Inorganic Chemistry

Article

pubs.acs.org/IC

2,2,2-Tris(pyrazolyl)ethoxide (Ep^{OX}) Ruthenium(II) Complexes, (Ep^{OX})RuCl(L)(L′): Synthesis, Structure, and Reactivity

Brandon Quillian,[†,∥] Evan E. Joslin,[†] T. Brent Gunnoe,*[,†] Michal Sabat,[‡] and William H. Myers[§]

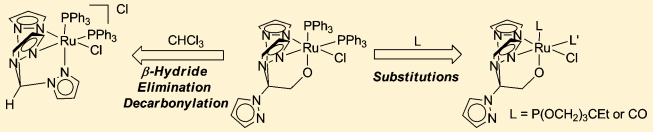
[†]Department of Chemistry, University of Virginia, Charlottesville, Virginia 22904, United States

[‡]Nanoscale Material Characterization Facility, Department of Materials Science and Engineering, University of Virginia, Charlottesville, Virginia 22904, United States

[§]Department of Chemistry, University of Richmond, Richmond, Virginia 23173, United States

Supporting Information

ABSTRACT: Treatment of $RuCl_2(PPh_3)_3$ with sodium 2,2,2-tris(pyrazolyl)ethoxide [$NaOCH_2C(pz)_3$; pz = pyrazolyl] affords the asymmetric heteroscorpionate complex *cis*-(Ep^{OX})-$RuCl(PPh_3)_2$ (**1**), (Ep^{OX} = κ^3-*N,N,O*-$OCH_2C(pz)_3$), which can be converted to Ru(II) compounds (**2**–**6**), (Ep^{OX})RuCl-(L)(L′) [(**2**) L = PPh_3, L′ = $P(OCH_2)_3CEt$; (**3**) L = L′ = $P(OCH_2)_3CEt$; (**5**) L, L′ = PPh_3, CO; (**6**) L = L′ = CO]. Compounds **1** and **3** react with $CHCl_3$ at 60 and 100 °C, respectively, to yield cationic tris(pyrazolyl)methane Ru(II) complexes, [(κ^3-*N,N,N*-Mp)$RuCl(L)_2$]Cl [Mp = $HC(pz)_3$; (**7**) L = PPh_3; (**8**) L = $P(OCH_2)_3CEt$]. The complexes have been characterized by ^1H, ^{13}C, and $^{31}P\{^1H\}$ NMR spectroscopy, elemental analysis, high resolution mass spectrometry, and cyclic voltammetry. Complexes **1** and **3** have also been characterized by single crystal X-ray analysis.



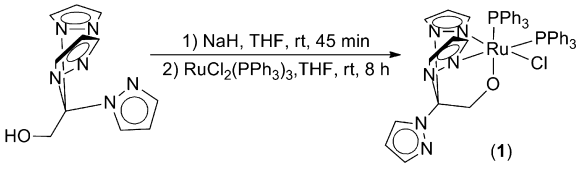
INTRODUCTION

Trofimenko's early studies of poly(pyrazolyl) ligands[1−3] has played a major role in the development of transition metal chemistry.[4−11] The $H_{(4-n)}B(pz)_n$ (n = 2, 3, 4) architecture is easily modified by varying the number and identity of the pyrazolyl fragments, which has allowed the preparation of a variety of poly(pyrazolyl)borate ligands.[11−13] In addition, poly(pyrazolyl) ligands with carbon[8,14,15] or silicon[16,17] have been prepared. Replacing one of the pyrazolyl substituents of $HE(pz^*)_3$ (E = B, C, Si; pz* = pyrazolyl or substituted pyrazolyl) with a nonpyrazolyl moiety provides mixed heteroscorpionate (HS) ligands.[18] The bis(pyrazolyl)methane heteroscorpionate ligands (HS^{Me}) [$HC(pz^*)_2X$, X = functional group] often possess anionic X functional groups such as phenoxide,[19−21] alkoxide,[20−24] thiolate,[20] acetate,[14,25−27] or dithioacetate.[24,27] These ligands have been used to prepare biomimetic models for enzyme active sites such as 2-his-1-carboxylate facial triad enzymes,[28,29] liver alcohol dehydrogenase,[22] and dimethylsulfoxide reductase.[19,20] The utility of the acetate functionalized HS^{Me} ligands has been especially well-documented in transition metal coordination chemistry;[23,30,31] however, less attention has been drawn to the study of alkoxy functionalized HS^{Me} ligands beyond the early transition metals.[20−24] Caulton et al. have studied the effects of alkoxy fragments on five-coordinate d^6-systems and found that $(PR_3)_2Ir(H)_2(OR)$ complexes are more stabilized by alkoxy functional groups than acetate, which is proposed to be a consequence of increased π-donation of the alkoxy lone pairs.[32,33] Although the alkoxy fragment induces relative stability, the influence does not engender inertness, but instead maintains "operational" unsaturation.[34,35] Obtaining a better understanding of the impact of alkoxy functionalized bis-(pyrazolyl)methane ligands on d^6-octahedral centers may provide insights into incorporating these ligands in catalytic processes that require such stabilization.[36,37]

We elected to study 2,2,2-*tris*(pyrazolyl)ethanol [$HOCH_2C(pz)_3$, {Ep^{OH}}][14] on ruthenium as a model system. Reger et al. initially disclosed the synthesis of Ep^{OH} as a synthon for the preparation of $^t Bu(C_6H_4)CH_2OCH_2C(pz)_3$,[14] and it has since been used as a building block for more elaborate ligands.[38−41] The parent ligand, Ep^{OH}, has had limited use as a κ^3-*N,N,N*-coordinating ligand in transition metal coordination chemistry,[42−44] but to our knowledge it has never been examined as a k^3-*N,N,O*-heteroscorpionate. Herein, we discuss the properties and some reactions of Ru(II) complexes supported by 2,2,2-*tris*(pyrazolyl)ethoxide (Ep^{OX}) bound in a κ^3-*N,N,O*-coordination mode.

RESULTS AND DISCUSSION

Preparation of *cis*-(Ep^{OX})$RuCl(PPh_3)_2$ and Reaction with $P(OCH_2)_3CEt$. The reaction of $RuCl_2(PPh_3)_3$ with $NaEp^{OX}$ (Ep^{OX} = $^-OCH_2C(pz)_3$) (eq 1),[38] prepared in situ



(1)

Received: November 8, 2012

   dx.doi.org/10.1021/ic3024474 | *Inorg. Chem.* XXXX, XXX, XXX−XXX

by treating 2,2,2-tris(pyrazolyl)ethanol[14] with excess sodium hydride, gives *cis*-(Ep^{OX})RuCl(PPh_3)$_2$ (**1**) in 48% isolated yield. NMR spectra (^{1}H, ^{13}C, and ^{31}P) of **1** are consistent with an asymmetric complex, which indicates a PPh_3 ligand trans to the alkoxide of the Ep^{OX} ligand. No evidence of a second isomer with the chloride ligand trans to the alkoxide fragment was detected. In a previous study, the similar heteroscorpionate ruthenium complex, (HS^A)RuCl(PPh_3)$_2$ [HS^A = bis(pyrazolyl)-acetate {HC(pz)$_2$CO$_2^-$}], was isolated as mixture of cis/trans isomers.[45]

Complex **1** decomposes above 70 °C to intractable products and exhibits air- and moisture-sensitivity at room temperature in both solution (methylene chloride, chloroform, benzene, tetrahydrofuran (THF), and toluene) and in the solid-state. The methylene protons of **1** are observed as two resonances at 4.32 ppm and 4.75 ppm (d, $^2J_{HH}$ = 8 Hz and dd, $^2J_{HH}$ = 8 Hz and $^4J_{HP}$ = 7 Hz, respectively). Solvent identity has a pronounced effect on the multiplicity and chemical shift of the ^{31}P resonances. ^{31}P NMR spectra recorded at room temperature in THF-d_8, $CDCl_3$, CD_2Cl_2, and $NCCD_3$ display two doublets exhibiting an AB splitting pattern ($^2J_{PP}$ = 26 Hz) (Figure 1). In contrast, in benzene and toluene only a single

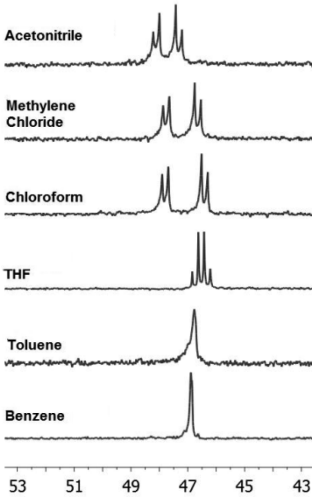
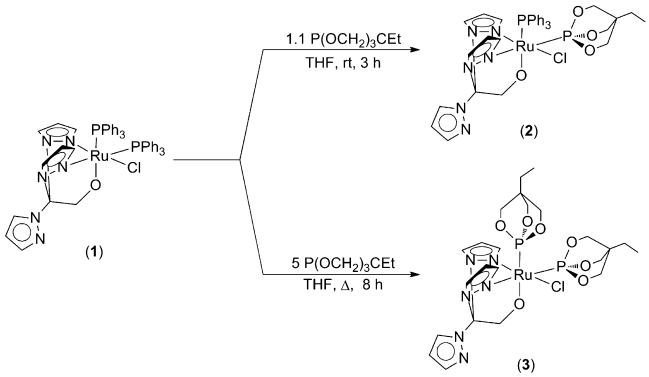


Figure 1. ^{31}P{^{1}H} NMR spectra of *cis*-(Ep^{OX})RuCl(PPh_3)$_2$ (**1**) showing different chemical shifts and multiplicities as a function of solvent identity.

resonance is observed, which we presume is a result of a dynamic exchange of the two phosphine ligands. Consistent with this suggestion, the single resonance in toluene decoalesces into two broad doublets in the ^{31}P NMR spectrum of **1** at −5 °C.

