| = 8.55$ Hz, C_o), 129.0 (s, C_p), 128.83 (s, C_p), 128.24 (apparent d, $|^3J_{PC} + {}^5J_{PC}| = 12.07$ Hz, C_γ), 127.69 (apparent t, $|^3J_{PC} + {}^5J_{PC}| = 8.17$ Hz, C_m), 127.16 (apparent t, $|^3J_{PC} + {}^5J_{PC}| = 9.43$ Hz, C_m), 117.57 (apparent t, $|^2J_{PC} + {}^4J_{PC}| = 7.9$ Hz, C_β), 90.14 (t, $^2J_{PC} = 2.14$ Hz, C_5Me_5), 33.95 (apparent t, $|^1J_{PC} + {}^3J_{PC}| = 21.37$ Hz, C_α), 9.27 (s, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 37.5 (s). IR (Nujol): ν(N−CS) 2100, ν(NCS) 805 cm^{-1}.

Preparation of $[(\eta^5\text{-}C_5Me_5)Ru(\eta^1\text{-}ADPP)_2(CO)][PF_6]$ (3). A 50 mL flask was charged with **1** (0.2 g, 0.24 mmol) and 20 mL of 1,2-dichloroethane. A Tygon tube, fitted to a gas inlet adapter, was inserted into the solution, and CO gas was slowly bubbled through the solution for 96 h at ambient temperature. The solvent was removed *in vacuo*, and the yellow residue was treated with 3 × 5 mL portions of Et_2O. The product was dried in high vacuum (0.1 mmHg) at 68 °C for 24 h to give 0.19 g (94%) of **3** as a yellow powder. Mp: 209−212 °C. Anal. Calcd for $C_{41}H_{45}F_6OP_3Ru$: C, 57.14; H, 5.26. Found: C, 56.95; H, 5.14. ^1H NMR ($CDCl_3$): δ 7.0−7.54 (m, 20H, Ph), 5.15 (m, 2H, H_a), 4.86 (m, 2H, H_c), 4.71 (m, 2H, H_b), 2.66 (m, 2H, CH_{2a}), 2.31 (m, 2H, CH_{2b}), 1.43 (t, $^4J_{PH}$ = 1.07 Hz, 15H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 206.39 (t, $^2J_{PC} = 16.97$ Hz, CO), 132.6 (apparent t, $|^2J_{PC} + {}^4J_{PC}| = 10.43$ Hz, C_o), 132.28 (apparent t, $|^2J_{PC} + {}^4J_{PC}| = 9.30$ Hz, C_o), 131.45 (s, C_p), 131.32 (m, C_i), 131.23 (s, C_p), 130.00 (AXX′, $^2J_{PP} = 29.85$ Hz, $^1J_{PC} = 42.88$ Hz, $^3J_{PC} = -3.63$ Hz, C_i), 129.61 (apparent t, $|^3J_{PC} + {}^5J_{PC}| = 10.18$ Hz, C_γ), 129.01 (apparent t, $|^3J_{PC} + {}^5J_{PC}| = 9.55$ Hz, C_m), 128.50 (apparent t, $|^3J_{PC} + {}^5J_{PC}| = 10.56$ Hz, C_m), 120.53 (apparent t, $|^2J_{PC} + {}^4J_{PC}| = 10.18$ Hz, C_β), 100.54 (t, $^2J_{PC} = 1.26$ Hz, C_5Me_5), 36.83 (AXX′, $^2J_{PP} = 29.85$ Hz, $^1J_{PC} = 27.84$ Hz, $^3J_{PC} = -2.85$ Hz, C_α), 9.67 (s, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 34.6 (s), −145.3 (septet, $^1J_{PF} = 712.6$ Hz, PF_6^-). IR (CH_2Cl_2): ν(CO) 1954 cm^{-1}.

