of the ligands L[17] in the complexes.

All the ruthenium and osmium clusters give singlets in the ^{31}P NMR (Table I, in D_2O) spectra at room temperature, suggesting that all the P atoms are equivalent (unfortunately the NMR data for the analogous PPh_3 complexes of Ru and Os, as well as crystallographic data, are not easily available[18]). Concerning the Ir cluster (**5**) (the X-ray structure is available for the PPh_3 analogue[19]), two ligands L adopt a radial configuration and one adopts an axial configuration like the analogous PPh_3 cluster (Figure 1).[16]

The number and position of the UV-Vis bands for the Ru clusters[6] suggest a triangular metal–metal-bonded framework as discussed by Gray et al.[20] for the analogous PPh_3-substituted clusters.

The catalytic properties in water for these clusters and derived related compounds are presently being investigated in our laboratories and will be described later.

Acknowledgment. We thank Rhône-Poulenc Ind. for a gift of tris(*m*-sulfonatophenyl)phosphine and the CNRS for a fellowship to B.F.

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(21) The periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

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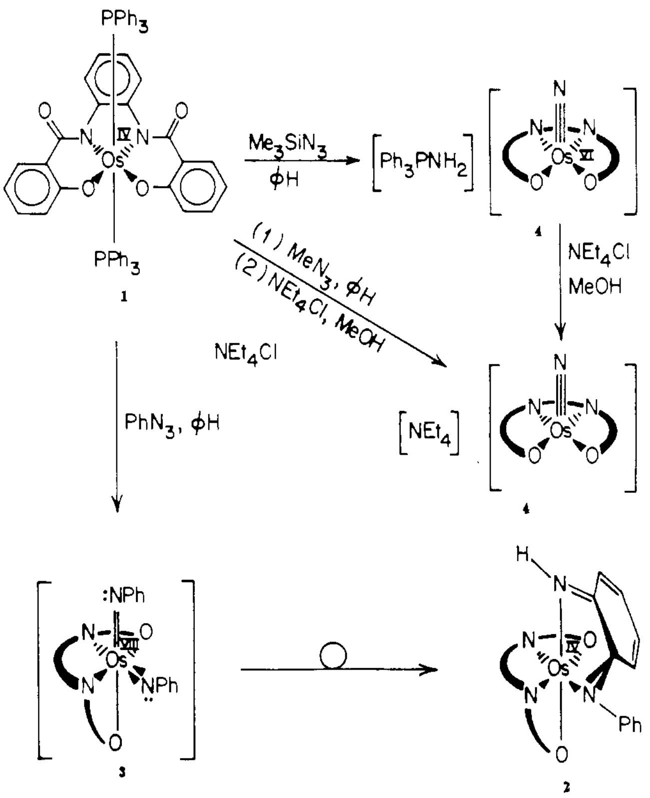
Reactions of Osmium(IV) Complexes of PAC Ligands with Azide Species

Sir:

The search for new oxidizing agents is an interdisciplinary theme.[1] We have been developing new highly oxidized and highly oxidizing inorganic complexes by utilizing oxidation-resistant polyanionic chelating (PAC) ligands.[2-6] As part of this work, we sought to incorporate multiply bonded nitrogen ligands[7] in the same coordination sphere as PAC ligands and discovered that organic azides react in several ways with the osmium(IV) complex *trans*-Os(η^4-HBA-B)(PPh_3)$_2$ (**1**) (Scheme I), depending upon the nature of the azide. Here we report a thermal C–H bond activation via a putative osmium(VIII) bis(imido) complex and the synthesis of a nitrido complex derived from methyl or trimethylsilyl azide.

The reaction of **1** with a twofold excess of phenyl azide (*caution!*) in benzene proceeds at room temperature[8] to yield the

Scheme I



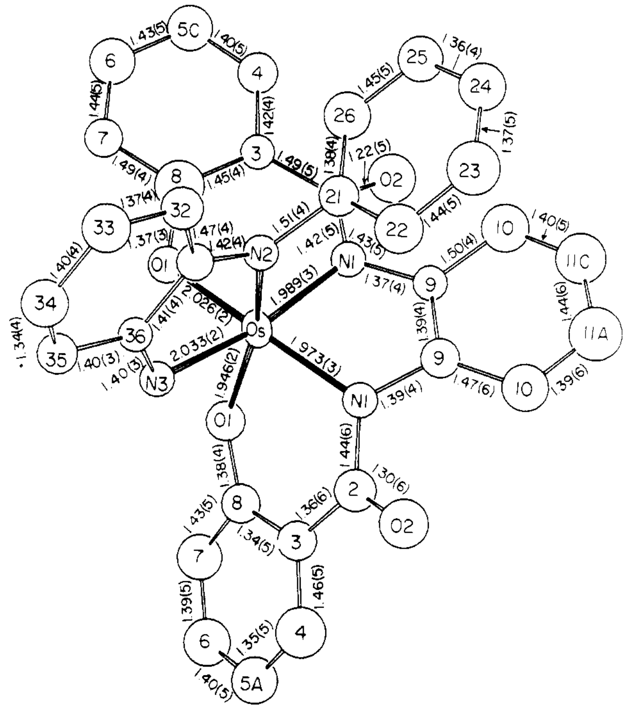


Figure 1. Molecular structure of *cis*-*β*-Os(η^2-NPhC$_6$H$_4$NH)(η^4-HBA-B) (**2**).