The reaction of **1** with 1.1 equiv of 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane [P(OCH$_2$)$_3$CEt][46] in THF results in the formation of the mixed phosphine/phosphite complex (Ep^{OX})RuCl[P(OCH$_2$)$_3$CEt](PPh_3) (**2**) in 83% isolated yield (Scheme 1). A diagnostic pair of doublets in the ^{31}P NMR spectrum (48 ppm and 129 ppm, $^2J_{PP}$ = 58 Hz) is consistent with phosphine and phosphite ligands in a *cis* conformation. Alternatively, combining **1** with excess P(OCH$_2$)$_3$CEt in refluxing THF results in the precipitation of (Ep^{OX})RuCl[P(OCH$_2$)$_3$CEt]$_2$ (**3**) (Scheme 1). The mixed phosphine/phosphite complex **2** is not observed (vide infra) while monitoring the formation of **3** by ^{1}H and ^{31}P NMR spectroscopy. The nine distinct signals for the pyrazolyl

Scheme 1. Reactions of 1 with P(OCH$_2$)$_3$CEt



protons and the resonances observed for the diastereotopic methylene protons of the alkoxy fragment of **3** are consistent with an asymmetric complex. A pair of doublets at 4.18 ppm and 4.26 ppm ($^3J_{PH}$ = 4 Hz) in the ^{1}H NMR spectrum is assigned to the phosphite methylene protons. These resonances collapse to singlets in the phosphorus decoupled ^{1}H NMR spectrum.

The reaction of **1** with excess of P(OCH$_2$)$_3$CEt (5 equiv) in CD_2Cl_2 at room temperature results in the formation of multiple products (determined by ^{31}P NMR spectroscopy), including free PPh_3. The ^{31}P spectrum also reveals a broad resonance (116 ppm), a virtual triplet (133 ppm), and a large singlet (130 ppm). In addition, two doublets at 129 ppm and 130 ppm are observed for complex **3**. No evidence of **2** is detected; however, the reaction of **2** with excess phosphite results in the formation of **3**. Cooling the solution to −50 °C results in decoalescence of the broad peak at 116 ppm into two doublet of doublets ($^2J_{PP}$ = 786 and 69 Hz) (Figure 2). The

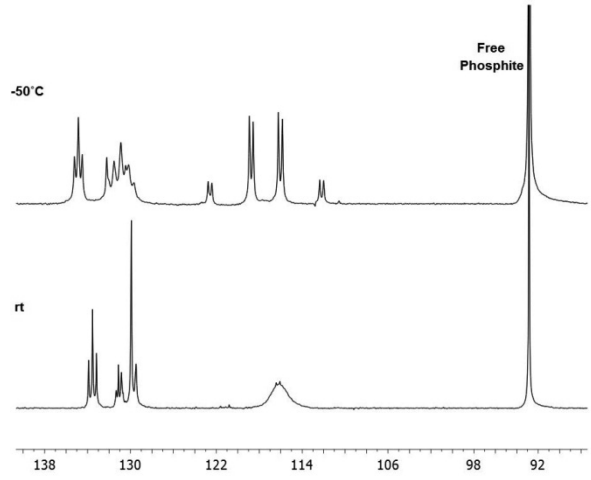
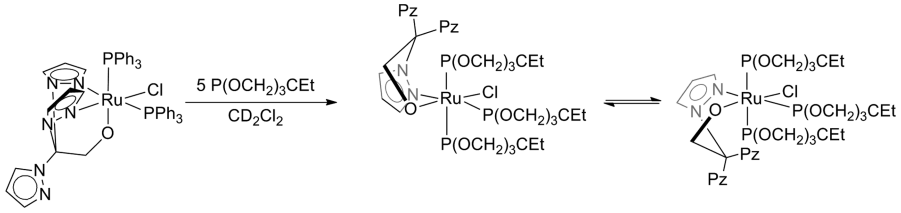


Figure 2. ^{31}P{^{1}H} NMR spectra of the reaction of **1** with excess P(OCH$_2$)$_3$CEt; room temperature (bottom) and −50 °C (top) spectra (units are in ppm).

large $^2J_{PP}$ coupling constant for the doublet of doublets (786 Hz) was validated by a ^{31}P COSY NMR experiment (see Supporting Information). Complexes with $^2J_{PP}$ couplings as large as 1100 Hz have been reported.[47,48] The two doublet of doublets at 119.0 ppm and 113.6 ppm are coupled to the virtual triplet at 133 ppm,[49,50] which remains a triplet at lower temperature. The sharp singlet at 130 ppm observed at room temperature broadens (128−132 ppm) and becomes a complex

dx.doi.org/10.1021/ic3024474 | *Inorg. Chem.* XXXX, XXX, XXX−XXX

Scheme 2. Reaction of 1 with Excess $P(OCH_2)_3CEt$ to Produce (*mer*-κ^2-*N,O*-Ep^{OX})RuCl$[P(OCH_2)_3CEt]_3$ and Proposed Fluxional Ring-Flip of the Ep^{OX} Ligand to Explain Variable Temperature ^{31}P NMR Spectra

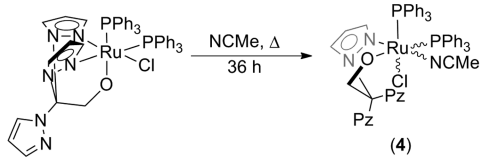


multiplet at lower temperature, indicative of a dynamic process.[51] These variable temperature spectra (Figure 2) are consistent with the complex (*mer*-κ^2-*N,O*-Ep^{OX})RuCl$[P(OCH_2)_3CEt]_3$ having three phosphite ligands about the metal center in a meridional configuration (Scheme 2). The additional singlet at ~130 ppm in the room temperature ^{31}P NMR spectrum is due to an uncharacterized species, which we were unable to isolate.

Transition metal complexes possessing multiple phosphorus ligands are commonly characterized on the premise that $^2J_{PP(cis)} < {}^2J_{PP(trans)}$.[52] On this basis, the small coupling constant ($^2J_{PP}$ = 67 Hz) for the triplet at 133 ppm is attributed to a phosphite ligand in the N−O−Cl plane coupled to the two cis-phosphite ligands, and the two doublets at 119.0 ppm and 113.6 ppm with a large $^2J_{PP(trans)}$ (786 Hz) and smaller $^2J_{PP(cis)}$ (67 Hz) coupling constant are assigned to the trans-phosphite ligands. The broad peak (116 ppm) at room temperature is a consequence of the two trans phosphite ligands approaching chemical equivalence, likely because of conformational fluxionality of the κ^2-*N,O*-Ep^{OX} ligand, where the complex rapidly converts between two conformers via a low-energy "flip" of the free noncoordinating pyrazolyl units (Scheme 2).

All efforts to isolate the *tris*-phosphite complex (*mer*-κ^2-*N,O*-Ep^{OX})RuCl$[P(OCH_2)_3CEt]_3$ led to the formation of **3**. This suggests (*mer*-κ^2-*N,O*-Ep^{OX})RuCl$[P(OCH_2)_3CEt]_3$ is only stable in the presence of excess phosphite. As evidence of this hypothesis, reaction of **3** with 1 equiv of $P(OCH_2)_3CEt$ revealed only minor formation of (*mer*-κ^2-*N,O*-Ep^{OX})RuCl$[P(OCH_2)_3CEt]_3$, signified by a broad peak at 116 ppm in the ^{31}P NMR spectrum. The resonances for (*mer*-κ^2-*N,O*-Ep^{OX})RuCl$[P(OCH_2)_3CEt]_3$ are much larger when **3** is reacted with 16 equiv of $P(OCH_2)_3CEt$. Using NMR spectra, an equilibrium constant of 4.1(4) × 10^{-3} was calculated for the formation of (*mer*-κ^2-*N,O*-EpOX)RuCl$[P(OCH_2)_3CEt]_3$.

Reaction of *cis*-$(Ep^{OX})RuCl(PPh_3)_2$ (1) with NCMe. Heating **1** in neat acetonitrile for 36 h produces (κ^2-*N,O*,-Ep^{OX})RuCl$(PPh_3)_2$(NCMe) (**4**) (characterized by ^1H and ^{31}P NMR spectroscopy) (eq 2). This complex is characterized by a



(2)

pair of doublets in the ^{31}P NMR spectrum (48.1 ppm and 50.1 ppm, $^2J_{PP}$ = 26 Hz), which are shifted upfield relative to those of **1**, and a singlet in the ^1H NMR spectrum at 2.34 ppm assigned to coordinated NCMe. The resonances attributed to the diastereotopic methylene hydrogen atoms of **4** are separated by more than 1 ppm (4.29 ppm and 3.25 ppm) and shifted upfield compared to those of **1** (4.75 and 4.31 ppm), suggesting a more electron-rich metal center. This is inconsistent with the formation of [(Ep^{OX})Ru-$(PPh_3)_2$(NCMe)][Cl] through chloride/NCMe exchange, as it is expected the cationic complex would result in a downfield chemical shift for the methylene hydrogen atoms. The ^{31}P NMR, in addition to the diastereotopic signals for the methylene hydrogen atoms, is consistent with an asymmetric complex with the PPh_3 ligands arranged in a cis-configuration. The absolute configuration of the ligands about ruthenium is not known. The isolation of **4** suggests the phosphine ligands in **1** are more strongly bound to Ru than the chelated nitrogen atoms. This reactivity is different from the reaction of (HS^A)RuCl$(PPh_3)_2$ with NCMe to produce the acetonitrile complex (k^3-*N,N,O,*-HS^A)RuCl(PPh_3)(NCMe).[53]

Single Crystal X-ray Structures of 1 and 3. Single crystal X-ray structural analyses were performed on yellow and colorless crystals of **1** (Figure 3) and **3** (Figure 4). The unit

