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Oxidative Addition of Water by an Iridium PCP Pincer Complex: Catalytic Dehydrogenation of Alkanes by $IrH(OH)\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t{}_2)_2\}$

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The dehydrogenation of $IrH_2\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t{}_2)_2\}$ (**1**) by *tert*-butylethylene followed by reaction with an excess of water leads to the isolation of $IrH(OH)\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t{}_2)_2\}$ (**2**) in nearly quantitative yield. The hydrido hydroxo complex has been characterized by multinuclear NMR spectroscopy as well as a single-crystal X-ray structure determination. An isotopic labeling study with D_2O indicates that **2** arises from the oxidative addition of water to the intermediate 14-electron complex $Ir\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t{}_2)_2\}$. The title complex is an efficient catalyst for the transfer dehydrogenation of cyclooctane to cyclooctene but shows no catalytic activity for the hydroxylation of the alkane by water. The conversion of **1** to **2** can be reversed by placing a solution of **2** under 1 atm of H_2 at 25 °C.

Introduction

The iridium PCP pincer complex $IrH_2\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t{}_2)_2\}$ (**1**) has been found to be a highly efficient and robust catalyst for the dehydrogenation of alkanes,[1] ethers,[2] and alkylarenes.[2] As part of our exploration of the scope of the functional group tolerance of the aliphatic dehydrogenation activity of **1**, we recently examined its reactivity with primary and secondary alcohols. We found that aliphatic dehydrogenation does not occur with these substrates but, rather, a process involving the activation of O−H bonds and the catalytic production of ketones and aldehydes.[3] The oxidative addition of water by late-transition-metal complexes has long been proposed to occur in several homogeneous catalytic processes, including the water-gas shift reaction,[4] nitrile hydration,[5,6] and Wacker-type reactions.[7] Thus, our finding that **1** was reactive with O−H bonds prompted us to follow up on preliminary observations of the reactivity of **1** with water. We have found that the dehydrogenation of **1** in the presence of water results in the formation of the hydrido hydroxo complex $IrH(OH)\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t{}_2)_2\}$ (**2**). We wish to report the isolation and characterization of **2**, including a single-crystal X-ray structure determination as well as our studies of the activity of **2** as a catalyst for the transfer dehydrogenation of alkanes.

Results and Discussion

The title complex was initially detected by ^1H and ^{31}P NMR spectroscopy as one of several products arising upon treatment of toluene solutions of **1** with excess *tert*-butylethylene (tbe) under 1 atm of argon. One of these products was identified as $[Ir\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t{}_2)_2\}]_2(\mu\text{-}N_2)$ (**3**).[8] We postulated that the 14-electron intermediate $Ir\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t{}_2)_2\}$, which arises upon the dehydrogenation of **1** by tbe,[8,9] reacts with traces of nitrogen that are present in the argon to produce **3**. Therefore, it seemed likely that the other product complexes arose from the reaction with other impurities in the argon, and we were able to link the formation of **2** with the presence of water. We have found that the title complex is produced in nearly quantitative yield upon addition of excess of water to a reaction mixture of **1** and tbe.

The signal for the hydride ligand of **2** is observed at high field in the ^1H spectrum of **2** as a triplet at −31.03 ppm; the multiplicity of the signal is due to the coupling of the hydride ligand with the two equivalent phosphorus nuclei of the PCP pincer ligand. The ^1H NMR also contains a signal for the hydroxyl hydrogen at 5.6 ppm as a broad singlet, which disappears upon D_2O addition. A similar broad resonance was observed for the hydroxyl hydrogen of the closely related 16-electron osmium complex $OsH(OH)(CO)(PPr^i{}_3)_2$ at 4.25 ppm.[10] These signals are markedly downfield from those observed for the hydroxyl hydrogens of the structurally characterized

