manganous porphyrin to a manganic porphyrin tethered to a PE molecule on the opposite side of the bilayer can occur. We have assumed that the PE-linked porphyrins can penetrate into the membrane up to the phosphoric acid head group of the lipid and the distance these porphyrins penetrate into the lipid bilayer should be different with different PE-C_n-TTP (n = 0, 5, 11). It is likely that this is the reason why PE-C_{11}-MnTTP and PE-C_5-MnTTP can catalyze the electron transfer more than PE-MnTTP (Figure 1) because the MnTTP portion of the C_{11} and C_5 derivatives can approach each other sufficiently for electron transfer to occur.[5]

In conclusion, these results showed that (1) PE-C_n-MnTTP exhibited a selective transmembrane electron transfer, depending not only on the length of spacer methylene groups of PE-C_n-MnTTP incorporated in the lipsome but also on the fluidity of the lipid bilayer and (2) **1** can be embedded into the lipid bilayer of liposome much more easily than MnTTP. Thus, these compounds are being utilized to systematically examine electron transport in selected liposomal systems.

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Planar "20-Electron" Osmium Imido Complexes. A Linear Imido Ligand Does Not Necessarily Donate Its Lone Pair of Electrons to the Metal

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We have been using the (2,6-diisopropylphenyl)imido ligand as a stabilizing ligand for high-oxidation-state Mo alkylidene,[1] W alkylidene,[2] Re alkylidene,[3] and Re alkylidyne[4] complexes. In order to explore the potential of a similar approach to the high-oxidation-state organometallic chemistry of later metals, and in view of the relative scarcity of imido complexes of group 8 and 9 metals,[5] we have begun to explore the preparation and chemistry of new imido complexes of osmium, the metal that yielded the first example of a transition-metal imido complex, Os(N-*t*-Bu)O_3.[6]

OsO_4 reacts with 3 equiv of ArNCO (Ar = 2,6-C_6H_3-*i*-Pr_2) smoothly over the course of ~20 h in refluxing heptane to afford deep red-brown, crystalline Os(N-2,6-C_6H_3-*i*-Pr_2)$_3$ (**1**) in 50% isolated yield.[7] An X-ray study[8] shows **1** to be a planar trigonal complex (Figure 1) in which a crystallographic 2-fold axis passes through Os, N(2), C(21), and C(24). Two of the phenyl rings are oriented roughly perpendicular to the OsN_3 plane (dihedral angle 81.62°), while the third lies in the OsN_3 plane (dihedral angle 1.90°). The two crystallographically distinct imido ligands are linear (Os-N(1)-C(11) = 178.0 (5)°, Os-N(2)-C(21) = 180° by symmetry). If we assume imido ligand linearity to indicate that the lone pair of electrons on nitrogen is donated to the metal, **1** is a "20-electron" complex. In D_{3h} symmetry, one can construct σ-bonding metal orbitals from s, p_x, and p_y orbitals, and five π-bonding metal orbitals, three using combinations of p_z (a_2''), d_{xz}, and d_{yz} (e'') and two using combinations of $d_{x^2-y^2}$ and d_{xy} (e') orbitals. Two electrons are left in the d_{z^2} (a_1') orbital on osmium, and the last remaining pair of electrons we propose is located in a nitrogen-centered nonbonding MO of a_2' symmetry made up of the "in-plane" p_x orbitals on the nitrogen atoms.[9] SCF-Xα-SW calculations on hypothetical Os(NH)$_3$ suggest that the HOMO is the metal-based a_1' (d_{z^2}) orbital, the ligand-based a_2' orbital being approximately 1 eV lower in energy.[10]

^1H and ^{13}C NMR data[11] indicate that all three imido ligands are equivalent in **1** in CD_2Cl_2 between 25 and −90 °C. Therefore

