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SYNTHESIS AND CHARACTERIZATION OF [(η^6-arene)Ru(R_3P)(CH_3CN)Cl]PF_6 COMPLEXES

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ABSTRACT

The synthesis and characterization of the complexes [(η^6-arene)Ru(R_3P)(CH_3CN)Cl]PF_6, [arene = C_6H_6, MeC_6H_5, *p*-$MeC_6H_4CHMe_2$, and C_6Me_6; R_3P = $Ph_2PCH{=}CH_2$ (DPVP); $PhP(CH{=}CH_2)_2$ (DVPP); $Ph_2PCH_2CH{=}CH_2$ (ADPP); and 1-phenyl-3,4-dimethylphosphole (DMPP)] are described. These complexes have been characterized by elemental analyses, physical properties, ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy, infrared spectroscopy, cyclic voltammetry, and in most cases, by X-ray crystallography.

INTRODUCTION

Arene ruthenium(II) complexes are of considerable current interest because they are useful catalysts or catalyst precursors for a variety of organic transformations.[1] Complexes of the type [(η^6-arene)Ru(R_3P)(CH_3CN)Cl]PF_6 were first reported in 1993.[2] We have found that the CH_3CN ligand in these complexes is labile and is easily replaced by a variety of two-electron donor ligands, making these complexes potentially more useful synthetic intermediates than their [(η^6-arene)Ru(R_3P)Cl_2] precursors.[3] We describe herein the synthesis of several [(η^6-arene)Ru(R_3P)(CH_3CN)Cl]PF_6 complexes and their characterization by a variety of techniques.

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a) Undergraduate Research Participant.

EXPERIMENTAL

A. Reagents and Physical Measurements

The [(η^6-arene)Ru(R_3P)Cl_2] complexes were prepared as previously described.[3] Melting points were determined on a Mel-Temp apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. NMR spectra were recorded for acetone-d_6 solutions on a Varian Unity Plus-500 FT NMR spectrometer operating at 500 MHz for ^{1}H, 202 MHz for ^{31}P, and 125 MHz for ^{13}C. Proton and carbon chemical shifts were referenced to residual solvent resonances and phosphorus chemical shifts were referenced to an external 85% aqueous solution of H_3PO_4. All shifts to low field, high frequency are positive. FT-IR spectra were recorded as Nujol mulls on CsI windows on a Perkin-Elmer BX Spectrometer. Cyclic voltammograms were recorded 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 a platinum disk, and the reference electrode was Ag/AgCl (aqueous) separated from the cell by a luggin capillary. The Fc/Fc$^+$ couple occured at 480 mV[4] under the same conditions.

B. Synthesis of [(η^6-arene)Ru(R_3P)(CH_3CN)Cl]PF_6

All the [(η^6-arene)Ru(R_3P)(CH_3CN)Cl]PF_6 complexes were prepared in the following manner. To a solution of 1.0 mmol of the appropriate [(η^6-arene)Ru(R_3P)Cl_2][3] complex in 25 mL of a 4:1 mixture of CH_3CN and CH_2Cl_2 was added 1.0 mmol (0.17 g) of $NaPF_6$. The solution was stirred under nitrogen at ambient temperature for 24 h. The initially deep red solution became yellow-orange as the reaction proceeded. The solution was gravity filtered and reduced to dryness on a rotary evaporator. The resulting gummy solid was extracted with 25 mL of acetone, the extract was filtered to remove NaCl and the filtrate volume was reduced to about 5 mL on a rotary evaporator. Addition of ether produced yellow-orange crystals that were isolated by filtration, washed with ether and dried under vacuum at ambient temperature. The yields, analytical data, and melting points of the complexes are given in Table I.

C. X-ray Data Collection and Processing

Yellow-orange crystals of the complexes were isolated from $CH_3OH/CH_3CN/CH_2Cl_2$ (**2**), acetone/ether [(**4**), (**7**), (**11**)-(**13**)], CH_3OH/ether (**5**), $CHCl_3$/ether (**6**), or CH_2Cl_2/ether (**10**). Suitable crystals were mounted on glass fibers and placed on a Siemens P4 diffractometer. Crystal data and details of data collection are given in Table II. Intensity data were taken in the ω-mode at 25° C with graphite monochromated MoK_α radiation (λ = 0.71073 Å). Three check reflections, monitored every 100 reflections, showed random (<2%) variation during the data

TABLE I. Preparative and Analytical Data for [(η^6-arene)Ru(R_3P)(CH_3CN)Cl]PF_6.

	Arene	R_3P	Formula	MW	%C (calc.),found	%H (calc.),found	%Cl (calc.),found	Mp, °C	Yield %
(1)	C_6H_6	ADPP	$C_{21}H_{24}ClF_6NP_2Ru$	626.72	(44.08), 43.93	(3.83), 3.71	(5.66), 5.72	164-165	72.7
(2)	C_6H_6	DPVP	$C_{22}H_{22}ClF_6NP_2Ru$	612.71	(43.13), 43.20	(3.59), 3.54	(5.79), 5.70	171-172	45.4
(3)	C_6Me_6	ADPP	$C_{29}H_{36}ClF_6NP_2Ru$	710.78	(49.00), 49.04	(5.06), 4.93	(4.99), 5.13	170-172	76.4
(4)	C_6Me_6	DPVP	$C_{28}H_{34}ClF_6NP_2Ru$	696.77	(48.27), 48.16	(4.88), 4.74	(5.09), 4.92	222-224	86.7
(5)	C_6Me_6	DVPP	$C_{24}H_{32}ClF_6NP_2Ru$	646.73	(44.57), 44.25	(4.95), 4.87	(5.48), 5.27	185-187	80.0
(6)	C_6Me_6	DMPP	$C_{26}H_{34}ClF_6NP_2Ru$	672.75	(46.42), 46.54	(5.05), 4.93	(5.27), 5.19	264-266	85.9
(7)	*p*-$MeC_6H_4CHMe_2$	ADPP	$C_{27}H_{32}ClF_6NP_2Ru$	682.76	(47.50), 47.41	(4.69), 4.58	(5.19), 5.02	162-163	74.2
(8)	*p*-$MeC_6H_4CHMe_2$	DPVP	$C_{26}H_{30}ClF_6NP_2Ru$	668.75	(46.70), 46.52	(4.49), 4.38	(5.30), 5.34	200-201	21.0
(9)	*p*-$MeC_6H_4CHMe_2$	DVPP	$C_{22}H_{28}ClF_6NP_2Ru$	618.71	(42.71), 42.57	(4.53), 4.61	(5.73), 5.68	105-107	25.5
(10)	*p*-$MeC_6H_4CHMe_2$	DMPP	$C_{24}H_{30}ClF_6NP_2Ru$	644.73	(44.71), 44.62	(4.65), 4.69	(5.50), 5.23	153-155	83.1
(11)	MeC_6H_5	ADPP	$C_{24}H_{26}ClF_6NP_2Ru$	640.73	(44.99), 44.84	(4.06), 4.13	(5.53), 5.41	152-154	90.4
(12)	MeC_6H_5	DPVP	$C_{23}H_{24}ClF_6NP_2Ru$	626.72	(44.08), 44.13	(3.83), 3.74	(5.66), 5.72	148-150	68.8
(13)	MeC_6H_5	DVPP	$C_{19}H_{22}ClF_6NP_2Ru$	576.67	(39.57), 39.44	(3.81), 3.75	(6.15), 6.02	145-146	56.9
(14)	MeC_6H_5	DMPP	$C_{21}H_{26}ClF_6NP_2Ru$	604.70	(41.71), 41.65	(4.30), 4.28	(5.86), 5.79	144-145	50.0

TABLE II. Crystallographic Data.

	(2)	(4)	(5)
chemical formula	$C_{22}H_{22}ClF_6NP_2Ru$	$C_{28}H_{34}ClF_6NP_2Ru$	$C_{24}H_{32}ClF_6NP_2Ru$
formula weight	612.87	697.02	674.98
color, habit	red-orange, block	yellow-orange, rod	yellow, block
crystal size (mm)	0.60 x 0.80 x 0.80	0.18 x 0.34 x 0.18	0.14 x 0.42 x 0.38
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$	C2/c
a (Å)	8.2765(9)	13.473(2)	23.078(2)
b (Å)	29.611(3)	13.924(1)	8.583(2)
c (Å)	10.3183(8)	16.633(2)	30.173(3)
α (deg.)	90	90	90
β (deg.)	98.84(1)	103.411(8)	95.374(8)
γ (deg.)	90	90	90
volume ($Å^3$)	2498.7(4)	3035.2(6)	5950.7(13)
Z	4	4	8
ρ calc ($g\ cm^{-3}$)	1.629	1.525	1.507
μ (mm^{-1})	0.918	0.766	0.781
F(ooo)	1224	1416	2736
2θ range (deg.)	4.22/45.0	3.52/50.0	3.54/45.0
Octants	h k ± l	h -k ± l	-h k ± l
reflections collected	4227	6646	4939
observed reflections (I>2σI)	3244	4640	2982
parameters	336	353	336
R (WR2)	0.0347/0.0827	0.0646/0.1254	0.1018/0.2215
GOF	1.075	1.025	1.057
data/parameters	9.6	13.1	8.9

TABLE II. (Cont.)

