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C−H Bond Activation in the Formation of an Osmium(IV) Metallacycle

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Summary: The osmium methylimido complex [(η^5-C_5H_5)Os(NCH_3)(CH_2SiMe_3)$_2$][SO_3CF_3], ***1****, reacts with PPh_3 to give both the methyleneamido complex (η^5-C_5H_5)Os(NCH_2)(CH_2SiMe_3)$_2$,* ***2****, and the unique osmium(IV) hydride [(η^5-C_5H_5)Os(H)(PPh_3){$CHSiMe_3PPh_2(C_6H_4)$}][SO_3CF_3],* ***4****. A single-crystal X-ray diffraction study of* ***4*** *shows that this molecule has a distorted square pyramidal structure with the center of the cyclopentadienyl ring at the apex. This molecule results from a series of reactions that includes two C−H activation steps: α-hydrogen elimination and orthometalation.*

Imido ligands in transition metal imido complexes can react with nucleophiles, electrophiles, and unsaturated molecules in a number of ways depending on the nature of the complex. Acids add to some imides, forming amide complexes.[1] Bases can deprotonate some imido groups to form alkylideneamido complexes.[2,3] In some cases, nucleophiles add to the imido nitrogen atom.[2,4] Alkenes and alkynes add to the amide ligand in a few complexes.[2,5] Studies on the reaction chemistry of organometallic imido complexes have an added complication because alkyl ligands may react under the same conditions as imido ligands.

We recently described the reaction chemistry of the osmium methylimido complex [(η^5-C_5H_5)Os(NCH_3)(CH_2SiMe_3)$_2$][SO_3CF_3], **1**.[2] Various bases deprotonate the methylimido ligand and form an osmium(IV) methyleneamido complex (η^5-C_5H_5)Os(N=CH_2)(CH_2SiMe_3)$_2$, **2**.

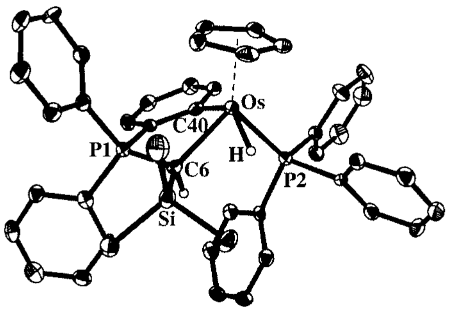

Figure 1. SHELXTL plot of **4** showing 35% probability ellipsoids for non-H atoms. H atoms have been left out for clarity except for the hydride and H6, which were both independently refined. Selected bond distances (Å): Os−C6 = 2.129(8), Os−C40 = 2.129(8), Os−H = 1.614(77), Os−Cp = 2.231(8), Os−P2 = 2.306(2). Selected bond angles (deg): C40−Os−C6 = 81.2(3), C40−Os−P2 = 84.7(2), C6−Os−P2 = 96.3(2), Cp−Os−C6 = 129.7(3), Cp−Os−P2 = 132.1(3), Cp−Os−C6 = 129.7(3), Cp−Os−P2 = 132.1(3). Cp is the centroid of carbon atoms in the cyclopentadienide ring.

Triphenylphosphine reacts with **1** as both a base and a nucleophile. The reaction of **1** with 1.5 equiv of triphenylphosphine gives nearly equal amounts of **2** and [(η^5-C_5H_5)Os(CH_2SiMe_3)$_2$(PPh_3)][SO_3CF_3], **3**, by ^{1}H NMR, along with [$HPPh_3$][SO_3CF_3] and MeN=PPh_3 (Scheme 1, R = CH_2SiMe_3). There is an intermediate species between **1** and **3**, which we presume to be [(η^5-C_5H_5)Os(CH_2SiMe_3)$_2$(MeN=PPh_3)][SO_3CF_3] on the basis of data from IR, ^{1}H NMR, and ^{31}P NMR spectroscopy of the reaction mixture.

However, when **1** reacts with an excess quantity of PPh_3 in dichloromethane solution, **3** is not a product. The organometallic products are the methyleneamido complex, **2**, and a new metallocycle [(η^5-C_5H_5)Os(H)(PPh_3){$CHSiMe_3PPh_2(C_6H_4)$}][SO_3CF_3], **4**. Complex **2** is readily extracted from the reaction mixture by removing the dichloromethane under vacuum and extracting the residue with hexane.[2] Complex **4** crystallizes from tetrahydrofuran/diethyl ether solutions at −30 °C. Complex **4** also forms by the reaction between **3** and PPh_3.

