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Reactions of an Amido Hydrido Complex of Osmium, $OsH(NHCMe_2CMe_2NH_2)(PPh_3)_2$: HX Addition, HX Transfer, and Ketone H_2 Hydrogenation

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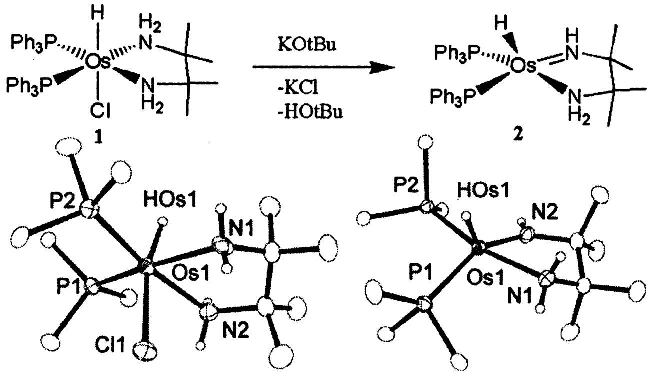
*Summary: The new amido complex $OsH(NHCMe_2CMe_2NH_2)(PPh_3)_2$ (**2**) reacts with weak acids HX to give complexes $OsHX(tmen)(PPh_3)_2$ (**1**; X = Cl, **3**; X = NCCHCN; and X = H; tmen = $NH_2CMe_2CMe_2NH_2$) and is an active ketone hydrogenation catalyst. HX is completely transferred from Os to Ru in the reactions of the amido complex $RuH(NHCMe_2CMe_2NH_2)(PPh_3)_2$ with complexes **1** and **3**.*

Ruthenium amido hydrido complexes have been identified as active catalysts for the H_2 hydrogenation and asymmetric hydrogenation of ketones and imines.[1−3] In this paper we make an initial comparison of the properties of the title osmium amido hydrido complex **2** with those[4] of the reported ruthenium analogue $RuH(NHCMe_2CMe_2NH_2)(PPh_3)_2$ (**4**)[1] as both a ketone hydrogenation catalyst and as a compound reactive toward weak acids. The reactivity of other late-transition-metal amido complexes toward weak acids has been studied[5−9] and is important in catalytic conjugate addition reactions.[10] We also report a novel HX transfer reaction that promises to allow us to rank the reactivity of amido groups on different metals.

Scheme 1. Synthesis of Complex 2 and Structures of 1 and 2 from X-ray Diffraction Studies[a]



[a] Most of the phenyl atoms have been removed for clarity.

The complex **2** is generated in two steps from $OsHCl(PPh_3)_3$[11] by first reacting it with 2,3-diamino-2,3-dimethylbutane to give $OsHCl(tmen)(PPh_3)_2$ (**1**; tmen = $NH_2CMe_2CMe_2NH_2$). The X-ray crystal structure (Scheme 1) has a distorted-octahedral geometry with trans hydride and chloride, cis phosphines, and cis amine ligands. The smaller Cl−Os−N angles of 80.78(12) and 82.95(12)° and the larger Cl−Os−P angles of 96.00(5) and 106.65(5)° indicate that the chloride ligand is moved away from the bulky triphenylphosphine ligands and toward the less bulky diamine ligand. The triplet at −20.9 ppm in the hydride region of the ^{1}H NMR spectrum and the singlet observed at 17.9 ppm in the $^{31}P\{^{1}H\}$ NMR spectrum suggest that this structure is maintained in solution. The dehydrohalogenation of **1** by reaction with potassium *tert*-butoxide produces the amido hydrido complex $OsH(NHCMe_2CMe_2NH_2)(PPh_3)_2$ (Scheme 1). A broad peak at −23.7 ppm in the ^{1}H NMR and two broad peaks at 29.8 and 27.1 ppm in the $^{31}P\{^{1}H\}$ NMR indicate that the complex is fluxional at room temperature with magnetically inequivalent phosphorus nuclei. The X-ray crystal structure of **2** (Scheme 1) is almost the same as the structure of the previously reported ruthenium analogue **4**: e.g. Os1=N2 = 1.958(3) Å, Os1−N1 = 2.181(2) Å, and P2−Os1−N1 = 165.97(8)° vs Ru=N = 1.967(2) Å, Ru−N = 2.176(1) Å, and P−Ru−N = 164.98(5)°.[1] The geometry around osmium in **2** is best viewed as distorted trigonal bipyramidal with axial atoms N1 and P2 and equatorial atoms N2, P1, and H1Os. The amido nitrogen N2 is trigonal planar and positioned for optimum dative $p\pi(N)\rightarrow d\pi(Os)$ bonding. This π bonding distorts the equatorial geometry from trigonal to Y-shaped with a small H1Os−Os1−P1 angle (80.3°).[12] As expected, the osmium−amido bond is significantly shorter than the osmium−amine bond.