	(6)	**(7)**	**(10)**
chemical formula	$C_{26}H_{34}ClF_6NP_2Ru$	$C_{27}H_{32}ClF_6NP_2Ru$	$C_{24}H_{30}ClF_6NP_2Ru$
formula weight	673.00	683.00	644.95
color, habit	orange, block	orange, block	yellow, plate
crystal size (mm)	0.22 x 0.46 x 0.34	0.26 x 0.54 x 0.34	0.08 x 0.44 x 0.24
crystal system	monoclinic	orthorhombic	monoclinic
space group	C2/c	$Pna2_1$	$P2_1/c$
a (Å)	29.926(4)	23.441(7)	11.426(1)
b (Å)	9.3307(8)	12.117(6)	15.738(1)
c (Å)	23.474(2)	10.338(8)	15.243(2)
α (deg.)	90	90	90
β (deg.)	115.040(8)	90	91.571(10)
γ (deg.)	90	90	90
volume (Å^3)	5938.6(10)	2950.0(3)	2470.0(5)
Z	8	4	4
ρ calc (g cm^{-3})	1.505	1.538	1.563
μ (mm^{-1})	0.780	0.786	0.841
F(ooo)	2736	1384	1304
2θ range (deg.)	3.74/50.0	3.78/50.0	3.56/50.0
Octants	h -k ± l	-h -k l	-h -k ±l
reflections collected	6357	3513	5975
observed reflections (I>2σI)	4510	2774	4185
parameters	331	344	316
R (WR2)	0.0693/0.1524	0.0702/0.1728	0.0758/0.1673
GOF	1.038	1.020	1.036
data/parameters	13.6	8.1	13.2

(continued)

TABLE II. (Cont.)

	(11)	(12)	(13)
chemical formula	$C_{24}H_{26}ClF_6NP_2Ru$	$C_{23}H_{24}ClF_6NP_2Ru$	$C_{19}H_{22}ClF_6NP_2Ru$
formula weight	640.92	626.89	576.84
color, habit	orange, wedge	yellow, plate	yellow, plate
crystal size (mm)	0.24 x 0.42 x 0.42	0.06 x 0.36 x 0.22	0.02 x 0.48 x 0.12
crystal system	monoclinic	orthorhombic	triclinic
space group	$P2_1/n$	$P2_12_12_1$	$P\bar{1}$
a (Å)	12.361(1)	7.6898(6)	8.1573(11)
b (Å)	11.047(1)	18.027(2)	10.6272(13)
c (Å)	20.092(2)	18.074(2)	14.125(2)
α (deg.)	90	90	94.349(10)
β (deg.)	106.09(1)	90	102.001(13)
γ (deg.)	90	90	99.948(10)
volume ($Å^3$)	2636.1(4)	2505.6(5)	1171.7(3)
Z	4	4	2
ρ calc ($g\ cm^{-3}$)	1.615	1.662	1.635
μ (mm^{-1})	0.874	0.917	0.973
F(ooo)	1288	1256	576
2θ range (deg.)	4.22/60.0	4.50/50.0	3.92/50.0
Octants	-h k ± l	h k l	-h ± k ± l
reflections collected	5987	3296	5085
observed reflections ($I>2\sigma I$)	4344	3092	3592
parameters	317	302	272
R (WR2)	0.0426/0.1010	0.0497/0.0763	0.0704/0.1359
GOF	1.040	1.025	1.005
data/parameters	13.7	10.2	13.2

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.[5] Calculations were performed with the Siemens SHELXTL Plus (Version 5.03) software package on a PC. The structures were solved by direct 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 R(F) and WR2 values given in Table II, where $\omega^{-1} = \sigma^2F + 0.001F^2$.

RESULTS AND DISCUSSION

A. Synthesis and Structures

The yellow-orange [(η^6-arene)Ru(R_3P)(CH_3CN)Cl]PF_6 complexes were readily prepared from the red [(η^6-arene)Ru(R_3P)Cl_2] complexes by reaction of the latter with $NaPF_6$ in CH_3CN-containing solutions (equation 1).

$$[(\eta^6\text{-arene})\text{Ru}(\text{R}_3\text{P})\text{Cl}_2] + \text{NaPF}_6 + \text{CH}_3\text{CN} \longrightarrow [(\eta^6\text{-arene})\text{Ru}(\text{R}_3\text{P})(\text{CH}_3\text{CN})\text{Cl}]\text{PF}_6 + \text{NaCl} \qquad (1)$$

Attempts to prepare them from [(η^6-arene)Ru(CH_3CN)$_2$Cl]PF_6[2] by equation 2 were uniformly unsuccessful even though [(η^6-arene)Ru(PPh_3)(CH_3CN)Cl]BF_4[2] has been prepared by reaction of [(η^6-arene)Ru(CH_3CN)$_2$Cl]BF_4 with PPh_3.

$$[(\eta^6\text{-arene})\text{Ru}(\text{CH}_3\text{CN})_2\text{Cl}]\text{PF}_6 + \text{R}_3\text{P} \longrightarrow [(\eta^6\text{-arene})\text{Ru}(\text{R}_3\text{P})(\text{CH}_3\text{CN})\text{Cl}]\text{PF}_6 + \text{CH}_3\text{CN} \qquad (2)$$

The [(η^6-arene)Ru(R_3P)(CH_3CN)Cl]PF_6 complexes are quite soluble in acetone, CH_3OH, and CH_3NO_2, but except for complexes (**5**)-(**10**), are only slightly soluble in CH_2Cl_2 or $CHCl_3$. They are not soluble in ether or hydrocarbons.

The crystal structures of nine of these complexes have been obtained (Figures 1-9). Their metrical parameters of interest are compared in Table III. The structures consist of isolated cations and anions with no unusual interionic contacts. They are typical three-legged piano-stool cations in which the Ru(II) atoms possess a pseudo-octahedral geometry. None of the Ru-P (2.346 Å, ave.), Ru-Cl (2.401 Å, ave.), Ru-N (2.055 Å, ave.), or C-N (1.119 Å, ave.) distances

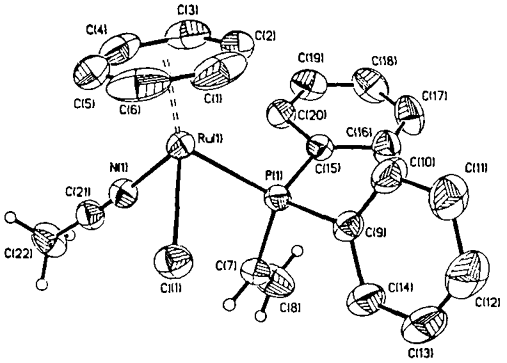

Figure 1. Perspective Drawing of the $[(\eta^6\text{-}C_6H_6)Ru(DPVP)(CH_3CN)Cl]^+$ Cation (**2**) Showing the Atom Numbering Scheme (40% Probability Ellipsoids). Hydrogen Atoms Have an Arbitrary Radius of 0.1 Å.