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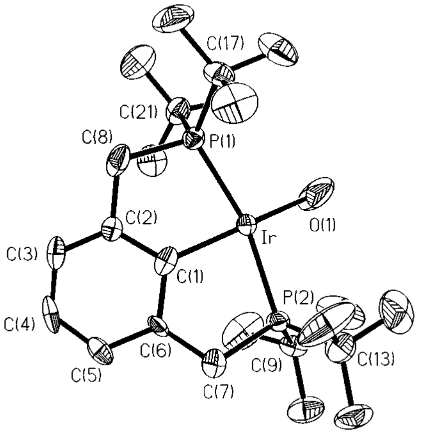


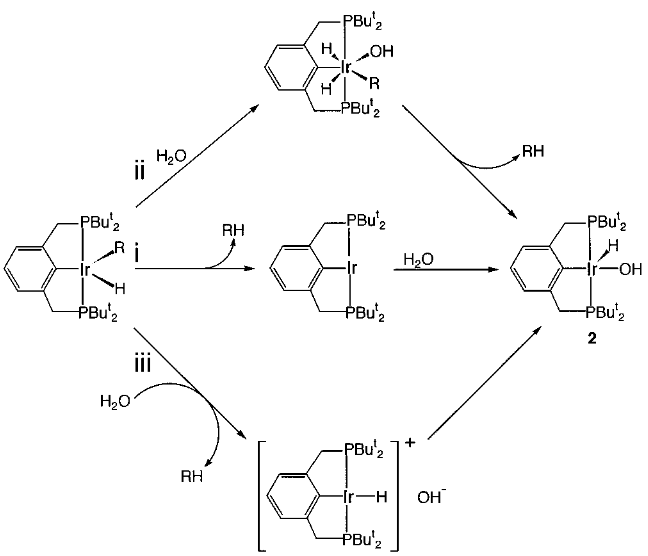
Figure 1. ORTEP diagram for IrH(OH){C_6H_3-2,6-($CH_2PBu^t{}_2)_2$} (**2**) with the thermal ellipsoids at 50% probability.

Table 1. Selected Bond Lengths and Angles for IrH(OH){C_6H_3-2,6-($CH_2PBu^t{}_2)_2$} (2)

Bond Lengths (Å)			
Ir−P(1)	2.304(4)	P(1)−C(17)	1.90(2)
Ir−P(2)	2.303(4)	P(1)−C(21)	1.89(2)
Ir−C(1)	2.01(2)	P(2)−C(7)	1.79(2)
Ir−O(1)	2.00(3)	P(2)−C(9)	1.88(2)
P(1)−C(8)	1.84(2)	P(2)−C(13)	1.88(2)
Bond Angles (deg)			
P(2)−Ir−P(1)	166.9(2)	C(1)−Ir−P(2)	83.9(5)
O(1)−Ir−P(1)	96.9(7)	C(1)−Ir−O(1)	163.8(13)
O(1)−Ir−P(2)	95.3(7)	C(8)−P(1)−Ir	102.6(6)
C(1)−Ir−P(1)	83.1(5)	C(7)−P(2)−Ir	102.8(6)

18-electron hydrido hydroxo complexes OsH(OH)(CO)(η^2-CH_2=$CHCO_2CH_3$)($PPr^i{}_3)_2$[10] and [*cis*-IrH(OH)($PMe_3)_4$][PF_6][11] at −4.5 and −1.4 ppm, respectively. A further variation in the ^1H NMR chemical shift of the hydrogen of a hydroxo ligand is provided by the rhodium analogue of **2**, RhH(OH){C_6H_3-2,6-($CH_2PBu^t{}_2)_2$}, which was reported at 16.4 ppm.[12] It may be significant that the spectrum of the rhodium complex was obtained from an unpurified sample prepared in situ by the reaction of RhHCl{C_6H_3-2,6-($CH_2PBu^t{}_2)_2$} with NaOH and, thus, the hydroxo ligand may be involved in hydrogen-bonding interactions. The appearance of absorptions at 3450 and 2086 cm^{-1} in the infrared spectrum of **2** provides further evidence for the presence of the hydroxo and hydrido ligands, respectively.