Elemental analysis and spectroscopic methods characterized complex **4**. The presence of a metal hydride is confirmed by the resonance at −11.63 ppm (dd, $^2J_{PH}$ = 37.8 Hz, $^3J_{PH}$ = 5.4 Hz, 1H, OsH) in the ^{1}H NMR spectrum. Integration shows that there is only one trimethylsilyl group. The inequivalent phosphorus atoms differ by 38.5 ppm in the ^{31}P NMR spectrum.

X-ray-quality crystals were obtained by slow addition of hexane to a tetrahydrofuran/dichloromethane (5:1 ratio) solution of **4** at −30 °C. Figure 1 shows the structure of **4**. The osmium center is in a four-legged

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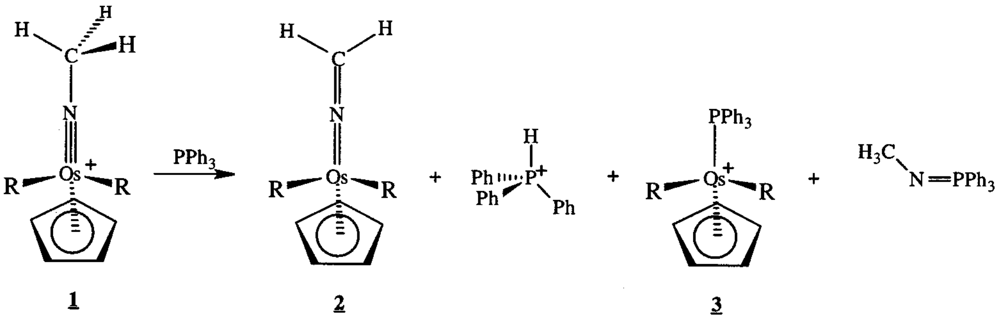
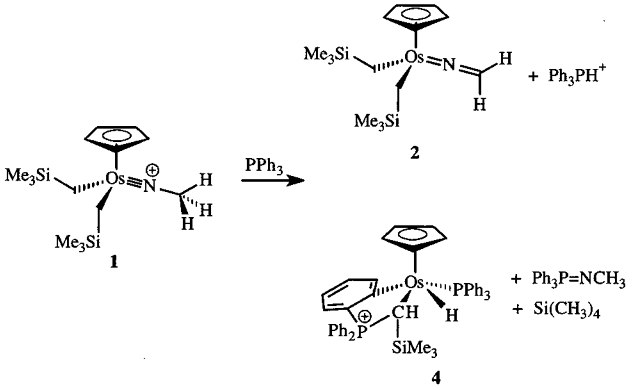
Scheme 1



Scheme 2



piano stool environment. The cyclopentadienyl ligand is bound to the osmium in an η^5 fashion and shows no distortion. Nitridoosmium(VI) cyclopentadienyl complexes show a significant distortion toward the η^3 coordination mode.[6]

The carbon and the hydrogen atom derived from the orthometalated phenyl group are trans to one another. Both C40 and H have smaller Cp-Os-L angles [CpOs$-$C(40) = 111.5(3)°; Cp$-$Os$-$H = 113.0(3)°],where Cp is the centroid of the cyclopentadienyl moiety, than do C6 and P2 [Cp$-$Os$-$C(6) = 129.7(3)°; Cp$-$Os$-$P(2) = 132.1-(3)°]. This distortion from ideal pseudo-square-pyramidal geometry is common in compounds of the general formula $CpML_4$ in which the four L ligands are not identical.[7] The metal-hydride was located and independently refined. The Os$-$H bond distance, 1.614(77) Å, falls within the expected range (1.62$-$1.68 Å) for terminal osmium hydrides.[8]

A proposal for the formation of **4** is shown in Scheme 3. Several transition metal imido complexes react with phosphines at the imido nitrogen to give either a coordinated or free phosphinimine and a reduced metal species.[9] In this case, nucleophilic attack of PPh_3 on the imido nitrogen of **1** likely forms a coordinated phosphinimine complex, $[(\eta^5\text{-}C_5H_5)Os(MeNPPh_3)(CH_2SiMe_3)_2][SO_3CF_3]$. This complex is unstable and in the presence of excess phosphine, the phosphinimine is lost, resulting in the formation of $[(\eta^5\text{-}C_5H_5)Os(PPh_3)(CH_2SiMe_3)_2][SO_3CF_3]$, **3**. Complex **3** is coordinatively unsaturated with a 16-electron count but it can be isolated from solution.