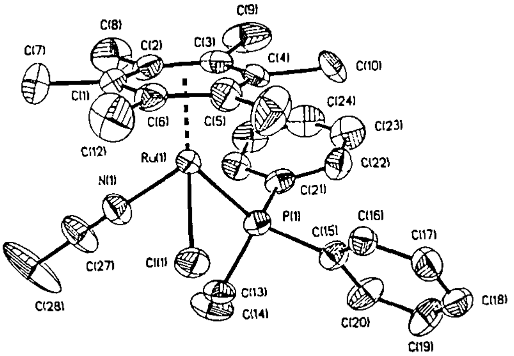

Figure 2. Perspective Drawing of the $[(\eta^6\text{-}C_6Me_6)Ru(DPVP)(CH_3CN)Cl]^+$ Cation (**4**) Showing the Atom Numbering Scheme (40% Probability Ellipsoids).

differ significantly from their average values, suggesting that the nature of the arene has no influence on these distances. Also, the Ru-P and Ru-Cl distances are similar to those of their $[(\eta^6\text{-arene})Ru(R_3P)Cl_2]$ precursors[3] (Ru-P, 2.334 Å, ave.; Ru-Cl, 2.411 Å, ave.). The average Ru-C distances of the C_6Me_6 complexes (2.249 Å, ave.) and $p\text{-}MeC_6H_4CHMe_2$ complexes (2.219 Å, ave.) are slightly greater than those of the C_6H_6 and MeC_6H_5 complexes (2.208 Å, ave.) and are all slightly greater than the comparable distances found for the $[(\eta^6\text{-arene})Ru(R_3P)Cl_2]$

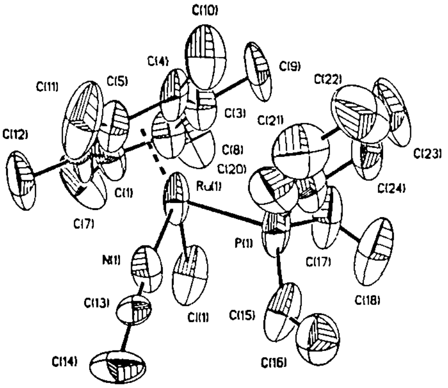

Figure 3. Perspective Drawing of the [(η^6-C$_6$Me$_6$)Ru(DVPP)(CH$_3$CN)Cl]$^+$ Cation (5) Showing the Atom Numbering Scheme (40% Probability Ellipsoids).

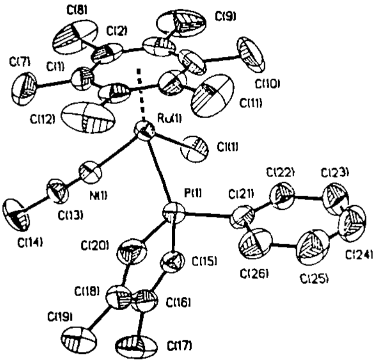

Figure 4. Perspective Drawing of the [(η^6-C$_6$Me$_6$)Ru(DMPP)(CH$_3$CN)Cl]$^+$ Cation (6) Showing the Atom Numbering Scheme (40% Probability Ellipsoids).

complexes[3] (C$_6$Me$_6$, 2.234 Å, ave.; MeC$_6$H$_5$, 2.208 Å, ave.; *p*-MeC$_6$H$_4$CHMe$_2$, 2.207 Å, ave.; C$_6$H$_6$, 2.194 Å, ave.). This is probably a result of the lower donor ability of CH$_3$CN compared to Cl$^-$ reducing the ruthenium electron density, thereby reducing the π-donor ability of the ruthenium to the η^6-arene ligands.

As can be seen in Figures 5 and 8, the RuPNCl cone is arranged such that each of the three vectors in the cone nearly bisect alternating C-C bonds of the η^6-arene ligand, independent of the nature of the arene.

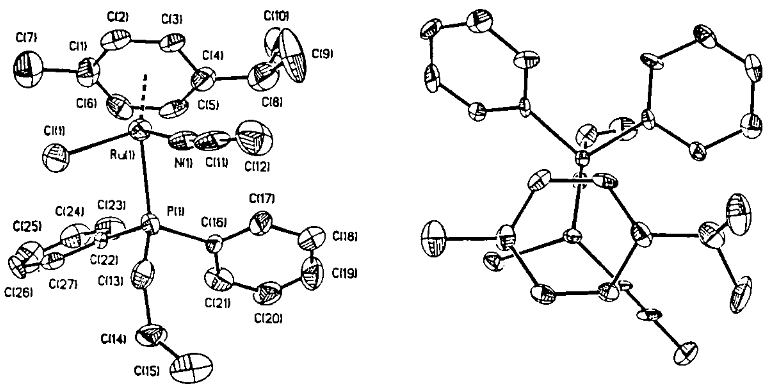

Figure 5. Perspective Drawings of the $[(\eta^6\text{-}p\text{-MeC}_6H_4CHMe_2)Ru(ADPP)(CH_3CN)Cl]^+$ Cation (**7**) Showing the Atom Numbering Scheme (40% Probability Ellipsoids).

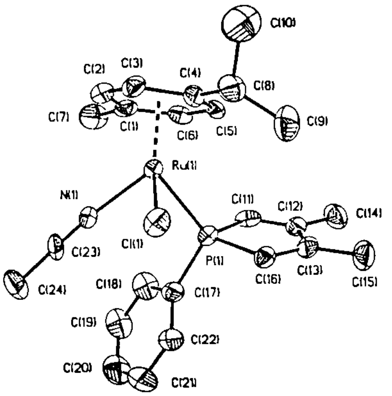

Figure 6. Perspective Drawing of the $[(\eta^6\text{-}p\text{-MeC}_6H_4CHMe_2)Ru(DMPP)(CH_3CN)Cl]^+$ Cation (**10**) Showing the Atom Numbering Scheme (40% Probability Ellipsoids).

B. Infrared Spectroscopy, $^{31}P\{^1H\}$ NMR Spectroscopy and Electrochemistry

The infrared spectra of the $[(\eta^6\text{-arene})Ru(R_3P)(CH_3CN)Cl]PF_6$ complexes display υ(RuN), υ(RuCl), and υ(PF) vibrations in the expected regions[6] (Table IV). The υ(CN) vibrations all occur at higher energy than observed[2] for $[(\eta^6\text{-}C_6H_6)Ru(Ph_3P)(CH_3CN)Cl]BF_4$ (2325 cm^{-1}). The υ(RuCl) vibration occurs in the same region as the two vibrations observed[3] for the $[(\eta^6\text{-arene})\text{-}Ru(R_3P)Cl_2]$ complexes (289 to 299 and 271 to 283 cm^{-1}).

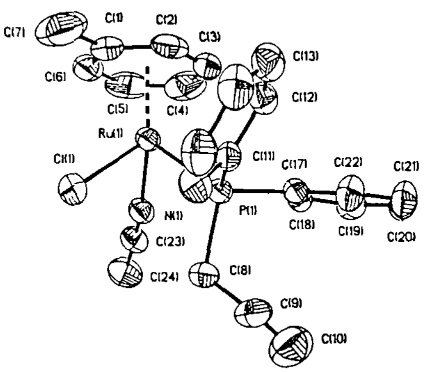

Figure 7. Perspective Drawing of the [(η^6-MeC$_6$H$_5$)Ru(ADPP)(CH$_3$CN)Cl]$^+$ Cation (**11**) Showing the Atom Numbering Scheme (40% Probability Ellipsoids).

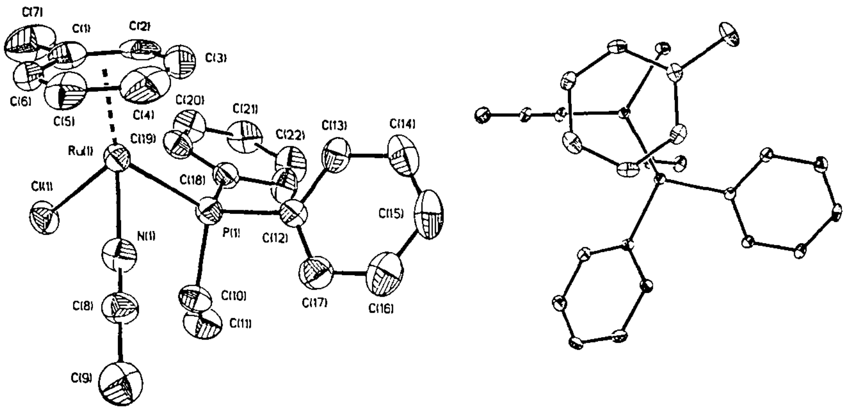

Figure 8. Perspective Drawings of the [(η^6-MeC$_6$H$_5$)Ru(DPVP)(CH$_3$CN)Cl]$^+$ Cation (**12**) Showing the Atom Numbering Scheme (40% Probability Ellipsoids).

The ^{31}P coordination chemical shift Δδ ^{31}P, defined as Δδ ^{31}P = δ ^{31}P complex - δ ^{31}P ligand, is generally about one to three ppm greater for the [(η^6-arene)Ru(R$_3$P)(CH$_3$CN)Cl]PF$_6$ complexes than for the [(η^6-arene)Ru(R$_3$P)Cl$_2$]^3 precursors as a result of the cationic nature of the former.

