J. Am. Chem. Soc. **1998,** *120,* 5595−5596

Direct Attack of Phenyl Anion at an Electrophilic Osmium−Nitrido Ligand

Thomas J. Crevier[1] and James M. Mayer*

Department of Chemistry, Box 351700
University of Washington
Seattle, Washington 98195-1700

Received February 18, 1998

The oxidation of organic compounds by metal−oxo species is widely practiced and the related chemistry of metal−nitrogen multiple bonds is receiving increasing attention.[2] Despite this interest, fundamental mechanistic issues concerning these reactions remain a matter of discussion.[3] In particular, does the substrate attack directly at the nitrogen or oxygen, or is initial coordination to the metal required?[4] We report here that carbanions add to the nitrido ligand in $TpOs(N)Cl_2$ (**1a**)[5] by a mechanism of direct attack at N and not via formation of an Os−C bond [Tp = hydrotris(1-pyrazolyl) borate, $HBpz_3$]. The direct addition of a carbanion has been observed for electrophilic carbene ligands,[6] but to our knowledge is unprecedented for other multiply bound ligands. This mechanism is potentially a valuable methodology for C−N bond formation.

Addition of 1 equiv of PhMgCl to an ethereal solution of $TpOs(N)Cl_2$ (**1a**) at −78 °C gives a dark orange solution, which turns bright red on exposure to the atmosphere. Aerobic workup and chromatography on silica gel gives the osmium(IV) amide complex $TpOs(NHPh)Cl_2$ (**2a**) in good yield (Scheme 1).[7] With 2 or 3 equiv of PhMgCl, TpOs(NHPh)(Ph)Cl (**2b**), or $TpOs(NHPh)Ph_2$ (**2c**) are isolated, respectively.[7] Compounds **2a**−**c** can be isolated in similar yields with PhMgBr, PhLi, or phenyl zincate reagents (*n*PhLi + $ZnCl_2$). Compounds **2a**−**c** are soluble in all common organic solvents and have been characterized by ^1H NMR, IR, and EI/MS.[7] Their formulation as Os(IV) is consistent with their narrow and mildly paramagnetic shifted ^1H NMR signals, a common feature of d^4 octahedral Os and Re complexes.[8] An X-ray crystal structure of **2a** (Figure 1) reveals an octahedral metal center with the amide phenyl group interleaved between two pyrazole rings.[9]

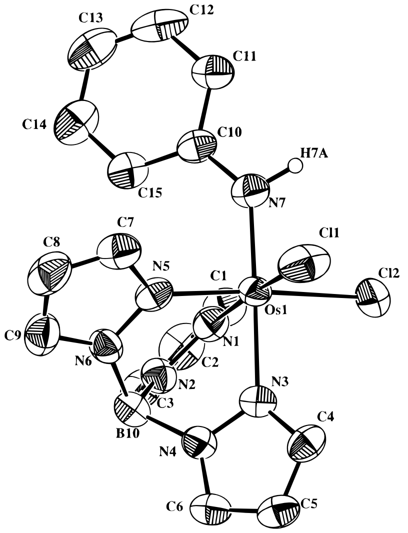
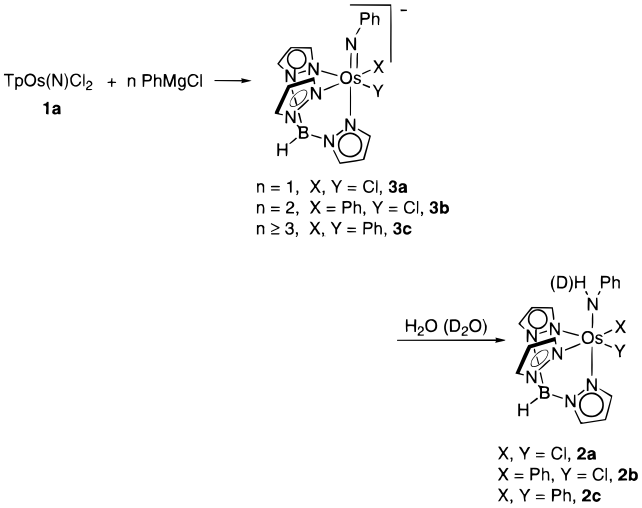


Figure 1. ORTEP diagram of one of the two unique molecules of **2a** (the other exhibits nearly identical structural parameters). All hydrogen atoms except the amido hydrogen are omitted for clarity. Selected bond lengths (Å) and angles (deg): Os(1)−N(7) 1.919(6); Os(1)−Cl(1) 2.363(2); Os(1)−Cl(2) 2.384(2); Os(1)−N(1) 2.039(6); Os(1)−N(3) 2.097(5); Os(1)−N(5) 2.052(6); Os(1)−N(7)−C(10) 133.8(5).

