An osmium nitrido complex as a π-acid ligand for late transition metals

Thomas J. Crevier, Scott Lovell and James M. Mayer*

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

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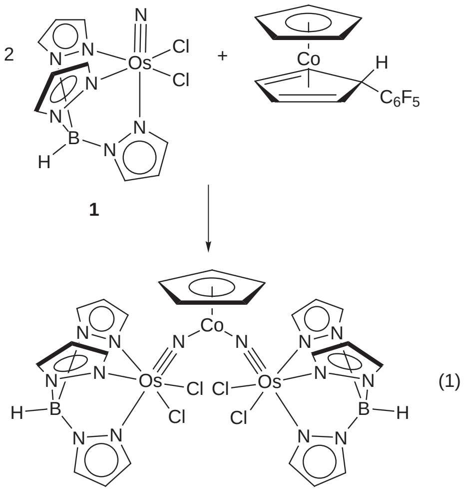
The Os(VI) nitrido complex, $TpOs(N)Cl_2$ (1), acts as a π-acid ligand in the cobalt and platinum complexes $CpCo[NOs(Tp)Cl_2]_2$ (2) and $(Me_2S)Cl_2Pt–N≡Os(Tp)Cl_2$ (3).

Transition metal nitrido complexes $L_nM≡N$ typically act as nucleophiles, being alkylated or binding to other metals.[1] The two dozen or so known hetero-bimetallic μ-nitrido complexes all involve nucleophilic nitrido complexes and are described as dative adducts $L_nM≡N \rightarrow M'L_m$ (**A**) or metalloimido complexes $L_nM\overset{-}{=}N–M'L_m$ (**B**).[2] We have recently prepared an Os(VI) nitrido complex, $TpOs(N)Cl_2$ [**1;** Tp = hydrotris(1-pyrazolyl)borate],[3] that acts as an electrophile. Electrophilic multiply-bonded ligands are less common but such ligands are important in various processes, including atom and group transfers, and dihydroxylation and aminohydroxylation of olefins.[4] Complex **1** is unreactive with protic acids, methyl triflate (MeOTf), $BF_3·Et_2O$, and $[Ph_3C][BF_4]$, but it reacts with PPh_3 and carbanions at nitrogen.[3] Despite its lack of reaction with simple electrophiles, we report here that **1** is a good ligand for Co(I) and Pt(II) centers. We propose that the complexes reported herein are a new type of μ-nitrido compound, in which the multiply bonded nitrido fragment is best described as a π acid ligand for the heterometal.

$CpCo(\eta^4-C_5H_5C_6F_5)$[5] was chosen as a source of the electron-rich CpCo(I) fragment since the η^4-diene should be easily displaced. Indeed, addition of **1** to a benzene solution of $CpCo(\eta^4-C_5H_5C_6F_5)$ causes an immediate darkening of the solution and precipitation of purple $CpCo[NOs(Tp)Cl_2]_2$ (**2**)† in good yield [eqn. (1)]. NMR data are consistent with a diamagnetic compound with two TpOs fragments per CpCo unit. Slow evaporation of a chloroform solution of **2** forms single crystals suitable for X-ray diffraction.‡ The structure (Fig. 1) shows a two-legged piano stool geometry about the cobalt atom with the two legs being octahedral osmium centers, connected to the cobalt by μ-nitrido ligands. The structure is quite similar to other $CpCoL_2$ complexes, such as $Cp^*Co(CO)_2$.[6] The Co–N–Os angles are essentially linear [171.6(6), 171.8(7)°], which is typical of such μ-nitrido linkages[1a] and indicates sp hybridization at nitrogen. The Os–N distances of 1.704(9) and 1.741(10) Å are indicative of substantial multiple bonding (as is the significant *trans* influence of the nitrido ligand), but these distances are longer than all crystallographically characterized terminal osmium–nitrido bonds (1.525–1.703, av. 1.629 Å).[7] The Co–N bonds are very short [1.696(11) and 1.737(9) Å], much shorter than would be expected for a simple dative interaction. For instance, they are substantially shorter than all reported cobalt–nitrile bonds, which also involve an sp hybridized nitrogen (Co–N 1.883–2.179, av. 1.997 Å).[7] The Co–N bonds in **2** are most similar to those in linear nitrosyl complexes (1.590–1.720, av. 1.658 Å) and are close to cobalt–carbonyl bond lengths (CpCo–CO 1.615–1.782, av. 1.721 Å).[7]



