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Isolation, Structural Characterization, and Dioxygen Reactivity of the Heterobimetallic Complex $[Os(N)(CH_2SiMe_3)_2(OCrO_3)(dppe)]^-$

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Summary: The heterobimetallic complex $[Y][Os(N)(CH_2SiMe_3)_2(\mu\text{-}O)_2CrO_2]$, *1 (Y =* $[PPh_4]$, $[N(n\text{-}Bu)_4]$*), reacts with* $Ph_2PCH_2CH_2PPh_2$ *(dppe) to form* $[Y][Os(N)(CH_2SiMe_3)_2(dppe)(OCrO_3)]$, *2. The structure of 2 was determined by X-ray diffraction. Complex 1 is a catalyst for the oxidation of dppe to* $Ph_2P(O)CH_2CH_2P(O)Ph_2$ *with molecular oxygen.*

Under ordinary conditions, dioxygen is kinetically unreactive toward most organic compounds. The use of metal catalysts to activate dioxygen is one goal of synthetic organic chemists. Many transition metal catalysts have been used to activate molecular oxygen for different organic transformations.[1] Transition metal oxides[2] and dioxygen complexes[3] can react with alkyl- and arylphosphines to generate phosphine oxides stoichiometrically. Catalysts have been developed for the oxidation of tertiary phosphines to phosphine oxides by dioxygen. The rhodium complex $RhCl(PPh_3)_3$ catalyzes the oxidation of PPh_3, $AsPh_3$, and 1,2-bis(diphenylarseno)ethane.[4] An EDTA complex of Ru(III) is a catalyst for the oxidation of triarylphosphines.[5] Tributylphosphine is oxidized catalytically with $Co(acac)_2$, and $Mo(O)_2(Et\text{-}L\text{-}cys)_2$ is an effective catalyst for the oxidation of tertiary phosphines.[6,7]

The heterobimetallic complexes $[Y][Os(N)(CH_2SiMe_3)_2(\mu\text{-}O)_2CrO_2]$ (Y = $[PPh_4]$, $[N(n\text{-}Bu)_4]$), **1**, are effective catalysts for the selective oxidation of alcohols to aldehydes and ketones by molecular oxygen.[8] Alcohols bind to the osmium center during the course of the catalytic oxidation process. Because the metal center in nitrido(alkyl)osmium(VI) complexes is not easily reduced by one electron, radical pathways leading to oxidation of substrate are eliminated and the reactions are therefore highly selective.[9] The alcohol oxidation catalyst, **1**, does not oxidize PPh_3, Me_2S, or olefins under reaction conditions.

Complex **1** does react slowly with 1,2-bis(diphenylphosphino)ethane (dppe). Here we report the syn-

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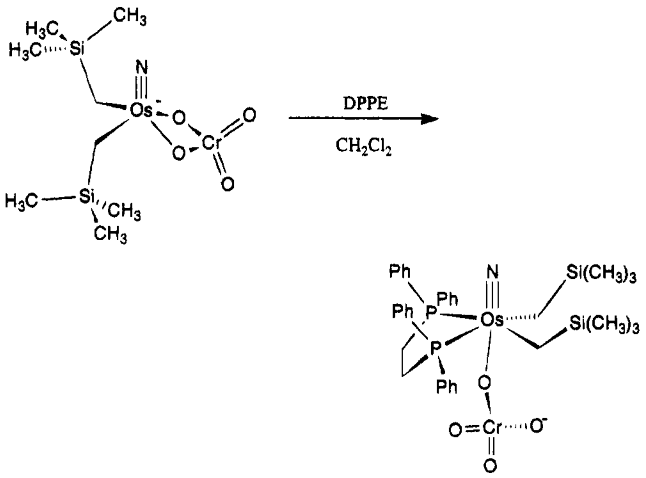
Scheme 1



thesis and characterization of the resulting dppe complex. Solutions of this complex yield the oxidized phosphine in the presence of dioxygen. Preliminary results on the catalytic oxidation of dppe to the corresponding phosphine oxide with **1** and molecular oxygen are reported.

