of the O_2^{2-} ligand being bonded to the boron center in a triangular bidentate (C_{2v}) manner,[2,8] and the complex anion $[B(O_2)F_3]^{2-}$ may be a pentacoordinated monomer; however, the possibility that the complex ion is tetrahedral with a terminal O–O group cannot be ruled out. The IR spectrum of the complex anion $[B_2(O_2)_3F_2]^{2-}$ shows a pattern generally similar to that of the $[B(O_2)F_3]^{2-}$ species, except for much greater broadening of the band at 1050 cm^{-1}. It is believed that the stereochemistry of boron in the $[B_2(O_2)_3F_2]^{2-}$ ion is tetrahedral, which is attained through coordination of one O_2^{2-} ligand in a triangular bidentate fashion, one terminal F^- ligand, and one end of a bridging O–O ligand. An alternate structure of the dimer, similar to that found for $NaBO_3 \cdot 4H_2O$, with two O–O bridges connecting the two boron atoms (i.e., a six-membered B_2O_4 ring), is also possible irrespective of the mode of coordination of the third peroxide group. In view of the structural study of the complex anion $[B_2(O_2)_2(OH)_4]^{2-}$, the latter structure appears more likely. The two extra bands at 3450 (m) and 1640 (m) cm^{-1} in the case of the Na^+ and K^+ salts were assigned to the ν_{O-H} and δ_{H-O-H} modes of uncoordinated water.[9] The broad nature of the ν_{O-H} band in each case indicates a fair possibility of hydrogen bonding through $F \cdots H \cdots F$ interactions. The bans at 1400 (s), 3045 (s), and 3155 (m) cm^{-1} in the spectrum of $(NH_4)_2B_2(O_2)_3F_2$ have been attributed to the ν_4, ν_1, and ν_3 modes of NH_4^+.

Thus, it is evident from the present work that, under the appropriate conditions, peroxyfluoroborates can be prepared and such complexes are appreciably stable.

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Registry No. $(NH_4)_2B_2(O_2)_3F_2$, 96455-71-9; $Na_2B(O_2)F_3$, 96455-72-0; $K_2B(O_2)F_3$, 96455-73-1.

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Preparative Uses of Hexaaquaruthenium(II): Synthesis of Phosphine Complexes

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While the chemistry of ruthenium(II) is vast, many of its complexes fall within two main classifications—chemical complexes containing simple amines as well as π-accepting heterocycles and molecules containing the wealth of soft ligands associated with organometallic chemistry. $RuCl_3 \cdot 3H_2O$ ultimately serves as the source of ruthenium in the preparation of many of the compounds within both of these classes. Although the versatility of this starting material is a matter of record, it does suffer two important limitations: (1) a reduction is required in order to obtain Ru(II) species; (2) the reaction must proceed in the presence of chloride ions. Hexaaquaruthenium(II) salts may function as alternative starting points for systems where it is desired to avoid either or both of these conditions. The structure of this ion is known,[1] the lability of the aqua ligands has been studied,[2] and a range of solvents is allowed depending upon the choice of anion. The utility of $[Ru(H_2O)_6](tos)_2$ (tos = *p*-toluenesulfonate) in the preparation of complexes containing nitrogenous ligands has been described previously.[3]

Experimental Section

Reagents. All solution manipulations were performed under argon by using Schlenk-type apparatus. Solvents were purified and dried by standard procedures and saturated with argon prior to use. $[Ru(H_2O)_6](tos)_2$[1] and $[Ru(H_2O)_3(C_6H_6)](tos)_2$[4] were prepared by literature methods. All other reagents were used as commercially supplied.

Physical Measurements. ^1H, $^{13}C\{^1H\}$, and ^{31}P NMR spectra were obtained on Bruker WP-80 CW and Varian XL-100 spectrometers, respectively. ^1H and ^{13}C chemical shifts are referenced to Me_4Si; ^{31}P chemical shifts are referenced relative to 85% H_3PO_4 with positive ppm values being downfield. IR and UV–vis spectra were obtained with Perkin-Elmer 599B and 551S spectrophotometers, respectively. Solution conductivities were measured in CH_3NO_2 ($\kappa = 0.73\ \mu\Omega$) at seven concentrations (10.2–0.77 mM) with a Philips PW 9505 conductivity bridge. Results were treated according to the method recommended by Geary.[5]