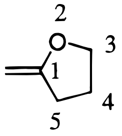
Preparation of $[(\eta^5\text{-}C_5Me_5)Ru(\eta^1\text{-}ADPP)_2\{C{=}C(H)(C_6H_5)\}][PF_6]$ (4). A 25 mL Schlenk flask was charged with **1** (0.21 g, 0.30 mmol), 25 mL of MeOH, and $HC{\equiv}C(C_6H_5)$ (0.05 mL, 0.45 mmol). The solution was stirred for 38 h at ambient temperature and turned from yellow to red. After the solution had been cooled to −25 °C for 48 h, an orange solid precipitated. The precipitate was collected on a glass frit, washed with 3 × 5 mL portions of Et_2O, and dried under vacuum to give 0.17 g (60%) of **4** as an orange powder. Anal. Calcd for $C_{48}H_{51}F_6P_3Ru$: C, 61.60; H, 5.49. Found: C, 61.42; H, 5.37. ^1H NMR ($CDCl_3$): δ 6.82−7.54 (m, 25H, Ph), 5.34 (t, $^4J_{PH}$ = 1.5 Hz, 1H, =C=CH), 5.00 (m, 2H, H_a), 4.73 (m, 2H, H_c), 4.53 (m, 2H, H_b), 2.83 (m, 2H, CH_{2a}), 2.29 (m, 2H, CH_{2b}), 1.50 (t, $^4J_{PH}$ = 1.50 Hz, 15H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 351.98 (t, $^2J_{PC} = 15.4$ Hz, Ru=C_α), 133.25 (apparent t, $|^2J_{PC} + {}^4J_{PC}| = 10.69$ Hz, C_o, ADPP), 133.18 (apparent t, $|^2J_{PC} + {}^4J_{PC}| = 8.55$ Hz, C_o, ADPP), 132.04 (s, C_i, =C=CPh), 131.64 (s, C_p, ADPP), 131.33 (s, C_p, ADPP), 130.57 (m, $|^1J_{PC} + {}^3J_{PC}| = 21$ Hz, C_i, ADPP), 130.17 (m, $|^1J_{PC} + {}^3J_{PC}| = 30.42$ Hz, C_i, ADPP), 129.93 (apparent t, $|^3J_{PC} + {}^5J_{PC}| = 8.8$ Hz, C_γ, ADPP), 129.40 (s, C_m, =C=CPh), 128.82 (apparent t, $|^3J_{PC} + {}^5J_{PC}| = 9.68$ Hz, C_m, ADPP), 128.33 (apparent t, $|^3J_{PC} + {}^5J_{PC}| = 10.18$ Hz, C_m, ADPP), 127.90 (s, C_p, =C=CPh), 127.33 (s, C_o, =C=CPh), 120.28 (apparent t, $|^2J_{PC} + {}^4J_{PC}| = 9.43$ Hz, C_β, ADPP), 115.47 (s, Ru=C=C_β), 104.33 (t, $^2J_{PC} = 1.0$ Hz, C_5Me_5), 37 (br m, C_α, ADPP), 10.20 (s, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 36.7 (s), −145.2 (septet, $^1J_{PF} = 712.6$ Hz, PF_6^-.

Table 2. Crystallographic Data for Compound **6**

empirical formula	$C_{29}H_{36}F_6OP_2Ru$
fw	677.59
cryst size (mm)	0.50 × 0.28 × 0.60
cryst syst	monoclinic
space group	$P2_1/n$
a (Å)	9.711(1)
b (Å)	12.418(2)
c (Å)	24.363(7)
β (deg)	99.60(2)
V (Å^3)	2896.9(10)
Z	4
d_{calcd} (g/cm^{-3})	1.554
μ (mm^{-1})	0.712
λ (Å) Mo Kα	0.717 03
temp (°C)	−106
max and min trans	0.959 and 0.870
data/restrnt/params	3795/0/347
R1,[a] wR2[b] [$I > 2\sigma(I)$]	0.0335, 0.0805
GOF (F^2)[c]	0.999

[a] $R1(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2(F^2) = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)]^2]^{0.5}$. [c] $GOF = S = [\sum[w(F_o^2 - F_c^2)^2]/(n - p)]^{0.5}$.