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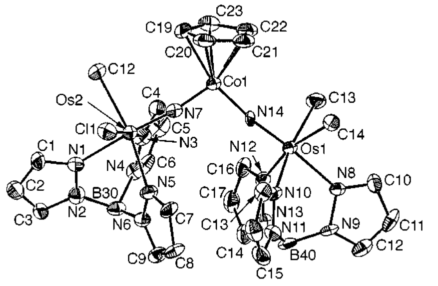
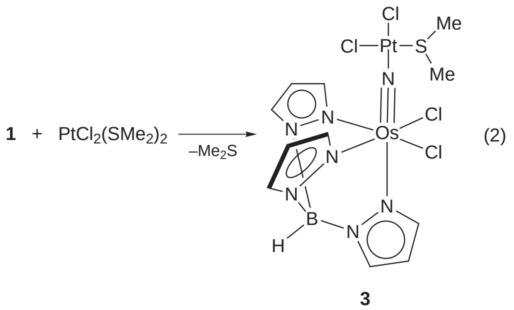


Fig. 1 ORTEP drawing of $CpCo[NOs(Tp)Cl_2]_2$ (**2**), with hydrogen atoms and two $CHCl_3$ of crystallization omitted for clarity. Selected bond lengths (Å) and angles (°): Os(1)–N(14) 1.704(9), Os(2)–N(7) 1.741(10), Co(1)–N(7) 1.696(11), Co(1)–N(14) 1.737(9), Os(2)–N(1) 2.189(11), Os(2)–N(3) 2.054(12), Os(2)–N(5) 2.086(10), Os(1)–N(8) 2.198(10), Os(1)–N(10) 2.070(10), Os(1)–N(12) 2.060(11), Os(1)–N(14)–Co(1) 171.6(6), Os(2)–N(7)–Co(1) 171.8(7), N(7)–Co(1)–N(14) 101.3(5).

Complex **2** is thermally robust, showing only minor decomposition over two weeks at 75 °C in chloroform solution by ^1H NMR. There is no reaction under these conditions with 1 equiv. of PPh_3. Since **1** reacts rapidly with PPh_3, this shows that **2** does not dissociate to **1** at 75 °C. There is also no reaction when a chloroform solution of **2** is heated under 100 Torr of CO at 75 °C for several days.

Complex **1** reacts slowly with $PtCl_2(SMe_2)_2$ in benzene with with loss of Me_2S to give $(Me_2S)Cl_2Pt–N≡Os(Tp)Cl_2$ (**3**) in good yield [eqn. (2)].† Single crystals of **3** were obtained by slow evaporation of a benzene solution. The X-ray structure (Fig. 2)‡ shows a molecule of **1** bound to a square planar platinum center. The Pt–N bond of 1.868(8) Å is at the short end of the range of Pt–N bonds in *cis*-dichloroplatinum complexes (1.848–2.371 Å),[7] again closer to those in nitrosyl rather than nitrile complexes. The Os–N bond [1.687(8) Å] is apparently



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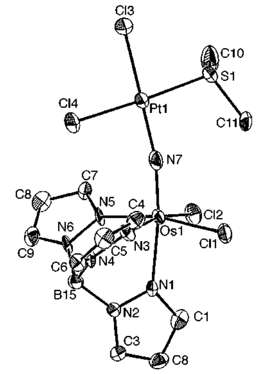

Fig. 2 ORTEP drawing of $(Me_2S)Cl_2Pt–N{\equiv}Os(Tp)Cl_2$ (**3**), with hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Os(1)–N(7) 1.687(8), Pt(1)–N(7) 1.868(8), Os(1)–N(1) 2.178(7), Os(1)–N(3) 2.071(7), Os(1)–N(5) 2.068(7), Pt(1)–S(1) 2.286(2), Pt(1)–Cl(3) 2.297(2), Pt(1)–Cl(4) 2.317(2), Os(1)–N(7)–Pt(1) 169.2(5).

shorter than those in **2**, although it is presumably slightly longer than in **1**.

The data are most consistent with **1** acting as a π acid ligand in **2** and **3**, as opposed to simply a dative (**A**) or σ only (**B**) ligand. The CpCo(I) fragment forms two legged piano stool structures only with soft and/or π-acid ligands; related CpCo(III) complexes adopt three-legged stool geometries.[8,9] The short Co–N and Pt–N distances and the kinetic inertness of the Co–N bonds are indicative of multiple bond character. The other known platinum μ-nitrido complexes are $(Et_2PhP)_3Cl_2Re{\equiv}N–PtCl_2(PEt_3)$,[2d] $(Me_3SiO)_3V{\equiv}N–Pt(Me)(PEt_3)_2$,[2a] and three complexes with $[Os(N)O_3]^-$.[10] The first is a labile adduct with dative bonding (resonance form **A**), while the others have N–Pt bond distances [VN–Pt, 2.030(7); O_3OsN–Pt, 2.03(4), 2.040(7), 1.958(7), 2.05(1) Å] which are indicative of single bonding (form **B**) and significantly longer than that in **3**. *Ab initio* DFT calculations on **1** show that the LUMO and LUMO+1 are low-lying Os–N π* orbitals, with significant density at nitrogen.[11] These empty orbitals are quite similar to the π* orbital of CO, the prototypical π acid (Fig. 3).§ The small apparent lengthening of the Os≡N bond in **2** is reminiscent of the small change in the C≡O distance on coordination. This lengthening is smaller if present in **3**, consistent with Pt(II) being a poorer π-donor than Co(I). The bonding in **2** and **3** could alternatively be described as a resonance hybrid of **A** or **B** with a multiple bond form $Os{=}N{\Leftarrow}M'$ or $Os{=}N{=}M'$, the latter well known for homonuclear μ-nitrido complexes.[1a]

