maximum conductivity (σ_{max}) observed during doping for 5 h was shown in Table VII. The film was allowed to stand in an atmosphere of SbF_5 vapor for 7 days to reach a constant value. Then, a supply of SbF_5 vapor was stopped, the excess of SbF_5 vapor was removed by a pump, and the film was exposed to air. The conductivity was immediately measured by the four-probe method.

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Registry No. *dl*-**1a**, 139102-54-8; *meso*-**1a**, 139102-59-3; *dl*-**2a**, 139102-55-9; *meso*-**2a**, 139102-60-6; *dl*-**3a**, 139102-56-0; *meso*-**3a**, 139102-61-7; *dl*-**4a**, 139130-62-4; *meso*-**4a**, 139102-62-8; **5a**, 139102-57-1; *cis-trans*-**1b**, 139236-44-5; (±)-*all-trans*-**1b**, 139236-45-6; *cis-trans*-**1b** (homopolymer), 139341-69-8; (±)-*all-trans*-**1b** (homopolymer), 139341-70-1; *cis-trans*-**2b**, 139236-46-7; (±)-*all-trans*-**2b**, 139236-48-9; *cis-trans*-**2b** (homopolymer), 139341-71-2; (±)-*all-trans*-**2b** (homopolymer), 139341-73-4; *cis-trans*-**3b**, 139102-58-2; (±)-*all-trans*-**3b**, 139236-49-0; *cis-trans*-**3b** (homopolymer), 139236-51-4; (±)-*all-trans*-**3b** (homopolymer), 139341-74-5; *cis-trans*-**4b**, 139236-47-8; (±)-*all-trans*-**4b**, 139236-50-3; *cis-trans*-**4b** (homopolymer), 139341-72-3; (±)-*all-trans*-**4b** (homopolymer), 139341-75-6; **5b**, 135020-33-6; **5b** (homopolymer), 135020-34-7; $Et(SiPhMe)_2Et$, 139102-48-0; $Cl(SiPhMe)_2Cl$, 29442-41-9; $Bu(SiPhMe)_2Bu$, 139102-49-1; $H(CH_2)_6(SiPhMe)_2(CH_2)_6H$, 139102-50-4; $Ph(SiEt_2)_2Ph$, 18586-57-7; $Et_2SiPhLi$, 139102-51-5; $ClEt_2SiPh$, 17876-59-4; $Cl(SiMeEt)_2Cl$, 111230-98-9; $Cl(SiBuMe)_2Cl$, 139102-52-6; $H(CH_2)_6(SiMeCl)_2(CH_2)_6H$, 139102-53-7; $Cl_2(SiEt_2)_2$, 85590-06-3; $(SiHMePh)_2C{\equiv}C$, 17964-73-7; ClSiHPhMe, 1631-82-9; $(ClMeSiPh)_2C{\equiv}C$, 17937-56-3; $(ClMeSiPh)_2C{\equiv}C$ (homopolymer), 139102-63-9; *n*-BuLi, 109-72-8; SbF_5, 7783-70-2.

Supplementary Material Available: Tables of fractional coordinates and isotropic temperature factors of all atoms, including hydrogen atoms, bond distances and angles, and anisotropic temperature factors of all the non-hydrogen atoms for *cis-trans*-**1b** and *all-trans*-**1b** (8 pages); listings of observed and calculated structure factors for *cis-trans*-**1b** and *all-trans*-**1b** (14 pages). Ordering information is given on any current masthead page.

Ruthenium-Catalyzed Arbuzov Rearrangement of (Allyloxy)phosphines: Isolation and X-ray Structure Analysis of an Intermediate Leading to Mechanistic Conclusions

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The $[CpRu(CH_3CN)_3]PF_6$-catalyzed classical Arbuzov rearrangement of (allyloxy)phosphines $Ph_nP(OC_3H_5)_{3-n}$ (n = 0–2) at room temperature in neat (allyloxy)phosphine proceeds to completion in a short time period and gives only the classical Arbuzov rearrangement products, $Ph_nP(O)(C_3H_5)(OC_3H_5)_{2-n}$ (n = 0–2). The reaction mechanism was studied in acetonitrile solution by $^{31}P\{^1H\}$ NMR spectroscopy and supported by isolation and characterization of intermediates and final products. In addition to the classical Arbuzov product, with $Ph_2P(OC_3H_5)$, the mono-chelation product $[CpRu(CH_3CN)\{\eta^3\text{-}Ph_2P(OC_3H_5)\}]PF_6$ (**6**) was isolated and characterized; with $PhP(OC_3H_5)_2$, the bis-chelation products $[CpRu\{\eta^5\text{-}PhP(OC_3H_5)_2\}]PF_6$ (**5a,b**) were isolated and characterized; with $P(OC_3H_5)_3$, the intermediate phosphite complex $[CpRu\{\eta^5\text{-}P(OC_3H_5)_3\}]PF_6$ (**2**), the final product of dealkylation $[CpRu\{\eta^5\text{-}P(O)(OC_3H_5)_2\}]$ (**4**), the alkylation product $[CpRu(\eta^3\text{-}C_3H_5)(CH_3CN)_2][PF_6]_2$ (**1**), and the hydrolysis product $[CpRu\{\eta^5\text{-}P(OH)(OC_3H_5)_2\}]PF_6$ (**3**) have been isolated and characterized by elemental analysis, infrared spectroscopy, and ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy. The structure of **2** was confirmed by X-ray crystallography. It crystallizes in the monoclinic space group $P2_1/n$ in a unit cell of dimensions a = 7.603 (5) Å, b = 20.507 (3) Å, c = 12.054 (2) Å, β = 97.45 (2)°, and ρ_{calcd} = 1.829 g cm^{-3} with Z = 4. Refinement converged to R = 0.041 and 1892 independent observed ($I/\sigma(I) \geq 3.0$) reflections. The two coordinated alkene moieties are inequivalent having different dihedral angles between the planes of the C_5H_5 rings and the C–C axes (4.8, 36.10°) and slightly different average Ru–C bond distances of 2.213 (8) and 2.239 (9) Å. The P–OH and P=O complexes, **3** and **4**, are interconvertible via simple acid–base reactions.

Introduction

The well-known Arbuzov rearrangement has been widely employed for the synthesis of phosphonate and phosphinic acid esters and phosphine oxides.[2] Arbuzov-like dealkylation reactions of transition metal phosphite complexes have also been reviewed,[3] and the rearrangement mechanisms, thoroughly discussed. However, metal-catalyzed rearrangements of allylic phosphites were not included in either review although thermal rearrangement of allylic

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Table I. $^{31}P\{^1H\}$ NMR Data

compd	$\delta(^{31}P)$	$\Delta\delta(^{31}P)^a$
$P(OC_3H_5)_3$	138.91[b]	
$O{=}P(OC_3H_5)_2(C_3H_5)$ (16)	22.29[b]	
$[CpRu(MeCN)_2\{P(OC_3H_5)_3\}]^+$ (15)	152.84[b]	13.93
$[CpRu(MeCN)\{\eta^3\text{-}P(OC_3H_5)_3\}]^+$ (14)	178.51[b]	39.60
$[CpRu\{\eta^5\text{-}P(OC_3H_5)_3\}]^+$ (2)	200.75[b]	61.84
$[CpRu\{\eta^5\text{-}P(OC_3H_5)_3\}]^+$ (2)	202.49[c]	63.84
$[CpRu\{\eta^5\text{-}P(OH)(OC_3H_5)_2\}]^+$ (3)	177.81[c]	38.90
$[CpRu\{\eta^5\text{-}P(O)(OC_3H_5)_2\}]$ (4)	145.83[c]	6.92
$PhP(OC_3H_5)_2$	159.38[b]	
$PhP(O)(C_3H_5)(OC_3H_5)$	39.74[b]	
$[CpRu(MeCN)_2\{PhP(OC_3H_5)_2\}]^+$	173.79[b]	14.41
$[CpRu(MeCN)\{\eta^3\text{-}PhP(OC_3H_5)_2\}]^+$ (5a′)	199.34[b]	39.96
$[CpRu(MeCN)\{\eta^3\text{-}PhP(OC_3H_5)_2\}]^+$ (5b′)	204.25[b]	44.87
$[CpRu\{\eta^5\text{-}PhP(OC_3H_5)_2\}]^+$ (5a)	222.11[c]	62.73
$[CpRu\{\eta^5\text{-}PhP(OC_3H_5)_2\}]^+$ (5b)	227.68[c]	68.30
$Ph_2P(OC_3H_5)$	111.67[b]	
$Ph_2P(O)(C_3H_5)$	30.52[b]	
$[CpRu(MeCN)_2\{Ph_2P(OC_3H_5)\}]^+$	146.18[b]	34.51
$[CpRu(MeCN)\{\eta^3\text{-}Ph_2P(OC_3H_5)\}]^+$ (6)	179.21[d]	67.33
$CpRh\{\eta^3\text{-}Ph_2P(OC_3H_5)\}$[e]	169.00[d]	57.33
$P(OMe)_3$	141.00[b]	
$[CpRu(MeCN)_2\{P(OMe)_3\}]^+$ (9)	153.05[b]	12.05
$P(OEt)_3$	138.19[b]	
$[CpRu(MeCN)_2\{P(OEt)_3\}]^+$ (10)	149.33[b]	11.14

[a] $\Delta\delta(^{31}P) = \delta(^{31}P)$(complex) − $\delta(^{31}P)$(ligand). [b] Recorded in CH_3CN. [c] Recorded in CD_3NO_2. [d] Recorded in $CDCl_3$. [e] See ref 9.

phosphites has been known since the early sixties.[4] Lu et al.[5] recently reported that allylic phosphites could be rearranged to their corresponding allylic phosphonates by nickel catalysts under mild conditions in moderate to high yields. They proposed a redox mechanism involving a coordinated allyl intermediate. However, no intermediates have been isolated or characterized.

We report herein the isolation and structural characterization of (allyloxy)phosphine and π-allyl intermediates, a dealkylated phosphonate complex, a hydrolyzed phosphite complex and a high-yield ruthenium-catalyzed rearrangement of the (allyloxy)phosphines $Ph_nP(OC_3H_5)_{3-n}$ (n = 0–2) in the absence of additional nucleophiles. Mechanistic studies of the reactions of $[CpRu(CH_3CN)_3]PF_6$ with (allyloxy)phosphines and the mechanism of the catalyzed Arbuzov rearrangement are also discussed.