Scheme 1



The structure of complex **2** was confirmed by a single-crystal X-ray structure determination. Deep orange crystals of complex **2** that were suitable for X-ray diffraction were obtained from slow evaporation of a pentane/cyclohexane solution of complex **2**. A projection of the structure is shown in Figure 1. The selected bond lengths (Å) and bond angles (deg) are listed in Table 1. The Ir−C(1) (2.01(2) Å), Ir−P(1) (2.304(4) Å), and Ir−P(2) (2.303(4) Å) bond lengths show no significant deviation from those determined for **1**,[1b] in which the two phosphorus atoms are situated trans to each other as expected for the chelate PCP pincer ligand (P(2)−Ir−P(1) = 166.9(2)°) and the hydroxo ligand is trans to the metalated carbon C(1) (C(1)−Ir−O(1) = 163.8(13)°). The complex apparently has a square-pyramidal coordination geometry in which P(1), C(1), P(2), and O(1) constitute the basal square plane and the hydrido ligand, which was not reliably located, is presumed to occupy the apical position. The preference of the hydroxo ligand for the basal rather than the apical site is expected, as this arrangement avoids the destabilization of the complex that would result from trans orientation of the strongly σ-donating aryl and hydrido ligands. The Ir−O(1) (2.00(3) Å) distance is substantially shorter compared to that observed in the 18-electron species [*cis*-IrH(OH)($PMe_3)_4$]PF_6 (Ir−O 2.119(5) Å).[11] Caulton has explained similar differences in Ir−O bond distances in related 16- and 18-electron alkoxo complexes in terms of O→Ir π donation in the formally unsaturated complex.[13] The molecular structures of several other hydrido hydroxo complexes have been carried out through single-crystal X-ray[10,11,14] and neutron diffraction[16] studies. However, to our knowledge, complex **2** is the first example of a structurally characterized 16-electron hydrido hydroxo complex.

Conceivable mechanisms for the formation of **2** following the initial insertion of tbe into an Ir−H bond are illustrated in Scheme 1. Mechanisms i and ii involve the oxidative addition of water to the metal center. There are a growing number of precedents for this reactivity, as several late-transition-metal hydrido hydroxo complexes have now been found to arise from this process.[6,11,14,15] In pathway i, the reductive elimination of alkane generates the 14-electron Ir(I) intermediate that is believed to be the precursor to **3**. This is followed by oxidative addition of water to produce **2**. The sequence of reductive elimination and oxidative addition is reversed in pathway ii. The initial oxidative addition of water to the iridium center gives rise to an 18-electron

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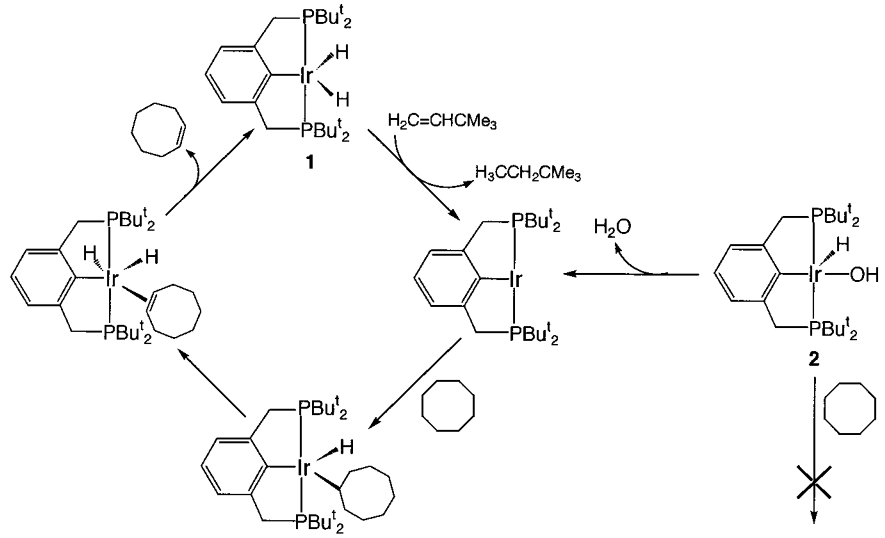
Scheme 2