Preparation of $[(\eta^5\text{-}C_5Me_5)Ru(\eta^3\text{-}ADPP)\{\overline{C(CH_2)_3O}\}][PF_6]$ (6). A 50 mL Schlenk flask was charged with **1** (0.40 g, 0.50 mmol), 20 mL of CH_2Cl_2 and $HC{\equiv}CCH_2CH_2OH$ (0.09 mL, 1.24 mmol). The solution was stirred at room temperature for 20 h and then subsequently refluxed for 19 h. The solvent was removed *in vacuo*, and the yellow residue was washed with 3 × 5 mL portions of Et_2O. The product was dried under high vacuum for 24 h to give 0.27 g (81%) of **6** as a yellow powder. Mp: 116−118 °C dec. Anal. Calcd for $C_{29}H_{36}F_6OP_2Ru$: C, 51.43; H, 5.32. Found: C, 51.28; H, 5.45. Crystallization from CH_2Cl_2/hexanes gave a few crystals suitable for X-ray crystallography.



atom labeling for NMR spectroscopy

^1H NMR ($CDCl_3$, 25 °C): δ 6.8−7.8 (m, 10H, Ph), 5.22 (m, 1H, H_a), 4.85 (m, 1H, H_b), 4.51 (m, 1H, H_c), 4.33 (m, 2H, OCH_2), 3.44 (m, 2H, $CH_{2'}$), 2.75 (m, 2H, C_4CH_2), 2.28 (m, 2H, C_5CH_2), 1.49 (s, 15H, CH_3). $^{13}C\{^1H\}$ NMR: ($CDCl_3$, 25 °C) δ 299.43 (d, $^2J_{PC} = 13.6$ Hz, Ru=C_1-ring), 135.3−127.7 (m, Ph, C_β), 119.64 (d, $^2J_{PC} = 8.67$ Hz, C_γ), 99.95 (s, C_5Me_5), 80.30 (s, C_3-ring), 55.68 (s, C_5-ring), 29.61 (d, $^1J_{PC} = 55.0$ Hz, $CH_{2'}$), 23.68 (s, C_4-ring), 10.49 (s, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 46.0 (br s), −145.1 (septet, $^1J_{PF} = 712.6$ Hz, PF_6^-). ^1H NMR ($CDCl_3$, −60 °C): δ 7.8−6.8 (m, 10H, Ph), 5.60 (m, 0.5H, H_a), 5.00 (m, 0.5H, H_b), 4.80 (m, 0.5H, $H_{a'}$), 4.76 (m, 0.5H, H_c), 4.70 (m, 0.5H, $H_{b'}$), 4.60 (m, 1H, OCH_2), 4.13 (m, 0.5H, $H_{c'}$), 3.80 (m, 1H, $OCH_{2'}$), 3.40 (m, 1H, $CH_{2'}$), 3.37 (m, 1H, C_4CH_2), 3.00 (m, 1H, $CH_{2'}$), 2.70 (m, 1H, $C_4CH_{2'}$), 2.48 (m, 1H, C_5CH_2), 2.00 (m, 1H, $C_5CH_{2'}$), 1.50 (m, 15H, CH_3).

C. X-ray Determination and Processing for 6. Crystal data and details of data collection are given in Table 2. Data were collected in the $\omega/2\theta$ mode at 167 K with Mo Kα graphite-monochromated radiation (λ = 0.710 73 Å) on a Siemens P4 diffractometer. Two check reflections monitored every 100 reflections showed random (<2%) variation during the data collection. Unit cell parameters were determined by least-squares refinement of 24 reflections. 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.[17] Calculations were performed with the Siemens SHELXTL Plus version 5.1 software package on a personal computer. The structure was solved by direct methods. Anisotropic thermal

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(17) *International Tables for X-Ray Crystallography*; D. Reidel Publishing Co.: Boston, MA, 1992; Vol. C.

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.

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Supporting Information Available: Partial representation of the 499.86 MHz variable temperature ^1H NMR spectra of **1** in $CDCl_3$ (1 page). An X-ray crystallographic file in CIF format for $[(\eta^5\text{-}C_5Me_5)\text{-}Ru(\eta^3\text{-ADPP})\{\overline{C(CH_2)_3O}\}][PF_6]$ (**6**) is available on the Internet only. Ordering and access information is given on any current masthead page.

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