Results

Reactions of $[CpRu(CH_3CN)_3]PF_6$ with $Ph_nP(OC_3H_5)_{3-n}$ (n = 0–2). It was anticipated that reaction of 1 equiv of $[CpRu(CH_3CN)_3]PF_6$ with 2 equiv of $Ph_nP(OC_3H_5)_{3-n}$ (n = 0–2), L, would lead to simple displacement of two CH_3CN ligands to form $[CpRuL_2(CH_3CN)]PF_6$ on the basis of previous studies.[6] However, when the reaction of $[CpRu(CH_3CN)_3]PF_6$ with 2 equiv of $P(OC_3H_5)_3$ was carried out at room temperature in CH_3CN, five compounds were isolated. These included $[CpRu\{\eta^5\text{-}P(OC_3H_5)_3\}]PF_6$ (2), $[CpRu\{\eta^5\text{-}P(OH)(OC_3H_5)_2\}]PF_6$ (3), $[CpRu\{\eta^5\text{-}P(O)(OC_3H_5)_2\}]$ (4), the unexpected $[CpRu(\eta^3\text{-}C_3H_5)(CH_3CN)_2][PF_6]_2$ (1), and the classical Arbuzov rearrangement product $(C_3H_5)P(O)(OC_3H_5)_2$. The ratio of these five compounds is a function of the ratio of $P(OC_3H_5)_3$ to $[CpRu(CH_3CN)_3]PF_6$. The relative amount of 1 increased with decreasing phosphite to ruthenium ratio and reached a maximum at a 1:1 ratio.

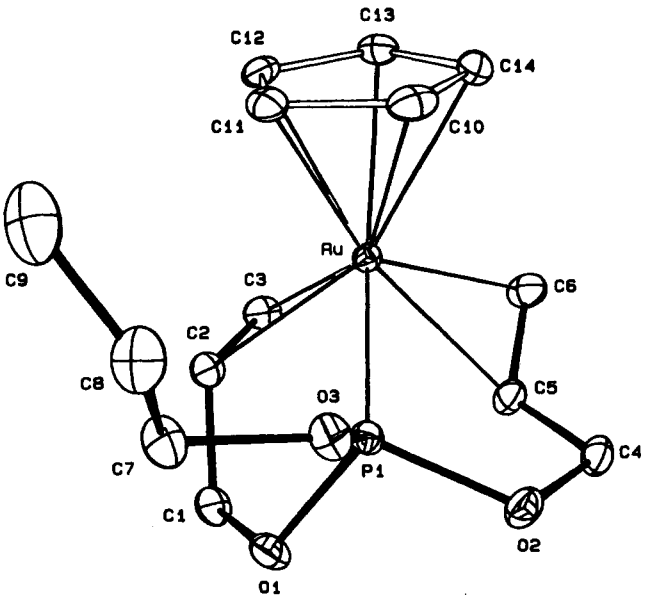

Figure 1. ORTEP drawing of the cation of complex 2, showing the atom-numbering scheme (50% probability ellipsoids). Hydrogen atoms are omitted.

The classical Arbuzov rearrangement product $(C_3H_5)P(O)(OC_3H_5)_2$ was isolated by extraction with ether and characterized by its $^{31}P\{^1H\}$ NMR spectrum, $\delta(CH_3CN)$ 22.29 ppm (Table I). The first isolated ruthenium complex, 1, is a yellow crystalline solid whereas most $CpRu^{IV}$ compounds are brown or red.[7,8] Its infrared spectrum displayed two ν(CN) vibrations (2342, 2318 cm^{-1}) for the two coordinated CH_3CN ligands. Its $^{31}P\{^1H\}$ spectrum showed a septet (δ = −144.95 ppm, $^1J(PF)$ = 713 Hz) for the two PF_6^- anions. Its ^1H NMR spectrum displayed three multiplets (δ 4.48, 4.81, and 5.72 ppm) in a 2:2:1 integrated ratio for the π-C_3H_5 protons in addition to singlets at δ 2.57 (6 H, 2 CH_3CN) and δ 6.35 (5 H, C_5H_5). Its $^{13}C\{^1H\}$ NMR spectrum showed five singlets for the five unique carbon nuclei. Thus, this compound possesses a mirror plane and the π-allyl ligand is symmetrically bound to ruthenium.

There are two possible orientations for the π-allyl ligand relative to the Cp ring, endo and exo.[7] Only one isomer is observed for complex 1, and it is not dynamic. Variable-temperature ^1H NMR spectra in CD_3NO_2 (−30 to 50 °C) showed only a slight temperature dependence of the chemical shifts with no change in the line shapes. Were the endo and exo isomers interconverting rapidly on the NMR time scale, the five allyl protons would change from an A_2M_2X to an AX_4 spin system as protons H_b and H_c are rendered equivalent by such a process. ^1H NOE difference spectra showed a positive NOE between the C_5H_5 and H_b protons, a negative NOE between the C_5H_5 and H_c protons, and no NOE between the C_5H_5 and H_a protons. Hence, this compound is present in solution as the endo isomer analogous to other ruthenium(IV) allyl complexes.[8]

The second ruthenium complex isolated in this reaction was $[CpRu\{\eta^5\text{-}P(OC_3H_5)_3\}]PF_6$ (2). It is a light-brown crystalline solid that is thermally stable in the solid state and in solution free of water and other nucleophiles. It

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Table II. X-ray Experimental Parameters for 2

formula	$C_{14}H_{20}O_3F_6P_2Ru$
fw	513.32
a, Å	7.603 (5)
b, Å	20.507 (3)
c, Å	12.054 (2)
β, deg	97.45 (2)
space group	$P2_1/n$
Z	4
d(calcd), g cm^{-3}	1.829
μ, cm^{-1}	10.611
abs factor range	0.76–1.38
temp, °C	20
final $R(F)^a$	0.041
final $R_w(F)^b$	0.058

$^a R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w(F) = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

Table III. Atom Coordinates for Complex 2

atom	x	y	z	B,^{a} Å^2
Ru	0.10539 (8)	0.16708 (3)	0.36916 (5)	3.44 (1)
P1	−0.0948 (3)	0.15477 (9)	0.2180 (2)	4.14 (4)
O1	−0.2192 (8)	0.0937 (3)	0.2282 (5)	6.2 (1)
C1	−0.182 (1)	0.0582 (4)	0.3338 (9)	6.9 (2)
C2	−0.002 (1)	0.0682 (4)	0.3888 (8)	6.0 (2)
C3	0.040 (1)	0.0942 (5)	0.4931 (7)	6.0 (2)
O2	−0.2206 (7)	0.2169 (3)	0.1978 (5)	5.7 (1)
C4	−0.215 (1)	0.2568 (4)	0.2977 (8)	5.9 (2)
C5	−0.143 (1)	0.2187 (40	0.3975 (7)	5.6 (2)
C6	−0.015 (1)	0.2389 (5)	0.4786 (8)	6.7 (2)
O3	−0.0426 (8)	0.1488 (3)	0.0960 (4)	5.4 (1)
C7	0.010 (1)	0.0851 (5)	0.0530 (8)	6.5 (2)
C8	0.124 (2)	0.0971 (5)	−0.0295 (9)	7.9 (3)
C9	0.283 (2)	0.0728 (6)	−0.024 (1)	10.5 (4)
C10	0.301 (1)	0.2106 (5)	0.2685 (8)	6.4 (2)
C11	0.343 (1)	0.1437 (5)	0.2884 (7)	5.9 (2)
C12	0.388 (1)	0.1357 (5)	0.4012 (8)	5.6 (2)
C13	0.379 (1)	0.1952 (5)	0.4518 (8)	5.6 (2)
C14	0.324 (1)	0.2414 (4)	0.3725 (8)	6.2 (2)
P2	0.6417 (3)	0.0781 (1)	0.7147 (2)	4.86 (5)
F1	0.3466 (8)	0.4365 (4)	0.2408 (6)	12.3 (2)
F2	0.4393 (8)	0.0921 (4)	0.6893 (5)	9.0 (2)
F3	0.1446 (8)	0.3874 (3)	0.3325 (4)	7.4 (1)
F4	0.594 (1)	0.0120 (3)	0.7686 (6)	11.0 (2)
F5	0.3640 (9)	−0.0439 (3)	0.4031 (4)	8.4 (2)
F6	0.674 (1)	0.1442 (3)	0.6578 (6)	10.4 (2)

^{a} B values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

Table IV. Selected Bond Distances (Å) for Complex 2

Ru–P1	2.231 (2)	P1–O2	1.593 (5)
Ru–C2	2.210 (8)	P1–O3	1.577 (6)
Ru–C3	2.215 (8)	O1–C1	1.46 (1)
Ru–C5	2.228 (8)	C1–C2	1.46 (1)
Ru–C6	2.249 (9)	C2–C3	1.36 (1)
Ru–C10	2.224 (8)	O2–C4	1.45 (1)
Ru–C11	2.210 (8)	C4–C5	1.48 (1)
Ru–C12	2.227 (8)	C5–C6	1.35 (1)
Ru–C13	2.263 (8)	O3–C7	1.48 (1)
Ru–C14	2.251 (8)	C7–C8	1.42 (1)
P1–O1	1.584 (6)	C8–C9	1.31 (2)

is soluble in CH_3NO_2 but not in $CHCl_3$ or CH_2Cl_2. It was characterized by infrared spectroscopy, ^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H}, ^{1}H/^{1}H COSY, and 2D-^{1}H/^{13}C HETCOR NMR spectroscopy (see Experimental Section), and X-ray crystallography. An ORTEP drawing is shown in Figure 1, and data collection parameters, atomic coordinates, selected bond distances, and angles are given in Tables II–V, respectively. Its 300-MHz ^{1}H NMR spectrum indicated that it is a chiral complex with two of the three carbon–carbon double bonds coordinated to ruthenium. The quite different chemical shifts and coupling constants for the two coordinated C_2H_3 moieties suggested quite different orientations for these two groups relative to the metal center, the cyclopentadienyl ring, and the Ru–P bond. As can be seen in Figures 2 and 3, one of the π-coordinated double bonds (C2–C3, Figure 2) is nearly parallel to the plane of the Cp ring (dihedral angle 4.8°) and perpendicular to the Ru–P bond. The other π-coordinated double bond (C5–C6) makes a dihedral angle of 36.1° with the Cp plane and is nearly parallel to the Ru–P bond (Figure 3).