Ir(V) intemediate which undergoes the reductive elimination of alkane. Pathway iii entails the hydrolytic cleavage of a metal alkyl followed by coordination of the resulting hydroxy anion. This pathway would not involve the oxidative addition of water and changing oxidation states of the iridium. To distinguish between these possibilities, we carried out an NMR tube reaction in which **1** was dehydrogenated by tbe in the presence of D_2O. Monitoring the reaction by ^{2}H NMR spectroscopy, we observed that the deuterium label was completely incorporated into the methyl groups of the pincer ligand of **2**. This reactivity parallels that observed for $IrD_2\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t{}_2)_2\}$, which was found to undergo complete H/D exchange between the hydride and pincer methyl positions. The lack of deuterated alkane formation clearly rules out both mechanisms ii and iii and suggests that **2**, like **3**, arises from the same 14-electron intermediate. We have also found that **2** can be obtained from the reaction of **3** with excess water at 25 °C. Although production of **2** through this method requires a much longer reaction time, 3 days, it demonstrates that the oxidative addition of water to an Ir(I) pincer complex is a viable pathway for the formation of **2**.

Having found that water undergoes facile activation at the iridium pincer center, it seemed plausible that this process might occur in concert with the well-established ability of this system to activate alkane C−H bonds[1,9] and result in the catalytic hydroxylation of alkanes. The conversion of an alkane and water to an alcohol in conjunction with the hydrogenation of a sacrificial alkene is exothermic by about 40 kcal/mol.[17] This possibility was probed by examining the reactivity of cyclooctane and water in the presence of a catalytic amount of **2**, both in the presence of tbe. A sealed tube containing the reaction mixture was immersed in a 200 °C bath for periods up to 24 h. Although no traces of oxygenated products were detected, cyclooctene was produced. In the absence of water, **2** was observed to catalyze the transfer dehydrogenation of cyclooctane to cycloctene at a rate of 1200 turnovers/h. This rate is nearly identical with that observed in analogous experiments with **1**[1b] and suggests that **2** is a precursor to an intermediate in the catalytic cycle by which **1** operates. This entry could be accomplished simply by the mircroreverse of the oxidative addition of water to $Ir\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t{}_2)_2\}$, as seen in Scheme 2. The reductive elimination of water from **2** appears, in fact, to be quite facile. We have observed that placing a pentane solution of **2** under 1 atm of H_2 at 25 °C results in a nearly quantitative conversion to **1**.

Conclusion

The unusual 16-electron hydrido hydroxo complex **2** is formed upon the oxidative addition of water to $Ir\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t{}_2)_2\}$. The complex functions efficiently as a catalyst for the transfer dehydrogenation of cyclooctane but shows no catalytic activity for the hydroxylation of the alkane by water. Apparently, the barrier to the reductive elimination of water from **2** is much lower than that for the oxidative addition of alkane C−H bonds to the 16-electron complex. It may be possible to reverse this situation through modification of the pincer ligand and thus open the door to novel catalytic pathways that incorporate the now established oxidative addition of both aliphatic C−H bonds and water by iridium PCP pincer complexes.

Experimental Section

General Considerations. All manipulations were carried out using standard Schlenk and glovebox techniques under purified argon. Solvents were degassed and dried using standard procedures. The complex $IrH_2\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t{}_2)_2\}$ was synthesized by the literature method.[1a,b] The ^{1}H NMR spectra were recorded on a Varian Unity Inova 400 spectrometer. Chemical shifts are reported in ppm downfield of TMS using the solvent as internal standard (cyclohexane-d_{12}, δ 1.38). ^{13}C and ^{31}P NMR spectra were recorded with complete proton decoupling and are reported in ppm downfield of TMS with solvent as internal standard (cyclohexane-d_{12}, δ 26.43) and external 85% H_3PO_4, respectively. GC analyses were carried out in HP 5890A flame ionization detector (FID) and HP 5890 SERIES II with an 5971A mass selective detector gas chromatographs and an HP-1 capillary column (25.0 m) from Hewlett-Packard.