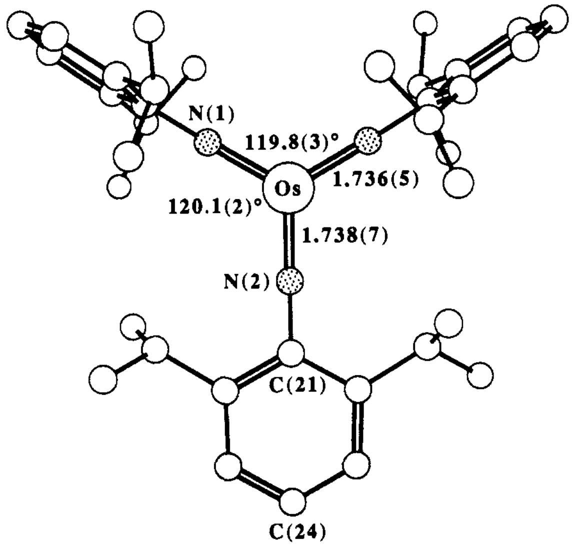

Figure 1. A drawing of the structure of Os(N-2,6-C_6H_3-*i*-Pr_2)$_3$. (Only "covalent" Os=N bonds are shown.)

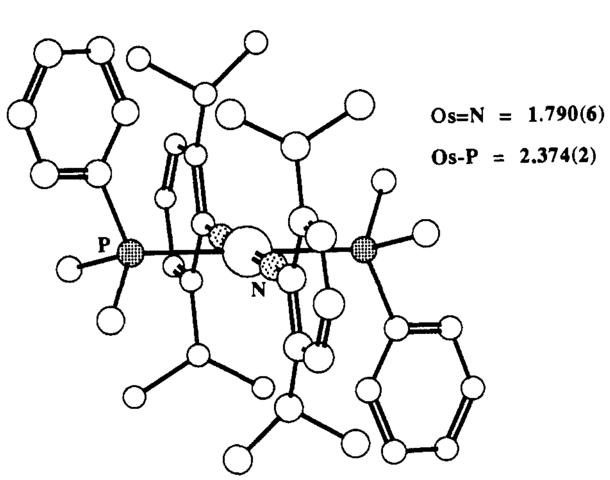

Figure 2. A drawing of *trans*-Os(N-2,6-C_6H_3-*i*-Pr_2)$_2$(PMe_2Ph)$_2$.

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(7) A solution of OsO_4 (2.0 g, 7.87 mmol) and ArNCO (4.8 g, 23.65 mmol) in heptane (40 mL) was refluxed under argon for 20 h, during which time the initial yellow solution became a dark brown. Red-brown crystals of **1** precipitated from solution upon cooling of the reaction mixture to −35 °C for ~2 h. The crude product was recrystallized from pentane (−35 °C) to obtain pure **1** in 50% yield. Anal. Calcd for $C_{36}H_{51}N_3Os$: C, 60.39; H, 7.18; N, 5.87. Found: C, 60.60; H, 7.22; N, 5.77.

(8) A crystal was mounted on a glass fiber in air. Data were collected on an Enraf-Nonius CAD-4 diffractometer at room temperature using Mo Kα radiation: space group $C2/c$ with a = 22.616 (2) Å, b = 10.2831 (4) Å, c = 16.185 (1) Å, β = 111.462 (6)°, Z = 4, FW = 716.02, and ρ = 1.357 g/cm^3. A total of 4291 reflections ($h,k,\pm l$) were collected in the range $3° < 2\theta < 55°$ with the 2824 having $I > 3.00\sigma(I)$ being used in the structure refinement by full-matrix least-squares techniques (180 variables) using the TEXSAN crystallographic software package from Molecular Structure Corporation. Final R_1 = 0.042, R_2 = 0.041. Full details can be found in the supplementary material.

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(11) ^1H NMR (C_6D_6): δ 7.33 (H_p), 7.03 (H_m), 3.84 (Me_2CH), 1.21 (Me_2CH). ^{13}C NMR (C_6D_6): δ 155.67 (C_{ipso}), 139.51 (C_o), 128.25 (C_m), 123.30 (C_p), 29.08 (Me_2CH), 22.92 (Me_2CH).

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the orientations observed in the crystal must be ascribed to relatively weak intramolecular interactions and/or intermolecular crystal packing forces.