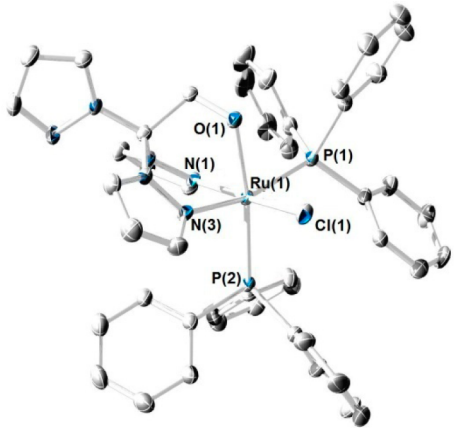


Figure 3. ORTEP of *cis*-(Ep^{OX})RuCl$(PPh_3)_2$ (**1**) (30% probability with hydrogen atoms omitted). Selected bond lengths (Å): Ru(1)−Cl(1), 2.4242(8); Ru(1)−P(1), 2.3218(9); Ru(1)−P(2), 2.3235(8); Ru(1)−O(1), 2.096(2); Ru(1)−N(1), 2.071(3), Ru(1)−N(3), 2.099(3). Selected bond angles (deg): N(1)−Ru(1)−O(1), 87.14(9); N(1)−Ru(1)−N(3), 85.9(1); O(1)−Ru(1)−N(3), 79.1(1); N(1)−Ru(1)−P(1), 96.38(8); O(1)−Ru(1)−P(1), 84.74(7); N(1)−Ru(1)−P(2), 90.23(7); P(1)−Ru(1)−P(2), 103.71(3); O(1)−Ru(1)−Cl(1), 86.99(6); N(3)−Ru(1)−Cl(1), 86.99(8); P(1)−Ru(1)−Cl(1), 89.21(3); P(2)−Ru(1)−Cl(1), 94.67(3); N(7)−Ru(2)−N(9), 86.7(1); N(7)−Ru(2)−O(2), 86.1(1); N(9)−Ru(2)−O(2), 81.8(1); N(7)−Ru(2)−P(4), 90.95(7).

cell of **1** contains two similar but crystallographically unique molecules, while that of **3** contains only one independent molecule. The initial discussion of **1** will be limited to one structure; differences between the two structures will be addressed below. The Ru(II) metal centers in **1** and **3** reside in a slightly distorted octahedral geometry and confirm an intact Ru−O bond with nearly identical bond lengths (Ru−O

dx.doi.org/10.1021/ic3024474 | Inorg. Chem. XXXX, XXX, XXX−XXX

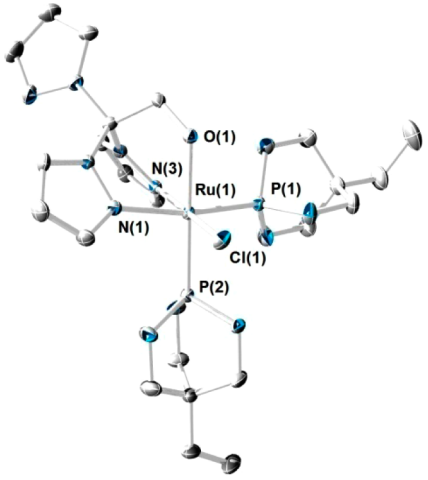


Figure 4. ORTEP of $(Ep^{OX})RuCl[P(OCH_2)_2CEt]_2$ (**3**) (30% probability with hydrogen atoms omitted). Selected bond lengths (Å): Ru(1)−Cl(1), 2.3990(9); Ru(1)−P(1), 2.1899(7); Ru(1)−P(2), 2.1905(8); Ru(1)−O(1), 2.086(2); Ru(1)−N(1), 2.140(2); Ru(1)−N(3). 2.055(3). Selected bond angles (deg): Cl(1)−Ru(1)−P(1), 96.03(3); Cl(1)−Ru(1)−P(2), 87.91(3); Cl(1)−Ru(1)−O(1), 84.85(6); Cl(1)−Ru−N(1), 90.75(7); Cl(1)−Ru−N(3), 172.80; P(1)−Ru−O(1), 92.45(6); P(1)−Ru(1)−P(2), 90.34(3); P(1)−Ru(1)−N(1), 169.18(7); P(1)−Ru(1)−N(3), 89.86(7); P(2)−Ru(1)−O(1), 172.48(6); O(1)−Ru(1)−N(1), 79.74(9).

bond = 2.092(2) Å in **1** and 2.086(2) Å in **3**). The close similarity between these bond lengths implies that the trans-effect influence of the different phosphorus ligands has little bearing on Ru−O bond distance. The Ru−O bonds of **1** and **3** are shorter than that found in $(HS^A)RuCl(PPh_3)_2$ (Ru−O = 2.181(2) Å) by almost 0.1 Å.[45] The shorter Ru−O bond distance found in **1** and **3** is expected since the oxygen atom of the alkoxy unit is not involved in delocalized π-bonding as with acetate.

The two independent molecules (vide supra) found in the unit cell of **1** have distinctions such as variation of the Ru−O−C−C dihedral angle and the orientation of the free pyrazolyl fragment (Figure 5). For example, the morphology of **1a** shown in Figure 5 displays a Ru(1)−O(1)−C(1)−C(2) dihedral angle of 37.21°, while that for **1b** [Ru(2)−O(2)−C(48)−C(49)] is 7.28°. The free pyrazolyl fragment of **1b** is nearly coplanar with the C(48)−C(49) bond, while it is slightly bent from

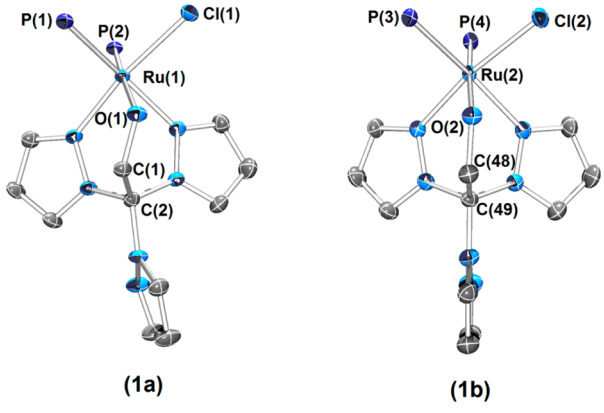
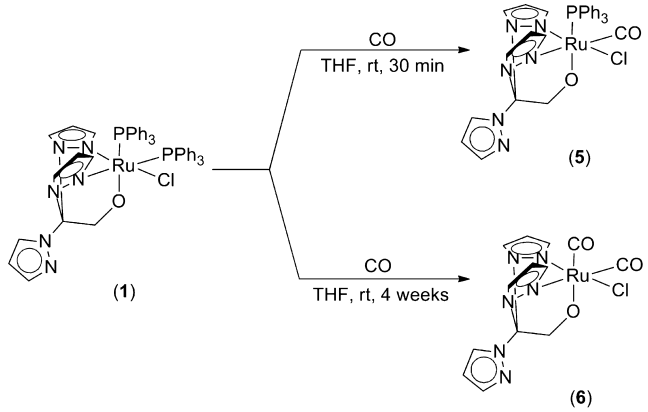


Figure 5. Depiction of dihedral angle of the C−C−O−Ru fragments of two crystallographically independent molecules found in the unit **1a** and **1b**. Atoms of the phosphorus ligands are omitted for clarity.

coplanarity relative to the C(1)−C(2) bond in **1a**. The Ru(2)−O(2)−C(48) bond angle [121.0(2)°] in **1b** is slightly larger than the Ru(1)−O(1)−C(1) bond angle [118.0(2)°] in **1a**. Transition metal M−O−R bond angles can vary greatly depending on the π-interaction of the −OR lone pairs with the metal or substituents, with larger bond angles usually correlating to a greater degree of π-bonding. For example, $TpRu(PMe_3)_2(OPh)$[54] has a larger Ru−O−R bond angle [Ru−O−C = 133.2(2)°] than $TpRu(PMe_3)_2(OMe)$, [Ru−O−C = 109.5(2)°],[55] possibly because of π-bonding of the oxygen lone pairs into the phenyl ring of $TpRu(PMe_3)_2(OPh)$.

Reaction of 1 with Carbon Monoxide. $(Ep^{OX})RuCl(PPh_3)(CO)$ (**5**) is isolated in 90% yield from the reaction of **1** with CO (60 psi) at room temperature (Scheme 3).

Scheme 3. Reactions of 1 with CO (60 psi) for 30 min and 4 weeks



Monitoring the reaction by ^{31}P NMR spectroscopy reveals complete conversion of **1** to **5** within 30 min. The nine well-resolved pyrazolyl resonances and the two resonances for methylene protons (two doublets; 4.98 ppm and 5.14 ppm, $^2J_{HH}$ = 9 Hz) in the ^1H NMR spectrum are consistent with an asymmetric complex. A single resonance (44.0 ppm) is observed in the ^{31}P NMR spectrum, while a strong absorption at 1940 cm^{-1} in the IR spectrum of **5** is assigned to the CO stretch. Comparison of the ν_{CO} (cm^{-1}) for **5** with those of similar octahedral Ru(II) complexes bearing CO, Cl, and PPh_3 ligands (Table 1) suggests the Ep^{OX} ligand is an overall better electron-donor than Tp[56] and Cp;[57] however, it appears that the electron donating ability of the Ep^{OX} ligand is less than that of Cp* ($C_5Me_5^-$).[58] As expected, the ν_{CO} (1940 cm^{-1}) stretch for **5** also implies that the Ep^{OX} ligand is a stronger electron-donating ligand than its acetate bearing analogue $(HS^A)RuCl(CO)(PPh_3)$ (ν_{CO} = 1969 cm^{-1}).[59]