The Ru (II/III) potentials for the [(η^6-arene)Ru(R$_3$P)(CH$_3$CN)Cl]PF$_6$ complexes are all about 0.5 Volt greater than for the [(η^6-arene)Ru(R$_3$P)Cl$_2$]^3 precursors reflecting a decrease in ruthenium electron density in the former relative to the latter series of complexes. As was

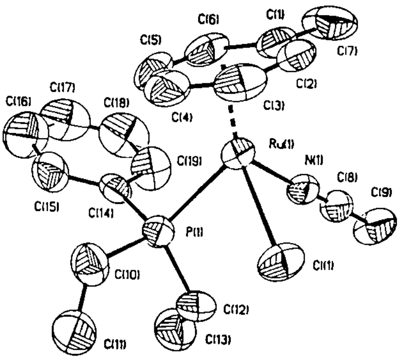

Figure 9. Perspective Drawing of the $[(\eta^6\text{-MeC}_6H_5)Ru(DVPP)(CH_3CN)Cl]^+$ Cation (**13**) Showing the Atom Numbering Scheme (40% Probability Ellipsoids).

observed for the $[(\eta^6\text{-arene})Ru(R_3P)Cl_2]$ complexes[3], the arene strongly influences the magnitude of the Ru (II/III) potential. Thus, the $\eta^6\text{-}C_6Me_6$ complexes are more easily oxidized (0.94 V, ave.) than the $\eta^6\text{-}p\text{-MeC}_6H_4CHMe_2$ complexes (1.14 V, ave.), the $\eta^6\text{-MeC}_6H_5$ complexes (1.21 V, ave.), and the $\eta^6\text{-}C_6H_6$ complexes (1.31 V, ave.).

C. ^1H and $^{13}C\{^1H\}$ NMR Spectroscopy

The ^1H and $^{13}C\{^1H\}$ NMR chemical shifts were assigned with the aid of COSY, $^1H/^{13}C$ HETCOR, APT, and $^1H\{^{31}P\}$ experiments. Figures 10 and 11 show expansions of typical COSY and $^1H/^{13}C$ HETCOR spectra, respectively.

In the COSY spectrum of $[(\eta^6\text{-}p\text{-MeC}_6H_4CHMe_2)Ru(DVPP)(CH_3CN)Cl]PF_6$ (**9**) (Figure 10) the diastereotopic nature of the two sets of vinyl protons, due to the lack of any symmetry in these complexes, is clearly evident. These vinyl resonances represent a tightly coupled AMRX (A, M, R = ^1H, X = ^{31}P) spin system. The $\eta^6\text{-}p\text{-MeC}_6H_4CHMe_2$ arene protons form a tightly coupled four-spin spin system centered at δ 5.8 ppm. The CH_3 and CH resonances are also clearly identifiable in the COSY spectrum. The $^1H/^{13}C$ HETCOR spectra (Figure 11 shows an example), together with the COSY and APT spectra allow for unambiguous assignment of the proton and carbon chemical shifts (Tables V and VI, respectively).

The ^1H and $^{13}C\{^1H\}$ NMR data for the $[(\eta^6\text{-arene})Ru(R_3P)(CH_3CN)Cl]PF_6$ complexes are similar to those for their $[(\eta^6\text{-arene})Ru(R_3P)Cl_2]$ precursors.[3] Both the ^1H and $^{13}C\{^1H\}$ data clearly evidence the complete lack of symmetry of the $[(\eta^6\text{-arene})Ru(R_3P)(CH_3CN)Cl]PF_6$

TABLE III. Selected Bond Lengths (Å) and Angles (deg.) For [(η^6-arene)Ru(R_3P)(CH_3CN)Cl]PF_6.

No	Arene	R_3P	Ru-P	Ru-Cl	Ru-N	C-N	Ru-C (ave.)	P-Ru-Cl	P-Ru-N	Cl-Ru-N
(2)	C_6H_6	DPVP	2.3505(11)	2.397(1)	2.051(4)	1.136(6)	2.202(5)	82.28(4)	88.68(10)	85.68(10)
(4)	C_6Me_6	DPVP	2.357(2)	2.396(2)	2.048(7)	1.105(10)	2.241(8)	83.37(7)	84.9(2)	85.9(2)
(5)	C_6Me_6	DVPP	2.338(5)	2.392(8)	2.050(2)	1.10(3)	2.28(3)	83.4(3)	83.6(5)	86.0(7)
(6)	C_6Me_6	DMPP	2.329(2)	2.401(2)	2.058(7)	1.127(10)	2.226(9)	85.14(9)	84.2(2)	87.4(2)
(7)	*p*-$MeC_6H_4CHMe_2$	ADPP	2.372(4)	2.407(4)	2.054(13)	1.11(2)	2.22(2)	84.4(2)	90.0(3)	86.2(4)
(10)	*p*-$MeC_6H_4CHMe_2$	DMPP	2.335(3)	2.413(3)	2.052(8)	1.129(12)	2.218(9)	85.54(9)	88.7(2)	82.8(2)
(11)	MeC_6H_5	ADPP	2.3496(12)	2.4068(13)	2.069(4)	1.124(6)	2.207(6)	83.71(4)	90.91(11)	87.19(11)
(12)	MeC_6H_5	DPVP	2.353(2)	2.401(2)	2.054(7)	1.104(9)	2.208(9)	86.33(8)	85.0(2)	86.8(2)
(13)	MeC_6H_5	DVPP	2.329(3)	2.394(3)	2.062(8)	1.132(10)	2.212(10)	85.48(9)	85.9(2)	85.2(2)
	Reference 2:								N-Ru-N	
	[(η^6-C_6H_6)Ru(CH_3CN)$_2$Cl]BF_4			2.379(2)	2.062(5)	1.135(7)	2.175(5)		85.8(3)	85.3(1)

TABLE IV. Infrared, Electrochemical, and $^{31}P\{^1H\}$ NMR Data for $[(\eta^6\text{-arene})Ru(R_3P)(CH_3CN)Cl]PF_6$.

No	Arene	R_3P	υ(CN) (cm^{-1})(w)^c	υ(RuN) (cm^{-1})(m)^c	υ(RuCl) (cm^{-1})(m)^c	υ(PF) (cm^{-1})(s)^c	$E_{1/2}$ Ru(II)/(III)(V)^a E_{pa}-E_{Pc} (mV)	$E_{1/2}$ Ru(III/IV)(V)^a E_{pa}-E_{Pc} (mV)
(1)	C_6H_6	ADPP	2362	457	278	832, 557	1.33(135)	No^b
(2)	C_6H_6	DPVP	2360	458	278	838, 556	1.29(75)	No
(3)	C_6Me_6	ADPP	2361	457	278	839, 558	0.98(78)	1.75(100)
(4)	C_6Me_6	DPVP	2360	462	278	842, 558	0.96(69)	1.60(90)
(5)	C_6Me_6	DVPP	2359	457	278	840, 556	0.96(113)	1.59(129)
(6)	C_6Me_6	DMPP	2360	458	278	842, 556	0.86(60)	1.58(117)
(7)	p-$MeC_6H_4CHMe_2$	ADPP	2360	459	278	838, 558	1.16(55)	1.65(151)
(8)	p-$MeC_6H_4CHMe_2$	DPVP	2364	456	290	842, 558	1.15(161)	No
(9)	p-$MeC_6H_4CHMe_2$	DVPP	2360	457	278	839, 557	1.13(66)	1.74(124)
(10)	p-$MeC_6H_4CHMe_2$	DMPP	2328	457	278	846, 557	1.11(48)	1.73(160)
(11)	MeC_6H_5	ADPP	2360	456	277	837, 556	1.23(101)	1.85(233)
(12)	MeC_6H_5	DPVP	2357	458	278	837, 557	1.22(70)	1.88(240)
(13)	MeC_6H_5	DVPP	2362	457	278	833, 557	1.20(90)	1.80(200)
(14)	MeC_6H_5	DMPP	2361	457	278	842, 558	1.19(65)	No

No	Arene	R_3P	δ ^{31}P (ppm)	δ ^{31}P ligand (ppm)	Δδ ^{31}P (ppm)^d	δ ^{31}P PF_6 (ppm) [$J_{(P-F)}$ (Hz)]
(1)	C_6H_6	ADPP	27.94	-17.00	44.94	-144.96[708]
(2)	C_6H_6	DPVP	27.70	-11.00	38.70	-145.04[707]
(3)	C_6Me_6	ADPP	28.86	-17.00	45.86	-145.04[712]
(4)	C_6Me_6	DPVP	28.85	-11.00	39.85	-145.02[707]
(5)	C_6Me_6	DVPP	20.57	-14.00	34.57	-145.05[708]
(6)	C_6Me_6	DMPP	34.44	-2.50	36.94	-144.98[712]
(7)	*p*-$MeC_6H_4CHMe_2$	ADPP	26.97	-17.00	43.97	-144.98[708]
(8)	*p*-$MeC_6H_4CHMe_2$	DPVP	25.78	-11.00	36.78	-145.03[708]
(9)	*p*-$MeC_6H_4CHMe_2$	DVPP	20.39	-14.00	34.39	-144.88[712]
(10)	*p*-$MeC_6H_4CHMe_2$	DMPP	32.62	-2.50	35.12	-144.99[709]
(11)	MeC_6H_5	ADPP	30.75	-17.00	47.75	-146.41[708]
(12)	MeC_6H_5	DPVP	28.54	-11.00	39.54	-144.94[709]
(13)	MeC_6H_5	DVPP	21.97	-14.00	35.97	-145.04[708]
(14)	MeC_6H_5	DMPP	35.85	-2.50	38.35	-146.43[708]

a) Measured in CH_2Cl_2 Solution at a Platinum Working Electrode, 0.1 M Tetrabutylammonium Hexafluorophosphate as Supporting Electrolyte. All Potentials are vs Fc/Fc^+. Scan Rate 100 mV s^{-1}.

b) No = Not Observed.

c) Abbreviations: s, strong: m, medium; w, weak.

d) Δδ ^{31}P = δ ^{31}P complex - δ ^{31}P ligand.