Preparations. $\mathbf{Ru(H_2O)_2(THF)_2(tos)_2}$. $[Ru(H_2O)_6](tos)_2$ (0.500 g, 0.907 mmol) was suspended in 25 mL of THF and stirred for 72 h. The pale pink solid was isolated by filtration, rinsed with THF, and dried under vacuum (78% yield). Anal. Calcd for $C_{22}H_{34}O_{10}S_2Ru$: C, 42.37; H, 5.49; S, 10.28; H_2O, 5.78. Found: C, 42.37; H, 5.43; S, 10.20; H_2O, 5.69.

$\mathbf{Ru(H_2O)_2(PPh_3)_2(tos)_2}$. **Method A.** $[Ru(H_2O)_6](tos)_2$ (2.00 g, 3.63 mmol) and PPh_3 (1.95 g, 7.43 mmol) were suspended in 40 mL of THF and stirred for 24 h. The deep red solution was filtered, reduced in volume by half, and treated with 30 mL of diethyl ether. When the mixture was cooled to −30 °C, a scarlet crystalline solid formed. This solid was collected by filtration and dried under vacuum (80% yield). Anal. Calcd for $C_{50}H_{48}O_8P_2S_2Ru$: C, 59.82; H, 4.82; P 6.17; S, 6.39; H_2O, 3.59. Found: C, 59.84; H, 5.00; P, 6.10; S, 6.21; H_2O, 3.56.

Method B. $Ru(H_2O)_2(THF)_2(tos)_2$ (0.362 g, 0.581 mmol) and PPh_3 (0.304 g, 1.16 mmol) were stirred in 25 mL of THF for 24 h, producing a deep red solution. Treatment of this solution as described above resulted in isolation of $Ru(H_2O)_2(PPh_3)_2(tos)_2$, as shown by comparison of its infrared spectrum with that of an authentic sample.

$\mathbf{Ru(dppe)_2(tos)_2}$. When a suspension of 1.00 g (1.81 mmol) of $[Ru(H_2O)_6](tos)_2$ and 1.45 g (3.64 mmol) of $Ph_2PCH_2CH_2PPh_2$ (dppe) in 40 mL of THF was stirred for 24 h, a yellow solid gradually precipitated. This solid was isolated by filtration and crystallized from a $CHCl_3/C_6H_6$ mixture (40% yield). Anal. Calcd for $C_{66}H_{62}O_6P_4S_2Ru \cdot 0.5H_2O$: C, 63.46; H, 5.08; P, 9.92; S, 5.13; H_2O, 0.72. Found: C, 63.45; H, 5.06; P, 9.57; S, 5.16; H_2O, 0.81.

***cis*-$\mathbf{RuH_2(dppe)_2}$.** A suspension containing 0.800 g (0.645 mmol) of $Ru(dppe)_2(tos)_2$ and 0.18 g (3.3 mmol) of $NaAlH_4$ in 35 mL of THF was stirred for 1 h at room temperature. During this period the yellow metal complex reacted, yielding a colorless solution containing a white precipitate. The solid was removed by filtration and the filtrate reduced in volume to 5 mL. When the filtrate was cooled to −30 °C, a white crystalline solid formed. This solid was isolated by filtration and dried under vacuum.

$\mathbf{Ru(PPh_3)(C_6H_6)(tos)_2}$. A suspension of 2.50 g (4.34 mmol) of $[Ru(H_2O)_3(C_6H_6)](tos)_2$ and 2.30 g (8.78 mmol) of PPh_3 in 40 mL of THF was stirred for 24 h, producing an orange solid. The mixture was warmed, yielding a red solution, which was filtered hot. When the solution was cooled to 5 °C, an orange microcrystalline solid formed, which was isolated by filtration, rinsed with cold THF, and dried under vacuum (80% yield). Anal. Calcd for $C_{38}H_{35}O_6PS_2Ru$: C, 58.23; H, 4.50; P, 3.95; S, 8.18. Found: C, 58.16; H, 4.65; P, 3.94; S, 8.35; H_2O, <0.3.