Table 1. Carbonyl Stretching Frequencies of Octahedral Ruthenium(II) Complexes with CO and PPh_3 Ligands

complex	ν_{CO} (cm^{-1})	ref.
$(Ep^{OX})RuCl(PPh_3)(CO)$ (**5**)	1940	this work
Cp*$RuCl(PPh_3)(CO)$	1918	58
(η^5-indenyl)$RuCl(PPh_3)(CO)$	1944	60
$CpRuCl(PPh_3)(CO)$	1958	57
$TpRuCl(PPh_3)(CO)$	1965	56
$(HS^A)RuCl(PPh_3)(CO)$	1969	59
[(η^6-C_6Me_6)$RuCl(PPh_3)(CO)$][PF_6]	2012	61
[(η^6-*p*-cymene)$RuCl(PPh_3)(CO)$][OTf]	2027	62

dx.doi.org/10.1021/ic3024474 | Inorg. Chem. XXXX, XXX, XXX−XXX

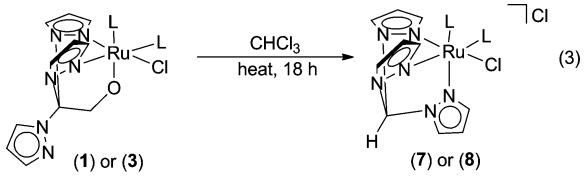
Prolonged reaction of **1** with CO (60 psi) at room temperature produces $(Ep^{OX})RuCl(CO)_2$ (**6**) over several weeks (Scheme 3). The half-life of this reaction at room temperature is approximately 21 days. Increasing CO pressure (100 psi) at room temperature and/or exposure to slightly elevated temperatures (50 °C) leads to the formation of multiple intractable products. Complex **6** is asymmetric, as indicated by the nine pyrazolyl and two methylene resonances (two doublets, 4.77 ppm and 4.94 ppm, $^2J_{HH}$ = 9 Hz). Two absorptions at 2060 cm^{-1} and 1986 cm^{-1} in the IR spectrum of **6** confirm the presence of cis-dicarbonyl ligands. Comparison of the average value of the symmetric and asymmetric absorptions for a series of Ru(II) complexes (Table 2) places

Table 2. Carbonyl Stretching Frequencies of Octahedral Ruthenium(II) Complexes with Bis-carbonyl Ligands

complex	ν_{CO} (cm^{-1})	avg ν_{CO} (cm^{-1})	ref
$(Ep^{OX})RuCl(CO)_2$ (**5**)	2060, 1986	2023	this work
$Cp^*RuCl(CO)_2$	2025, 1975	2000	63
(η^5-indenyl)$RuCl(CO)_2$	2052, 1995	2023	64
$CpRuCl(CO)_2$	2059, 2008	2033	65
$TpRuCl(CO)_2$	2071, 2011	2041	66
$(bdmpza)RuCl(CO)_2$	2066, 1996	2031	67

the donor ability of the Ep^{OX} ligand greater than Tp and Cp, similar to indenyl, and less than Cp*. The recently reported $(bdmpza)RuCl(CO)_2$ (bdmpza =2,5-dimethylpyrazolyl acetate) complex,[67] which bears an acetate heteroscorpionate ligand, has a slightly higher energy average CO absorption than **6**.

Reactivity of $(Ep^{OX})RuCl(L)_2$ Complexes with Chloroform. Heating **1** in chloroform at 60 °C results in the formation of the previously reported[68] tris(pyrazolyl)methane ruthenium(II) complex $[\{HC(pz)_3\}RuCl(PPh_3)_2]Cl$ (**7**) (eq 3). The identity of compound **7** was confirmed by independent

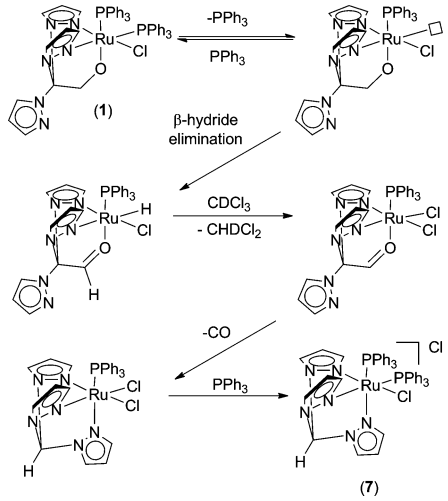


a) (**1**) or (**7**) L = PPh_3, 60 °C; b) (**3**) or(**8**) L = $P(OCH_2)_3CEt$, 100 °C

synthesis. Monitoring the reaction of **1** with $CHCl_3$ to generate **7** by ^{31}P NMR spectroscopy revealed initial appearance of free PPh_3, followed by the emergence of a singlet at 39.2 ppm for complex **7**. Ruthenium intermediates were not observed by ^{31}P or ^1H NMR spectroscopy, although during the reaction resonances in the ^1H NMR spectrum were broadened. Upon completion of the reaction, the free PPh_3 was completely consumed. Performing the reaction in $CDCl_3$ results in the production of $CHDCl_2$ (1:1:1 triplet, 5.32 ppm). Additionally, when heating **1** in the presence of excess PPh_3 the rate of formation of **7** is reduced. For example, heating **1** in the presence of PPh_3 (5 equiv) in $CDCl_3$ for 2 h results in 10% conversion of **1** into **7**, whereas heating **1** without added PPh_3 results in a more expedient reaction with 33% conversion in 2 h. These observations are consistent with a mechanism that involves PPh_3 dissociation.

Given that the addition of free PPh_3 slows the reaction and the precedent for Ru(II)-based decarbonylation reactions,[69] the alkoxide fragment of the Ep^{OX} ligand is likely converted into a carbonyl unit upon phosphine dissociation followed by β-hydride elimination.[70,71] The net loss of the CHO fragment of the Ep^{OX} ligand could involve decarbonylation.[72−74] The observation of $C(D)HCl_2$ in the ^1H NMR spectrum in $CDCl_3$ is evidence of hydrogen/chloride exchange between **1** and solvent.[75] Reactions with metal-hydrides with chloroform to generate a metal-chloride and methylene chloride are known.[76,77] Thus, the observation of $CHDCl_2$ is consistent with the formation of a Ru−H intermediate. The intimate details for the conversion of **1** to **7** cannot be known with available data, but Scheme 4 portrays a pathway consistent with experimental observations and established precedent.

Scheme 4. Possible Pathway for the Conversion of 1 to 7



Similar to the formation of **7**, heating a $CHCl_3$ solution of **3** (100 °C) yields $[\{\kappa^3\text{-}HC(pz)_3\}RuCl[P(OCH_2)_3CEt]_2]Cl$ (**8**) in quantitative yield (determined by ^1H NMR spectroscopy). Monitoring the reaction with ^1H and ^{31}P NMR spectroscopy suggests differences in formation pathways for **7** and **8**. For example, while free PPh_3 is observed during the formation of **7**, no evidence of $P(OCH_2)_3CEt$ dissociation is obtained during the formation of **8**. In addition, the reaction of **3** with $CDCl_3$ produces $[\{DC(pz)_3\}RuCl\{P(OCH_2)_3CEt\}_2]Cl$ (**8**-d_1), as indicated by the absence of the methine proton resonance at 12.36 ppm for the tris(pyrazolyl)methane ligand, and $C(D)HCl_2$ is not observed when $CDCl_3$ is used as reaction medium for the conversion of **3** to **8**. This suggests that the deuterium/proton incorporation at the methine position in **8** comes directly from the solvent. Heating **3** in $^{13}CHCl_3$ does not afford a ^{13}C-labeled complex **8**.

Electrochemistry. To determine relative electron density of the Ru(II) complexes we sought to compare redox potentials. The results of cyclic voltammetry studies of complexes **1**−**3**, **5**, **7**, and **8** are listed in Table 3 (reported versus NHE). Cyclic voltammogram (CV) data for all complexes show either irreversible or quasi-reversible Ru(III/II) redox potentials. A quasi-reversible couple at +0.47 V is assigned to the Ru(III/II) redox potential of **1**. As expected, based on the ν_{CO} stretch of $TpRuCl(CO)(PPh_3)$ and $(Ep^{OX})RuCl(PPh_3)(CO)$ (**3**) (ν_{CO} = 1965 cm^{-1} and 1940 cm^{-1}, respectively), the Ru(III/II) potential of **1** is negative to that of the less electron-rich $TpRuCl(PPh_3)_2$,[78] observed at 0.84 V. In relation to **1**, Ru (III/II) potentials of compounds **2**

dx.doi.org/10.1021/ic3024474 | Inorg. Chem. XXXX, XXX, XXX−XXX

Table 3. Cyclic Voltammetry Data for (κ^3-L)RuCl(L′)(L″) Complexes [L = Ep^{OX} or tris(pyrazolyl)methane (Mp)]

complex [L′/L″]	ligand	$E_{1/2}$, {$E_{p,a}$}
1 $[PPh_3]_2$	Ep^{OX}	+0.47
2 $[PPh_3/P(OCH_2)_3CEt]$	Ep^{OX}	{+0.70}
3 $[P(OCH_2)_3CEt]_2$	Ep^{OX}	{+0.73}
5 $[PPh_3/CO]$	Ep^{OX}	{+1.21}
7 $[PPh_3]_2$	Mp	+1.24
8 $[P(OCH_2)_3CEt]_2$	Mp	{+1.29}

and **3** are more positive, showing irreversible Ru(III/II) potentials at +0.70 V and +0.73 V, respectively. These data suggest that the net result of substituting PPh_3 with $P(OCH_2)_3CEt$ is a reduction of electron-density at the metal center. This correlates well with the known π-accepting ability of bicyclic phosphites.[79] The CV of **5** reveals a Ru(III/II) potential at +1.21 V, which reflects the expected reduction of electron-density upon coordinating CO. The CVs for the cationic tris(pyrazolyl)methane ruthenium compounds, **7** and **8**, show considerably more positive Ru(III/II) redox potentials (+1.24 V and +1.29 V, respectively) compared to the neutral Ep^{OX} ruthenium complexes **1**−**5**.