In a typical preparation, a solution of 0.039 g of $[PPh_4][Os(N)(CH_2SiMe_3)_2(\mu\text{-}O)_2CrO_2]$ in 5 mL of methylene chloride was added dropwise to a stirred solution of 0.020 g of dppe in 5 mL methylene chloride over a period of 5 min. The solution was stirred for an additional 0.5 h and filtered through Celite, and the solvent was removed under vacuum to yield a yellow oil. The oil was crystallized from methylene chloride/hexane at −30 °C to yield yellow crystals of $[PPh_4][Os(N)(CH_2SiMe_3)_2OCrO_3(dppe)]$, **2a**, in 86% yield (0.050 g)[10] (Scheme 1). The $[N(n\text{-}Bu)_4]$ salt was prepared in an analogous fashion from **1b** and dppe.[11]

The molecular structure of **2a** was determined by X-ray diffraction.[12] The bright yellow complex crystallizes in the space group $P\bar{1}$ with two molecules of **2a** and three disordered solvent molecules per unit cell. The complex has a distorted octahedral arrangement of ligands around the osmium center (Figure 1). The chromium center has a distorted tetrahedral arrangement of oxygen atoms with the bridging oxygen bond being longer than that of the other chromium−oxygen bonds.

The cationic complex $[Os(N)(CH_2SiMe_3)_2(dppe)(NCMe)][BF_4]$ has a structure similar to that of **2**.[13] This complex has a distorted octahedral geometry with the nitride and neutral acetonitrile ligands in the axial positions with the equatorial ligands bent toward the acetonitrile ligand. The osmium−nitride bond distance is 1.638(5) Å, which is similar to that of **2a**. The osmium−phosphorus distances are essentially identical with averages of 2.453 and 2.463 Å for the acetonitrile and chromate complexes, respectively.

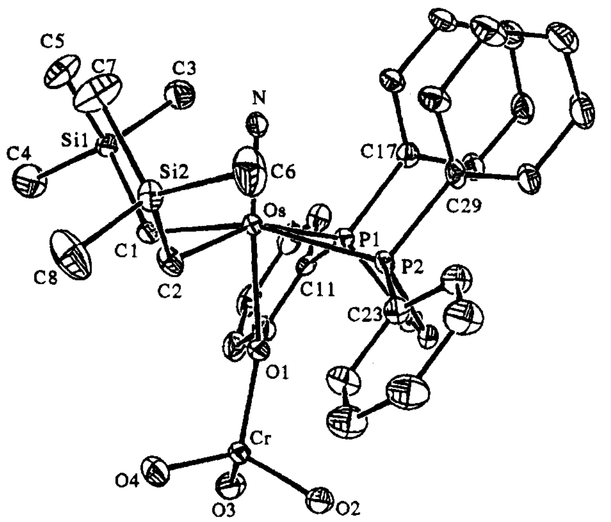


Figure 1. ORTEP diagram for $[PPh_4][Os(N)(CH_2SiMe_3)_2OCrO_3(dppe)]$. Selected bond distances (Å) are as follows: Os−N = 1.656(3), Os−C1 = 2.152(4), Os−C2 = 2.158(4), Os−O1 = 2.157(2), Os−P1 = 2.4665(11), Os−P2 = 2.4600(11), Cr−O1 = 1.705(2), Cr−O2 = 1.634(3), Cr−O4 = 1.632(3), Cr−O3 = 1.626(3). Selected bond angles (deg) are as follows: N−Os−C1 = 101.23(14), N−Os−C2 = 99.48(14), N−Os−P1 = 101.04(11), N−Os−P2 = 97.11(11), N−Os−O1 = 174.55(12), Os−O1−Cr = 159.8(2), O1−Cr−O2 = 108.01(13), O2−Cr−O3 = 109.7(2), O3−Cr−O4 = 110.1(2).