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$IrH(OH)\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t{}_2)_2\}$ (2). A pentane (5 mL) solution of $IrH_2\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t{}_2)_2\}$ (20 mg, 0.034 mmol) was treated with *tert*-butylethylene (66 μL, 0.51 mmol) under 1 atm of argon at 25 °C. After 1 h of reaction, the resulting red-purple solution was treated with degassed, deionized H_2O (0.1 mL, 5.6 mmol). Removal of the solvent in vacuo yields the title complex as a deep orange solid in nearly quantitative yield. ^1H NMR (400.00 MHz, cyclohexane-d_{12}): δ 6.59 (d, $J_{HH} = 7.3$ Hz, 2H, *m*-H), 6.45 (d, $J_{HH} = 7.3$ Hz, 1H, *p*-H), 5.6 (brs, 1H, Ir−O*H*), 3.05 (d of vt, $J_{HH} = 18.3$ Hz, $J_{PH} = 3.7$ Hz, 2H, CH_2), 2.95 (d of vt, $J_{HH} = 16.5$ Hz, $J_{PH} = 3.7$ Hz, 2H, CH_2), 1.32, 1.28 (vt, $J_{PH} = 6.4$ Hz, 18H, $C(CH_3)_3$), −31.03 (vt, $J_{PH} = 11.9$ Hz, Ir-*H*). ^{13}C NMR (100.60 MHz, cyclohexane-d_{12}): δ 148.3 (vt, $J_{PC} = 7.3$ Hz, *o-C*), 140.6 (s, *C-1*), 121.4 (vt, $J_{PC} =$ 7.3 Hz, *m*-**C**), 121.0 (s, *p-C*), 36.3 (vt, $J_{PC} = 14.6$ Hz, CH_2P), 36.9 (vt, $J_{PC} = 10.1$ Hz, $C(CH_3)_3$), 35.1 (vt, $J_{PC} = 11.0$ Hz, $C(CH_3)_3$), 30.2, 30.1 (s, $C(CH_3)_3$). ^{31}P NMR (161.90 MHz, cyclohexane-d_{12}): δ 64.6 (s). IR (cyclohexane) ν_{OH} 3450 (broad), ν_{IrH} 2086 (w) cm^{-1}. Anal. Calcd for $C_{24}H_{45}OP_2Ir$ (603.78): C, 47.74; H, 7.51. Found: C, 47.71; H, 7.49.

Reaction of $IrH_2\{C_6H_3\text{-}2,6\text{-}(CH_2Bu^t{}_2)_2\}$ with D_2O in the Presence of tbe. A pentane (1.0 mL) solution of $IrH_2\{C_6H_3\text{-}2,6\text{-}(CH_2Bu^t{}_2)_2\}$ (**1**; 3 mg, 0.0051 mmol) was treated with *tert*-butylethylene (0.010 mL, 0.076 mmol) in a NMR tube under 1 atm of argon at 25 °C. After 1 h of reaction, the resulting red-purple solution was treated with degassed deuterium oxide (0.05 mL, 2.76 mmol). Analysis by ^2H NMR showed the deuterium label to be completely incorporated into the methyl groups of the pincer ligand.

Reaction of $[Ir\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t{}_2)_2]_2(\mu\text{-}N_2)$ with H_2O. A cyclohexane (5 mL) solution of $[Ir\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t{}_2)_2]_2(\mu\text{-}N_2)$ (10 mg, 0.083 mmol) was freeze−pump−thaw degassed three times. The solution was then treated with a 10-fold excess of degassed, deoxygenated water and stirred at 25 °C for 3 days. Removal of the solvent in vacuo gave $IrH(OH)\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t{}_2)_2$ (**2**) as a deep orange solid in nearly quantitative yield.