Like the ruthenium analogue **4**, the new osmium amido complex **2** is an active ketone hydrogenation catalyst. With an acetophenone concentration of 0.17 M in benzene, a ratio of acetophenone to **2** of 347:1, and

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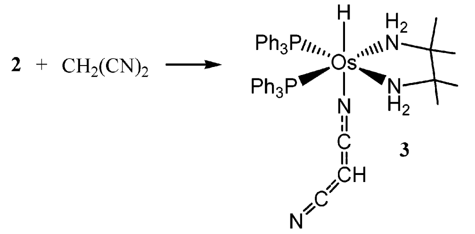
the mild conditions of 5 atm of hydrogen and 20 °C, the TOF continuously increases, reaching a maximum of 0.4 s^{-1} with 98% conversion to 1-phenylethanol in 20 min. Under the same conditions using the ruthenium catalyst **4**, the TOF continuously decreases from an initial maximum TOF of 1 s^{-1}, achieving 99% conversion in 20 min. The differences in the kinetic behavior and the mechanism of hydrogenation are under study. The hydrido chloro complex **1** is a precatalyst that is activated by reaction with KOtBu. This combination can be used to hydrogenate neat acetophenone to 1-phenylethanol under the mild conditions of 1 atm of dihydrogen and room temperature. Reported osmium catalysts for the hydrogenation of ketones require higher temperatures (>80 °C).[13,14]

Like the ruthenium analogue **4**,[1] complex **2** in benzene under 1 atm of H_2(g) splits dihydrogen, a very weak acid with $pK_\alpha^{THF} > 44$,[15] into a hydride on osmium and a proton on the nitrogen of the diamine ligand, to produce the reactive *trans*-dihydride complex *trans*-OsH_2(tmen)(PPh_3)$_2$. This has a triplet at −6.8 ppm (J_{PH} = 12 Hz) for the hydride in the ^1H NMR spectrum and a singlet in the $^{31}P\{^1H\}$ spectrum at 36.8 ppm.

Malononitrile is a weak acid with $pK_\alpha^{THF} = 24$.[15] It reacts with **2** according to eq 1 to give OsH(NCCHCN)(tmen)(PPh_3)$_2$ (**3**). The triplet at −15.9 ppm in the hydride region of the ^1H NMR spectrum and the singlet at 19.7 ppm in the $^{31}P\{^1H\}$ NMR spectrum indicate equivalent phosphorus atoms. The ν(C−N) signal at 2126 cm^{-1} is lower than that reported for the carbon-bound dicyanomethyl complex Co(salpn)(CH(CN)$_2$)(py) (salpn = the dianion of *N*,*N*′-bis(salicylideneimine)-1,2-propane), suggesting that the NCCHCN ligand is bonded via nitrogen to osmium in **3**.[16,17] Indeed, the X-ray crystal structure of **3** (Figure 1) is the first to show a dicyanomethyl ligand that is not carbon-bonded to a transition metal. A structure has been reported for a dimeric palladium complex with two dicyanomethyl ligands that bridge by forming Pd−N and Pd−C bonds.[18] We conclude that the negative charge on the dicyanomethyl ligand in **3** is delocalized over the entire ligand on the basis of the following bond angle and distance data. The central carbon, C9, has a planar geometry with a C7−C9−C8 angle of 123.3(4)°. The C−N bonds C7−N4 = 1.156(5) Å and C8−N3 = 1.151(4) Å are similar, as are the C−C bonds C7−C9 = 1.389(6) Å and C8−C9 = 1.388(5) Å. In the crystal lattice the molecules of **3** occur in hydrogen-bonded pairs with the terminal nitrogen of the dicyanomethyl ligand of one molecule forming a hydrogen bond with the amine proton of a partner molecule and vice versa.