SUMMARY

Ruthenium(II) compounds **1**−**6** supported by 2,2,2-*tris*(pyrazolyl)ethoxide ($NaOCH_2C(pz)_3$, {Ep^{OX}}, pz = pyrazolyl) with phosphorus and CO ligands have been reported. For complexes **1**, **3**, and **6**, the asymmetric *cis*-isomers with the chloride ligand cis to the alkoxy ligand are isolated. Compounds **1** and **3** react with $CHCl_3$ at 60 and 100 °C, respectively, to produce cationic tris(pyrazolyl)methane Ru(II) products (**7** and **8**). Conversions of the ruthenium(II) Ep^{OX} complexes **1** and **3** to tris(pyrazolyl)methane Ru(II) products **7** and **8** highlight the potential incompatibility of the Ep^{OX} ligand with late transition metal complexes that can mediate β-hydride elimination and decarbonylation. Using ν_{CO} of monocarbonyl complexes as a gauge, the Ep^{OX} ligand is more electron-donating than Cp, Tp and η^6-arenes.

EXPERIMENTAL SECTION

Unless otherwise noted, all synthetic procedures were performed under anaerobic conditions in a nitrogen filled glovebox or by using standard Schlenk techniques. Glovebox purity was maintained by periodic nitrogen purges and was monitored by an oxygen analyzer (O_2 < 15 ppm for all reactions). Tetrahydrofuran was dried by distillation from sodium/benzophenone. Pentane was distilled over P_2O_5. Acetonitrile and diethyl ether were dried by distillation from CaH_2. Benzene, hexanes, and methylene chloride were purified by passage through a column of activated alumina. Acetonitrile-d_3, benzene-d_6, chloroform-d_1, methylene chloride-d_2 and toluene-d_8 were stored under a nitrogen atmosphere over 4 Å molecular sieves. ^{1}H NMR spectra were recorded on a Varian Mercury Plus 300 MHz or a Varian Inova 500 MHz spectrometer, and ^{13}C NMR spectra were recorded on Varian Mercury Plus 300 MHz and Varian Inova 500 MHz spectrometers (operating frequency 75 and 126 MHz, respectively). All ^{1}H and ^{13}C NMR spectra are referenced against residual proton signals (^{1}H NMR) or the ^{13}C resonances of the deuterated solvent (^{13}C NMR). ^{31}P NMR spectra were obtained on a Varian Mercury Plus 300 MHz (operating frequency 121 MHz) spectrometer and referenced against an external standard of H_3PO_4 (δ = 0). Variable Temperature ^{31}P NMR and ^{31}P COSY experiments were recorded on a Varian Inova 500 MHz spectrometer (202 MHz). Pyrazolyl has been abbreviated as pz. Resonances due to the pyrazolyl residues of the Ep^{OX} ligand are listed by chemical shift and multiplicity only (all coupling constants are less than 3 Hz).

Electrochemical experiments were performed under a nitrogen atmosphere using a BAS Epsilon Potentiostat. Cyclic voltammograms were recorded in NCMe using a standard three electrode cell from −1700 to 1700 mV at 100 mV/s (unless otherwise noted) with a glassy carbon working electrode and tetrabutylammonium hexafluorophosphate as electrolyte. All potentials are reported versus NHE (normal hydrogen electrode) using cobaltocenium hexafluorophosphate as the internal standard. High-resolution electrospray ionization mass spectrometry (ESI-MS) analyses were obtained on a Bruker BioTOF-Q spectrometer at the University of Richmond. Samples were dissolved in acetonitrile then mixed 3:1 with 0.1 M aqueous sodium trifluoroacetate (NaTFA) using $[Na(NaTFA)_x]^+$ clusters as an internal standard. These data are reported using the most intense peaks from the isotopic envelope for either $[M]^+$, $[M + H]^+$, or $[M + Na]^+$. The data are listed as m/z with the intensity relative to the most abundant peak of the isotopic envelope given in parentheses for both the calculated and the observed peaks. The difference between calculated and observed peaks is reported in ppm. Single crystal X-ray intensity data were collected on a Bruker SMART APEX II CCD diffractometer using MoKα radiation. The structure was solved by direct methods in Bruker SHELXTL.[80] Hydrogen atoms were included in calculated positions without further refinement. The preparation and characterization of 2,2,2-(pyrazol-1-yl)ethanol,[14,40] 2,2,2-(pyrazol-1-yl)ethoxide sodium[38] and $RuCl_2(PPh_3)_3$[81] have been reported. $P(OCH_2)_3CEt$ was obtained from a commercial source and purified by extraction and recrystallization in hexane. All other reagents were used as purchased from commercial sources.

***cis*-(Ep^{OX})RuCl(PPh_3)$_2$ (1).** To a 100 mL round-bottom flask containing $HOCH_2C(pz)_3$ (643 mg, 2.52 mmol) in THF (18 mL), a slurry of NaH (73.8 mg, 3.08 mmol) in THF (8 mL) was added. The reaction mixture was stirred at room temperature for 45 min. The solution was passed through a short column of Celite to remove excess NaH, and the filtrate was added to a THF solution (20 mL) of $RuCl_2(PPh_3)_3$ (2.35 g, 2.45 mmol). The reaction was stirred at room temperature overnight then all volatiles were removed in vacuo. The remaining red-brown residue was reconstituted in a minimum amount of methylene chloride, loaded on a short column of Celite, and washed with additional methylene chloride (15 mL). The filtrate was collected and reduced to ∼3−5 mL in vacuo, and hexane was added to induce precipitation. The yellow precipitate was collected on medium porosity frit and washed with diethyl ether and pentane. The solid was collected, reconstituted in methylene chloride, and loaded on a silica column (prewashed with diethyl ether). A red material was eluted with diethyl ether and discarded. The column was then washed with THF to elute a yellow band. This eluate was collected, reduced in vacuo unto dryness, reconstituted in methylene chloride (5 mL), and treated with hexanes to precipitate a yellow solid. The yellow solid was collected on a fine frit, washed with a minimum amount of diethyl ether followed by copious amounts of pentane, and dried in vacuo (791 mg, 35%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.31 (d, 1H, $-CH_2$ORu-, $^2J_{HH}$ = 7 Hz), 4.75 (dd, 1H, $-CH_2$ORu-, $^2J_{HH}$ = 8 Hz and $^4J_{HP}$ =7 Hz), 5.35 (m, 2H, overlapping 3- or 5-pz), 5.96 (dd, 1H, 4-pz), 6.61 (m, 2H, overlapping, 4-pz), 6.96−7.06 (m, 12H, PPh_3), 7.06−7.18 (m, 6H, PPh_3), 7.20−7.26 (m, 6H, overlapping pz and PPh_3), 7.47 (br s, 1H, 3- or 5-pz), 7.80 (t, 6H, *o*-PPh_3, $^3J_{HH}$ = 9 Hz), 7.88 (d, 1H, 3- or 5-pz), 7.99 (br s, 1H, 3- or 5-pz). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 75.6 (s, -$OCH_2C(pz)_3$), 91.2 (s, -$OCH_2C(pz)_3$), 105.7, 106.6, 108.4 (each a singlet, 4-pz), 127.2, 127.6 (each d, $^3J_{CP}$ = 9 Hz, *m*-PPh_3), 128.5, 128.9 (each a singlet, *p*-PPh_3), 130.7, 130.9, 130.8 (each a singlet, 3- or 5-pz), 134.4, 135.1 (each a doublet, $^2J_{CP}$ = 9 Hz, *o*-PPh_3), 136.0 (s, $^1J_{CP}$ = 6 Hz, *i*-PPh_3), 136.4 (s, *i*-PPh_3, $^1J_{CP}$ = 2 Hz), 142.9, 145.8, 148.9 (each s, 3- or 5-pz). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$) δ: 46.9 (d, $^2J_{PP}$ = 27 Hz), 48.1 (d, $^2J_{PP}$ = 27 Hz). CV: $E_{1/2}$ = +0.47 V, [Ru(III/II), quasi-reversible]. HRMS: $[M + H]^+$ obs'd (%), calc'd (%), ppm: 903.16439 (43.7), 903.1638 (41.9), 0.7; 904.16405 (66), 904.16389 (61.4), 0.2; 905.16457 (100), 905.16313 (100), 1.6; 906.16477 (67.3), 906.16462 (56.8), 0.2; 907.16289 (77.7), 907.163 (75.9), −0.1.