Reaction of $IrH(OH)\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t{}_2)_2$ with H_2. A cyclohexane (5 mL) solution of $IrH(OH)\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t{}_2)_2$ (10 mg, 0.017 mmol) was placed under 1 atm of hydrogen at 25 °C for 1 min. Removal of the solvent in vacuo gave $IrH_2\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t{}_2)_2$[1b] as a dark brown solid in nearly quantitative yield.

General Procedure for the Catalytic Reactions. Solutions of cyclooctane (4.0 mL, 37.0 mmol), tbe (0.20 mL, 1.5 mmol), and, in select experiments, degassed, deoxygenated water (0.027 mL, 1.5 mmol) were charged with $IrH(OH)\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t{}_2)_2\}$ (3 mg, 0.05 mmol) in sealed Schlenk tubes in a Vacuum Atmospheres glovebox under argon. The tubes were then fully immersed in a constant-temperature bath at 200 °C for the prescribed reaction times. Quantification of the cyclooctene produced in these reactions was accomplished by gas chromatographic analysis.

X-ray Structure Analysis of $IrH(OH)\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t{}_2)_2\}$. A crystalline yellow prism of $IrH(OH)\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t{}_2)_2\}$ obtained from a concentrated solution in a pentane/cyclohexane (1:1) solvent mixture was glued to a glass fiber. Intensity data were measured at room temperature using a Nicolet P3 diffractometer, with a graphite monochromator ($\lambda = 0.710$ 73 Å, Mo Kα). The unit cell was determined from the angular coordinates of 25 reflections with 2θ values between 15 and 30°. The diffractometer autoindexing routine found an orthorhombic unit cell, which was confirmed by axial photographs. Three check reflections, monitored every 100 reflections, showed no significant decay. The data were processed using the SHELXTL program package, and a semiempirical ellipsoid absorption correction from ψ-scans was applied. The structure was solved by Patterson methods using the SHELXTL-93 computer program. The remainder of the structure was easily developed via a few cycles of least-squares refinement and difference Fourier maps. Hydrogen atoms were input at calculated positions and allowed to ride on the atoms to which they are attached. Two group thermal parameters were refined for hydrogen atoms, one each for methylene and methyl protons. The final cycle of refinement was carried out on all nonzero data using SHELXL-97[18] and anisotropic thermal parameters for all non-hydrogen atoms. Crystal data are collected in Table 2.

Table 2. Crystallographic Data for $IrH(OH)\{C_6H_3\text{-}2,6\text{-}(CH_2PBu^t{}_2)_2\}$ (2)

formula	$C_{24}H_{45}OIrP_2$
fw	603.74
temp, K	293(2)
cryst syst	orthorhombic
space group	*Pbca*
cryst dimens, mm	0.5 × 0.3 × 0.2
a, Å	11.520(7)
b, Å	16.094(10)
c, Å	28.53(2)
α, deg	90
β, deg	90
γ, deg	90
V, Å^3	5291(6)
Z	8
μ, cm^{-1}	51.80
transmissn coeff: min, max	0.055, 0.127
λ (Mo Kα radiation), Å	0.710 73
2θ range, deg	3−40
no. of indep rflns	2429
no. of unique data with $I > 2\sigma(I)$	1547
no. of params refined	272
goodness of fit[a]	0.920
ρ_{calcd}, g/cm^3	1.516
scan type	ω
R,[b] %	4.42
R_w,[c] %	9.78

[a] $GOF = [w\Sigma(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$. [b] $R = \Sigma|F_o| - |F_c|/\Sigma|F_o|$. [c] $R_w = [w\Sigma(|F_o| - |F_c|)^2/\Sigma wF_o{}^2]^{1/2}$.

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Supporting Information Available: Tables of crystallographic parameters, atomic coordinates, all bond distances and angles, anisotropic displacement coefficients, and coordinates of hydrogen atoms for complex **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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