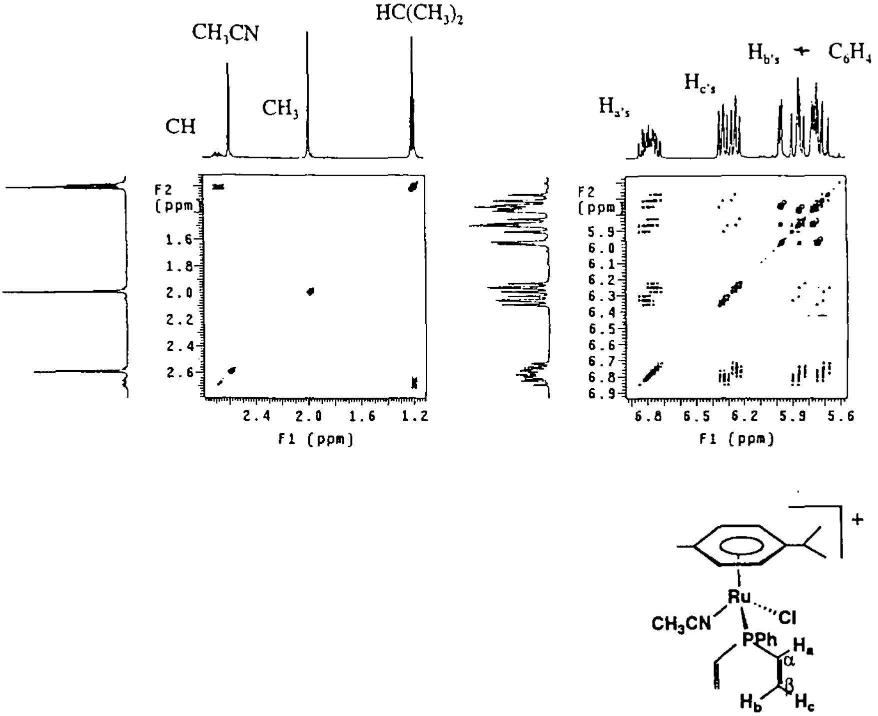

Figure 10. Expansions of the 500 MHz ^{1}H COSY-45 Spectrum of [(η^6-*p*-MeC$_6$H$_4$CHMe$_2$)Ru(DVPP)Cl]PF$_6$ (**9**) in Acetone-d$_6$.

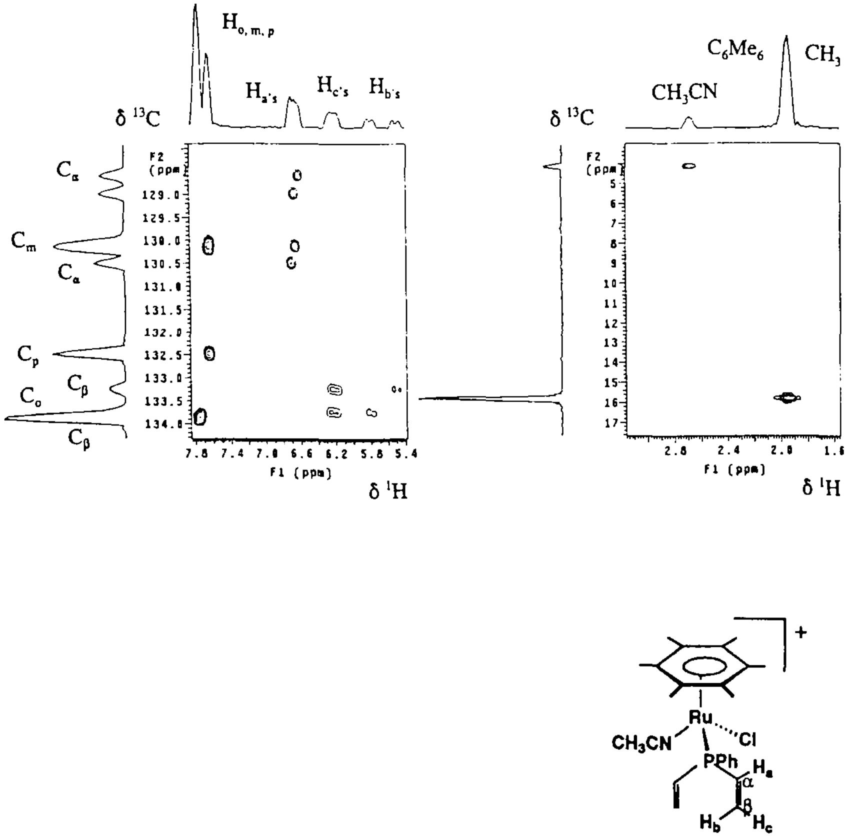

Figure 11. Expansions of the ^{1}H/^{13}C HETCOR Spectrum of [(η^6-C_6Me_6)Ru(DVPP)(CH_3CN)Cl]PF_6 (**5**) in Acetone-d_6.

TABLE V. 500 MHz ^1H NMR Data for $[(\eta^6\text{-arene})Ru(R_3P)(CH_3CN)Cl]PF_6$.ª

Data for the η^6-C_6H_6 Arene

No	R_3P	δ CH_3CN ($^5J_{P\text{-}H}$)	R_3P Resonances	Arene Resonances
(1)	ADPP	2.47(1.5)	7.82 (m, 4H, H_o), 7.59 (m, 6H, $H_{m,p}$), 5.62 (ddtd, $^3J_{(HaHb)}$ = 17.3 $^3J_{(HaHc)}$ = 10.3, $^3J(CH_2H_a)$ = 7.0, $^1J_{(PH)}$ = 4.5, 1H, H_a). 5.03 (dddt, $^3J_{HaHc}$ = 10.3, $^2J_{(HbHc)}$ = 3.0, $^4J_{(PH)}$ = 1.5, $^4J(CH_2H_c)$ = 1.5, 1H, H_c), 4.98 (dddt, $^3J_{(HaHb)}$ = 17.3, $^4J_{(PH)}$ = 3.0, $^2J_{(HbHc)}$ = 3.0, $^4J(CH_2H_b)$ = 1.5, 1H, H_b), 3.57 (ABdddd, $^2J_{(AB)}$ = 15.0, $^2J_{(PH)}$ = 2.5, $^3J(H_AH_c)$ = 7.0, $^4J(H_AH_b)$ = 1.5, $^4J(H_AH_c)$ = 1.5, 1H, H_A). 3.47 (ABdddd, $^2J_{(AB)}$ = 15.0, $^2J_{(PH)}$ = 7.5, $^3J(H_BH_a)$ = 7.0, $^4J(H_BH_b)$ = 1.5, $^4J(H_BH_c)$ = 1.5, 1H, H_B).	5.90 (d, 6H, $J_{(PH)}$ = 1.0)
(2)	DPVP	2.40(1.5)	7.78 (m, 4H, H_o), 7.60 (m, 6H, $H_{m,p}$), 6.97 (ddd, $^2J_{(PH)}$ = 23.9, $^3J_{(HaHb)}$ = 18.1, $^2J_{(HaHc)}$ = 12.2, 1H, Ha), 6.26 (ddd, $^3J_{(PH)}$ = 40.0, $^3J_{(HaHc)}$ = 12.2, $^2J_{(HbHc)}$ = 1.0, 1H, H_c), 5.49 (ddd, $^3J_{(PH)}$ = 20.0, $^3J_{(HaHb)}$ = 18.1, $^2J_{(HbHc)}$ = 1.0, 1H, H_b).	6.01 (d, 6H, $J_{(PH)}$ = 1.0)