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(7) For recent pertinent reviews see: (a) Nugent, W.; Haymore, B. *Coord. Chem. Rev.* **1980**, *31*, 123–175. (b) Griffith, W. *Coord. Chem. Rev.* **1972**, *8*, 369–396.

(8) Reaction proceeds identically in presence or absence of laboratory lighting.

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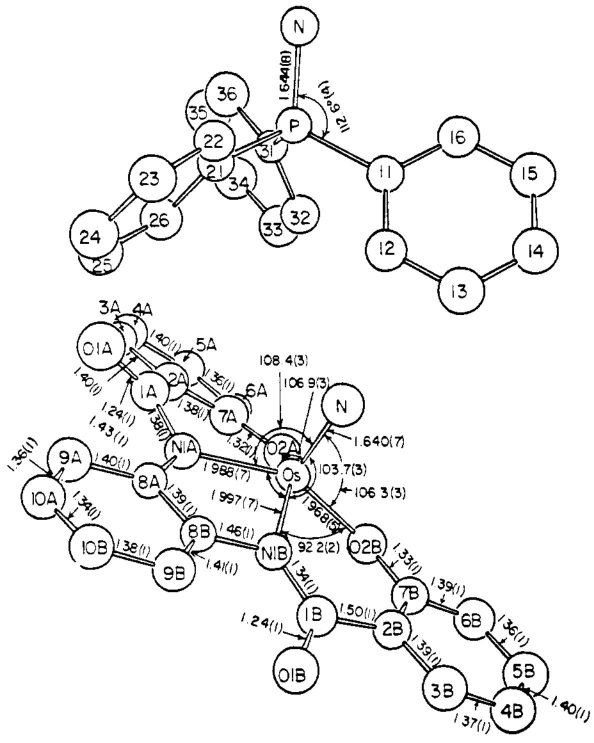

Figure 2. Molecular structure of $[Ph_3PNH_2][OsN(\eta^4\text{-HBA-B})]$ (**4**).

intensely colored purple product, **2**, together with a red as yet unidentified paramagnetic species. Complex **2** can be isolated following preparative TLC on silica gel plates in 30% yield. Recrystallization from ethanol/hexane affords small deep purple crystals. An X-ray analysis was performed.[9] The X-ray structural study (Figure 1)[10] reveals that the PAC ligand has isomerized to the cis-β geometry and a bidentate ligand has been produced. One plausible mechanism for the formation of the bidentate ligand involves the intermediacy of an Os(VIII) bis(imido) complex **3** (see Scheme I). Insertion of an imido nitrogen of **3** into the aryl C–H bond of the second imido ligand followed by proton migration would yield the bidentate ligand. Analogous reactions have been observed by Trogler et al. in photochemically initiated reactions of cobalt tetraazadiene complexes. High-valent diimido intermediates (cobalt(V)) were also invoked.[11] The identical ligand was found for the complex $[HOs_5(CO)_{13}(PhNC_6H_4NH)]$, obtained from the reaction of $H_2Os_3(CO)_{10}$ with azobenzene.[12] Examples of this insertion reaction are also found in purely organic systems.[13] Attempts are under way to trap the supposed Os(VIII) intermediate.

In contrast, reaction of **1** with 2 equiv of trimethylsilyl azide (*caution!*) in benzene at room temperature for 4 h yields the yellow nitrido complex **4**, which precipitates in pure form as the $[Ph_3PNH_2]^+$ salt (>90% yield).[14] Recrystallization from CH_2Cl_2 affords X-ray-quality crystals.[15] The results of an X-ray crystal structure determination are shown in Figure 2.[16] The Os–$N_{nitrido}$ bond distance (1.64 (1) Å) is consistent with an osmium–nitrogen triple bond.[17] The osmium atom sits 0.56 Å above the PAC ligand plane with an average NML angle of 106.4°. Cation metathesis with $[Et_4N][Cl]$ gives the tetraethylammonium salt of the nitrido complex anion. When methyl azide (*caution!*) is passed through a solution of **1** in benzene, followed by workup with $[Et_4N][Cl]$, the same nitrido complex anion can be isolated in good yield (80%) as the tetraethylammonium salt.

Acknowledgment. We acknowledge the Rohm and Haas Co., the Atlantic Richfield Corp. of America, and the National Science Foundation (Grant CHE-84-06198) for generous support of this research. We thank Dr. Peter J. Desrosiers for helpful discussions and John T. Keech for assitance with NMR measurements. Upgrade of the Divisional X-ray Diffraction Facility was supported by the National Science Foundation (Grant CHE-82-19039).