Table V. Selected Bond Angles (deg) for Complex 2

P1–Ru–C2	76.2 (3)	O1–P1–O2	107.0 (3)
P1–Ru–C3	106.6 (3)	O1–P1–O3	103.6 (3)
P1–Ru–C5	71.2 (2)	O2–P1–O3	97.9 (3)
P1–Ru–C6	105.5 (3)	P1–O1–C1	114.2 (5)
C2–Ru–C3	35.9 (3)	O1–C1–C2	113.1 (7)
C2–Ru–C5	95.1 (3)	C1–C2–C3	124.6 (9)
C2–Ru–C6	110.8 (4)	P1–O2–C4	111.8 (5)
C3–Ru–C5	87.1 (3)	O2–C4–C5	110.2 (7)
C3–Ru–C6	84.4 (4)	C4–C5–C6	125.7 (9)
C5–Ru–C6	35.1 (3)	P1–O3–C7	120.5 (5)
C7–C8–C9	123.1 (1)	O3–C7–C8	107.9 (8)

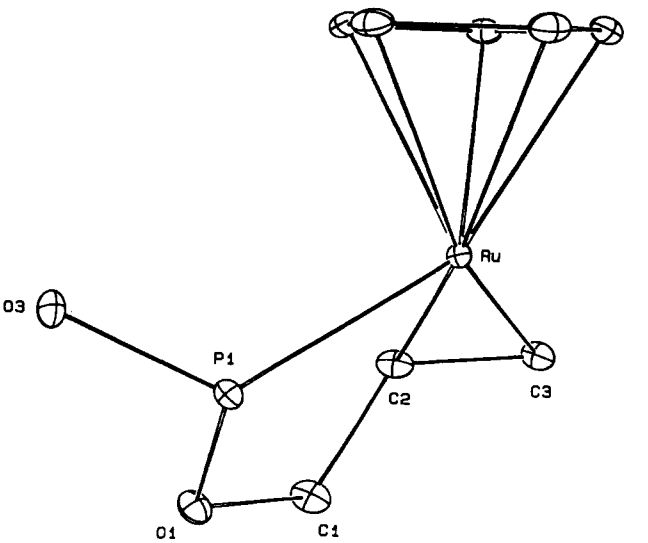

Figure 2. Partial projection of complex **2** showing the relative orientation of the coordinated double bond C2–C3 to the Cp plane and the Ru–P bond.

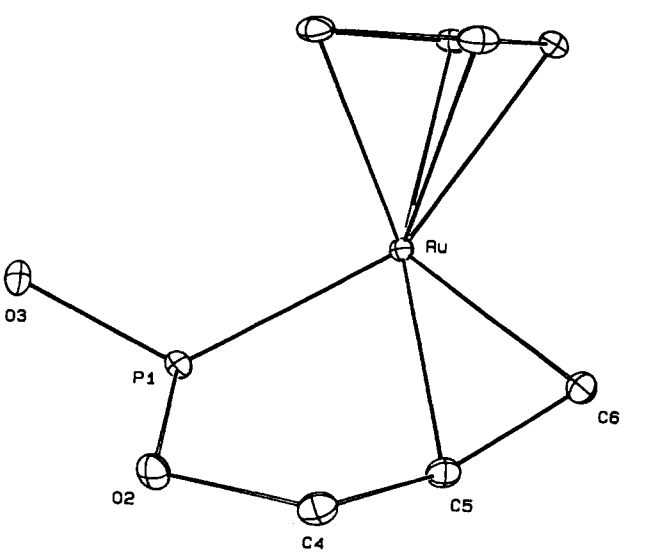

Figure 3. Partial projection of complex **2** showing the relative orientation of the coordinated double bond C5–C6 to the Cp plane and the Ru–P bond.

Similar coordination models have been proposed[9] for $Ph_2P(OC_3H_5)$ and found in the crystal structures of $[Rh\{Ph_2PCH_2CH_2CH{=}CH_2)\}_2Cl]$[10] and $[Rh\{\eta^5\text{-}P(CH_2CH_2CH{=}CH_2)_3\}Cl]$.[11] The carbon–carbon double bond is slightly more strongly bound to ruthenium when it is nearly parallel to the Cp ring (average Ru–C2,C3 = 2.213 (8) Å) than when this dihedral angle increases (average Ru–C5,C6 = 2.239 (9) Å). The slight shortening of the Ru–P bond distance (2.239 (9) Å) compared to normal Ru–P bond distances (~2.28 Å) results from formation of the two chelate rings in $\eta^5\text{-}P(OCH_2CH{=}CH_2)_3$. Similar Rh–P bond shortening was observed in the crystal structures[10,11] of rhodium(I) complexes of chelating alkenylphosphines.

The third ruthenium complex isolated, $[CpRu\{\eta^5\text{-}P(OH)(OC_3H_5)_2\}]PF_6$ (**3**), was probably formed by hydrolysis of **2** by adventitious H_2O and/or by protonation of **4** by HPF_6 (vide infra). Its IR spectrum displayed a strong ν(OH) vibration at 3450 cm^{-1}. Its $^{31}P\{^1H\}$ NMR spectrum exhibited a singlet (δ 177.81 ppm). The loss of the free allyl group was evidenced in its ^1H and $^{13}C\{^1H\}$ NMR spectra, where there were only two sets of resonances for the two chelate allyl groups and no resonances for the free allyl group. However, the resonance for the OH proton could not be assigned.

The similarities in the chemical shifts and coupling constants in the ^1H and $^{13}C\{^1H\}$ spectra of **2** and **3** suggested that **3** is also chiral and possesses orientations of its coordinated carbon–carbon double bonds that are similar to those in **2**. The presence of the POH functionality was supported by quantitative conversion of **3** to **4** upon reaction with KOH.

The last ruthenium complex to be isolated, $[CpRu\{\eta^5\text{-}P(O)(OC_3H_5)_2\}]$ (**4**), is exactly the same as the base conversion product from **3**. It can also be obtained by reaction of **2** with strong bases. Its IR spectrum shows a strong ν(P=O) vibration (1175 cm^{-1}) in addition to two ν(P–O) vibrations at 1012 and 1048 cm^{-1}. The ^{31}P chemical shift of its phosphonate phosphorus resonance is shielded by 50 ppm relative to the phosphite resonance of **2**. This shielding has been previously reported[3] for transition metal phosphite/phosphonate pairs of complexes. Furthermore, there was no PF_6^- resonance in the $^{31}P\{^1H\}$ NMR spectrum of **4**. Its ^1H and $^{13}C\{^1H\}$ NMR spectra were similar to those of **3**, indicating a chelate structure similar to that of **2**.

The P=O bond of **4** is a strongly Lewis basic site and is easily protonated by HCl as has previously been reported[12] to occur with $[(Cp\text{–}R)Co(PMe_3)\{P(O)(OMe_3)_2\}Li]PF_6$ though it was not silylated by reaction with $(CH_3)_3SiCl$.

In order to verify that the formation of **3** and **4** involves cleavage of a C–O bond of the uncoordinated allyloxy group of **2**, $PhP(OC_3H_5)_2$ and $Ph_2P(OC_3H_5)$ were reacted with $[CpRu(CH_3CN)_3]PF_6$. The reaction with 2 equiv of $PhP(OC_3H_5)_2$ produced two ruthenium complexes (**5a** and **5b** in a 1:7 ratio) in addition to the classical Arbuzov product $PhP(O)(C_3H_5)(OC_3H_5)$ without formation of analogues of **3** and **4**. The small ^{31}P chemical shift difference (5 ppm) observed for **5a,b** suggested that they are isomers of one another. The ^1H and $^{13}C\{^1H\}$ NMR data for the major isomer (**5b**; see Experimental Section) suggested that it contains an $\eta^5\text{-}PhP(OC_3H_5)_2$ ligand in a complex whose structure is similar to that of **2**. The minor isomer is achiral possessing a plane of symmetry. The results of this reaction suggest that a free allyloxy group is necessary in order to form **1** and analogues of **3** and **4**. Similarly, $[CpRu(CH_3CN)_3]PF_6$ reacted with 2 equiv of $Ph_2P(OC_3H_5)$ to form $Ph_2P(O)(C_3H_5)$ and $[CpRu\{\eta^3\text{-}Ph_2P(OC_3H_5)(CH_3CN)\}]PF_6$ (**6**).

Oxidative Addition of CH_2=$CHCH_2Cl$ to $[CpRu(CH_3CN)_3]PF_6$. In order to grain further insight concerning the mechanism of the reaction of $[CpRu(CH_3CN)_3]PF_6$ with $P(OC_3H_5)_3$, this complex was reacted with CH_2=$CHCH_2Cl$ in refluxing CH_3CN. The oxidative addition product $[CpRu(\eta^3\text{-}C_3H_5)Cl_2]$[8] (**7**) was formed in high yield in this reaction. When this same reaction was repeated in a mixture of CH_3NO_2 and CH_3CN in addition to **7**, another oxidative addition product $[CpRu(\eta^3\text{-}C_3H_5)(CH_3CN)Cl]PF_6$ (**8**) was formed. Thus, $[CpRu(CH_3CN)_3]PF_6$ readily undergoes oxidative additions with allyl chloride, and its reaction with $P(OC_3H_5)_3$ may involve an oxidative addition.

Reaction of $[CpRu(CH_3CN)_3]PF_6$ with Trialkyl Phosphites. Reaction of $[CpRu(CH_3CN)_3]PF_6$ with excess $P(OCH_3)_3$ or $P(OC_2H_5)_3$ for short time periods produced only $[CpRu(CH_3CN)_2\{P(OR)_3\}]PF_6$ (**9**, R = CH_3, and **10**, R = C_2H_5,[13] respectively). Reactions for long time periods and/or at elevated temperatures produced $[CpRu(CH_3CN)\{P(OR)_3\}_2]PF_6$[13] and $[CpRu\{P(OR)_3\}_3]PF_6$.[13] No Arbuzov rearrangement products were reported in these reactions.