Data for the η^6-C_6Me_6 Arene

No	R_3P	δ CH_3CN ($^5J_{P\text{-}H}$)	R_3P Resonances	Arene Resonances
(3)	ADPP	2.47(1.0)	7.62 (m, 10H, Ph), 5.32 (ddtd, $^2J_{(HaHb)}$ = 17.0, $^3J_{(HaHc)}$ = 10.0, $^3J(CH_2H_a)$ = 7.5, $^3J_{(PH)}$ = 4.5, 1H, H_a), 4.84 (ddd, $^3J_{(HaHc)}$ = 10.0, $^4J_{(PH)}$ = 3.5, $^2J_{(HbHc)}$ = 1.3, 1H, H_c), 4.71 (ddd, $^3J_{(HaHb)}$ = 17.0, $^4J_{(PH)}$ = 4.5, $^2J_{(HbHc)}$ = 1.3, 1H, H_b), 3.19 (ABXY, $^2J(H_AH_B)$ = 14.5, $^2J_{(PH)}$ = 10.5, $^3J(CH_2H_a)$ = 7.5, 1H, H_A), 3.15 (ABXY, $^2J(H_AH_B)$ = 14.5, $^2J_{(PH)}$ = 10.5, $^3J(CH_2H_a)$ = 7.5, 1H, H_B).	1.81 (d, 18H, $J_{(PH)}$ = 1.0)
(4)	DPVP	2.80(16.5)	7.57-7.74 (M, 10h, Ph), 6.79 (ddd, $^2J_{(PH)}$ = 24.0, $^3J_{(HaHb)}$ = 18.0, $^3J_{(HaHc)}$ = 12.0, 1H, H_a), 6.14 (ddd, $^3J_{(PH)}$ = 38.5, $^3J_{(HaHc)}$ = 12.0, $^2J_{(HbHc)}$ = 1.3, 1H, H_c), 5.54 (ddd, $^3J_{(PH)}$ = 19.0, $^3J_{(HaHb)}$ = 18.0, $^2J_{(HbHc)}$ = 1.3, 1H, H_b).	1.96 (d, 18H, $J_{(PH)}$ = 0.5)
(5)	DVPP	2.70(1.5)	7.76 (m, 2H, H_o), 7.65 (m, 3H, $H_{m,p}$), 6.68 (ddd, $^2J_{(PH)}$ = 23.0, $^3J_{(HaHb)}$ = 18.3, $^3J_{(HaHc)}$ = 12.3, 1H, H_a), 6.65 (ddd, $^2J_{(PH)}$ = 25.0, $^3J_{(HaHb)}$ = 18.5, $^3J_{(HaHc)}$ = 12.3, 1H, H_a), 6.23 (ddd, $^3J_{(PH)}$ = 38.5, $^3J_{(HaHc)}$ = 12.3, $^2J_{(HbHc)}$ = 1.0, 1H, H_c), 6.22 (ddd, $^3J_{(PH)}$ = 39.0, $^3J_{(HaHc)}$ = 12.3, $^2J_{(HbHc)}$ = 1.0, 1H, H_c), 5.80 (ddd, $^3J_{(PH)}$ = 19.5, $^3J_{(HaHb)}$ = 18.3, $^2J_{(HbHc)}$ = 1.0, 1H, H_b), 5.51 (ddd, $^3J_{(PH)}$ = 19.5, $^3J_{(HaHb)}$ = 18.5, $^2J_{(HbHc)}$ = 1.0, 1H, H_b).	1.97 (d, 18H, $J_{(PH)}$ = 1.0)
(6)	DMPP	2.09(1.0)	7.74 (m, 2H, H_o), 7.36 (m, 3H, $H_{m,p}$), 6.85 (d, $^2J_{(PH)}$ = 32.5, 1H, H_a), 2.18 (s, 3H, CH_3), 2.12 (s, 3H, CH_3).	2.02 (d, 18H $J_{(PH)}$ = 1.0)

TABLE V. (Cont.)

Data for the η^6-*p*-$MeC_6H_4CHMe_2$ Arene

No	R_3P	δ CH_3CN ($^5J_{P\text{-}H}$)	R_3P Resonances	Arene Resonances
(7)	ADPP	2.63(0)	7.86 (m, 4H, H_o), 7.62 (m, 6H, $H_{m,p}$), 5.47 (ddtd, $^3J_{(HaHb)}$ = 17.3, $^3J_{(HaHc)}$ = 10.5, $^3J(CH_2H_a)$ = 7.5, $^3J_{(PH)}$ = 5.0, 1H, H_a), 4.93 (dddt, $^3J_{(HaHc)}$ = 10.5, $^4J_{(PH)}$ = 3.5, $^2J_{(HbHc)}$ = 1.5, $^4J(CH_2H_c)$ = 1.5, 1H, H_c), 4.83 (dddt, $^3J_{(HaHb)}$ = 17.3, $^4J_{(PH)}$ = 4.5, $^2J_{(HbHc)}$ = 1.5, $^4J(CH_2H_b)$ = 1.5, 1H, H_b), 3.49 (ABdddd, $^2J_{(AB)}$ = 15.0, $^2J_{(PH)}$ = 8.0, $^3J(H_AH_a)$ = 7.5, $^4J(H_AH_b$ = $^4J(H_AH_c)$ = 1.5, 1H, H_A), 3.34 (ABdddd, $^2J_{(AB)}$ = 15.0, $^2J_{(PH)}$ = 8.0, $^3J(H_BH_a)$ = 7.5, $^4J(H_BH_b)$ = $^4J(H_BH_c)$ = 1.5, 1H, H_B).	5.84 (d, $^3J_{(HH)}$ = 6.5), 5.80 (d, $^3J_{(HH)}$ = 6.5), 5.71 (d, $^3J_{(HH)}$ = 6.5), 5.58 (d, $^3J_{(HH)}$ = 6.5), 2.48 (sp, $^3J_{(HH)}$ = 6.5, CH), 2.00 (s, 3H, CH_3), 1.02 (d, $^3J_{(HH)}$ = 6.5, 3H, CH_3), 1.00 (d, $^3J_{(HH)}$ = 6.5, 3H, CH_3).
(8)	DPVP	2.48(1.5	7.82-7.56 (m, 10H, Ph), 7.02 (ddd, $^2J_{(PH)}$ = 24.5, $^3J_{(HaHb)}$ = 18.0, $^3J_{(HaHc)}$ = 12.0, 1H, H_a), 6.22 (ddd, $^3J_{(PH)}$ = 34.0, $^3J_{(HaHc)}$ = 12.0, $^2J_{(HbHc)}$ = 1.0, 1H, H_c), 5.41 (ddd, $^3J_{(PH)}$ = 19.5, $^3J_{(HaHb)}$ = 18.0, $^2J_{(HbHc)}$ = 1.0, 1H, H_b).	5.97 (d, $^3J_{(HH)}$ = 6.5), 5.79 (m, 3H), 2.64 (sp, $^3J_{(HH)}$ = 1.0), 2.01 (s, 3H, CH_3), 1.17 (d, $^3J_{(HH)}$ = 7.0, 3H, CH_3), 1.13 (d, $^3J_{(HH)}$ = 7.0, 3H, CH_3).
(9)	DVPP	2.59(1.0	7.72 (m, 2H, H_o), 7.58 (m, 3H, $H_{m,p}$), 6.79 (ddd, $^2J_{(PH)}$ = 25.5, $^3J_{(HaHc)}$ = 18.3, $^3J_{(HaHb)}$ = 12.0, 1H, H_a), 6.78 (ddd, $^2J_{(PH)}$ = 23.5, $^3J_{(HaHc)}$ = 18.3, $^3J_{(HaHb)}$ 12.0, 1H, H_a), 6.30 (ddd, $^3J_{(PH)}$ = 40.0, $^3J_{(HaHc)}$ = 12.0, $^3J_{(HbHc)}$ = 1.0, 1H, H_c), 6.28 (ddd, $^3J_{(PH)}$ = 39.5, $^3J_{(HaHc)}$ = 12.0, $^2J_{(HbHc)}$ = 1.0, 1H, H_c), 5.86 (ddd, $^3J_{(PH)}$ = 20.5, $^3J_{(HaHb)}$ = 18.3, $^2J_{(HbHc)}$ = 1.0, 1H, H_b), 5.71 (ddd, $^3J_{(PH)}$ = 20.5, $^3J_{(HaHb)}$ = 18.3, $^2J_{(HbHc)}$ = 1.0, 1H, H_b).	5.97 (d, $^3J_{(HH)}$ = 6.0), 5.86 (d, $^3J_{(HH)}$ = 6.0), 5.77 (d, $^3J_{(HH)}$ = 6.0), 5.75 (d, $^3J_{(HH)}$ = 6.0), 2.68 (sp, $^3J_{(HH)}$ = 7.0, CH), 1.99 (s, 3H, CH_3), 1.21 (d, $^3J_{(HH)}$ =7.0, 3H, CH_3), 1.20 (d, $^3J_{(HH)}$ = 7.0, 3H, CH_3).
(10	DMPP	2.31(1.5)	7.78 (m, 2H, H_o), 7.48 (m, 3H, $H_{m,p}$), 7.01 (d, $^2J_{(PH)}$ = 34.5, H_α), 6.94 (d, $^2J_{(PH)}$ = 33.5, H_α), 2.23 (s, 6H, $2CH_3$).	6.01 (d, $^3J_{(HH)}$ = 6.0), 6.00 (d, $^3J_{(HH)}$ = 6.5), 5.91 (d, $^3J_{(HH)}$ = 6.5), 5.58 (d, $^3J_{(HH)}$ = 6.0), 2.81 (s, 3H, CH_3), 2.70 (sp, $^3J_{(HH)}$ = 7.0, CH), 1.23 (d, $^3J_{(HH)}$ = 7.0, 3H, CH_3), 1.17 (d, $^3J_{(HH)}$ = 7.0, 3H, CH_3).