dx.doi.org/10.1021/ic3024474 | Inorg. Chem. XXXX, XXX, XXX−XXX

(Ep^{OX})RuCl(PPh_3)[$P(OCH_2)_3CEt$] (2). $P(OCH_2)_3CEt$ (46.4 mg, 0.286 mmol) dissolved in THF was added to a THF solution (25 mL) of **1** (235 mg, 0.260 mmol) and stirred for 3 h at room temperature. All solvent was removed under vacuum, the yellow residue was taken up in a minimum amount of methylene chloride, and hexanes were added to induce precipitation. The pale-yellow solid was collected on a fine porosity frit, washed with pentane, and dried under reduced pressure (173 mg, 83%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ: 0.73 (t, 3H, $-CH_2CH_3$, $^3J_{HH}$ = 7 Hz), 1.09 (q, 2H, $-CH_2CH_3$, $^3J_{HH}$ = 7 Hz), 3.96 (d, 6H, $(POCH_2)_3$-, $^3J_{HP}$ = 5 Hz), 4.82 (d, 1H, $-CH_2$ORu-, $^2J_{HH}$ = 8 Hz), 5.04 (t, 1H, $-CH_2$ORu-, $^2J_{HH}$ = 8 Hz), 5.69 (dd, 1H, 3- or 5-pz), 6.40 (br s, 1H, 4-pz), 6.63 (m, 2H, overlapping 4-pz), 6.67 (d, 1H, 3- or 5-pz), 7.17 (d, 1H, 3- or 5-pz), 7.20–2.30 (m, 9H, PPh_3), 7.86–7.95 (m, 6H, PPh_3), 7.97 (d, 1H, 3- or 5-pz), 8.06 (d, 1H, 3- or 5-pz), 8.29 (d, 1H, 3- or 5-pz). ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2) δ: 7.2 (s, $-CH_2CH_3$), 23.8 (s, $-CH_2CH_3$), 35.1 (d, $(-CH_2)_3CEt$, $^3J_{CP}$ = 31 Hz), 74.1 (d, $P(OCH_2)_3$, $^2J_{CP}$ = 7 Hz), 92.0 (s, $C(pz)_3$), 106.0, 106.6, 108.7 (each a singlet, 4-pz) 127.4 (d, *o*-PPh_3, $^2J_{CP}$ = 9 Hz), 130.8 (s, *p*-PPh_3), 131.2 (s, 3- or 5-pz), 135.1 (d, *m*-PPh_3, $^3J_{CP}$ = 10 Hz), 136.5 (d, *i*-PPh_3, $^1J_{CP}$ = 42 Hz), 143.3, 145.8, 148.4 (each a singlet, 3- or 5-pz). ^{31}P{^{1}H} NMR (121 MHz, CD_2Cl_2) δ: 48.1 (d, PPh_3, $^2J_{PP}$ = 57 Hz), 129.1 (d, $P(OCH_2)_3CEt$, $^2J_{PP}$ = 57 Hz). CV: $E_{p,a}$ = +0.70 V [Ru(III/II), irreversible]. HRMS: [M+H$^+$] obs'd (%), calc'd (%), ppm: 804.11488 (50.5), 804.11706 (60.8), −2.7; 805.11449 (100), 805.11626 (100), −2.2; 806.11614 (49.6), 806.11763 (48.3), −1.8; 807.11501 (81.2), 807.11603 (75.6), −1.3; 808.11862 (24.1), 808.11864 (27.9), 0.

(Ep^{OX})RuCl[$P(OCH_2)_3CEt]_2$ (3). Compound **1** (101 mg, 0.111 mmol) and $P(OCH_2)_3CEt$ (101 mg, 0.623 mmol) were combined, dissolved in THF (40 mL), and refluxed for 8 h. The flask was allowed to cool to room temperature, and hexanes were added to induce precipitation. The white solid was collected on a fine porosity frit, washed successively with diethyl ether and pentane, and dried under reduced pressure (72.1 mg, 93%). ^{1}H NMR (300 MHz, CD_2Cl_2) δ: 0.81 (overlapping triplets, 6H, $-CH_2CH_3$, $^3J_{HH}$ = 7 Hz), 1.18 (q, 2H, $-CH_2CH_3$, $^3J_{HH}$ = 7 Hz), 1.20 (q, 2H, $-CH_2CH_3$, $^3J_{HH}$ = 7 Hz), 4.21 (d, 6H, $P(OCH_2)_3$-, $^2J_{HP}$ = 4 Hz), 4.26 (d, 6H, $P(OCH_2)_3$-, $^2J_{HP}$ = 4 Hz), 4.58 (d, 1H, $-CH_2$ORu-, $^2J_{HH}$ = 9 Hz), 4.77 (t, 1H, $-CH_2$ORu-, $^2J_{HH}$ = 9 Hz), 6.16 (dt, 1H, 4-pz), 6.39 (br s, 1H, 4-pz), 6.61 (dt, 1H, 4-pz), 6.71 (d, 1H, 3- or 5-pz), 7.15 (d, 1H, 3- or 5-pz), 7.88 (d, 1H, 3- or 5-pz), 7.98 (br s, 2H, overlapping resonances, 3- or 5-pz), 8.26 (br s, 1H, 3- or 5-pz). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ: 7.3 (s, $-CH_2CH_3$), 23.7 (s, $-CH_2CH_3$), 35.1 (dd, $^3J_{CP}$ = 20 Hz, $(-CH_2)_3CEt$), 74.0 (d, $(P(OCH_2)_3$, $^2J_{CP}$ = 6 Hz), 76.0 (s, $OCH_2C(pz)_3$), 91.7 (s, $C(pz)_3$), 105.9, 106.6, 108.4 (each a singlet, 4-pz), 130.4, 131.0, 142.9, 146.0, 148.7 (each a singlet, 3- or 5-pz). ^{31}P{^{1}H} NMR (121 MHz, CD_3CN) δ: 129.2 (d, $^2J_{PP}$ = 99 Hz), 130.7 (d, $^2J_{PP}$ = 99 Hz). EA calcd (found) for $C_{24}H_{34}Cl_4N_6O_7P_2Ru$: C, 35.01(35.46); H, 4.16(4.52); N, 10.29(10.01). Note: contains 1 equiv of $CHCl_3$ determined by ^{1}H NMR. CV: $E_{p,a}$ = +0.73 V Ru(III/II) (irreversible), +1.10 V (irreversible). HRMS: [M+H$^+$] obs'd (%), calc'd (%), ppm: 804.11488 (50.5), 804.11706 (60.8), −2.7; 805.11449 (100), 805.11626 (100), −2.2; 806.11614 (49.6), 806.11763 (48.3), −1.8; 807.11501 (81.2), 807.11603 (75.6), −1.3; 808.11862 (24.1), 808.11864 (27.9), 0.

(κ^2-*N,O*-Ep^{OX})RuCl(PPh_3)$_2$(NCMe) (4). Compound **1** (99.0 mg, 0.110 mmol) was dissolved in NCMe (10 mL) and stirred at room temperature for 36 h. The yellow solution was filtered through a plug of Celite. The filtrate was collected, and then solvent removed under reduced pressure. The residue was reconstituted in a minimum amount of methylene chloride and treated with hexanes to give a pale yellow solid. The solid was collected by filtration on a fine porosity frit and dried in vacuo (72.2 mg, 70%). ^{1}H NMR (CD_2Cl_2, 300 MHz) δ: 2.34 (s, 3H, NCMe), 3.22 (d, 1H, $-CH_2$ORu-, $^2J_{HH}$ = 9 Hz), 4.29 (dd, 1H, $-CH_2$ORu-, $^2J_{HH}$ = 9 Hz, $^4J_{HP}$ = 7 Hz), 5.75 (dd, 1H, 4-pz), 6.18 (dd, 1H, 4-pz), 6.20 (br dd, 1H, 4-pz), 6.38 (d, 1H, 3- or 5-pz), 6.56 (d, 1H, 3- or 5-pz), 6.69 (d, 1H, 3- or 5-pz), 7.06 (t, 6H, *p*-PPh_3, $^3J_{HH}$ = 9.06), 7.18–7.49 (m, 25H, overlapping *o*-*m*-PPh_3 and one 3- or 5-pz), 7.74 (d, 1H, 3- or 5-pz,), 8.04 (d, 1H, 3- or 5-pz). ^{31}P{^{1}H} NMR (CD_2Cl_2, 121 MHz) δ: 48.1 (d, $^2J_{PP}$ = 25 Hz), 50.1 (d, $^2J_{PP}$ = 25 Hz).

(Ep^{OX})RuCl(CO)(PPh_3) (5). *cis*-(Ep^{OX})RuCl(PPh_3)$_2$ (**1**) (101 mg, 0.111 mmol) was dissolved in THF (30 mL) and added to a glass pressure reactor equipped with a stir bar. The reactor was pressurized with CO (60 psi) and stirred at room temperature for 30 min. The initial homogeneous yellow solution became colorless. The contents of the reactor were transferred to a round-bottom flask, and the solvent was removed under reduced pressure to afford a brown residue. The residue was dissolved in methylene chloride, loaded on a short column of silica gel, and eluted with THF. The eluate was collected, reduced in vacuo ~3 mL, and hexanes were added to give a precipitate. The white precipitate was collected on a fine porosity frit, washed with diethyl ether and pentane, and dried in vacuo (67.1 mg, 90%). IR (Thin film KBr): ν_{CO} = 1940 cm^{-1}. ^{1}H NMR (CD_2Cl_2, 500 MHz), δ: 4.98 (dd, 1H, $-CH_2$ORu- $^2J_{HH}$ = 9 Hz and $^4J_{HP}$ =1 Hz), 5.15 (d, 1H, $-CH_2$ORu-, $^2J_{HH}$ = 9 Hz), 5.90 (vt, 1H, 4-pz), 6.45 (m, 1H, 3- or 5-pz), 6.63 (dd, 1H, 3- or 5-pz), 6.68 (vt, 1H, 4-pz), 6.91 (dd, 1H, 3- or 5-pz), 7.28 (dd, 1H, 3- or 5-pz), 7.29 (m, 6H, PPh_3), 7.41 (m, 3H, PPh_3), 7.74–7.93 (m, 6H, PPh_3), 8.02 (d, 1H, 3- or 5-pz), 8.09 (d, 1H, 3- or 5-pz), 8.19 (br s, 1H, 3- or 5-pz). ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2) δ: 76.1 (s, $C(pz)_3$), 92.9 (s,-CH_2ORu-), 107.8, 108.0, 109.9 (each a singlet, 4-pz), 128.7 (d, *m*-PPh_3, $^2J_{CP}$ = 10 Hz), 131.0 (s, *p*-PPh_3), 134.1 (d, *i*-PPh_3, $^1J_{CP}$ = 48 Hz), 134.9 (d, *o*-PPh_3, $^2J_{CP}$ = 10 Hz) 132.0, 132.1, 132.7, 144.5, 145.4, 147.5 (each a singlet, 3- or 5-pz), 201.6 (d, CO, $^2J_{CP}$ = 15 Hz). ^{31}P{^{1}H} NMR (CD_2Cl_2, 121 MHz) δ: 44.00. HRMS: [M + Na]$^+$ obs'd (%), calc'd (%), ppm: 692.04849 (50), 692.04921 (60.6), −1; 693.04907 (100), 693.04838 (100), 1; 694.05024 (33.3), 694.04963 (44.1), 0.9; 695.04545 (85.7), 695.04812 (75.3), −3.8; 696.04491 (12.5), 696.05077 (24.4), −8.4. CV: $E_{1/2}$ = +1.21 V.