In this proposed mechanism, complex **3** reacts with additional PPh_3 in solution. Phosphine coordination induces α-hydrogen elimination and loss of tetramethylsilane from the complex.[10] Triphenyl phosphine adds to the electron-deficient carbon of the resulting alkylidene. Examples of attack by a tertiary phosphine on an unsaturated carbon producing a phosphoylide are known, and this type of reaction has been used to trap methylidene intermediates.[11] The phosphoylide intermediate in this reaction forms the observed metallacycle, **4**, via orthometalation.

The reaction between triphenylphosphine and $[(\eta^5\text{-}C_5H_5)Os(NCH_3)(CH_2SiMe_3)_2][SO_3CF_3]$ is complex and depends strongly on the concentration and relative quantity of the phosphine. The methylimido ligand is acidic and the phosphine deprotonates it. The nitrogen atom of the methylimido ligand is also electrophilic and the nucleophilic phosphine adds to form an unstable coordinated phosphinimine complex. If additional PPh_3 is available, it adds to the osmium center and displaces the phosphinimine. Excess PPh_3 promotes α-hydride elimination, adds to the resulting alkylidene at the alkylidene carbon, and ultimately leads to the formation of a stable metallocycle $[(\eta^5\text{-}C_5H_5)Os(H)(PPh_3)\{CHSiMe_3\text{-}PPh_2(C_6H_4)\}][SO_3CF_3]$.

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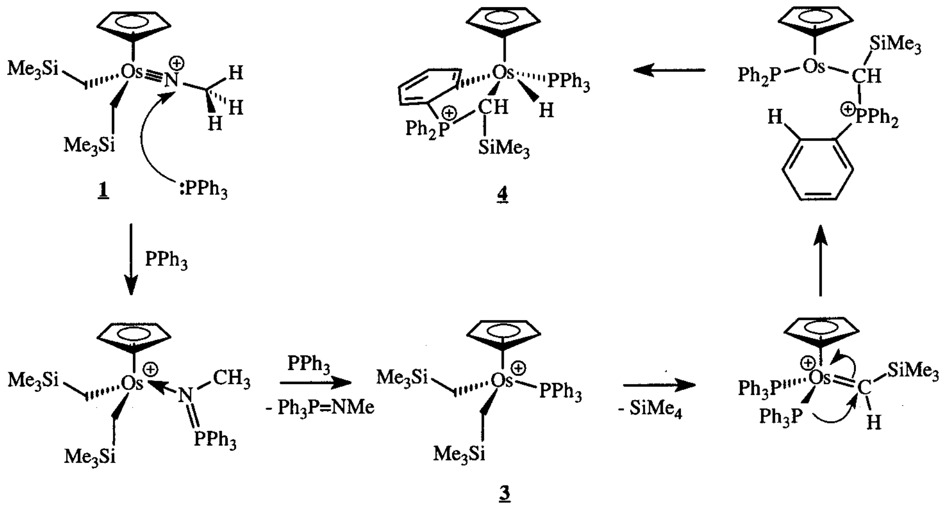
Scheme 3



Experimental Data

All reactions were done under nitrogen atmosphere, using standard air-sensitive techniques with a Schlenk line or in a Vacuum Atmospheres glovebox unless otherwise stated. Diethyl ether, THF, and hexane were distilled from Na/benzophenone. Methylene chloride was distilled from CaH_2. All solvents were stored over 4 Å molecular sieves. Deuterated methylene chloride was purchased from Cambridge Isotope Laboratories and was used without further purification. $[CpOs(NCH_3)(CH_2SiMe_3)_2][SO_3CF_3]$ was synthesized according to literature procedure.[2] All reagents were purchased from Aldrich.

NMR spectra were recorded on a Varian Unity 500, a Varian Unity 400, or a General Electric QE-300. Chemical shifts for ^1H and ^{13}C NMR spectra were referenced to internal solvent resonances. IR spectra were recorded on a Perkin-Elmer 1600 series FTIR. Mass spectra were recorded on a VG ZAB-SE (FAB). Elemental analyses were performed by the University of Illinois microanalytical service.