Reaction of $[CpRu(CH_3CN)_3]PF_6$ with $PhP(CH_2CH{=}CH_2)_2$. Previous reports[6,7,10,11] together with this research indicated that alkenylphosphines are potential chelating ligands. As with most phosphines studied, $[CpRu(CH_3CN)_3]PF_6$ reacts with 2 equiv of $PhP(CH_2CH{=}CH_2)_2$ (DAPP) in CH_3CN solution to liberate two CH_3CN ligands forming $[CpRu(CH_3CN)(DAPP)_2]PF_6$ (**11**). However, when the solvent is removed with a rotary evaporator and **11** is dissolved in $CHCl_3$ or CH_2Cl_2, the third CH_3CN spontaneously dissociates forming $[CpRu(\eta^3\text{-DAPP})(\eta^1\text{-DAPP})]PF_6$ (**12a,b**) as two isomers in a 19:1 ratio. Complex **12** readily converts to **11** upon addition of CH_3CN to a solution of **12** in $CDCl_3$. Similarly, **12** reacts with carbon monoxide quantitatively to form $[CpRu(DAPP)_2(CO)]PF_6$ (**13**).

Discussion

Mechanism of the Reactions of $[CpRu(CH_3CN)_3]PF_6$ with $Ph_nP(OC_3H_5)_{3-n}$. The reactions of $[CpRu(CH_3CN)_3]PF_6$ with $Ph_nP(OC_3H_5)_{3-n}$ (n = 0–2) were monitored as a function of time by $^{31}P\{^1H\}$ NMR spectroscopy. Within 5 min after addition of 1 equiv of $P(OC_3H_5)_3$ to a solution of $[CpRu(CH_3CN)_3]PF_6$ in CH_3CN at ambient temperature, ^{31}P resonances appeared at δ 178.51, 174.52, 152.84, 138.91, 26.89, and –144.95 ppm representing two isomers of $[CpRu(CH_3CN)\{\eta^3\text{-}P(OC_3H_5)_3\}]^+$ (**14a,b**), $[CpRu(CH_3CN)_2\{P(OC_3H_5)_3\}]^+$ (**15**), $P(OC_3H_5)_3$, $(C_3H_5)P(O)(OC_3H_5)_2$ (**16**), and PF_6^-, respectively, in a 1:2:23.2:22.3:3.3:52 ratio. Over a period of 20 h the resonances for **15** and **14b** disappeared, those of **14a** and **16** augmented, and a new resonance at δ 202.49 ppm representing **2** appeared. After 2 days the reaction was complete and only **2**, **14a**, and **16** were present in solution in a 1:2:1 ratio. These results are consistent with sequential replacement of CH_3CN (reactions 1–3). Complexes **14a,b** could not be isolated; they are converted to **2** upon removal of CH_3CN solvent.

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$$[CpRu(CH_3CN)_3]PF_6 + P(OC_3H_5)_3 \rightarrow [CpRu(CH_3CN)_2\{P(OC_3H_5)_3\}]PF_6 + CH_3CN \quad (1)$$
15

$$15 \rightarrow [CpRu(CH_3CN)\{\eta^3\text{-}P(OC_3H_5)_3\}]PF_6 + CH_3CN \quad (2)$$
14a,b

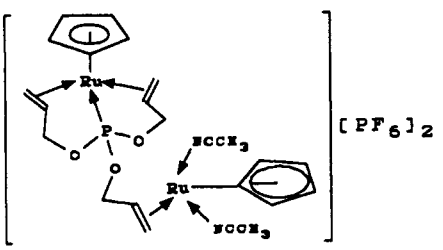
$$14 \rightarrow [CpRu\{\eta^5\text{-}P(OC_3H_5)_3\}]PF_6 + CH_3CN \quad (3)$$
2

Similar stepwise replacements of acetonitrile were observed in reactions of $[CpRu(CH_3CN)_3]PF_6$ with $PhP(OC_3H_5)_2$ and $Ph_2P(OC_3H_5)$ except that the latter ligand only replaces two CH_3CN molecules. Neither hydrolysis products analogous to **3** and **4** nor the π-allyl product, **1**, was observed in these two reactions.

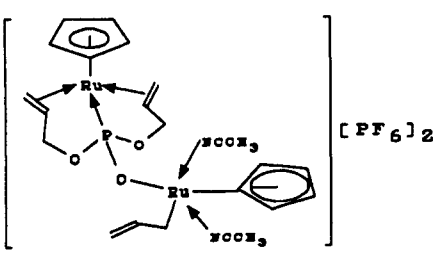
The isolation of **1** and **4** in the first reaction suggested that in addition to stepwise replacement of CH_3CN by $P(OC_3H_5)_3$ another reaction occurs. It was independently shown that reaction 4 occurs. Reaction 4 was monitored

$$[CpRu(CH_3CN)_3]PF_6 + 2 \rightarrow 1 + 4 + \text{other products} \quad (4)$$

by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy as a function of time in CD_3NO_2. $[CpRu(CH_3CN)_3]PF_6$ slowly decomposes in CD_3NO_2 or other polar solvents in which **2** is soluble such that this reaction could not be quantitated in this way. Despite this limitation, it is clearly evident that **1** and **4** are quickly formed together with **3**, an intermediate species ($\delta(^{31}P)$ 183.49), and an unidentified species ($\delta(^{31}P)$ 189.06) (compound **3** is formed because the CD_3NO_2 contains adventitious H_2O). After 24 h, **3** and the unidentified species are the only phosphorus-containing species present in solution and they are present in equal amounts. Thus, **1** and **4** are presumably formed by sequential oxidative addition and reductive elimination by way of intermediates such as I and II. Reaction of $[CpRu(CH_3CN)_3]PF_6$ with $P(OC_3H_5)_3$ gave **1** in isolated amounts that depended upon the phosphite to ruthenium ratio. Increasing this ratio decreased the amount of **1** isolated. This may be rationalized in the following way. $[CpRu(CH_3CN)_3]PF_6$ undergoes ligand substitution at a moderate rate,[14] and in the absence of an excess of $P(OC_3H_5)_3$ both $[CpRu(CH_3CN)_3]PF_6$ and $[CpRu\{\eta^5\text{-}P(OC_3H_5)_3\}]PF_6$ would be simultaneously present in solution. As the phosphite to ruthenium ratio increases, the rate of formation of $[CpRu\{\eta^5\text{-}P(OC_3H_5)_3\}]PF_6$ should increase and the probability of the bimolecular reaction 4 should decrease. Thus, the ratio of the products is kinetically controlled.



I



II

Mechanism of Catalyzed Arbuzov Reactions. Addition of a catalytic amount (1%) of $[CpRu(CH_3CN)_3]PF_6$ to neat $P(OC_3H_5)_3$ at room temperature under nitrogen produced $(C_3H_5)P(O)(OC_3H_5)_2$ quantitatively in less than 50 h. Thus, $[CpRu(CH_3CN)_3]PF_6$ is a better catalyst for this reaction than either $Ni(COD)_2$[5a] or $NiCl_2$,[5b] which both catalyze this reaction at 80 °C or higher with yields that are 80% or less. In addition, $[CpRu(CH_3CN)_3]PF_6$ also catalyzes the quantitative rearrangements of $Ph_2P(OC_3H_5)_2$ or $Ph_2P(OC_3H_5)$ under the same mild conditions. It does not however catalyze the rearrangement of $P(OCH_3)_3$ or $P(OC_2H_5)_3$. Hence, at least one allyloxy functionality is required. The mechanism could involve nucleophilic attack of Ru(II) on the $Ru\text{-}P(R_2)\text{-}OC_3H_5$ moiety to form a bridging intermediate containing one Ru(II) bonded to phosphorus and another Ru(II) π-bound to the carbon–carbon double bond. This intermediate could then undergo oxidative addition followed by reductive transfer of an allyl group from ruthenium to phosphorus. A more plausible mechanism is shown in Scheme I.

Experimental Section

General Methods. All preparations were conducted in reagent grade solvents. The preparations involving free phosphines were carried out under nitrogen. All chemicals were reagent grade and were used as received. The $^{31}P\{^1H\}$ NMR spectra were recorded at 40.26 MHz on a JEOL FX-100 spectrometer or at 121.66 MHz on a General Electric GN-300 spectrometer in the FT mode. Around a 2 ppm difference was observed for ^{31}P chemical shifts in different solvents. The ^1H, $^1H\{^{31}P\}$, $^{13}C\{^1H\}$, and APT NMR spectra were recorded at 300, 300, 75, and 75 MHz, respectively on a General Electric GN-300 spectrometer. Proton and carbon chemical shifts are relative to internal Me_4Si, and phosphorus chemical shifts are relative to internal PF_6^- (δ = -144.95 ppm) or external 85% H_3PO_4 (δ = 0) with a positive value being downfield of the respective reference. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Infrared spectra were recorded on a Perkin-Elmer 1800 FT-infrared spectrometer as KBr pellets. $[CpRu(CH_3CN)_3]PF_6$,[13] $PhP(OCH_2CH{=}CH_2)_2$,[15] and $Ph_2P(OCH_2CH{=}CH_2)$[16] were synthesized by literature procedures. $P(OCH_2CH{=}CH_2)_3$ was a gift from Western Chemical Inc.