Scheme 1



The initially formed dark orange complex **3c** can be observed by ^1H NMR spectra when a solution of **1a** in C_6D_6 is added to an excess of solid PhMgCl in the absence of air. It displays a paramagnetic (mildly shifted) ^1H NMR spectrum with two sets of phenyl and two sets of pyrazolyl resonances, both in 2:1 ratios.[10] Condensing a small amount of H_2O into the solution results in the rapid formation of **2c**, as happens on aerobic workup. Quenching with D_2O gives $TpOs(NDPh)Ph_2$ (**2c**-d_1); $TpOs(NMePh)Ph_2$ is formed with methyl triflate. These data suggest that the orange species is the anionic Os(IV) phenylimido complex $[TpOs(NPh)Ph_2]^-$ (**3c**). With less PhMgCl, the analogous compounds $[TpOs(NPh)Cl_2]^-$ and $[TpOs(NPh)(Ph)Cl]^-$ are likely formed given their hydrolysis to **2a** and **2b**. Compounds **3** are quite basic and are undoubtedly associated with magnesium

---

[1] University of Washington Saeggebarth Fellow, 1993−1994. University of Washington David M. Ritter Fellow, 1995−1996.

[2] (a) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic Press: New York, 1981. (b) *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon: New York, 1991; Vol. 7 (Oxidation). (c) Du Bois, J.; Tomooka, C. S.; Hong, J.; Carreira, E. M. *Acc. Chem. Res.* **1997**, *30*, 364−72.

[3] DelMonte, A. J.; Haller, J.; Houk, K. N.; Sharpless, K. B.; Singleton, D. A.; Strassner, T.; Thomas, A. A. *J. Am. Chem. Soc.* **1997**, *119*, 9907−8 and references therein.

[4] Sharpless, K. B.; Teranishi, A. Y.; Bäckvall, J.-E. *J. Am. Chem. Soc.* **1977**, *99*, 3120−8.

[5] Prepared from $K[Os(N)O_3]$, KTp, and HCl in EtOH/H_2O; see the Supporting Information.

[6] Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

[7] Complete experimental data are given in the Supporting Information. For **2a**: PhMgX was added dropwise to a −78 °C solution of **1a**; workup in the air (column chromatography using 50% CH_2Cl_2/hexanes and silica gel) yielded 81% **2a**. ^1H NMR ($CDCl_3$): −3.27 (d, 2 H), 8.70 (t, 2H), 0.32 (t, 1H.; all three 7.5 Hz, NC_6H_5, *o, m, p*); 5.87 (br s, 1H, N−H); 6.14 (t, 1H), 6.32 (d, 1H) 6.51 (d, 1H) 6.68 (t, 2H) 6.85 (d, 2H), 4.71 (d, 2H; all six 2 Hz, pz and pz′). IR (thin film, NaCl plates): 3519 cm^{-1} (N−H), 2508 cm^{-1} (B−H). Anal. Calcd (found) for $C_{15}H_{16}BCl_2N_7Os$: C, 31.81 (31.87); H, 2.85 (2.98); N, 17.33 (16.87).

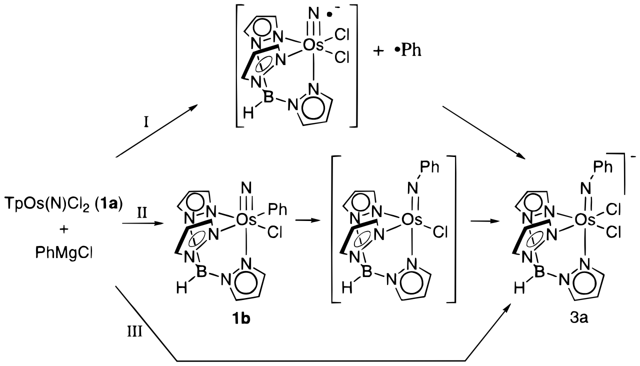
[8] See, for example: Randall, E. W.; Shaw, D. *J. Chem. Soc. A* **1969**, 2867−72.

[9] Crystal data: $C_{15}H_{16}BN_7Cl_2Os$, MW 566.26, triclinic, $P\bar{1}$, T = 296 K, $a = 9.2480(1)$ Å, $b = 11.9370(2)$ Å, $c = 18.2650(3)$ Å, $\alpha = 88.336(1)°$, $\beta = 88.147(1)°$, $\gamma = 71.989(1)°$, $V = 1916.14(5)$ Å^3, $Z = 4$, $D_{calc} = 1.963$ g/cm^3, $R = 0.0493$, $R_w = 0.1287$.