(continued)

TABLE V. (Cont.)

Data for the η^6-MeC_6H_5 Arene

No	R_3P	δ CH_3CN ($^5J_{P\text{-}H}$)	R_3P Resonances	Arene Resonances
(11)	ADPP	2.49(1.5)	7 81 (m, 4H, H_o), 7 59 (m, 6H, $H_{m,p}$), 5.60 (ddtd $^3J_{(HaHb)} = 17.5$, $^3J_{(HaHc)} = 10.3$, $^3J(H_AH_a) = {^3J}(H_BH_a) = 7$ 5, $^3J_{(PH)} = 5$ 0, H_a), 5.01 (dddt, $^3J_{(HaHc)} = 10.3$, $^4J_{(PH)} = 3.5$, $^2J_{(HbHc)} = 3.0$, $^4J(H_AH_c) = {^4J}(H_BH_c) = 1.2$, H_c), 4.96 (dddt, $^3J_{(HaHb)} = 17.5$, $^3J_{(HbHc)} = 3.0$, $^4J_{(PH)} = 3.0$, $^4J(H_AH_c) = {^4J}(H_BH_c) = 1.3$, H_b), 3.54 (ABdddd, $^2J_{(AB)} = 14.5$, $^3J(H_AH_a) = 7.5$, $^2J_{(PH)} = 7.0$, $^3J(H_AH_b) = {^3J}(H_AH_c) = 1.3$, H_A), 3 48 (ABdddd, $^2J_{(AB)} = 14$ 5, $^3J(H_BH_a) = 7.5$, $^2J_{(PH)} = 7.0$, $^3J(H_BH_b) = {^3J}(H_BH_c) = 1.3$, H_B).	6.08 (t, $^3J_{(HH)} = {^3J}_{(HH)} = 6.0$), 5.98 (dd, $^3J_{(HH)} = 6.0$, $^4J_{(HH)} = 0$ 5), 5.68 (td, $^3J_{(HH)} = {^3J}_{(HH)} = 6.0$, $J_{(PH)} = 2.5$), 5 33 (dd, $^3J_{(HH)} = 6.0$, $^4J_{(HH)} = 6.0$, $^4J_{(HH)} = 0.5$), 5.24 (tdt, $^3J_{(HH)} = {^3J}_{(HH)} = 6.0$, $J_{(PH)} = 1.5$, $^4J_{(HH)} = {^4J}_{(HH)} = 0.5$), 2.18 (s, CH_3).
(12)	DPVP	2.36(1.0)	7 75 (m, 4H, H_o), 7.58 (m, 6H, $H_{m,p}$), 6.98 (ddd, $^2J_{(PH)} = 23.5$, $^3J_{(HaHb)} = 18.0$, $^3J_{(HaHc)} = 12.0$, H_a), 6.25 (ddd, $^3J_{(PH)} = 40.0$, $^3J_{(HaHc)} = 12.0$, $^2J_{(HbHc)} = 1.0$, H_c), 5.48 (ddd, $^3J_{(PH)} = 20.5$, $^2J_{(HbHc)} = 18.0$, $^2J_{(HbHc)} = 1.0$, H_b).	6.05 (t, $^3J_{(HH)} = {^3J}_{(HH)} = 6.0$), 5.99 (d, $^3J_{(HH)} = 6.0$), 5.80 (td, $^3J_{(HH)} = {^3J}_{(HH)} = 5.5$, $J_{(PH)} = 3.0$), 5.63 (d, $^3J_{(HH)} = 6.0$), 5.30 (t, $^3J_{(HH)} = {^3J}_{(HH)} = 5.5$), 2.25 (d, $J_{(PH)} = 0.5$, CH_3).
(13)	DVPP	2.54(1.5)	7 80 (m, 2H, H_o), 7.60 (m, 3H, $H_{m,p}$), 6.75 (ddd, $^2J_{(PH)} = 24.5$, $^3J_{(HaHb)} = 18.5$, $^3J_{(HaHc)} = 12.0$, H_a), 6.72 (ddd, $^2J_{(PH)} = 22.0$, $^3J_{(HaHb)} = 18$ 5, $^2J_{(HaHc)} = 12.0$, H_a), 6.29 (ddd, $^3J_{(PH)} = 40$ 5, $^3J_{(HaHc)} = 12.0$, $^2J_{(HbHc)} = 1$ 0, H_c), 6.26 (ddd, $^3J_{(PH)} = 40.0$, $^3J_{(HaHc)} = 12.0$, $^2J_{(HbHc)} = 1.0$, H_c), 5.88 (ddd, $^3J_{(PH)} = 20.5$ $^3J_{(HaHb)} = 18$ 5, $^2J_{(HbHc)} = 1.0$, H_b).	6.10 (td, $^3J_{(HH)} = {^3J}_{(HH)} = 5.8$, $^4J_{(HH)} = 1.0$),6.03 (ddd, $^3J_{(HH)} = 5$ 8, $^4J_{(HH)} = 1.0$, $^4J_{(HH)} = 0.5$), 5.82 (tdd, $^3J_{(HH)} = {^3J}_{(HH)} = 5$ 8, $J_{(PH)} = 3.0$, $^4J_{(HH)} = 1.0$), 5 55 (dt, $^3J_{(HH)} = 5.5$, $^4J_{(HH)} = {^4J}_{(HH)} = 0.5$), 5.40 (td, $^3J_{(HH)} = {^3J}_{(HH)}$ 5.8, $^4J_{(HH)} = 0.5$), 2.25 (s, CH_3).
(14)	DMPP	2.27(1.0)	7 79 (m, 2H, H_o), 7.46 (m, 3H, $H_{m,p}$), 6.96 (d, $^2J_{(PH)} = 33.0$, H_α), 6.87 (d, $^2J_{(PH)} = 32.5$, H_α), 2.21 (d, $^4J_{(PH)} = 2.0$, CH_3), 2.21 (d, $^4J_{(PH)} = 1.5$, CH_3).	6.09 (d, $^3J_{(HH)} = 5.8$), 6.04 (t, $^3J_{(HH)} = {^3J}_{(HH)} = 5.8$), 5.80 (td, $^3J_{(HH)} = {^3J}_{(HH)} = 5.8$, $J_{(PH)} = 3$ 0), 5.62 (t, $^3J_{(HH)} = {^3J}_{(HH)} = 5.8$), 5 37 (d, $^3J_{(HH)} = 5.8$), 2.19 (s, CH_3).

a) Abbreviations; s, singlet; d, doublet; t, triplet; sp, septet; m, multiplet, δ in ppm, J in Hz. Measured in Acetone-d_6.

TABLE VI. 125 MHz $^{13}C\{^1H\}$ NMR Data for [(η^6-arene)Ru(R_3P)(CH_3CN)Cl]PF_6 [a]

Data for the η^6-C_6H_6 Arene.