Both the osmium and chromium atoms in **1** are coordinatively unsaturated with 16 and 12 electron counts, respectively, and would be expected to interact with donor molecules. Hard−soft acid−base theory predicts that the softer osmium center would hold more affinity for the soft phosphorus atoms than the harder chromium center leading to the observed product **2**.[14] This requires a change in the coordination mode of the chromate unit from bidentate in **1** to monodentate in **2**. Polyoxoanions coordinate to transition metals as either monodentate, bidentate, or tridentate ligands in similar organometallic complexes.[15]

Complex **2** reacts with molecular oxygen to give **1** and the phosphine oxide $Ph_2P(O)CH_2CH_2P(O)Ph_2$ (Scheme 2). At room temperature the reaction is slow, requiring several days for completion.

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(10) IR (KBr, cm^{-1}): 3054−2888 (m, ν_{CH}), 1436 (s, δ_{CH}), 1108 (s, δ_{PC} and ν_{OsN}), 937 (vw, ν_{CrO}), 912 (vw, ν_{CrO}), 854 (m, γ_{SiMe}), 829 (m, γ_{SiMe}), 746 (m, $\delta_{Ar\text{-}CH}$ oop), 724 (s, $\delta_{ar\text{-}CH}$ oop), 692 (s, $\delta_{ar\text{-}CH}$ oop), 528 (s). Mass spectrum (ES): $Os(N)CrO_2(dppe)^-$, *m/e* 688.0. ^1H NMR (300 MHz, 293 K, $CDCl_3$): δ 7.6−7.9 (m, 24 H, Ph), 7.0−7.4 (m, 20 H, Ph), 3.36 (m, 2H, CH_2), 2.54 (m, 2 H, CH_2), 2.25 (m, 2 H, CH_2), 1.79 (m, 2H, CH_2), −0.22 (s, 18 H, $SiCH_3$). ^{31}P NMR ($CDCl_3$, 121.65 MHz, 299 K): δ (ppm) 38.88 (s). Anal. Calcd for $C_{58}H_{66}NCrO_4OsP_3Si_2{\cdot}{}^1/_3CH_2Cl_2$: C, 55.57; H, 5.33; N, 1.11; Cl, 1.87. Found: C, 55.54; H, 5.34; N, 1.10; Cl, 1.32.

(11) IR (KBr, cm^{-1}): 3055−2875 (m, ν_{CH}), 1436 (m, δ_{CH}), 1239 (m, δ_{Si-C} sym), 1121 (m, ν_{OsN}), 1094 (m), 905 (vw, ν_{CrO}), 890 (vw, ν_{CrO}), 859 (m, γ_{SiCH3}), 829 (s, γ_{SiCH3}), 743 (m, $\delta_{ar\text{-}CH}$ oop), 692 (s, $\delta_{ar\text{-}CH}$ oop), 533 (m). ^{31}P NMR ($CDCl_3$, 121.65 MHz): δ (ppm) 38.91 (s). Mass spectrum (EI, 70 eV): $(M - C_3H_7)^+$, *m/e* 1093. Anal. Calcd for $C_{54}H_{90}N_2Cl_8CrO_4OsP_2Si_2{\cdot}4CH_2Cl_2$: C, 43.97; H, 6.15; N, 1.9; Cr, 3.52. Found: C, 43.77; H, 6.23; N, 1.64; Cr, 3.68.

(12) Data were measured on an Enraf-Nonius CAD4 diffractometer. The structure was solved by a combination of direct methods (SHELXS-86) and Fourier techniques. Crystallographic data for $[PPh_4][Os(N)(CH_2SiMe_3)_2(dppe)(OCrO_3)]$ (198 K): space group $P\bar{1}$; molecules per unit cell (Z) = 2; cell dimensions a = 13.333(3) Å, b = 13.505(4) Å, c = 20.852(4) Å, α = 87.80(2)°, β = 79.56(2)°, γ = 62.38(2)°; V = 3267.2(14) Å^3; Z = 2; R = 0.0293, R_w = 0.0697 for 9644 observed reflections.