$Os(NAr)_3$ is soluble and stable in most common organic solvents and is stable to moist air in both the solid state and solution for days at 25 °C. It is insoluble and stable in water. It does not react at 25 °C with pyridine, tetrahydrofuran, tertiary amines, triphenylphosphine, gaseous HCl in ether, $Ph_3P{=}O$, propylene oxide, norbornene, cyclopentene, or styrene. However, **1** does react readily with PMe_2Ph in pentane to give violet, crystalline $Os(NAr)_2(PMe_2Ph)_2$ (**2**) and $Me_2PhP{=}NAr$ in high yield.[12] (Products that probably are related to **2** are obtained from analogous reactions between **1** and PMe_3, $P(OMe)_3$, or $P(OPh)_3$.) An X-ray study[13] showed **2** to be a square-planar complex in which there is a crystallographic inversion center (Figure 2). The bond lengths $Os{=}N = 1.790\ (6)$ Å and $Os{-}P = 2.374\ (2)$ Å are not unusual. The imido ligands are virtually linear ($Os{-}N{-}C$ angle of 177.9 (5)°). Therefore **2** also might be called a "20-electron" complex, but again, an electron pair can be said to be in a nitrogen-based nonbonding MO (b_{3u} in D_{2h} symmetry) made up of the symmetric combination of the two in-plane p orbitals on the nitrogen atoms. (The b_{3u} orbital on osmium probably is used primarily for σ bonding to the phosphine ligands.)

Compound **1** reacts with Me_3NO to give red-black crystalline $OsO(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_3$ (**3**),[14] an analogue of previously reported $OsO(N\text{-}t\text{-}Bu)_3$.[15] **3** readily transfers an oxygen atom to PPh_3 to generate Ph_3PO and **1** and reacts with norbornene, cyclopentene, and ethylene[16] to give orange, crystalline products that contain a plane of symmetry (by NMR) and therefore are postulated to be Os(VI) metallaimidazolidine complexes analogous to those postulated as intermediates in reactions between $OsO(N\text{-}t\text{-}Bu)_3$ and olefins.[15] The structure of $Os[(Ar)NCH_2CH_2N(Ar)](O)(NAr)$ has been confirmed by an X-ray study, details of which will be published later.

To our knowledge, **1** is the first example of a "pure" homoleptic imido complex[17] and a rare example of trigonal coordination.[18] The unusual square-planar geometry of **2** is reminiscent of square-planar complexes of the type $M(O\text{-}2,6\text{-}C_6H_3R_2)_4$ (M = W[19] or Re;[20] R = *i*-Pr or Me) where strong π bonding is believed to enforce the square-planar geometry. The structures of **1** and **2** challenge the notion that linearity or near linearity of an imido ligand implies donation of the electron pair on nitrogen to the metal.[5] The structure of a recently reported "20-electron" zirconium complex would justify a similar conclusion.[21]

Acknowledgment. R.R.S. thanks the National Science Foundation for research support (CHE 88-22508) and the U.S. Department of Energy, Division of University and Industry Programs, for funds to purchase the X-ray diffractometer (Grant DE-FG05-86ER75292). J.T.A. thanks the Deutscher Akademischer Austauschdienst for a NATO Postdoctoral Fellowship, and T.P.K. thanks the Science and Engineering Research Council for a NATO Postdoctoral Fellowship. We thank Dr. W. M. Davis for collecting the data set for 1 and Molecular Structure Corporation for collecting the data set for 2.

Supplementary Material Available: Description of the X-ray study, an ORTEP drawing, and a fully labeled drawing and tables of final positional parameters and final thermal parameters for **1** and **2** (21 pages); tables of final observed and calculated structure factors for **1** and **2** (52 pages). Ordering information is given on any current masthead page.

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(12) Anal. Calcd for $C_{32}H_{45}N_2O_2Os$: C, 58.80; H, 6.91; N, 3.43. Found: C, 58.62; H, 7.14; N, 3.45. ^1H NMR (C_6D_6): δ 4.32 ($CHMe_2$), 1.53 (virtual t, $PPhMe_2$), 1.13 ($CHMe_2$); aryl proton resonances not listed.