$\mathbf{RuH_2(PPh_3)(C_6H_6)}$. A solution containing 1.00 g (1.28 mmol) of $Ru(PPh_3)(C_6H_6)(tos)_2$ in 50 mL of THF was slowly added with stirring to a suspension of $NaAlH_4$ (0.36 g, 6.6 mmol) in 20 mL of THF. Reaction was rapid with formation of a white precipitate and a pale yellow solution. The solid was removed by filtration and the clear filtrate reduced in volume of 5 mL. Addition of diethyl ether and cooling to −30 °C resulted in the formation of a yellow microcrystalline solid, which was isolated by filtration and dried under vacuum.

Results and Discussion

$\mathbf{[Ru(H_2O)_6](tos)_2}$ **Derivatives.** The high solubility of $[Ru(H_2O)_6]^{2+}$ in a variety of weakly coordinating solvents together

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Table I. Spectroscopic Data for Ru(II) Complexes

	solvent	^{1}H NMR,[a] ppm	^{31}P{^{1}H} NMR,[b] ppm	J_{PP}, Hz	IR,[c] cm^{-1}
$Ru(H_2O)_2(PPh_3)_2(tos)_2$	THF-d_8	7.5–6.8 m (PPh_3, tos) 5.03 s (H_2O) 2.33 s (tos)	51.9 s		ν_{SO} 1150, 1220
[Ru(dppe)$_2$(tos)]tos	$CDCl_3$	8.2–6.2 m (dppe, tos) 2.2 br (dppe, tos)	59.8 t 46.5 t	18.0 18.0	ν_{SO} 1200, 1250
$RuH_2(dppe)_2$	THF		79.3 t 64.8 t	16.0 16.0	ν_{Ru-H}[d] 1850 (br), 1890 (sh)
[RuCl(dppp)$_2$]BPh$_4$[e]	$CDCl_3$		45.7 t 2.95 t	32 32	
$Ru(PPh_3)(C_6H_6)(tos)_2$[f]	$CDCl_3$	7.7–6.8 m (PPh_3, tos) 5.80 s (C_6H_6) 2.30 s (tos)	32.6 s		ν_{SO} 1150, 1255
$RuH_2(PPh_3)(C_6H_6)$	THF-d_8	7.5–7.0 m (PPh_3) 5.13 s (C_6H_6) −10.2 d, J_{HP} = 44.0 Hz (Ru–H)	65.2 s [65.2 t][g]	 [~40 Hz][g]	
$RuH_2(P\text{-}i\text{-}Pr_3)(C_6H_6)$[h]	C_6D_6	5.28 m (C_6H_6) 1.69 m (P-*i*-Pr$_3$) 1.13 dd −10.44 d, J_{HP} = 43.0 Hz (Ru–H)	90.48 s		

[a] Relative to Me_4Si. [b] Downfield from 85% H_3PO_4. [c] Nujol. [d] Reported as 1880 cm^{-1}.[10] [e] Taken from ref 7. [f] ^{13}C{^{1}H} −85.66 (d), $^2J_{CP}$ = 3.2 Hz, C_6H_6. [g] Slightly reduced J_{HP} due to selective decoupling. [h] Taken from ref 13.

with the favorable exchange rate of the water ligands makes the hexaaqua salts of ruthenium(II) attractive candidates to employ in metalloorganic syntheses.

PPh_3 readily reacts with $[Ru(H_2O)_6](tos)_2$, yielding a complex of stoichiometry $Ru(H_2O)_2(PPh_3)_2(tos)_2$, regardless of the ratio of reactants. NMR and infrared spectra (Table I) are consistent with octahedrally coordinated Ru(II). The observation of electrical conductivity in nitromethane is attributed to the substitution lability of the coordinated tosylate being similar to that in Ru(dppe)$_2$(tos)$_2$ (vide infra).

A singlet in the ^{31}P{^{1}H} spectrum, along with virtual triplets for the ortho, meta, and ipso carbons in the ^{13}C{^{1}H} spectrum, suggests the presence of trans phosphine ligands. This might be expected on the basis of the trans effect and steric demands of PPh_3.