(Ep^{OX})RuCl(CO)$_2$ (6). Compound **1** (444 mg, 0.491 mmol) was dissolved in THF (30 mL) and added to a pressure reactor equipped with a stir bar. The reactor was pressurized with CO (60 psi) and allowed to stir at room temperature for 30 days. The initial homogeneous yellow reaction solution became colorless. The contents were placed in a round-bottom flask, and the solvent was removed under reduced pressure to afford a brown residue. The residue was dissolved in minimal THF and eluted with THF through a short column of silica. This portion contained complex **5**. The column was then washed with a THF/MeOH (90/10, v/v%) mixture to elute a reddish-brown band. The filtrate was collected, and the solvent was removed in vacuo. The residue was taken up in methylene chloride, and hexanes were added to induce precipitation. The off-white solid was collected on a frit by filtration, washed with pentane and dried under reduced pressure (12.3 mg, 5%). IR (thin film on KBr): ν_{CO} = 2060 cm^{-1} and 1986 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 4.77 (d, 1H, $-CH_2$ORu-, $^2J_{HH}$ = 9 Hz), 4.94 (d, 1H, $-CH_2$ORu-, $^2J_{HH}$ = 9 Hz) 6.45 (t, 1H, 4-pz), 6.53 (t, 1H, 4-pz), 6.72 (dd, 1H, 4-pz), 7.11(dd, 1H, 3- or 5-pz), 7.20 (dd, 1H, 3- or 5-pz), 7.77 (dd, 1H, 3- or 5-pz), 8.02 (d, 1H, 3- or 5-pz), 8.08 (d, 1H, 3- or 5-pz), 8.28 (d, 1H, 3- or 5-pz). HRMS: [M + Na]$^+$obs'd (%), calc'd (%), ppm: 457.9524 (56.3), 457.95263 (59.9), −0.5; 458.95164 (100), 458.95169 (100), −0.1; 459.95238 (13.1), 459.95218 (29.9), 0.4; 460.95174 (79.5), 460.9515 (77.1), 0.5; 462.95523 (26.3), 462.95036 (16.6), 10.5.

[$HC(pz)_3$RuCl(PPh_3)$_2$]Cl (7). A solution of compound **1** (302 mg, 0.334 mmol) in chloroform (25 mL) was placed in a pressure tube and stirred at 60 °C overnight. The solvent was removed under reduced pressure, and the remaining residue was reconstituted in a minimum amount of methylene chloride. Hexanes were added to induce precipitation of pale-yellow solid, which was collected on a fine porosity frit and washed with diethyl ether followed by pentane. The crude product was reconstituted in THF and eluted through a short column of silica. The filtrate was collected, solvent reduced in vacuo until ~3–5 mL remained, and hexanes were added to induce precipitation. The pale-yellow solid was collected on a fine porosity frit and washed with diethyl ether and pentane and dried under reduced pressure (236 mg, 71%). The spectroscopic data for **7** is identical to that previously reported.[68] CV: $E_{1/2}$ = +1.24 V Ru(III/II)(quasi-reversible).

[$HC(pz)_3$RuCl[$P(OCH_2)_3CEt]_2$]Cl (8). Compound **3** (140 mg, 0.199 mmol) was dissolved in $CHCl_3$ (10 mL), transferred to a pressure

dx.doi.org/10.1021/ic3024474 | *Inorg. Chem.* XXXX, XXX, XXX–XXX

tube, and heated at 100 °C overnight. The solution was treated with hexanes and a white solid formed. The solid was collected on a fine porosity frit, washed with diethyl ether and pentane, and dried under reduced pressure (86.7 mg, 62%). ^{1}H NMR (CD_2Cl_2, 300 MHz) δ: 0.83 (t, 6H, $-CH_2CH_3$, $^{3}J_{HH}$ = 8 Hz), 1.24 (q, 4H, $-CH_2CH_3$, $^{3}J_{HH}$ = 8 Hz), 4.30 (vt, 12H, $-(OCH_2)_3$, $^{3}J_{PH}$ = 3 Hz), 6.27 (t, 1H, 4-pz), 6.40 (vt, 2H, 4-pz), 7.84 (d, 1H, 3- or 5-pz), 8.13 (d, 1H, 3- or 5-pz), 8.70 (br s, 2H, 3- or 5-pz), 8.80 (br s, 1H, 3- or 5-pz), 12.36 (br s, 1H, $HC(pz)_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 126 MHz) δ: 7.3 ($-CH_2CH_3$), 23.6 ($-CH_2CH_3$), 35.8 (t, $C(CH_2CH_3)_3$, $^{3}J_{CP}$ = 16 Hz), 74.1 ($C(pz)_3$), 75.0 ($\{OCH_2\}_3$), 107.4, 107.7 (each a singlet, 4-pz), 133.5, 135.0, 146.6, 150.0 (each a singlet, 3- or 5-pz). ^{31}P{H} ($CDCl_3$, 121 MHz) δ: 131.0 (s). CV: $E_{1/2}$ = +1.5 V Ru(III/II) (quasi-reversible), $E_{p,a}$ = +1.28 (irreversible). HRMS: $[M]^+$obs'd (%), calc'd (%), ppm: 672.0607 (29.6), 672.0603 (32.9), 0.6; 673.0592 (37.6), 673.0593 (40), 0.1; 674.0588 (58.3), 674.0597 (60.3), 1.3; 675.0589 (100), 675.0588 (100), 0.1; 676.0598 (35.8), 676.0598 (38.2), 0; 677.0581 (74.6), 677.0586 (76.3), 0.7.

■ ASSOCIATED CONTENT

Supporting Information

Crystallographic data in CIF format. Further details are given in Figures S1−S7. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: tbg7h@virginia.edu.

Present Address

[‖]Department of Chemistry and Physics, Armstrong Atlantic State University, 11935 Abercorn St., Savannah, Georgia 31419, United States.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the Department of Energy (DE-SC0000776) for support of this work. B.Q. thanks the Ford Foundation for support through a postdoctoral fellowship. We acknowledge Dr. John G. Verkade (Iowa State University) for helpful discussions.