[10] For **3c**: ^1H NMR (C_6D_6): 2.86 (d, 2H), 8.21 (t, 2H), 4.25 (t, 1H; all three 7.5 Hz NC_6H_5, *o, m, p*), 5.75 (d, 4H) 7.88 (t, 4H) 6.02 (t, 2H; all three 7.5 Hz, Os−C_6H_5, *o, m, p*), 5.88 (t, 1H) 6.14 (d, 1H) 6.78 (d, 1H) 6.12 (t, 2H) 6.81 (d, 2H) 6.85 (d, 2H; all six 2 Hz, pz and pz′).

S0002-7863(98)00548-4 CCC: $15.00

Scheme 2



cations in these solutions, based on their high solubility in benzene and the different ^{1}H NMR chemical shifts for products from PhLi vs PhMgCl. They are perhaps better described as metalla−amido complexes.[11] Related phenyl−boryl−amido complexes, with both Ph and BX_2 groups attached to nitrogen, are formed from **1a** and BPh_3 or Ph_2BOBPh_2 (as shown by X-ray crystallography).[12] Compounds **3** without an associated cation would be rare examples of d^4 octahedral imido complexes, in which 2 electrons would occupy Os═N π^* orbitals.[13] This antibonding interaction is minimized on decreasing the Os−N−Ph angle and binding a cation. Attempts to isolate compounds **3** have so far been unsuccessful.

Three mechanisms have been considered for the formation of the C−N bond (Scheme 2).[14] Initial electron transfer to give free phenyl radicals (path I) is ruled out by the reaction proceeding in high yield in THF solvent. An osmium species of concentration $\leq 10^{-3}$ M would have to react with $Ph^\bullet$ faster than the diffusion limit ($\geq 10^{11}$ M^{-1} s^{-1}) to compete with trapping by THF solvent (4.8×10^6 M^{-1} s^{-1}).[15] Alternatively, the amido complexes could be formed by initial phenyl addition to the osmium center to give TpOs(N)(Ph)Cl (**1b**) or $TpOs(N)Ph_2$ (**1c**), followed by phenyl migration to the nitrido ligand (path II). Aryl metal-to-nitrido migration is without precedent but a closely related rearrangement of a rhenium−oxo−phenyl complex has been described.[16] Independently synthesized **1b** and **1c**[17] undergo no observable migration or decomposition at 80 °C in C_6D_6 or $CDCl_3$. They react slowly with Ph-d_5-MgBr, with only 5% conversion to partially deuterated **2c** after 1 day. Since this is much slower than the conversion of **1a** to **3a**−**c**, **1b** and **1c** are not kinetically competent to be intermediates. In addition, ^{1}H NMR spectra of the products after workup show TpOs[NH(Ph-d_5)](Ph-d_5)(Ph) from **1b** and TpOs[NH(Ph-d_5)]Ph_2 from **1c**, with no evidence for protio phenyl groups being transferred to the nitrogen. Thus, osmium-to-nitrido migration (path II) is not the operative mechanism and osmium−aryl species are not intermediates. We conclude that the mechanism is the direct addition of the phenyl anion to the nitrido ligand (path III). This is consistent with the first phenyl group added to **1a** being bonded to the nitrido and with the absence of halide exchange when PhMgBr is used.

The observation of direct Ph^- addition indicates that the nitrido ligand in **1a** is electrophilic. Consistent with this, **1a** reacts rapidly with PPh_3 to give $TpOs(NPPh_3)Cl_2$.[18] Complex **1a** exhibits no nucleophilic reactivity, as it is inert to $BF_3 \cdot Et_2O$ and methyl triflate. Preliminary DFT calculations support this picture: the LUMO in **1a** is a low-lying Os−N π^* orbital, with significant density on the nitrido ligand, while the nitrogen lone pair is at quite low energy.[19] The electrophilicity is strongly influenced by the ancillary ligands, as **1c** reacts very slowly with PhMgX and PPh_3, which instantly reduce **1a**. The character of osmium nitrido ligands is known to vary from electrophilic—$[Os(N)Cl_2(trpy)]^+$ adds phosphines at N[20]—to nucleophilic, such as methyl triflate alkylating the nitride of $Tp^*Os(N)Ph_2$ [$Tp^* = HB(3,5\text{-}Me_2pz)_3$].[21] $[Os(N)Cl_4]^-$ is alkylated at osmium by MgR_2 without evidence for attack at N.[22] The reactivity of imido ligands on osmium is equally variable: the very basic compounds **3** in this system react rapidly with trace water to give compounds **2**, while the isoelectronic d^4 imido dication $[Os(NH)(trpy)(bpy)]^{2+}$ is water stable and electrophilic.[20b]

In sum, PhMgCl and related reagents deliver phenyl anion directly to the electrophilic nitrido ligand in $TpOs(N)Cl_2$ (**1a**), without the intermediacy of osmium aryl complexes or free phenyl radicals. We know of no precedence for such a direct carbanion addition to nitrido, oxo, imido, or sulfido ligands.[23,24] These results indicate that substrates need not coordinate to a metal center prior to oxidation by combining with a multiply bonded ligand.