Free sulfonate anions normally display an intense absorption in the infrared associated with a doubly degenerate S–O stretch. Upon ion pairing or coordination, the symmetry of the anion is lowered and this degeneracy lifted.[6] For free tosylate this band is centered at 1200 cm^{-1}. While strong hydrogen bonding of this anion in solid $[Ru(H_2O)_6](tos)_2$ is sufficient to produce two broad adsorbances, in $Ru(H_2O)_2(PPh_3)_2(tos)_2$ discrete and sharp absorptions at 1150 and 1220 cm^{-1}, which persist in solution ($CDCl_3$), indicate coordination of the anions to ruthenium via an oxygen atom. Unfortunately simple infrared and NMR experiments are incapable of distinguishing between an all trans and a trans–cis stereochemistry.

Even the weakly coordinating solvent THF can induce reaction with $[Ru(H_2O)_6]^{2+}$. When a suspension of the tosylate salt is stirred in THF, $Ru(H_2O)_2(THF)_2(tos)_2$ is isolated in high yield. Again, absorbances at 1150 and 1230 cm^{-1} indicate that the tosylates are oxygen bound. PPh_3 reacts with this complex, $Ru(H_2O)_2(PPh_3)_2(tos)_2$ again being isolated.

Ru(dppe)$_2$(tos)$_2$ is cleanly isolated from mixtures of $PPh_2CH_2CH_2PPh_2$ and $[Ru(H_2O)_6](tos)_2$. The presence of a sharp infrared absorbance at 1250 cm^{-1} in addition to a broad band centered at 1200 cm^{-1} in both the solid state and $CDCl_3$ solution is suggestive of a combination of free and coordinated tosylate. Its room-temperature ^{31}P{^{1}H} ($CDCl_3$; Figure 1) NMR spectrum consists of a pair of sharp triplets resulting from mutually cis dppe chelates; however, variable-temperature ^{13}C{^{1}H} NMR experiments indicate that the tosylate anions are involved in some type of exchange process.

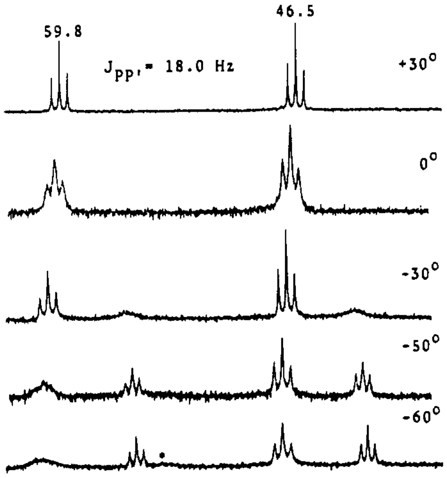
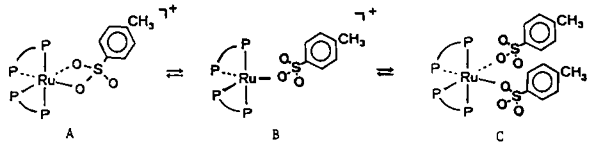


Figure 1. ^{31}P{^{1}H} NMR spectra of Ru(dppe)$_2$(tos)$_2$.

Scheme I



At −50 °C, six separate resonances assignable to the ring carbons of tosylate (presumably two more are hidden within the envelopes of the dppe phenyl resonances) attest to the presence of two distinct tosylate environments. At higher temperatures these signals broaden beyond detection; however, the limiting spectrum corresponding to rapid exchange could not be obtained due to solvent limitation.

Upon cooling, the phosphorus spectrum undergoes an even more dramatic evolution. Exchange broadening is evident at 0 °C with two new signals being observed upon further cooling. At −50 °C each of the new signals is clearly resolved into a triplet; however, the lowest field triplet of the original pair continues to broaden, suggesting the presence of a third species and a second exchange process. Finally at −60 °C, as both of the original signals broaden further, an additional broad and weak resonance is observed (starred in Figure 1). Once again the limiting spectrum could not be obtained due to the freezing point of $CDCl_3$.

The results of these experiments seem most consistent with the equilibria presented in Scheme I. It allows for the exchange of tosylate while equilibrating three species possessing cis-dppe stereochemistry, two of which are clearly indicated by ^{31}P NMR.