Synthesis. Reaction of $[CpRu(CH_3CN)_3]PF_6$ with Triallyl Phosphite. Method a. Under a purge of nitrogen, 1.0 mL (5.1 mmol) of triallyl phosphite was added to a solution containing $[CpRu(CH_3CN)_3]PF_6$ (1.0 g, 2.30 mmol) in acetonitrile (20 mL) with a syringe. The solution color lightened immediately. The solution was degassed for another 3 min, and the flask was then stoppered with a septum. The mixture was stirred with a magnetic stirring bar at ambient temperature overnight. The solvent was removed on a rotary evaporator. The Arbuzov product was extracted with ether several times, and the residue was dissolved in dichloromethane. Some yellowish solid which was not soluble in dichloromethane was isolated by filtration and identified as $[CpRu(CH_3CN)_2(C_3H_5)][PF_6]_2$ (**1**). After saturation of the dichloromethane solution with ether the flask was put in a freezer overnight. The first batch of yellow crystalline solid which formed in solution was collected by filtration and dried under vacuum. It was identified as $[CpRu\{\eta^5\text{-}P(OCH_2CH{=}CH_2)_3\}]PF_6$ (**2**). The second batch of pale yellow crystalline solid that formed later was also collected by filtration and dried under vacuum. It was identified as $[CpRu\{\eta^5\text{-}P(OH)(OCH_2CH{=}CH_2)_2\}]PF_6$ (**3**). The third batch of yellow solid formed much later and was isolated by the same method and identified as $[CpRu\{\eta^5\text{-}P(O)$-

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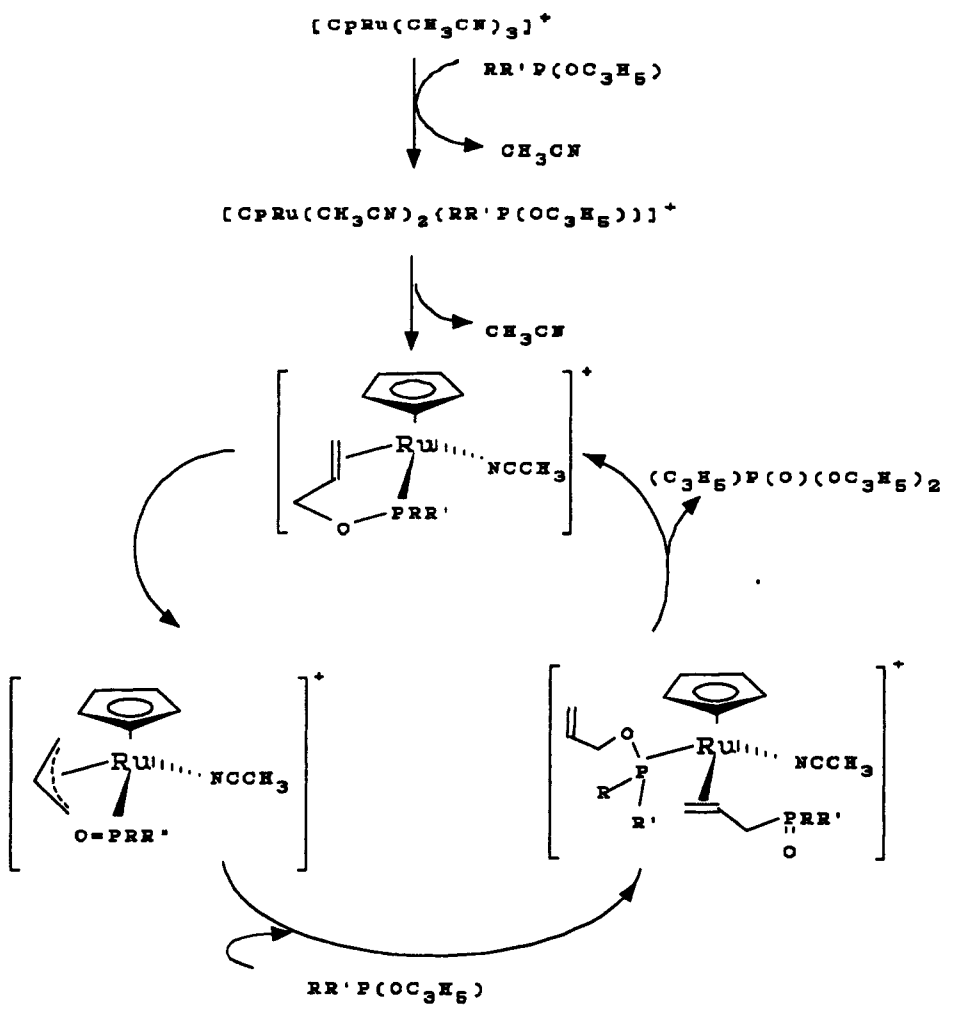
Scheme I

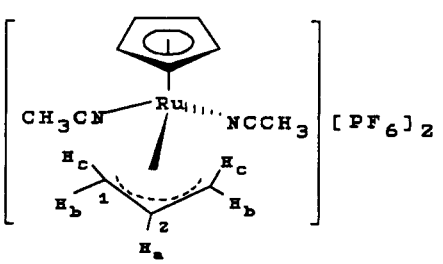


A. R=R'=OC_3H_5; B. R=Ph, R'=OC_3H_5; C. R=R'=Ph

$(OCH_2CH{=}CH_2)_2$] (**4**). The first three complexes (1–3) when pure are not soluble in either dichloromethane or chloroform, and they were recrystallized from a nitromethane/dichloromethane/ether mixture. The fourth complex is soluble in common solvents such as chloroform and dichloromethane. Total isolated yield is in the range 35–50%.

Method b. When a 1:1 molar ratio of $[CpRu(CH_3CN)_3]PF_6$ to triallyl phosphite was used, the major product isolated was complex 1. Under these conditions the four complexes 1–4 were isolated in a ratio of 8:4:2:1.

Complex 1. $^{31}P\{^1H\}$ NMR (CD_3NO_2): δ −144.95 (septet, $^1J(PF)$ = 713 Hz, PF_6^-). ^1H NMR (CD_3NO_2): δ 2.57 (s, 6 H, CH_3CN),

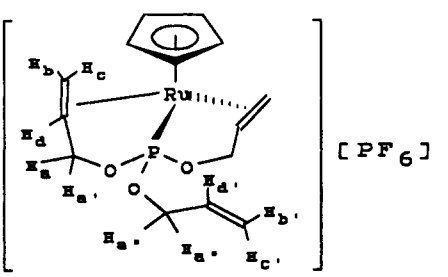


1

4.48 (d, $^3J(H_aH_c)$ = 11.42 Hz, 2 H, H_c), 4.81 (d, $^3J(H_aH_b)$ = 6.31 Hz, 2 H, H_b), 5.72 (tt, $^3J(H_aH_c)$ = 11.42 Hz, $^3J(H_aH_b)$ = 6.31 Hz, 1 H, H_a), 6.35 (s, 5 H, C_5H_5). $^{13}C\{^1H\}$ NMR (CD_3NO_2): δ 4.59 (s, CH_3CN), 70.95 (s, C_1), 97.57 (s, C_5H_5), 101.96 (s, C_2), 136.86 (s, CN).

Anal. Calcd for $C_{12}H_{16}N_2F_{12}P_2Ru$: C, 24.88; H, 2.78. Found: C, 24.96; H, 2.81. Mp: 179–181 °C.

Complex 2. $^{31}P\{^1H\}$ NMR (CD_3NO_2): δ 202.49 (s), −144.95 (septet, $^1J(PF)$ = 713 Hz, PF_6^-). ^1H NMR (CD_3NO_2): δ 1.17 (dd,



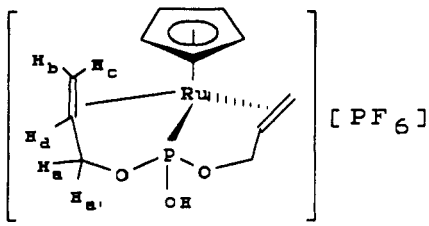
2

$^2J(bc)$ = 0.90, $^3J(cd)$ = 12.02 Hz, 1 H, H_c), 2.88 (ddd, $^3J(PH)$ = 0.90, $^2J(aa')$ = 10.61, $^3J(ad)$ = 10.31 Hz, 1 H, H_a), 3.42 (apparent td, $^3J(PH)$ = 1.20, $^3J(ad)$ = 10.37, $^2J(aa')$ = 10.37 Hz, 1 H, H_a), 3.63 (apparent dt, $^3J(PH)$ = 0.90, $^2J(bc)$ = 0.90, $^3J(bd)$ = 8.41 Hz, 1 H, H_b), 3.71 (m, $^4J(PH)$ = 0.90, $^3J(a'd)$ = 4.36, $^3J(bd)$ = 7.81, $^3J(ad)$ = 10.37, $^3J(cd)$ = 12.02 Hz, 1 H, H_d), 4.13 (dd, $^2J(bc)$ = 0.90, $^3J(bd)$ = 7.81 Hz, 1 H, H_b), 4.33 (dd, $^3J(cd)$ = 12.02, $^2J(bc)$ = 0.90 Hz, 1 H, H_c), 4.58 (ddd, $^3J(a'd)$ = 4.36, $^2J(aa')$ = 10.37, $^3J(PH)$ = 45.38 Hz, 1 H, $H_{a'}$), 4.70 (ddd, $^3J(a'd)$ = 5.71, $^2J(aa')$ = 10.61, $^3J(PH)$ = 46.58 Hz, 1 H, $H_{a'}$), 4.91 (m, $^4J(a''b')$ = 1.26, $^4J(a''c')$ = 1.50, $^3J(a''d')$ = 5.40, $^3J(PH)$ = 8.41 Hz, 2 H, $H_{a''}$), 5.05 (m, $^3J(a'd)$ = 5.71, $^3J(bd)$ = 8.41, $^3J(ad)$ = 10.31, $^3J(cd)$ = 12.02 Hz, 1 H, H_d), 5.39 (dddd, $^4J(a''b')$ = 1.26, $^2J(b'c')$ = 0.30, $^3J(b'd')$ = 10.52, $^5J(PH)$ = 2.70 Hz, $H_{b'}$), 5.53 (dddd, $^4J(a''c')$ = 1.50, $^2J(b'c')$ = 0.30, $^3J(c'd')$ = 17.13, $^5J(PH)$ = 3.0 Hz, 1 H, $H_{c'}$), 5.54 (s, 5 H, C_5H_5), 6.16 (apparent ddt, $^3J(a''d')$ = 5.40, $^3J(b'd')$ = 10.52, $^3J(c'd')$

= 17.13 Hz, 1 H, $H_{d'}$). $^{13}C\{^1H\}$ NMR (CD_3NO_2): δ 53.42 (s, $=CH_2$), 53.53 (s, $=CH_2$), 69.63 (d, $^2J(PC)$ = 6.95 Hz, OCH_2), 70.67 (d, $^2J(PC)$ = 7.41 Hz, OCH_2), 71.73 (d, $^2J(PC)$ = 8.16 Hz, OCH_2), 73.49 (s, =CH), 83.67 (s, =CH), 90.02 (s, C_5H_5), 119.58 (s, $=CH_2$), 134.03 (d, $^3J(PC)$ = 3.48 Hz, =CH). IR (KBr): ν(P–O), 1015 (s), 985 (s), 970 (s) cm^{-1}; ν(C–H), 3138 (m), 2965 (w), 2910 (w) cm^{-1}.