No	R_3P	δ CH_3CN (J_{PC})	R_3P Resonances: δ ($^nJ_{PC}$, assignment)	Arene Resonances: δ ($^nJ_{PC}$)
(1)	ADPP	129.09(0) 3.93(0.8)	134.50(9.3, C_o), 133.78 (8.8, C_o), 132.63 (48.9, C_i), 132.37 (2.6, C_p), 132.29 (2.6, C_p), 130.91 (47.3, C_i), 130.44 (9.9, C_α), 129.73 (10.2, C_m), 121.03 (10.7, C_β), 32.74 (28.3, CH_2).	92.03(2.9)
(2)	DPVP	128.25(0) 3.80(0.8)	135.14 (10.1, C_o), 134.43 (9.4, C_o), 132.99 (2.5, C_β), 132.56 (2.6, C_p), 132.36 (2.8, C_p), 131.70 (47.5, C_α), 131.22 (54.6, C_i), 130.58 (51.5, C_i), 129.83 (10.6, C_m), 129.69 (11.4, C_m).	92.04(3.0)
			Data for the η^6-C_6Me_6 Arene	
(3)	ADPP	126.83 (43.5) 4.10(0)	133.90 (9.7, C_o), 133.24 (8.7, C_o), 131.73 (2.5, C_p), 131.36 (2.6, C_p), 129.49 (10.1, C_α), 129.03 (10.1, C_m), 128.63 (9.9, C_m), 128.53 (126.3, C_i), 119.97 (9.9, C_β), 33.80 (27.2, CH_2).	100.11(2.5) 15.27(0)
(4)	DPVP	128.43(0) 4.22(0.8)	135.46 (9.8, C_o), 135.07 (8.7, C_o), 132.73 (45.3, C_α), 132.73 (45.3, C_α), 132.32 (1.9, C_p), 131.07 (1.0, C_β), 129.82 (9.9, C_m), 129.53 (10.4, C_m), 129.08 (50.7, C_i)	101.15(2.8) 15.78(0)
(5)	DVPP	127.93(0) 4.15(0)	133.86 (9.3, C_o), 133.75 (2.9, C_β), 133.24 (2.8, C_β), 132.48 (2.6, C_p), 130.32 (46.8, C_α), 130.12 (10.2, C_m), 129.43 (48.8, C_i), 128.79 (49.3, C_α).	100.76(2.9) 15.85(0)
(6)	DMPP	128.16(9.8) 3.45(0)	154.16 (10.3, C_β), 152.27 (8.5, C_β), 132.98 (8.4, C_o), 130.58 (0, C_p), 128.42 (10.6, C_m), 127.65 (50.4, C_i), 125.13 (48.8, C_α), 120.65 (51.9, C_α), 17.65 (CH_3), 17.55 (CH_3).	99.32(2.5) 15.64(0)

a) δ in ppm, J in Hz, Measured in Acetone-d_6.

(continued)

TABLE VI. (Cont.)

Data for the η^6-p-$MeC_6H_4CHMe_2$ Arene

No	R_3P	δ CH_3CN (J_{PC})	R_3P Resonances: δ ($^nJ_{PC}$, assignment)	Arene Resonances: δ ($^nJ_{PC}$)
(7)	ADPP	128.70(12.5) 4.08(1.9)	134.33 (9.1, C_o), 134.23 (8.8, C_o), 132.40 (0, C_p), 132.38 (0, C_p), 132.01 (48.1, C_i), 130.96 (45.9, C_i), 130.19 (11.1, C_α), 129.77 (10.1, C_m), 129 55 (10.2, C_m), 120.89 (9.9, C_β), 32.13 (26.9, CH_2).	111.89(0), 100.61(0), 95.48(4.4), 91.25(2.9), 90.27(0), 89.64(4.7), 31.52(0), 22.08(0), 21.82(0), 18.05(1.8).
(8)	DPVP	128.69(0) 3.85(0)	134 97 (9.9, C_o), 134.42 9.9, C_o), 132.71 (2.8, C_β), 132.27 (2.8, C_p), 131.72 (46.9, C_α), 131.54 (52.8, C_i), 130.62 (49.8, C_i), 129.76 (10.3, C_m), 129.62 (10.4, C_m).	112.84(1.9), 102 0(0), 93.33(4.0), 90.64(4.3), 90.13(5.8), 90.10(2.6), 31.68(CH), 22.31(CH_3), 22.04(CH_3), 18.11(CH_3).
(9)	DVPP	128 32(0) 3.93(0)	134.44 (2.0, C_β), 133.60 (3.3, C_β), 133.60 (9.3, C_o), 132.44 (2.6, C_p), 131.06 (52.4, C_i), 120.90 (10.3, C_m), 129.88 (47.9, C_α), 129.83 (49.9, C_α).	112.15(1.5), 101.42(0), 93 36(4.1), 90.11(4.3), 89.96(2.9), 89.55(4.4), 31.73 (CH), 22.29(CH_3) 18.18(CH_3).
(10)	DMPP	126.88(0) 3.19(0)	1154 55 (10.2, C_β), 154.29 (10.9, C_β), 133.26 (8.7, C_o), 131.81 (2.9, C_p), 129.53 (10.6, C_m), 129.45 (50.4, C_i), 125.42 (51 9, C_α), 124.70 (53.2, C_α), 17.74 (3.6, CH_3), 17.63 (4.0, CH_3)	110.03(0), 101.50(0), 93.56(4.9), 90.50(4.8), 90.24(3.0), 88.63(3.4), 31.83(CH), 22.47(CH_3), 22.18(CH_3), 18.48(CH_3)
			Data for the η^6-MeC_6H_5 Arene	
(11)	ADPP	128.90(0) 3 89(0)	134.54 (9.3, C_o), 133.70 (8.8, C_o), 132.96 (48 6, C_i), 132.35 (2.6, C_β), 132.24 (2.5, C_p), 130.99 (47.0, C_i), 130.50 (9.7, C_α), 129.73 (10.2, C_m), 129.63 (10.6, C_m), 120.92 (10.9, C_β), 32.95 (27.9, CH_2).	113.03(4.3), 93.04(2.1), 92.77(0), 92.69(7.3), 88.64(2.5), 83 49(0), 19.06(0, CH_3).
(12)	DPVP	127.85(0) 3.65(0)	134.91 (10.1, C_o), 134.21 (9.4, C_o), 132.71 (2.1, C_β), 132.36 (2.1, C_p), 132.15 (2.6, C_p), 131.66 (47.1, C_α), 131.15 (53.9, C_i), 130.46 (51.0, C_i), 129.68(10.6, C_m), 129 54 (10.6,C_m	113.86(4.7), 92.78(1.3), 92.62(0), 91.87(7.3), 87.86(0), 83.48(0), 19.07(0, CH_3).
(13)	DVPP	127.86(0) 3.93(0)	134.70 (1.5, C_β), 133.89 (9.7, C_o), 133.37 (2.9, C_β), 132.50 (2.8, C_p), 130.68 (53.4, C_i), 130.23 (50.7, C_α), 130.15 (48.0, C_α), 129.91 (10.6, C_m).	113.42(4.3), 93.02(1.6), 92.74(0), 91.97(7.4), 87.41(0), 82.81(0), 19.17(0, CH_3).
(14)	DMPP	126.59(0) 3.39(0)	154.38 (10.3, C_β), 154.28 (10.9, C_β), 133.35 (8.9, C_o), 131.85 (2.9, C_p), 129.49 (10.7, C_m), 129.07 (51.2, C_i), 125.73 (52.3, C_α), 125.03 (53 3. C_α), 117.74(7.9, CH_3), 17.64(7.8, CH_3)	111.45(3.8), 92.82(7.2), 92.23(0), 91.37(0), 87.83(0), 82.07(0), 19.06(0, CH_3).

complexes and show that the solution and the solid-state structures of these complexes are the same.

In the ^{1}H NMR spectra the resonances for the coordinated CH_3CN molecules generally appear as doublets in the δ 2.09 to 2.8 ppm region, downfield of free CH_3CN (δ 1.94 ppm) with $^5J_{(PH)}$ generally 1.0 to 1.5 Hz. In the $^{13}C\{^1H\}$ NMR spectra the resonances for the coordinated CH_3CN molecules generally appear in the 126.59 to 129.09 ppm (CH_3CN) and 3.39 to 4.22 ppm (CH_3CN) regions, also downfield of the resonances for free CH_3CN (118.69 and 1.39 ppm). The downfield shifts for the CH_3CN resonances, together with the general observation of spin correlation between phosphorus-31 and the coordinated CH_3CN protons and carbons demonstrate that the CH_3CN molecules do not dissociate from these ruthenium complexes on the NMR time scale.

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SUPPLEMENTARY MATERIAL

Listings of crystal and refinement data, bond distances and angles, H atom coordinates, and thermal parameters (U) are available from the authors.

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