Supplementary Material Available: Complete details of data collection and refinement and listings of bond distances and angles and of fractional atomic coordinates and Gaussian amplitudes (10 pages); listings of structure factor amplitudes (72 pages). Ordering information is given on any current masthead page.

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[9] ^1H NMR spectrum assigned following decoupling and NOE experiments. For assignments see Figure 1. ^1H NMR ($CDCl_3$), δ: 11.6 (s), N(3A)–H; 8.35 (dd), C(10A)–H; 8.05 (d), C(4C)–H; 7.3 (t), C(6C)–H, C(6A)–H; 7.0 (m), C(7C)–H, C(7A)–H, C(11A)–H, C(11C)–H, C(25A)–H, C(24A)–H, C(23A)–H; 6.92 (d), C(35A)–H; 6.8 (t), C(5C)–H, C(5A)–H; 6.48 (t), C(34A)–H; 6.35 (t), C(32A)–H; 6.28 (br t), C(33A)–H; 6.0 (d), C(26A)–H, C(22A)–H. Anal. Calcd for $OsC_{32}H_{22}O_4$: C, 53.62; H, 3.09; N, 7.82. Found: C, 53.49; H, 3.19; N, 7.65.

[10] Structure determination of **2**: space group $P\bar{1}$, $Z = 4$, $\lambda = 0.7107$ Å, Enraf-Nonius CAD4 diffractometer, $a = 9.259$ (2) Å, $b = 16.025$ (5) Å, $c = 17.883$ (10) Å, $\alpha = 95.37$ (4)°, $\beta = 94.49$ (4)°, $\gamma = 98.68$ (3)°, $V = 2600$ (2) Å^3. Heavy-atom solution, full-matrix least-squares refinement on all coordinates and anisotropic Gaussian amplitudes of the non-hydrogen atoms minimizing $\sum w\Delta^2$, $w = \sigma_F^{-2}$, $\Delta = F_o^2 - (F_c/k)^2$, resulted in the goodness-of-fit $S = [\sum w\Delta^2/(n - v)]^{1/2} = 1.73$, $n = 8144$ reflections and $p = 739$ parameters (3 blocks, 246–247–246), $R_F = \sum||F_o| - |F_c||/\sum|F_o| = 0.114$ (7143 reflections, $I > 0$), $R_F = 0.067$ (4378 reflections, $I > 3\sigma_I$). All calculations were carried out on a VAX 11/750 with the CRYM crystallographic system. The crystal of this compound was of poor diffracting quality so that counting rates and hence data precision were of low quality: the value of this determination lies principally in establishing the connectivity of the atoms. Additional details are given in the supplementary material.

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[14] Nitrido complexes have been produced from the reaction of trimethylsilyl azide and a metal complex: Chatt, J.; Dilworth, J. *J. Indian Chem. Soc.* **1977**, *106*, 13–18.

[15] ^1H NMR ($(CD_3)_2CO$), δ: 9.2 (dd), 2 H; 8.45 (dd), 2 H; 7.7 (m), 15 H; 7.1 (m), 8 H; 6.3 (br s), 2 H. $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$) δ: 42.1 (s). Anal. Calcd for $OsC_{38}H_{29}N_4O_4P$: C, 55.20; H, 3.53; N, 6.78. Found: C, 55.00; H, 3.67; N, 6.78.

[16] Structure determination of **4**: space group $P2_1/n$, Enraf-Nonius CAD4 diffractometer, $\lambda = 0.7107$ Å, $a = 9.555$ (2) Å, $b = 23.675$ (3) Å, $c = 14.375$ (3) Å, $\beta = 93.26$ (2)°, $V = 3247$ (1) Å^3, $Z = 4$; refinement and structure solution, as described above, led to $S = 1.75$ ($n = 5703$ reflections, $p = 433$ parameters), $R_F = 0.082$ ($n = 5153$ reflections, $I > 0$), $R_F = 0.049$ ($n = 3520$ reflections, $I > 3\sigma_I$). Additional details are given in the supplementary material.

[17] Compare for example with the structure of $K_2[OsNCl_5]$ where the Os–N bond distance is 1.614 (13) Å: Bright, D.; Ibers, J. *Inorg. Chem.* **1969**, *8*, 709–715.

[18] Contribution No. 7338.

[19] Alfred P. Sloan Research Fellow, 1986–1988; Dreyfus Teacher-Scholar, 1986–1990.

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Syntheses of Stabilized Linear Tetraphosphazanes

Sir:

The development of linear P(III)–phosphazane chemistry has been severely limited by the absence of phosphazane $[(PR-NR')_n]$ members of significant ($n > 2$) chain extension.[1] This dearth occurs because reactions from which linear phosphazanes could

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