Acknowledgment. We are grateful to the National Science Foundation for financial support, to Mr. Scott Lovell for assistance with the X-ray crystallography, and to Dr. A. Sattleberger for assistance.

Supporting Information Available: Full preparative procedures and spectroscopic data for **1**−**3**, and X-ray crystallographic tables for $TpOs(NHPh)Cl_2$ (**2a**) (19 pages, print/PDF). An X-ray crystallographic file, in CIF format, is available via the Web only. See any current masthead page for ordering information and Web access instructions.

JA980548U

---

[11] See, for example: (a) Dewey, M. A.; Stark, G. A.; Gladysz, J. A. *Organometallics* **1996**, *15*, 4798−807. (b) Powell, K. R.; Pérez, P. J.; Luan, L.; Feng, S. G.; White, P. S.; Brookhart, M.; Templeton, J. L. *Organometallics* **1994**, *13*, 1851−64.

[12] Crevier, T. J.; Mayer, J. M. *Angew. Chem.* **1988** In press.

[13] (a) Nugent, W. A.; Mayer, J. M. *Metal−Ligand Multiple Bonds*; Wiley-Interscience: New York, 1988. (b) Arndtsen, B. A.; Sleiman, H. F.; Chang, A. K.; McElwee-White, L. *J. Am. Chem. Soc.* **1991**, *113*, 4871−6. (c) See also, ref 11b.

[14] A reviewer suggested another possibility, addition of Ph^- to **1a** without chloride loss to form the seven-coordinate intermediate $[TpOs(N)Cl_2(Ph)^-]$, which then undergoes Os → N migration. But such seven-coordinate species are very unusual for d^2 nitrido and oxo complexes,[13a] and phenyl addition and migration would have to be regiospecific in order to account for the lack of protio phenyl migration in the reactions of **1b** and **1c** with Ph-d_5-MgBr.

[15] Scaiano, J. C.; Stewart, L. C. *J. Am. Chem. Soc.* **1983**, *105*, 3609−14.

[16] Brown, S. N.; Mayer, J. M. *J. Am. Chem. Soc.* **1996**, *118*, 12119−33.

[17] Arylation of $[^nBu_4N][Os(N)Cl_4]$ followed by treatment with KTp gives **1b** and **1c** (Supporting Information), following Koch, J. L.; Shapley, P. A. *Organometallics* **1997**, *16*, 4071−6.

[18] The synthesis, spectroscopy, and X-ray structure of $TpOs(NPPh_3)Cl_2$ will be reported in a future publication.

[19] Hrovat, D.; Crevier, T. J.; Borden, W. T.; Mayer, J. M. Work in progress.

[20] (a) Bakir, M.; White, P. S.; Dovetoglou, A.; Meyer, T. J. *Inorg. Chem.* **1991**, *30*, 2835−6; trpy = 2,2′:6′:2″-terpyridine. (b) See also: Coia, G. M.; Devenney, M.; White, P. S.; Meyer, T. J. *Inorg. Chem.* **1997**, *36*, 2341−51.

[21] (a) Shapley, P. A. Personal communication. (b) See also: Marshman, R. W.; Shusta, J. M.; Wilson, S. R.; Shapley, P. A. *Organometallics* **1991**, *10*, 1671−1676.

[22] Belmonte, P. A.; Own, Z.-Y. *J. Am. Chem. Soc.* **1984**, *106*, 7493−6. Shapley, P. A.; Marshman, R. M.; Shusta, J. M.; Gebeyehu, Z.; Wilson, S. R. *Inorg. Chem.* **1994**, *33*, 498.

[23] Hydride addition to electrophilic imido ligands occurs via initial attack at a carbonyl ligand. Luan, L.; Brookhart, M.; Templeton, J. L. *Organometallics* **1992**, *11*, 1433−5.

[24] Perhaps other reactions that have been proposed to form C−X bonds via [1, 2] migrations (see discussion in ref 16) should be reexamined in light of this new mechanism.