Since the ^{31}P resonances of the two species that are evidenced at lower temperature clearly exchange with the room-temperature

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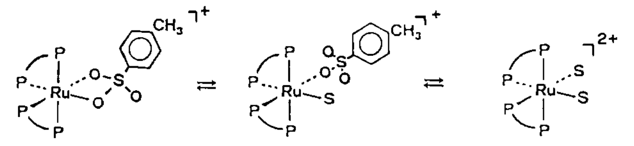
Table II. Solution Conductivity[a] and UV–Vis Spectral Data[b]

	$\Lambda_{0.001M}$	Λ_o	A	abs max, nm (ϵ_M)
$Ru(H_2O)_2(PPh_3)_2(tos)$	100	119	592	367 (960), 476 (190)
$Ru(PPh_3)(C_6H_6)(tos)_2$	71	78	320	333 (2360), 360 (sh)
$Ru(dppe)_2(tos)_2$	109	125	481	336 (2100), 376 (2180)
$[RuCl(dppe)_2]PF_6$[c]	86	91	173	357 (sh), 448 (2440), 549 (640)
NEt_4ClO_4	112	118	190	

[a] CH_3NO_2; $\Lambda_o - \Lambda_e = A \times N^{1/2}$; Λ in cm^2 Ω^{-1} equiv^{-1} and A in cm^2 Ω^{-1} equiv^{-1} $N^{-1/2}$. [b] $CHCl_3$. [c] Taken from ref 9; 1,2-dichloroethane solvent.

Scheme II



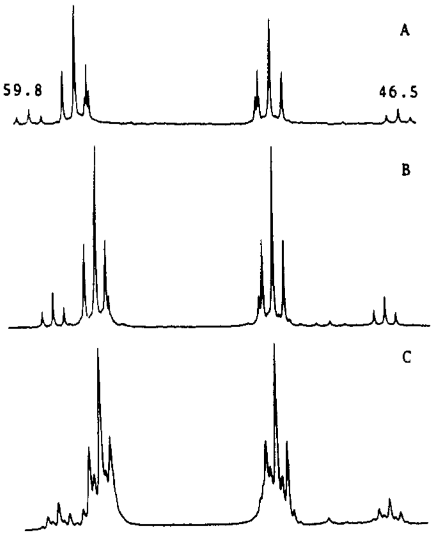


Figure 2. $^{31}P\{^1H\}$ NMR spectra of $Ru(dppe)_2(tos)_2$ in CD_3NO_2. Concentrations were increased by approximately a factor of 2 for successive measurements.

species while not appearing to exchange directly with each other, it would seem logical to propose that this complex is the pentacoordinate cation labeled B in Scheme I, However, the low-energy transition (550–680 nm) typical of the electronic spectra of other pentacoordinate complexes of Ru(II) is absent[7-9] (Table II). Additionally, although less importantly, attempts to prepare the dppe analogue of the known species $[Ru(dppe)_2Cl]^+$ were fruitless.[9]

For these reasons we propose that the predominant species present at room temperature is the hexacoordinate complex A containing a chelating tosylate ligand. We further propose that the second observed species is complex C. In order that this be consistent with the ^{31}P NMR, it is required that B have an extremely short lifetime in solution. This in fact seems quite reasonable since re-formation of A should be a low-energy intermolecular process. Thus on the NMR time scale, species C appears to be directly exchanging with A—species B essentially functioning as an activated complex. If this is indeed the correct interpretation, at some temperature below −60 °C all signals should broaden prior to attainment of the limiting spectrum consisting of three pairs of triplets.

In nitromethane solution $Ru(dppe)_2(tos)_2$ is in equilibrium with several solvated species. Conductivity data (Table II) are inconsistent with the simpler formation of a 1:1 electrolyte upon dissolution. $^{31}P\{^1H\}$ NMR spectra of CD_3NO_2 solutions across a range of concentrations show the presence of several species in addition to complex A observed in $CHCl_3$ (Figure 2). P–P couplings suggest the maintenance of the cis-dppe configuration, which is in agreement with the species formulated in Scheme II, although other species, possibly polynuclear, might also be involved.

cis-$RuH_2(dppe)_2$ is isolated in high yield upon treatment of $Ru(dppe)_2(tos)_2$ with $NaAlH_4$. The structure of this species has already been determined by X-ray crystallography.[10] The similarity between their $^{31}P\{^1H\}$ spectra [δ_P–$\delta_{P'}$(hydride) = 14.5, $J_{PP'}$ = 16.0 Hz; δ_P–$\delta_{P'}$(tos) = 13.3, $J_{PP'}$ = 18.0 Hz] is further evidence for a close structural relationship. It is hoped in the future to exploit this tendency toward maintenance of the cis-dppe configuration in other synthetic pathways stemming from $Ru(dppe)_2(tos)_2$.