Anal. Calcd for $C_{14}H_{20}F_6O_3P_2Ru$: C, 32.76; H, 3.93. Found: C, 32.50; H, 3.97. Mp: 127–128 °C.

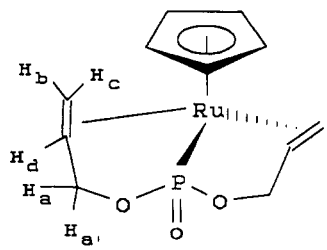
Complex 3. $^{31}P\{^1H\}$ NMR (CD_3NO_2): δ 177.81 (s), −144.95 (septet, $^1J(PF)$ = 713 Hz, PF_6^-). ^1H NMR (CD_3NO_2): δ 0.85 (dd,



3

$^2J(bc)$ = 0.60, $^3J(cd)$ = 11.57 Hz, 1 H, H_c), 2.68 (apparent td, $^3J(PH)$ = 1.20, $^2J(aa')$ = 10.07, $^3J(ad)$ = 10.07 Hz, 1 H, H_a), 3.18 (ddd, $^3J(PH)$ = 1.80, $^2J(aa')$ = 10.52, $^3J(ad)$ = 10.67 Hz, 1 H, H_a), 3.35 (dddd, $^3J(a'd)$ = 4.61, $^3J(bd)$ = 7.96, $^3J(ad)$ = 10.67, $^3J(cd)$ = 12.17 Hz, 1 H, H_d), 3.42 (ddd, $^2J(bc)$ = 0.60, $^3J(PH)$ = 0.90, $^3J(bd)$ = 7.96 Hz, 1 H, H_b), 3.81 (dd, $^2J(bc)$ = 0.60, $^3J(bd)$ = 8.11 Hz, 1 H, H_b), 4.09 (dd, $^2J(bc)$ = 0.60, $^3J(cd)$ = 12.17 Hz, 1 H, H_c), 4.38 (ddd, $^3J(a'd)$ = 4.61, $^2J(aa')$ = 10.07, $^3J(PH)$ = 43.28 Hz, 1 H, $H_{a'}$), 4.48 (ddd, $^3J(a'd)$ = 5.71, $^2J(aa')$ = 10.52, $^3J(PH)$ = 44.78 Hz, 1 H, $H_{a'}$), 4.82 (dddd, $^3J(a'd)$ = 5.71, $^3J(bd)$ = 8.11, $^3J(ad)$ = 10.07, $^3J(cd)$ = 11.57 Hz, 1 H, H_d), 5.47 (s, 5 H, C_5H_5). $^{13}C\{^1H\}$ NMR (CD_3NO_2): δ 50.00 (s, $=CH_2$), 50.51 (s, $=CH_2$), 67.42 (d, $^2J(PC)$ = 6.20 Hz, OCH_2), 70.01 (d, $^2J(PC)$ = 6.58 Hz, OCH_2), 71.23 (s, =CH), 82.75 (s, =CH), 90.25 (s, C_5H_5). IR (KBr): ν(O–H), 3440 cm^{-1}; ν(=C–H), 3120, 2968, 2910 cm^{-1}; ν(P–O), 1010, 975 cm^{-1}.

Complex 4. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 150.0 (s). ^1H NMR ($CDCl_3$): δ 0.37 (d, $^3J(cd)$ = 11.86 Hz, 1 H, H_c), 2.51 (ddd, $^3J(PH)$

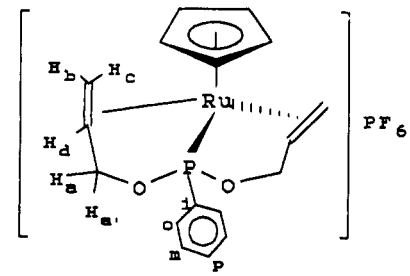


4

= 1.80, $^2J(aa')$ = 10.22, $^3J(ad)$ = 10.62 Hz, 1 H, H_a), 2.86 (dddd, $^3J(a'd)$ = 4.81, $^3J(bd)$ = 7.81, $^3J(cd)$ = 11.86, $^3J(ad)$ = 10.62 Hz, 1 H, H_d), 2.97 (ddd, $^3J(PH)$ = 3.91, $^2J(aa')$ = 10.22, $^3J(ad)$ = 10.07 Hz, 1 H, H_a), 3.16 (d, $^3J(bd)$ = 8.26 Hz, 1 H, H_b), 3.39 (dd, $^3J(PH)$ = 1.2, $^3J(bd)$ = 7.81 Hz, 1 H, H_b), 3.64 (d, $^3J(cd)$ = 11.27 Hz, 1 H, H_c), 4.31 (ddd, $^3J(a'd)$ = 4.81, $^2J(aa')$ = 10.22, $^3J(PH)$ = 40.87 Hz, 1 H, $H_{a'}$), 4.39 (ddd, $^3J(a'd)$ = 6.01, $^2J(aa')$ = 10.22, $^3J(PH)$ = 38.47 Hz, 1 H, H_a), 4.59 (dddd, $^3J(a'd)$ = 6.01, $^3J(bd)$ = 8.26, $^3J(ad)$ = 10.07, $^3J(cd)$ = 11.27 Hz, 1 H, H_d), 5.26 (s, 5 H, C_5H_5). $^{13}C\{^1H\}$ ($CDCl_3$): δ 45.10 (s, $=CH_2$), 46.47 (s, $=CH_2$), 64.75 (d, $^2J(PC)$ = 4.23 Hz, OCH_2), 67.20 (s, =CH), 67.94 (d, $^2J(PC)$ = 4.23 Hz, OCH_2), 79.42 (s, =CH), 89.01 (s, C_5H_5). IR (KBr): ν(=C–H), 3080, 2940, 2890 cm^{-1}; ν(P=O), 1175 cm^{-1}; ν(P–O), 1043, 1009 cm^{-1}.

Reaction of $[CpRu(CH_3CN)_3]PF_6$ with $PhP(OC_3H_5)_2$ (5a,b). To a yellow acetonitrile solution (20 mL) containing 0.39 g (0.90 mmol) of $[CpRu(CH_3CN)_3]PF_6$ was added 0.4 mL (3.05 mmol) of $PhP(OCH_2CH{=}CH_2)_2$ by syringe under nitrogen. After the mixture was stirred for about 20 min, the solvent was then removed on a rotary evaporator. The residue was washed with ether several times to remove excess phosphite and Arbuzov product and crystallized from dichloromethane and ether. The yellow crystalline solid which formed was collected by filtration and washed with chloroform, dichloromethane, and ether, respectively. A proton-decoupled phosphorus NMR spectrum showed that it was a mixture of two complexes (**5a** and **5b**). Attempted separation on a silica gel column with dichloromethane caused partial decomposition. Attempted fractional crystallization from dichloromethane/ether or chloroform/petroleum ether was not successful. Crystallization from acetone/chloroform afforded a mixture of two complexes in a ratio of 7:1. Yield: 116 mg (ca. 24%) of $[CpRu(\eta^5\text{-}PhP(OCH_2CH{=}CH_2)_2]PF_6$ (**5a,b**).

Complex 5a. $^{31}P\{^1H\}$ NMR (CD_3NO_2): δ 222.11 (s), −144.95 (septet, $^1J(PF)$ = 708.3 Hz, PF_6^-). ^1H NMR (CD_3NO_2): δ 1.25



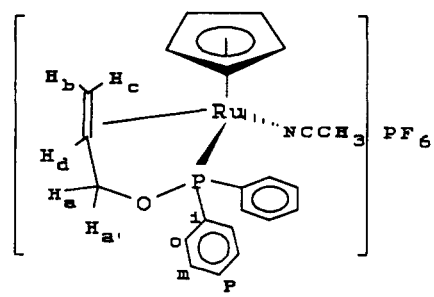
5

(d, $^3J(cd)$ = 12.02 Hz, 1 H, H_c), 3.05 (apparent td, $^3J(PH)$ = 0.40, $^2J(aa')$ = $^3J(ad)$ = 10.22 Hz, 1 H, H_a), 3.13 (apparent td, $^3J(PH)$ = 3.91, $^2J(aa')$ = $^3J(ad)$ = 10.52 Hz, 1 H, H_a), 3.92 (dddd, $^3J(a'd)$ = 4.67, $^3J(bd)$ = 7.81, $^3J(ad)$ = 10.52, $^3J(cd)$ = 12.02 Hz, 1 H, H_d), 4.17 (d, $^3J(bd)$ = 7.81 Hz, 1 H, H_b), 4.37 (d, $^3J(cd)$ = 12.32 Hz, 1 H, H_c), 4.70 (d, $^3J(bd)$ = 8.41 Hz, 1 H, H_b), 4.85 (ddd, $^2J(aa')$ = 10.52, $^3J(a'd)$ = 4.67, $^3J(PH)$ = 38.47 Hz, 1 H, $H_{a'}$), 4.90 (ddd, $^3J(a'd)$ = 5.41, $^2J(aa')$ = 10.22, $^3J(PH)$ = 47.18 Hz, 1 H, $H_{a'}$), 5.57 (dddd, $^3J(cd)$ = 12.32, $^3J(a'd)$ = 5.41, $^3J(bd)$ = 8.41, $^3J(ad)$ = 10.22 Hz, 1 H, H_d), 5.15 (s, 5 H, C_5H_5), 7.65–8.15 (m, 5 H, Ph). $^{13}C\{^1H\}$ NMR (CD_3NO_2): δ 53.87 (s, $=CH_2$), 54.90 (s, $=CH_2$), 72.26 (s, OCH_2), 75.12 (d, $^2J(PC)$ = 12.24 Hz, OCH_2), 78.29 (s, =CH), 85.37 (s, =CH), 90.69 (s, C_5H_5), 130.78 (d, $^3J(PC)$ = 12.47 Hz, C_m), 131.70 (d, $^1J(PC)$ = 12.77 Hz, C_i), 132.18 (d, $^2J(PC)$ = 12.40 Hz, C_o), 134.65 (d, $^4J(PC)$ = 2.72 Hz, C_p).