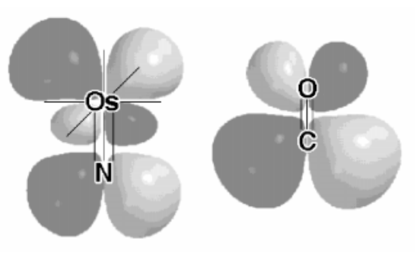

Fig. 3 Calculated LUMOs for **1** and CO.§

The ability of **1** to act as a strong ligand to late transition metals is perhaps surprising in light of its lack of reaction with main group Lewis acids such as $BF_3{\cdot}Et_2O$ and $[Ph_3C][BF_4]$. Complex **1** should be contrasted with the more nucleophilic hydrocarbyl derivatives $TpOs(N)Ph_2$[3a,12] and $CpOs(N)(CH_2SiMe_3)_2$.[2c] The latter forms a BF_3 adduct with $BF_3{\cdot}Et_2O$, is alkylated by MeOTf, and binds to Ag^+ giving a μ-nitrido complex $[Cp(R)_2OsN]_2Ag^+$.[2c] The Ag–N distances [2.15(1), 2.12(2) Å] are 0.27 Å longer than the Pt–N distances in **3**, much larger than the differences in ionic radii (2-coordinate Ag^+, 0.81 Å; 4-coordinate Pt^{2+}, 0.74 Å[13]). $TpOs(N)Ph_2$ does not react with $CpCo(\eta^4\text{-}C_5H_5C_6F_5)$ and an analog of **2** is not observed. The observation that the more nucleophilic osmium nitrides bind more poorly and form longer M–N bonds is not consistent with **1** acting as a simple σ donor ligand (type **A** or **B** bonding). We propose that the osmium nitrido unit in **1** acts as a π-acid ligand as a result of the low lying empty Os–N π* orbitals (Fig. 3). Further studies of **2** and **3**, and preparations of other compounds containing **1** as a ligand, are in progress.

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Notes and references

† Full preparative, spectroscopic, and calculational details for **1**, **2**, **3**, and $TpOs(NPPh_3)Cl_2$ will be reported in an upcoming full paper. *Selected NMR data*: for **2,** ^{1}H NMR ($CDCl_3$) 5.96 (2H, t), 7.32 (2H, d), 7.49 (2H, d), 6.17 (4H, t), 7.51 (4H, d), 7.55 (4H, d), 5.40 (5H, s); ^{13}C NMR ($CDCl_3$) 107.8, 136.0, 146.0 (pz *trans* to μ-N), 108.5, 137.8, 144.4 (pz *trans* to Cl), 91.2 (Cp). For **3**, ^{1}H NMR ($CDCl_3$) 6.03 (1H, t), 7.42 (1H, d), 7.54 (1H, d), 6.47 (2H, t), 7.75 (2H, d), 8.12 (2H, d), 2.85(6H, s).

‡ Data for both structures were collected on a Nonius KappaCCD with Mo-Kα (λ = 0.71070 Å). *Crystal data*: for **2**$\cdot 2CHCl_3$ at 161 K, $C_{25}H_{27}B_2Cl_{10}Co_1N_{14}Os_2$, M = 1339.06, triclinic, $P\bar{1}$ (no. 2), a = 11.3261(8), b = 14.2844(10), c = 15.3497(10) Å, α = 64.666(5), β = 75.612(5), γ = 68.010(5)°, V = 2069.7(2) Å^3, D_c = 2.149 g cm^{-3}, Z = 2, μ = 72.07 cm^{-1}. Of the 70903 reflections, 7908 unique reflections were used in the final least-squares refinement to yield R = 0.0651 and R_w = 0.1821. For **3** at 161 K, $C_{11}H_{16}B_1Cl_4S_1N_7Pt_1Os_1$, M = 815.26, triclinic, $P\bar{1}$ (no. 2), a = 8.5517(3), b = 10.9693(3), c = 13.2976(3) Å, α = 95.4985(19), β = 92.2917(19), γ = 104.4479(12)°, V = 1199.74(6) Å^3, D_c = 2.257 g cm^{-3}, Z = 2, μ = 116.56 cm^{-1}. Of the 17880 reflections, 4459 unique reflections were used in the final least-squares refinement to yield R = 0.0364 and R_w = 0.1283. CCDC 182/1026.

§ Minor contributions of other atoms to the LUMO in **1** are omitted for the sake of clarity. Full details of the calculations will be published in a forthcoming report.[11]

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