(1)

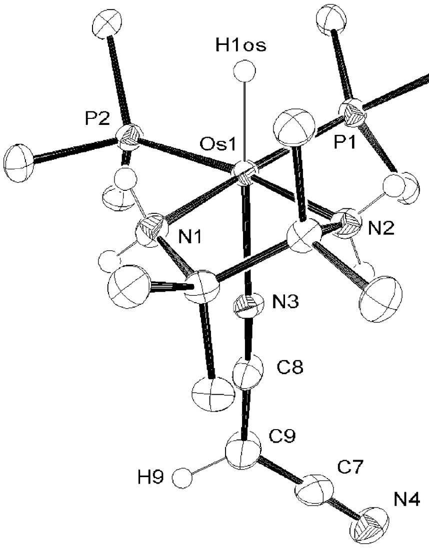
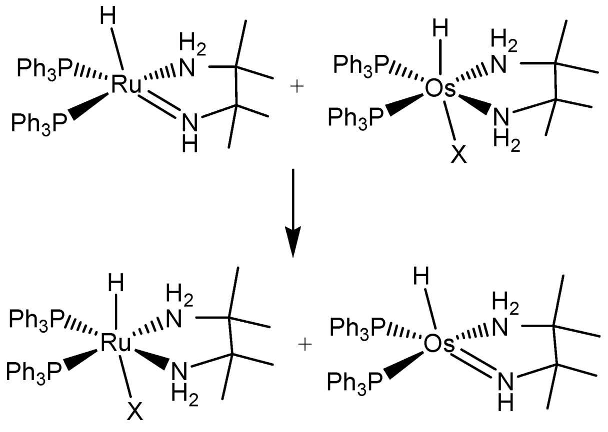


Figure 1. X-ray crystal structure of **3**. Some atoms have been removed for clarity.

Scheme 2. Transfer of HX from OsHX(tmen)(PPh$_3$)$_2$ to 4 (X = Cl, NCCHCN)



With analogous amido complexes of ruthenium and osmium and their adducts in hand, we were interested in determining, by competition experiments, which amido complex has the higher affinity for the weak acid HX. A slight excess of **1** was added with **4** to an NMR tube, and both were dissolved in benzene-d_6. The reaction mixture was observed by ^1H and $^{31}P\{^1H\}$ NMR. Over a period of 24 h all of **4** was converted to RuHCl(tmen)(PPh_3)$_2$, while **1** was converted to **2** (Scheme 2, X = Cl). The excess **1** remained at the end of this period. Similarly, after a slight excess of **3** was added to an NMR tube with **4** dissolved in benzene-d_6, all of **4** was converted to *trans*-RuH(NCCHCN)(tmen)(PPh_3)$_2$ [4] while **3** was converted to **2** within 20 min. It is somewhat surprising that HX is transferred completely from osmium to ruthenium. With the greater extent of their valence orbitals, third-row transition metals generally form stronger bonds than second-row transition metals. The formation of a stronger Os=N bond versus Ru=N

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bond appears to drive these novel HX transfer reactions. It is known that 5d metals form stronger multiple bonds than 4d metals.[19,20] This will be checked in future calculations.

In summary, the new osmium complex **1** with added base, or complex **2** without added base, actively catalyzes the hydrogenation of ketones under milder conditions than for other known osmium catalysts. Complex **3** has a novel nitrogen-bonded dicyanomethyl ligand. The complexes **1** and **3** display the interesting behavior of donating HCl and $CH_2(CN)_2$, respectively, to the ruthenium analogue of **2**. This may be attributed to a strong $2p\pi \rightarrow 5d\pi$ bond formed between the amido nitrogen and osmium(II).

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Supporting Information Available: Text and a figure giving experimental details and a CIF file giving X-ray crystallographic data. This information is available free of charge via the Internet at http://pubs.acs.org.

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