Preparation of $[Cp(PPh_3)Os(CHSiMe_3PPh_2(C_6H_4))][SO_3CF_3]$, 4. One equivalent of $[CpOs(NCH_3)(CH_2SiMe_3)_2][SO_3CF_3]$, **1**, (0.092 g, 0.201 mmol) was dissolved in 30 mL of CH_2Cl_2. Two equivalents of PPh_3 (0.105 g, 0.400 mmol) was added to the CH_2Cl_2 solution, and the reaction mixture was stirred for 24 h. The reaction was then filtered through Celite, and the solvent was removed from the filtrate. The residue was washed with diethyl ether to extract $CpOs(NCH_2)(CH_2SiMe_3)_2$, **2**, and $MeN{=}PPh_3$. The remaining residue was taken up in either CH_2Cl_2 or THF. Crystals were obtained by slowly adding diethyl ether or hexane to the solution (0.025 g, 0.025 mmol, 12.4%). ^1H NMR data (400 MHz, CD_2Cl_2, 18.9 °C): δ 7.96−6.72 (m, 29H, $P(C_6H_5)$ and $P(C_6H_4)$), 4.94 (s, 5H, C_5H_5), 1.05 (d, $J = 21.6$ Hz, 1H, $CHSiMe_3$), −0.14 (s, 9H, $Si(CH_3)_3$), −11.63 (dd, $^2J_{PH} = 37.8$ Hz, $^3J_{PH} = 5.4$ Hz, 1H, Os*H*). Crystals grown from THF/hexane solution also had two multiplets at δ 3.85 and 1.80 in the ^1H NMR spectrum due to residual THF, while crystals grown from $CHCl_3$ had a singlet at δ 7.25 due to residual $CHCl_3$. ^{13}C NMR data (125.7 MHz, CD_2Cl_2, 19.9 °C): δ 298.2 (m, **C**$HSiMe_3$), 146.91−123.80, 83.42 (s, C_5H_5), 3.12 (s, $Si(CH_3)_3$). $^{31}P\{^1H\}$ NMR data (161.9 MHz, CD_2Cl_2, 18.9 °C): δ 57.7, 19.2. IR (KBr pellet, cm^{-1}): 3059 (m, Cp ν_{CH}), 2961 (m, ν_{CH}), 1435 (m, δ_{CH}), 1422 (m), 1271 (s), 1221 (m), 1150 (s, ν_{SO}), 1033 (s, ν_{SO}), 833 (m, ν_{SiC}), 638 (m, Cp δ_{CC}). Mass spectroscopy (FAB, MB, *m/z*): 867.2 (M^+), 605.2 ($M^+ - PPh_3$). Anal. Calcd for $OsC_{46}H_{45}P_2SiSO_3F_3{\cdot}C_4H_8O$: C, 55.24: H, 4.91; P, 5.7. Found: C, 55.13; H, 5.15; P, 5.79.

Crystal Data and Structure Refinement Summary for $4{\bullet}(CH_2Cl_2)_2$. The data crystal was mounted using oil (Paratone-N, Exxon) to a thin glass fiber. Diffraction data were collected at 198 K on a Siemens Platform/CCD automated diffractometer. Crystal and refinement details are given in Table 1 (Supporting Information). Systematic conditions suggested the ambiguous space group $P\bar{1}$; refinement confirmed the presence of a symmetry center. Standard intensities showed no decay during frame collection. Intensity data were reduced by 3D-profile analysis using SAINT and corrected for Lorentz−polarization effects and for absorption. Scattering factors and anomalous dispersion terms were taken from standard tables.

The structure was solved by direct methods; correct positions for 47 non-H atoms were deduced from an E-map. One cycle of isotropic least-squares refinement followed by an unweighted difference Fourier synthesis revealed positions for the remaining non-H atoms. Atomic parameters for atoms H and H(6) were independently refined. Methyl H atom positions, $Si-CH_3$, were optimized by rotation about Si−C bonds with idealized C−H, Si−H, and H−H distances. Remaining H atoms were included as fixed idealized contributors. H atom U's, were assigned as 1.2 times U_{eq} of adjacent non-H atoms. Non-H atoms were refined with anisotropic thermal coefficients. Successful convergence of the full-matrix least-squares refinement on F^2 was indicated by the maximum shift/error for the last cycle. The highest peaks in the final difference Fourier map were in the vicinity of Os and Cl atoms; the final map had no other significant features. A final analysis of variance between observed and calculated structure factors showed no dependence on amplitude or resolution.

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Supporting Information Available: For **4**, tables of additional crystal data collection and refinement parameters, atomic coordinates, thermal parameters, and complete tables of distances and angles are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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