Complex 5b. $^{31}P\{^1H\}$ NMR (CD_3NO_2): δ 227.68 (s), −144.95 (septet, $^1J(PF)$ = 712 Hz, PF_6^-).

Reaction of $[CpRu(CH_3CN)_3]PF_6$ with $Ph_2P(OCH_2CH{=}CH_2)$ (6). To a yellow acetonitrile solution (20 mL) containing 0.32 g (0.74 mmol) of $[CpRu(CH_3CN)_3]PF_6$ was added 0.9 mL (3.35 mmol) of $Ph_2P(OCH_2CH{=}CH_2)$ by syringe under nitrogen. The mixture was stirred at ambient temperature for about 2 h. The solvent was removed on a rotary evaporator, and the residue was washed with ether several times to remove excess phosphite and Arbuzov product. The residue was then dissolved in dichloromethane, and the solution was set aside overnight. The product that formed was purified on a silica gel column by eluting with chloroform followed by acetone (some decomposition occurred on the column). Crystallization from chloroform/ether gave shiny, leaflike yellow crystals, which were dried in a vacuum oven at ambient temperature overnight. Yield: 110 mg (26%) of $[CpRu(NCMe)(Ph_2P(OCH_2CH{=}CH_2)]PF_6$. Mp: 181–182 °C.

$^{31}P\{^1H\}$ NMR of **6** ($CDCl_3$): δ 179.21 (s), −144.95 (septet, $^1J(PF)$ = 713.0 Hz, PF_6^-). ^1H NMR ($CDCl_3$): δ 1.89 (d, $^5J(PH)$ = 1.20



6

Hz, 3 H, CH_3), 2.91 (dd, $^3J(cd)$ = 11.42, $^2J(bc)$ = 0.60 Hz, 1 H, H_c), 2.97 (apparent td, $^3J(PH)$ = 2.10, $^2J(aa')$ = $^3J(ad)$ = 10.37 Hz, 1 H, H_a), 4.52 (apparent dt, $^3J(bd)$ = 8.11, $^3J(PH)$ = $^2J(bc)$ = 0.60 Hz, 1 H, H_b), 4.84 (s, 5 H, C_5H_5), 4.96 (ddd, $^3J(PH)$ = 36.96, $^2J(aa')$ = 10.37, $^3J(a'd)$ = 5.11 Hz, 1 H, $H_{a'}$), 5.03 (dddd, $^3J(cd)$ = 11.42, $^3J(ad)$ = 10.37, $^3J(bd)$ = 8.11, $^3J(a'd)$ = 5.11 Hz, 1 H,

H_d), 7.45–7.80 (m, 10 H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 3.61 (s, CH_3CN), 52.23 (s, $=CH_2$), 72.05 (s, =CH), 72.81 (s, OCH_2), 84.54 (s, C_5H_5), 129.08 (m, C_m), 129.78 (s, CN), 131.21 (s, C_p), 131.60 (m, C_o), 132.32 (d, ^1J(PC) = 43.31 Hz, C_i), 140.44 (d, ^1J(PC) = 62.05 Hz, C_i).

Reaction of 2 with $[CpRu(CH_3CN)_3]PF_6$. To 21.7 mg (0.05 mmol) of $[CpRu(CH_3CN)_3]PF_6$ and 25.7 mg (0.05 mmol) of **2** in a 10-mm NMR tube was added 3 mL of CD_3NO_2. After dissolution was complete, the reaction was followed by ^1H (300 MHz) and $^{31}P\{^1H\}$ (40.26 MHz) NMR spectroscopy at ambient temperature. The ^{31}P resonance at δ 202.49 (**2**) disappeared immediately and was replaced by resonances at δ 189.06 (unidentified), 183.49 (an intermediate), 177.68 (**3**), and 145.83 (**4**). After 24 h only the resonances at 189.06 and 177.68 remained with 1:1 relative intensities. Over the same period of time the C_5H_5 ^1H NMR resonance δ 5.54 (**2**) disappeared and was replaced by resonances at δ 6.35 (**1**), 5.47 (**3**), and 5.26 (unknown) with 1:2:1 relative intensities.

Reaction of $[CpRu(CH_3CN)_3]PF_6$ with Diallylphenylphosphine (DAPP). Under a purge of N_2, 0.5 mL (2.36 mmol) of DAPP was added to an orange solution containing $[CpRu(CH_3CN)_3]PF_6$ (0.5 g, 1.15 mmol) in 30 mL of CH_3CN. The solution lightened in color immediately. The flask was stoppered, and the solution was stirred with a magnetic stirring bar overnight. A ^{31}P NMR spectrum of the reaction mixture showed that a single compound (**11**) was formed (δ 29.92 (s), −144.95 septet, ^1J(PF) = 713 Hz). It presumably was $[CpRu[PhP(C_3H_5)_2]_2(CH_3CN)]PF_6$. After the solvent was removed on a rotary evaporator, the residue was washed with ether several times and crystallized from CH_2Cl_2/Et_2O. A mixture of two new compounds (**12a,b**) was obtained in a 19:1 ratio (calculated from the phosphorus NMR spectrum). The major product was obtained as a yellow crystalline solid by recrystallization from CH_2Cl_2/Et_2O in 90% yield (0.72 g). Mp: 196–197 °C.

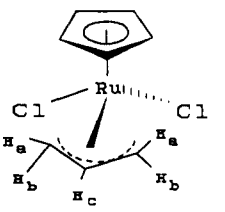
Anal. Calcd for $C_{29}H_{35}F_6P_3Ru$: C, 50.37; H, 5.10. Found: C, 50.09; H, 5.14.

$^{31}P\{^1H\}$ NMR ($CDCl_3$): **12a**, δ 28.04 (d, ^2J(PP′) = 39.05 Hz, 1 P, η^1-DAPP), −60.87 (d, ^2J(PP′) = 39.05 Hz, 1 P, η^3-DAPP), −144.95 (septet, ^1J(PF) = 713 Hz, 1 P, PF_6^-); **12b**, δ 30.15 (d, ^2J(PP′) = 43.06 Hz, 1 P, η^1-DAPP), −65.03 (d, ^2J(PP′) = 43.06 Hz, 1 P, η^3-DAPP), −144.95 (septet, ^1J(PF) = 713 Hz, 1 P, PF_6^-). ^1H NMR ($CDCl_3$) for **12a**: δ 2.02–3.06 (m, 11 H, PCH_2 and three coordinated vinyl protons), 4.58–5.60 (m, 9 H, vinyl protons), 5.10 (s, 5 H, C_5H_5), 7.10–7.50 (m, 10 H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$) for **12a**: 28.51 (d, ^1J(PC) = 34.01 Hz, CH_2), 34.92 (d, ^1J(PC) = 27.81 Hz, CH_2), 34.96 (d, ^1J(PC) = 27.81 Hz, CH_2), 39.62 (d, ^1J(PC) = 27.13 Hz, CH_2), 40.75 (d, ^2J(PC) = 22.37 Hz, HC=), 43.38 (t, ^2J(PC) = 4.95 Hz, $=CH_2$), 84.60 (s, C_5H_5), 120.40 (d, ^3J(PC) = 10.20 Hz, $=CH_2$), 120.53 (d, ^3J(PC) = 9.67 Hz, $=CH_2$), 121.11 (d, ^3J(PC) = 10.43 Hz, $=CH_2$), 128.37 (d, ^2J(PC) = 12.47 Hz, =CH), 128.56 (d, ^3J(PC) = 10.05 Hz, C_m), 129.07 (d, ^3J(PC) = 10.05 Hz, C_m), 129.92 (d, ^2J(PC) = 7.86 Hz, =CH), 130.18 (d, ^4J(PC) = 1.89 Hz, C_p), 130.03 (d, ^2J(PC) = 10.20 Hz, C_o), 131.23 (d, ^4J(PC) = 2.12 Hz, C_p), 129.10 (d, ^1J(PC) = 30.86 Hz, C_i), 135.16 (d, ^1J(PC) = 40.13 Hz, C_i).

Reaction of $[CpRu(CH_3CN)_3]PF_6$ with Allyl Chloride To Yield 7 and 8. To a yellow acetonitrile solution (20 mL) containing 0.50 g (1.15 mmol) of $[CpRu(CH_3CN)_3]PF_6$ was added 4 mL (40 mmol) of allyl chloride. The mixture was then heated at reflux under nitrogen for 4 h. Upon evaporation of the solvent, a reddish crystalline solid was obtained. It was collected by filtration and washed with chloroform and dried in vacuo. Yield: 0.16 g (50%) of $CpRu(C_3H_5)Cl_2$ (**7**).[8] Mp: 170–173 °C dec.

On another occasion, 6 mL of nitromethane was added to a yellow solution of 0.5 g of $[CpRu(CH_3CN)_3]PF_6$ and 6 mL of allyl chloride in 20 mL of acetonitrile. After the solution was heated at reflux for 6 h, the solvent was removed on a rotary evaporator to give a mixture of reddish crystalline solid and yellow powder. The yellow powder was extracted with chloroform and acetonitrile; it was isolated in 30% yield as $[CpRu(CH_3CN)(C_3H_5)Cl][PF_6]$ (**8**). The reddish crystalline solid left behind was isolated in 50% yield and characterized as the same product (**7**) as in the above reaction. Mp for **7**: 170–173 °C dec.

Complex 7. ^1H NMR (CD_3NO_2): δ 3.89 (d, ^3J(bc) = 10.81 Hz, 2 H, H_b), 4.20 (d, ^3J(ac) = 6.01 Hz, 2 H, H_a), 4.73 (tt, ^3J(ac) = 6.01, ^3J(bc) = 10.81 Hz, 1 H, H_c), 5.70 (s, 5 H, C_5H_5). $^{13}C\{^1H\}$ NMR (CD_3NO_2): δ 66.85 (s, CH_2), 95.60 (s, C_5H_5), 101.21 (s, CH).