(13) A crystal was mounted in a glass capillary. Data were collected on a Rigaku AFC6R diffractometer at room temperature using graphite-monochromated Mo Kα radiation: space group $P2_1/c$ with $a = 9.605\ (2)$ Å, $b = 9.314\ (7)$ Å, $c = 21.996\ (3)$ Å, $\beta = 96.56\ (2)°$, $Z = 2$, FW = 817.04, and $\rho = 1.388$ g/cm³. A total of 3914 reflections ($h,k,\pm l$) were collected in the range $0° < 2\theta < 48°$ with the 2206 having $I > 3.00\sigma(I)$ being used in the structure refinement by full-matrix least-squares techniques (206 variables) using the TEXSAN crystallographic software package from Molecular Structure Corporation. Final $R_1 = 0.029$, $R_2 = 0.044$. Full details can be found in the supplementary material.

(14) A suspension of **1** (0.2 g, 0.24 mmol) and Me_3NO (0.063 g, 0.84 mmol) in toluene (20 mL) was stirred under dinitrogen at room temperature for 24 h. Solvents were removed in vacuo, and the residue was extracted and recrystallized from pentane to afford red-brown crystals of **2** in 63% yield: ^1H NMR (C_6D_6) δ 7.00 (H_m), 6.88 (H_p), 3.47 (Me_2CH), 1.08 (Me_2CH); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 153.77 (C_{ipso}), 141.33 (C_o), 128.59 (C_m), 122.51 (C_p), 29.31 (Me_2CH), 23.55 (Me_2CH). Anal. Calcd for $C_{36}H_{51}N_3OOs$: C, 59.07; H, 7.02; N, 5.74. Found: C, 58.75; H, 7.17; N, 5.65.

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(16) Anal. Calcd for $C_{38}H_{55}N_3OOs$: C, 60.05; H, 7.29; N, 5.53. Found: C, 60.18; H, 7.44; N, 5.70. ^1H NMR (C_6D_6): δ 7.15–6.80 (m, 9, aryl protons), 4.05 (AA′BB′ pattern, 4, C_2H_4), 3.79 (sept, 2, $CHMe_2$), 2.81 (sept, 2, $CHMe_2$), 2.41 (sept, 2, $CHMe_2$), 1.54 (d, 6, $CHMe_2$), 1.20 (d, 6, $CHMe_2$), 1.14 (d, 6, $CHMe_2$), 0.93 (d, 6, $CHMe_2$), 0.90 (d, 12, $CHMe_2$). ^{13}C NMR (C_6D_6): δ 70.48 (C_β); $\nu(Os{=}O)$ 896 cm^{-1}.

(17) (a) Closely related complexes that contain lithium–nitrogen bonds are $Li_2W(N\text{-}t\text{-}Bu)_4$ and $Li(tmeda)Re(N\text{-}t\text{-}Bu)_4$.[17b] "$Re(N\text{-}t\text{-}Bu)_3$" is actually a dimer, $[Re(N\text{-}t\text{-}Bu)_2(\mu\text{-}N\text{-}t\text{-}Bu)]_2$.[17c] $Os(N\text{-}t\text{-}Bu)_3(NSO_2aryl)$ was characterized by elemental analysis and by its reactions with olefins,[17d] but not crystallographically characterized. (b) Danopoulos, A. A.; Wilkinson, G.; Hussain, B.; Hursthouse, M. B. *J. Chem. Soc., Chem. Commun.* **1989**, 896. (c) Danopoulos, A. A.; Longley, C. J.; Wilkinson, G.; Hussain, B.; Hursthouse, M. B. *Polyhedron*, in press. (d) Hentges, S. G.; Sharpless, K. B., unpublished results.

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X-ray Absorption Edge Spectroscopy of Ligands Bound to Open-Shell Metal Ions: Chlorine K-Edge Studies of Covalency in $CuCl_4^{2-}$

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Information on electronic structure can be obtained from analysis of X-ray absorption edge spectra.[1] This approach has been used to obtain information from edges of transition metals like Cu, Fe, Ni, and Mo.[2] It is also possible to directly study the absorption edge of ligands such as Cl and S bound to the metal.[2e,3] These edges fall in the 2–3-keV energy region where edge features are very well resolved.[4] We report here the observation of an intense preedge transition associated with ligands bound to open-shell central atoms. We further show that the

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