$[Ru(H_2O)_3(C_6H_6)](tos)_2$ Derivatives. In reactions analogous to those of $RuCl_3$,[11] $[Ru(H_2O)_6](tos)_2$ reacts with cyclohexadienes, yielding η^6-arene complexes containing aqua ligands. Much of the chemistry of these compounds formulated as $[Ru(H_2O)_3(\eta^6\text{-arene})](tos)_2$ parallels that of $[RuCl_2(\eta^6\text{-arene})]_2$, especially upon reaction with Ag^+ or other Cl^- abstracting reagents.

A single equivalent of PPh_3 adds to the benzene derivative, yielding the molecular species $Ru(PPh_3)(C_6H_6)(tos)_2$ showing properties similar to those of $Ru(PPh_3)(C_6Me_6)(O_2CR)_2$ (R = Me, CF_3).[12] A singlet at 5.80 ppm in the proton spectrum attests to the η^6 mode of benzene coordination while the S–O stretching frequencies at 1150 and 1255 cm^{-1} confirm the presence of coordinated tosylate. This species is a 1:1 electrolyte in CH_3NO_2; however, regardless of solvent it fails to react with CO (<3 atm).

$Ru(PPh_3)(C_6H_6)(tos)_2$ reacts with excess $NaAlH_4$, producing an air-sensitive yellow microcrystalline solid. Spectroscopic results are consistent with its formulation as $RuH_2(PPh_3)(C_6H_6)$. The $^{31}P\{^1H\}$ NMR spectrum consists of a singlet that splits into a triplet upon selective decoupling of the phenyl hydrogens. The ^1H NMR spectrum contains resonances appropriate for PPh_3 and η^6-C_6H_6 in addition to a hydrido doublet at −10.2 ppm.

Analogous ruthenium dihydrides $[RuH_2(PR_3)(\eta^6\text{-arene})]$ have been prepared and studied by Maitlis[13] and Werner,[14] but interestingly, only with the extremely bulky triisopropylphosphine could a benzene adduct be isolated. In light of the relative ease with which the PPh_3 complex is isolated via the tosylato species, reactions with other less bulky phosphine ligands are currently under investigation.

In conclusion, while similar to those with $RuCl_3$, syntheses via aquaruthenium reagents can afford significantly different products. These products, as well as their reactivities, may then provide a means for obtaining a better understanding of the chemistry of their chloro analogues.

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National Science Foundation, Grant No. INT-8304329, for additional support.

Registry No. $Ru(H_2O)_2(THF)_2(tos)_2$, 96826-78-7; $[Ru(H_2O)_6](tos)_2$, 15694-44-7; $Ru(H_2O)_2(PPh_3)_2(tos)_2$, 96826-79-8; $Ru(dppe)_2(tos)_2$, 96826-80-1; *cis*-$RuH_2(dppe)_2$, 41753-60-0; $Ru(PPh_3)(C_6H_6)(tos)_2$, 96826-81-2; $[Ru(H_2O)_3(C_6H_6)](tos)_2$, 96826-82-3; $RuH_2(PPh_3)(C_6H_6)$, 96826-83-4.

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Heterobimetallic Complexes. 2.[1] Preparation and Crystal and Molecular Structure of $(C_5H_5)_2Zr(\mu\text{-}P(C_6H_5)_2)_2Mo(CO)_4$

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Heterobinuclear transition-metal complexes have been the subject of numerous recent studies.[1-25] The interest in such species stems from both the relevance of bimetallic compounds to bioinorganic systems[3,4] and the potential for applications in catalysis.[5-25] Of particular interest is the incorporation of both early and late transition metals into the same complex.[1,21-25] Such compounds are expected to exhibit the ability to activate and polarize substrates like CO.