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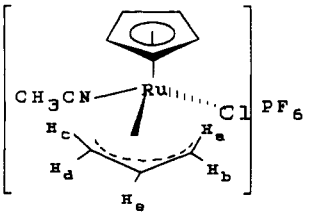

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Complex 8. ^1H NMR (CD_3NO_2): δ 2.51 (s, 3 H, CH_3), 4.05 (d, ^3J(de) = 10.97 Hz, 1 H, H_d), 4.27 (d, ^3J(be) = 10.97 Hz, 1 H, H_b), 4.36 (dd, ^3J(ce) = 6.31, ^4J(ac) = 3.76 Hz, 1 H, H_c), 4.51 (dd, ^3J(ae) = 6.31, ^4J(ac) = 3.76, 1 H, H_a), 5.15 (apparent tt, ^3J(ae) = ^3J(ce) = 6.31, ^3J(de) = ^3J(be) = 10.97 Hz, 1 H, H_e). $^{13}C\{^1H\}$ NMR (CD_3NO_2): δ 4.29 (s, CH_3), 72.90 (s, CH_2), 96.37 (s, C_5H_5), 101.54 (s, CH), 133.46 (s, CN).

$[CpRu(CH_3CN)_3]PF_6$-Catalyzed Arbuzov Rearrangement of $P(OC_3H_5)_3$. Under a purge of N_2, 50 mg (0.12 mmol) of $[CpRu(CH_3CN)_3]PF_6$ was added to 2.5 mL of $P(OC_3H_5)_3$ in a 10-mm NMR tube. The NMR tube was sealed with PTFE tape, and the reaction was monitored by $^{31}P\{^1H\}$ NMR (40.26 MHz) spectroscopy at ambient temperature. The ^{31}P resonance δ 137.75 $[P(OC_3H_5)_3]$ rapidly decreased in intensity as a resonance at δ 26.33 $[C_3H_5P(O)(OC_3H_5)_2]$ rapidly increased in intensity. The reaction was 85% complete after 20 h and 98% complete after 50 h.

$[CpRu(CH_3CN)_3]PF_6$-Catalyzed Arbuzov Rearrangements of $PhP(OC_3H_5)_2$ and $Ph_2POC_3H_5$. These two reactions were conducted in a similar manner. In each case only one product, $PhP(O)(C_3H_5)(OC_3H_5)$, δ 38.58, and $Ph_2P(O)C_3H_5$, δ 29.36, respectively, was formed at about the same rate as for the above reaction.

X-ray Data Collection and Processing. Suitable single crystals of **2** were obtained from $CH_3NO_2/CH_2Cl_2/Et_2O$ at low temperature. A single crystal was cut out from a cluster of crystals. A systematic search in reciprocal space using an Enraf-Nonius CAD4-F automatic diffractometer showed that crystals of **2** belong to the monoclinic system.

Quantitative data were obtained at room temperature. All experimental parameters used are given in Table II. The resulting data set was transferred to a VAX computer, and for all subsequent calculations the Enraf-Nonius SDP/VAX package[17] was used.

Three standard reflections measured every 1 h during the entire data collection period showed no significant trend.

The raw data were converted to intensities and corrected for Lorentz and polarization factors.

The structure was solved using the heavy-atom method. After refinement of the heavy atoms, a difference-Fourier map revealed maxima of residual electronic density close to the positions expected for hydrogen atoms; they were introduced in structure factor calculations by their computed coordinates (C–H = 0.95 Å) and isotropic temperature factors such as $B(H) = 1.3B_{eqv}(C)$ Å^2 but were not refined. At this stage empirical absorption corrections were applied using the method of Walker and Stuart[18] since face indexation was not possible. Full least-squares refinements proceeded with $\sigma^2(F^2) = \sigma^2_{counts} + (pI)^2$. A final difference map revealed no significant maxima. The scattering factor coefficients and anomalous dispersion coefficients come respectively from ref 19a,b.

Acknowledgment. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to Johnson Matthey Aesar/Alfa for

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(19) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; 1974, Vol IV, The Kynoch Press: Birmingham, England, 1974; Vol. IV: (a) Table 2.2b; (b) Table 2.3.1.

their generous loan of ruthenium.

Registry No. 1, 139565-54-1; 2, 139565-56-3; 3, 139565-58-5; 4, 139565-57-4; 5, 139565-60-9; 5′, 139565-76-7; 6, 139565-62-1; 7, 91083-16-8; 8, 139565-64-3; 9, 80049-65-6; 10, 139565-66-5; 11, 139565-68-7; 12, 139565-70-1; 14, 139565-72-3; 15, 139565-74-5; 16, 3479-30-9; DAPP, 29949-75-5; $[CpRe(CH_3CN)_3]PF_6$, 80049-61-2; $P(OCH_2CH{=}CH_2)_3$, 102-84-1; $PhP(OC_3H_5)_2$, 833-57-8; $Ph_2P(OC_3H_5)$, 14655-53-9; $ClCH_2CH{=}CH_2$, 107-05-1; $PhP(O)(C_3H_5)(OC_3H_5)$, 14655-46-0.

Supplementary Material Available: Listings of crystal and refinement data, bond distances and angles, H atom coordinates, and thermal parameters (U's) (5 pages); a listing of observed and calculated structure factors (×10) (7 pages). Ordering information is given on any current masthead page.

Photochemical Ring-Opening and Expansion Reaction of 2,4-Dineopentyl-1,1,3-triphenyl-3-vinyl-1,3-disilacyclobutane

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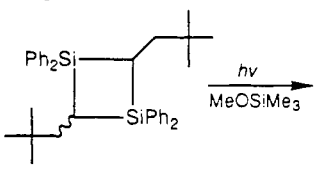
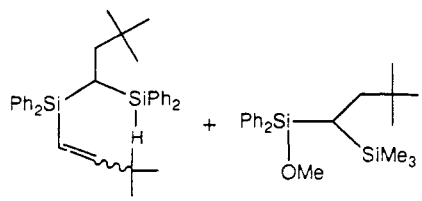
Photolysis of 2,4-dineopentyl-1,1,3-triphenyl-3-vinyl-1,3-disilacyclobutane (1) in the presence of methanol and methoxytrimethylsilane gives three major products, ring-opened alkenylsilanes, trapping products of silaethenes, and six-membered-ring products. The results are consistent with the initial formation of 1,4-biradical intermediates which undergo three competing reactions: intramolecular hydrogen abstraction leading to alkenylsilanes, fragmentation to silaethenes, and ring closure to six-membered-ring silenes. This is the first evidence for the generation of a six-membered-ring silene by the novel ring-closure reaction involving the vinyl group on silicon.

Introduction

The photochemical behavior of 1,3-disilacyclobutanes has received little attention.[2,3] The first photochemical study of 1,3-disilacyclobutanes was reported by Jutzi.[2] The photolysis of *cis*- or *trans*-2,4-diphenyl-1,1,3,3-tetramethyl-1,3-disilacyclobutane in methanol gave the methanol adduct of the ring-opened 1,4-biradical as the only isolated product. However, 1,1,3,3-tetraphenyl-1,3-disilacyclobutane gave no apparent reaction under the same conditions.[2] In order to look into this conflict, we investigated the photochemical behavior of *trans*- and *cis*-2,4-dineopentyl-1,1,3,3-tetraphenyl-1,3-disilacyclobutane.[3] The photolysis of the cyclohexane solution of *trans*- or *cis*-2,4-dineopentyl-1,1,3,3-tetraphenyl-1,3-disilacyclobutane in the presence of methoxytrimethylsilane gave *trans*- and *cis*-alkenylsilanes as major products from an intramolecular hydrogen shift reaction in the ring-opened 1,4-biradical intermediate and the trapping adduct of 1,1-diphenyl-2-neopentylsilene as a minor product:

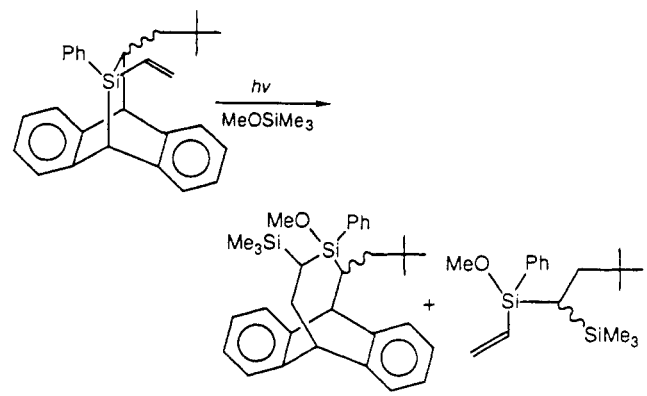


trans or *cis*



trans and *cis*

We also recently reported that the photolysis of the silabicyclo[2.2.2]octadiene having a vinyl group on the silicon atom gave the novel cyclic eight-membered-ring silene formed by the ring closure of the 1,6-biradical through vinyl involvement:[4]



In extension of these reactions, we wish to report the results of photochemical reactions of the vinyl-substituted 1,3-disilacyclobutanes 2,4-dineopentyl-1,1,3-triphenyl-3-vinyl-1,3-disilacyclobutanes (**1a–c**) in the absence and presence of trapping agents such as methanol and methoxytrimethylsilane.

Results and Discussion

The compounds *cis*-2,4-dineopentyl-1,1,3-triphenyl-*trans*-3-vinyl-1,3-disilacyclobutane (**1a**), *trans*-2,4-dineopentyl-1,1,3-triphenyl-3-vinyl-1,3-disilacyclobutane (**1b**), and *cis*-2,4-dineopentyl-1,1,3-triphenyl-*cis*-3-vinyl-1,3-disilacyclobutane (**1c**) were obtained in yields of 4.2%, 9.2%, and 6.2%, respectively, from the reaction of *tert*-butyllithium with a 1:1 mixture of chlorodivinylphenylsilane and chlorodiphenylvinylsilane in hexane at low temperature.[5]

(1) (a) Korea Institute of Science and Technology. (b) Yonsei University.
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(3) Jung, I. N.; Pae, D. H.; Yoo, B. R.; Lee, M. E.; Jones, P. R. *Organometallics* **1989**, *8*, 2017.
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0276-7333/92/2311-1626$03.00/0