■ REFERENCES

(1) Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 6288−6294.
(2) Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 3170−3177.
(3) Trofimenko, S. *J. Am. Chem. Soc.* **1970**, *92*, 5118−5126.
(4) Etienne, M. *Coord. Chem. Rev.* **1996**, *156*, 201−236.
(5) Slugovc, C.; Padilla-Martinez, I.; Sirol, S.; Carmona, E. *Coord. Chem. Rev.* **2001**, *213*, 129−157.
(6) Lobbia, G. G.; Hanna, J. V.; Pellei, M.; Pettinari, C.; Santini, C.; Skelton, B. W.; White, A. H. *Dalton. Trans.* **2004**, 951−958.
(7) Pettinari, C.; Cingolani, A.; Lobbia, G. G.; Marchetti, F.; Martini, D.; Pellei, M.; Pettinari, R.; Santini, C. *Polyhedron* **2004**, *23*, 451−469.
(8) Pettinari, C.; Pettinari, R. *Coord. Chem. Rev.* **2005**, *249*, 525−543.
(9) Pettinari, C.; Pettinari, R. *Coord. Chem. Rev.* **2005**, *249*, 663−691.
(10) Trofimenko, S.; Rheingold, A. L.; Sands, L. M. L. *Inorg. Chem.* **2002**, *41*, 1889−1896.
(11) Trofimenko, S. *J. Chem. Educ.* **2005**, *82*, 1715−1720.
(12) Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943−980.
(13) Trofimenko, S. *Scorpionates: The Coordination Chemistry of Polypyrazolylborate Ligands*; Imperial College Press: London, U.K., 1999.
(14) Reger, D. L.; Grattan, T. C. *Synthesis-Stuttgart* **2003**, 960−960.
(15) Bigmore, H. R.; Lawrence, S. C.; Mountford, P.; Tredget, C. S. *J. Chem. Soc., Dalton Trans.* **2005**, 635−651.
(16) Vepachedu, S.; Stibrany, R. T.; Knapp, S.; Potenza, J. A.; Schugar, H. J. *Acta Crystallogr., Sect. C* **1995**, *51*, 423−426.
(17) Pullen, E. E.; Rabinovich, D.; Incarvito, C. D.; Concolino, T. E.; Rheingold, A. L. *Inorg. Chem.* **2000**, *39*, 1561−1567.
(18) Otero, A.; Fernández-Baeza, J.; Antiñolo, A.; Tejeda, J.; Lara-Sánchez, A. *Dalton Trans.* **2004**, 1499−1510.
(19) Kail, B. W.; Basu, P. *Dalton. Trans.* **2006**, 1419−1423.
(20) Hammes, B. S.; Chohan, B. S.; Hoffman, J. T.; Einwachter, S.; Carrano, C. J. *Inorg. Chem.* **2004**, *43*, 7800−7806.
(21) Tran, B. L.; Carrano, C. J. *Inorg. Chim. Acta* **2007**, *360*, 1961−1969.
(22) Hoffman, J. T.; Carrano, C. J. *Inorg. Chim. Acta* **2006**, *359*, 1248−1254.
(23) Otero, A.; Fernández-Baeza, J.; Tejeda, J.; Antonío, A.; Carrillo-Hermosilla, F.; Díez-Barra, E.; Lara-Sánchez, A.; Fernández-López, M. *J. Chem. Soc., Dalton Trans.* **2000**, 2367−2374.
(24) Otero, A.; Fernandez-Baeza, J.; Antinolo, A.; Tejeda, J.; Lara-Sanchez, A.; Sanchez-Barba, L.; Martinez-Caballero, E.; Rodriguez, A. M.; Lopez-Solera, I. *Inorg. Chem.* **2005**, *44*, 5336−5344.
(25) Otero, A.; Fernandez-Baeza, J.; Tejeda, J.; Carrillo-Hermosilla, F.; Diez-Barra, E.; Lara-Sanchez, A.; Fernandez-Lopez, M.; Lanfranchi, M.; Pellinghelli, M. A. *J. Chem. Soc., Dalton Trans.* **1999**, 3537−3539.
(26) Otero, A.; Fernandez-Baeza, J.; Tejeda, J. B.; Antinolo, A.; Carrillo-Hermosilla, F.; Diez-Barra, E.; Lara-Sanchez, A.; Fernandez-Lopez, M. *J. Chem. Soc., Dalton Trans.* **2000**, 2367−2374.
(27) Otero, A.; Fernandez-Baeza, J.; Antinolo, A.; Tejeda, J.; Lara-Sanchez, A.; Sanchez-Barba, L.; Rodriguez, A. M. *Dalton. Trans.* **2004**, 3963−3969.
(28) Papish, E. T.; Taylor, M. T.; Jernigan, F. E., III; Rodig, M. J.; Shawhan, R. R.; Yap, G. P. A.; Jove, F. A. *Inorg. Chem.* **2006**, *45*, 2242−2250.
(29) Beck, A.; Barth, A.; Hubner, E.; Burzlaff, N. *Inorg. Chem.* **2003**, *42*, 7182−7188.
(30) Higgs, T. C.; Ji, D.; Czernuscewicz, R. S.; Carrano, C. J. *Inorg. Chim. Acta* **1999**, *286*, 80−92.
(31) Burzlaff, N.; Hegelmann, I.; Weibert, B. *J. Organomet. Chem.* **2001**, *626*, 16−23.
(32) Riehl, J. F.; Jean, Y.; Eisenstein, O.; Pelissier, M. *Organometallics* **1992**, *11*, 729−737.
(33) Lunder, D. M.; Lobkovsky, E. B.; Streib, W. E.; Caulton, K. G. *J. Am. Chem. Soc.* **1991**, *113*, 1837−1838.
(34) Poulton, J. T.; Folting, K.; Streib, W. E.; Caulton, K. G. *Inorg. Chem.* **1992**, *31*, 3190−3191.
(35) Johnson, T. J.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1992**, *114*, 2725−2726.
(36) Caulton, K. G. *New J. Chem.* **1994**, *18*, 25−41.
(37) Mayer, J. M. *Comments Inorg. Chem.* **1988**, *8*, 125−135.
(38) Reger, L. B.; Grattan, T. C.; Brown, K. J.; Little, C. A.; Lamba, J. J. S.; Rheingold, A. L.; Sommer, R. D. *J. Organomet. Chem.* **2000**, *607*, 120−128.
(39) Reger, D. L.; Brown, K. J.; Smith, M. D. *J. Organomet. Chem.* **2002**, *658*, 50−61.
(40) Sanchez-Mendez, A.; Silvestri, G. F.; de Jesus, E.; de la Mata, F. J.; Flores, J. C.; Gomez, R.; Gomez-Sal, P. *Eur. J. Inorg. Chem.* **2004**, 3287−3296.
(41) Maria, L.; Cunha, S.; Videira, M.; Gano, L.; Paulo, A.; Santos, I. C.; Santos, I. *Dalton. Trans.* **2007**, 3010−3019.
(42) Boujemaa, M.; Leita, B. A.; Halder, G. J.; Batten, S. R.; Jensen, P.; Smith, J. P.; Cashion, J. K.; Létard, J.-F.; Murray, K. s. *Dalton Trans.* **2007**, 4413−4426.
(43) Silva, T. F. S.; Mishra, G. S.; da Silva, M. F. G.; Wanke, R.; Martins, L. M. D. R. S.; Pombeiro, A. J. L. *Dalton. Trans.* **2009**, 9207−9215.
(44) Silva, T. F. S.; Guedes da Silva, F. M.; Mishra, G. S.; Martins, L. M. D. R. S.; Pombeiro, A. J. L. *J. Organomet. Chem.* **2011**, *696*, 1310−1318.
(45) Lopez-Hernandez, A.; Muller, R.; Kopf, H.; Burzlaff, N. *Eur. J. Inorg. Chem.* **2002**, 671−677.

(46) Wadsworth, W. S. J.; Emmons, W. D. *J. Am. Chem. Soc.* **1962**, *84*, 610−617.
(47) Rest, A. J. *J.Chem. Soc. A.* **1968**, 2212−2215.
(48) Goodfell, R. G. *Chem. Commun.* **1968**, 114−115.
(49) Note: The chemical shift positions were calculated by adding half of the geometrical mean of the distances between the outer and inner signals to the center frequency to obtain the upfield chemical shift and subtracted to obtain more downfield chemical shift.
(50) Friebolin, H. *Basic One- and Two-Dimensional NMR Spectroscopy*, 4th ed.; Wiley-VCH: Weinheim, Germany, 2005.
(51) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 2nd ed.; John Wiley and Sons: New York, 1994.
(52) Kühl, O. *Phosphoru-31 NMR Spectroscopy: A Concise introduction for the Synthetic Organic and Organometallic Chemist*; Springer-Verlag: Berlin, Germany, 2008.
(53) Tampier, S.; Müller, R.; Thorn, A.; Hübner, E.; Burzlaff, N. *Inorg. Chem.* **2008**, *47*, 9624−9641.
(54) Feng, Y. E.; Lail, M.; Foley, N. A.; Gunnoe, T. B.; Barakat, K. A.; Cundari, T. R.; Petersen, J. L. *J. Am. Chem. Soc.* **2006**, *128*, 7982−7994.
(55) Feng, Y.; Lail, M.; Barakat, K. A.; Cundari, T. R.; Gunnoe, T. B.; Petersen, J. L. *J. Am. Chem. Soc.* **2005**, *127*, 14174−14175.
(56) Sun, N.-Y.; Simpson, S. J. *J. Organomet. Chem.* **1992**, *434*, 341−349.
(57) Blackmore, T.; Bruce, M. I.; Stone, F. G. A. *J. Chem. Soc. (A)* **1971**, 2376−2382.
(58) Conroy-Lewis, F. M.; Simpson, S. J. *J. Organomet. Chem.* **1987**, *322*, 221−228.
(59) Kopf, H.; Pietraszuk, C.; Hübner, E.; Burzlaff, N. *Organometallics* **2006**, *25*, 2533−2546.
(60) Park, J. H.; Koh, J. H.; Park, J. *Organometallics* **2001**, *20*, 1892−1894.
(61) Hansen, H. D.; Nelson, J. H. *Organometallics* **2000**, *19*, 4740−4755.
(62) Bustelo, E.; Dixneuf, P. H. *Adv. Synth. Catal.* **2005**, *347*, 393−397.
(63) Nagashima, H.; Mukai, K.; Shiota, Y.; Yamaguchi, K.; Ara, K.; Fukahori, T.; Suzuki, H.; Akita, M.; Morooka, Y.; Itoh, K. *Organometallics* **1990**, *9*, 799−807.
(64) Sridevi, V. S.; Leong, W. K. *J. Organomet. Chem.* **2007**, *692*, 4909−4916.
(65) Dev, S.; Selegue, J. P. *J. Organomet. Chem.* **1994**, *469*, 107−110.
(66) Bruce, M. I.; Sharrocks, D. N.; Stone, F. G. A. *J. Organomet. Chem.* **1971**, *31*, 269−273.
(67) Türkoglu, G.; Tampier, S.; Strinitz, F.; Heinemann, F. W.; Hübner, E.; Burzlaff, N. *Organometallics* **2012**, *31*, 2166−2174.
(68) Field, L. D.; Messerle, B. A.; Soler, L.; Buys, I. E.; Hambley, T. W. *J. Chem. Soc., Dalton Trans.* **2001**, 1959−1965.
(69) Domazetis, G.; Tarpey, B.; Dolphin, D.; James, B. R. *J. Chem. Soc., Chem. Commun.* **1980**, 939−940.
(70) Backvall, J. E.; Chowdhury, R. L.; Karlsson, U. *J. Chem. Soc., Chem. Commun.* **1991**, 473−475.
(71) Aranyos, A.; Csjernyik, G.; Szabo, K. J.; Backvall, J. E. *Chem. Commun.* **1999**, 351−352.
(72) Chen, Y.-Z.; Chan, W. C.; Lau, C. P.; Chu, H. S.; Lee, H. L. *Organometallics* **1997**, *16*, 1241−1246.
(73) Lee, J. P.; Pittard, K. A.; DeYonker, N. J.; Cundari, T. R.; Gunnoe, T. B.; Petersen, J. L. *Organometallics* **2006**, *25*, 1500−1510.
(74) Coalter, J. N., III; Huffman, J. C.; Caulton, K. G. *Organometallics* **2000**, *19*, 3569−3578.
(75) Chowdhury, R. L.; Backvall, J. E. *J. Chem. Soc., Chem. Commun.* **1991**, 1063−1064.
(76) James, B. R.; Morris, R. H.; Kvintovics, P. *Can. J. Chem.* **1986**, *64*, 897−903.
(77) Fischer, P. J.; Neary, M. C.; Avena, L.; Sullivan, K. P.; Hackbarth, K. C. *Organometallics* **2012**, *31*, 2437−2444.
(78) Alcock, N. W.; Burns, I. D.; Claire, K. S.; Hill, A. F. *Inorg. Chem.* **1992**, *31*, 2906−2908.
(79) Verkade, J. G.; McCarley, R. E.; Hendricker, D. G.; King, R. W. *Inorg. Chem.* **1965**, *4*, 228−231.
(80) Sheldrick, G. M., *SHELXTL-97*, version 5.12; Bruker AXS: Madison, WI.
(81) Stephens., T.; G., W. *J. Inorg. Nucl. Chem.* **1966**, *28*, 945−956.

dx.doi.org/10.1021/ic3024474 | *Inorg. Chem.* XXXX, XXX, XXX−XXX