Table I. Summary of Crystal Data, Intensity Collection, and Structure Refinement for $(C_5H_5)_2Zr(\mu\text{-}P(C_6H_5)_2)_2Mo(CO)_4$

formula	$MoZrP_2O_4C_{38}H_{30}$
cryst color, form	yellow, blocks
a, Å	18.418 (2)
b, Å	18.435 (3)
c, Å	10.082 (1)
cryst system	orthorhombic
space group	$P2_12_12_1$
vol, $Å^3$	3423 (1)
d_{calcd}, g/cm^3	1.55
Z	4
cryst faces	(001), (001), (100), (010), (010)
cryst dimens, mm	0.27 × 0.31 × 0.73
abs coeff μ, cm^{-1}	7.12
radiation (λ, Å)	Mo Kα (0.710 69)
temp, °C	24
scan speed, deg/min	2.0–5.0 ($\theta/2\theta$ scan)
scan range, deg	1.0 below Kα_1 to 1.0 above Kα_2
bkgd/scan time ratio	0.5
data collcd	3285: 20 of 4.5° to 50 ($+h,+k,+l$)
no. of unique data ($F_o^2 > 3\sigma(F_o^2)$)	2961
no. of variables	415 (2 blocks)
R	2.34
R_w	2.62

Our research is aimed at the development of synthetic methods for the incorporation of early transition elements into heterobimetallic complexes. To this end we are exploring the chemistry of early-transition-metal "metalloligands", that is complexes that are early-transition-metal species and yet have the capability of acting as ligands for other metals. We have recently reported the synthesis of the titanium species $(C_5H_5)_2Ti(SCH_2CH_2P(C_6H_5)_2)_2$,[1] which is capable of acting as a "metalloligand" for complexation of Cu(I). In this paper we describe the use of the complex $(C_5H_5)_2Zr(P(C_6H_5)_2)_2$ (**1**) as a "metalloligand". The preparation, the characterization, and the results of an X-ray crystallographic investigation of the $Mo(CO)_4$ complex of **1** are presented herein. The implications of these results are discussed below.

Experimental Section

All preparations were done under an atmosphere of dry, O_2-free, N_2. Solvents were reagent grade and were distilled from the appropriate drying agents N_2 and degassed by the freeze–thaw method at least three times prior to use. ^1H NMR spectra were recorded on Bruker CXP-80 and CXP-100 spectrometers using $Si(CH_3)_4$ as the reference. ^{31}P NMR spectra were recorded on a Bruker CXP-100 spectrometer operating at 36.44 MHz with broad band proton decoupling. Samples were sealed in 5-mm tubes under a N_2 atmosphere. The ^{31}P chemical shifts are reported relative to 85% H_3PO_4. Infrared data were recorded on a Beckman IR-12 spectrometer. Melting points were recorded on a Fisher melting point apparatus and were not corrected. UV–vis spectra were recorded on a Shumadzu 240 spectrometer. Combustion analyses were performed by Guelph Chemical Laboratories, Guelph, Ontario, Canada. $(C_5H_5)_2ZrCl_2$ and $Mo(CO)_6$ were purchased from Aldrich Chemical Co. $(C_6H_5)_2PH$ was purchased from Strem Chemical Co. *cis*-$Mo(CO)_4(NHC_5H_{10})_2$ was prepared by literature methods.[26]

Preparation of $(C_5H_5)_2Zr(P(C_6H_5)_2)_2$ (1). Initially we employed the method of Baker et al.[27] to prepare **1**. This required the reaction of $(C_5H_5)_2ZrCl_2$ with 2 equiv of $LiP(C_6H_5)_2$ at −80 °C in THF. Wade and co-workers[28] recently reported the preparation of **1** at room temperature. In subsequent preparations of **1** this method was used. **1** was found to be an extremely air-sensitive and reactive compound; thus all isolation procedures and subsequent manipulations were performed in an inert-atmosphere glovebox (N_2 atmosphere).

Preparation of $(C_5H_5)_2Zr(\mu\text{-}P(C_6H_5)_2)_2Mo(CO)_4$ (2). *cis*-$Mo(CO)_4(NHC_5H_{10})_2$ (0.34 g, 0.90 mmol) dissolved in benzene was slowly added to a benzene solution of $(C_5H_5)_2Zr(P(C_6H_5)_2)_2$ (0.513 g, 0.87 mmol). The solution changed from a dark purple to a very clear orange-yellow upon stirring for 1 h. The volume was slowly reduced, and

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