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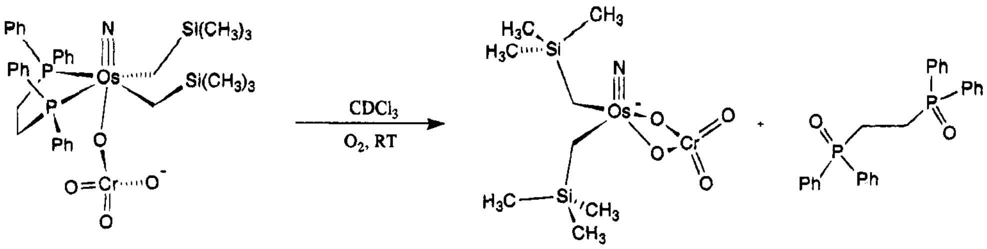
Scheme 2



The diphosphine is catalytically oxidized in toluene solution by 1 under air at 60 °C with a turnover number of 13/h at 25% conversion.[16] More than 40 equiv of phosphine/equiv of catalyst, 1, are oxidized without loss of catalytic activity. Experiments run under identical conditions in the absence of 1 show no measurable oxidation of the dppe. No $Ph_2P(O)CH_2CH_2PPh_2$ was produced. Meyer and Dovletoglou reported that the reduction of ruthenium and osmium oxides by dppe produced the monooxide $Ph_2P(O)CH_2CH_2PPh_2$.[17]

Related osmium complexes $[N(n\text{-}Bu)_4][Os(N)(CH_2SiMe_3)_2(SO_4)]$ and $[N(n\text{-}Bu)_4][Os(N)(CH_2SiMe_3)_2(CO_3)]$[18] react with dppe and O_2 at 60−70 °C in toluene to give a 20−30% yield of $Ph_2P(O)CH_2CH_2P(O)Ph_2$, but the oxidations are not catalytic. The dppe complex $[Os(N)(CH_2SiMe_3)_2(dppe)(NCMe)][BF_4]$ decomposes in the presence of O_2 under these conditions to give small amounts of $Ph_2P(O)CH_2CH_2P(O)Ph_2$ and a black, insoluble solid. The quantity of the phosphine oxide is not increased when the decomposition reaction is carried out in the presence of excess dppe. There is no reaction between $Os(N)(CH_2SiMe_3)_2(dppe)Cl$ and O_2.[13]

Because some $Ph_2P(O)CH_2CH_2P(O)Ph_2$ is formed in the reaction of dppe with molecular oxygen and several monometallic osmium complexes, the chromium center is not necessary for the oxidation. The CrO_4^{2-} group probably serves as an oxidatively stable ligand that can stabilize the osmium complex and allow it to survive multiple catalytic turnovers. The chromate ligand can switch between monodentate to bidentate coordination modes to accommodate substrate coordination at osmium. We do not observe free chromate under these reaction conditions. Mechanistic studies of the catalytic oxidation reaction are currently in progress.

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Supplementary Material Available: Text giving details of the syntheses of **2a,b** and tables of crystallographic data, atomic coordinates, thermal parameters, and selected distances and angles for **2a** (10 pages). Ordering information is given on any current masthead page.

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[16] A 0.0177 M solution of dppe in toluene-d_8 was heated to 60 °C with 0.000427 M **1b** as catalyst. Anisole (1 μL) was added as an internal standard. The reaction was monitored by watching the disappearance of dppe and growth of $Ph_2P(O)CH_2CH_2P(O)Ph_2$ by ^1H and ^{31}P NMR.

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