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[4 + 1] Cycloadditions of Cyclohexadienes with Osmium Nitrides

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Reactions in which atoms or groups multiply bonded to a transition metal are added to an alkene are among the most common and important reactions of these species.[1] Familiar examples include epoxidation by oxo complexes,[2] aziridination by imido complexes,[3] cyclopropanation by metal carbenes,[4] and dihydroxylation by polyoxo complexes such as osmium tetroxide.[5] In contrast, additions of multiply bonded groups in soluble metal complexes across the termini of dienes are very rare, with examples restricted to a few specialized reactions of Fischer carbene complexes[6] and metal phosphinidenes.[7] In heterogeneous reactions, addition of metal-bound oxygen atoms across 1,3-butadiene has been proposed in reactions on silver surfaces[8] and over vanadyl pyrophosphates, where it may play a role in the oxidation of butane to maleic anhydride.[9] There is also precedent for reactions that form dienes by extruding metal−ligand multiple bonds, for instance in the deoxygenation of 2,5-dihydrofuran to form a tungsten−oxo complex[10] and particularly in the recent demonstration of the extrusion of anthracene from a chromium amide derived from deprotonated dibenzo-7-azanorbornadiene to form a terminal nitride.[11] Here we report the [1,4]-addition of a variety of osmium nitrido complexes to 1,3-cyclohexadienes, a reaction which simultaneously forms two new carbon−nitrogen bonds. The addition reaction shares some features with the Diels−Alder reaction, with which it is formally isoelectronic.

The osmium(VI) tris(1-pyrazolyl)borate complex $TpOsNCl_2$ (**1**)[12] reacts with 1,3-cyclohexadiene in acetonitrile at 65 °C over the course of 4 days to afford the bicyclic osmium amido complex $TpOs(NC_6H_8)Cl_2$ (**2a**) in 80% yield by NMR (eq 1).

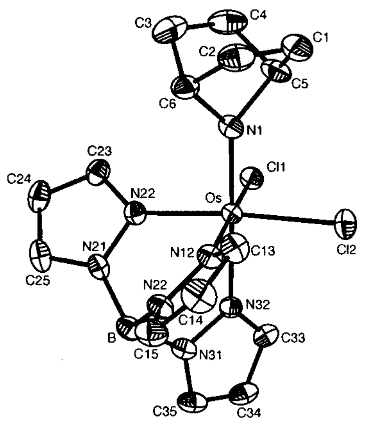
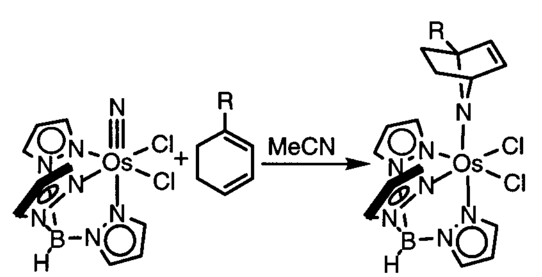


Figure 1. Thermal ellipsoid plot of $TpOs(NC_6H_8)Cl_2$ (**2a**, 30% thermal ellipsoids). Selected bond distances (Å) and angles (deg): Os−N1, 1.859 (3); Os−N12, 2.053 (3); Os−N22, 2.063 (3); Os−N32, 2.094 (3); Os−Cl1, 2.3879 (10); Os−Cl2, 2.3689 (11); C5−N1−Os, 131.0 (3); C6−N1−Os, 132.9 (3); C5−N1−C6, 96.1 (4).



(1)

1   R = H (**2a**), OMe (**2b**)

The air-stable compound has been characterized spectroscopically and analytically,[13] and its structure was confirmed by a single-crystal X-ray structure (Figure 1).[14] The complex is octahedral and contains a very short bond from osmium to a planar nitrogen atom of the bicyclic amide (sum of angles = 360.0°). The Os−N bond of 1.859(3) Å is within the range found for osmium−nitrogen double bonds in azavinylidene complexes (1.81−1.88 Å)[15,16] and is significantly shorter than the corresponding distance in the anilido complex $TpOs(NHPh)Cl_2$ (1.919(6) Å).[12] The π-bonding in the bicyclic amide also appears to be stronger than in the anilide, insofar as **2a** is diamagnetic (as judged by its sharp, unshifted ^1H and ^{13}C NMR resonances), while $TpOs(NHPh)Cl_2$ is paramagnetic. A similar difference in bond lengths

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[13] Partial spectroscopic data for selected compounds (for full experimental details, see the Supporting Information): **2a**: ^1H NMR ($CDCl_3$): δ 2.84, 3.12 (m, 2H ea.; C*HH*′C*HH*′), 3.74 (m, 2H; bridgehead C-*H*), 6.33 (t, 2 Hz, 1H; pz 4-H trans to amide), 6.36 (t, 2 Hz, 2H; pz 4-H trans to Cl), 6.78 (t, 1.5 Hz, 2H; alkene C-*H*). FABMS: 569 (M^+). **4b**: ^1H NMR (CD_3CN): δ 2.35 (ddd, 11.5, 9.5, 4 Hz, 1H, C*H*H′CH″H‴), 2.58 (s, 3H, OCH_3), 2.76 (ddt, 12, 9.5, 4.5 Hz, 1H, CH*H*′CH″H‴), 2.87 (ddd, 11.5, 10.5, 4 Hz, 1H, CHH′C*H*″H‴), 3.00 (ddd, 12, 10.5, 4 Hz, 1H, CHH′CH″*H*‴), 4.38 (dd, 4.5, 3 Hz, 1H, bridgehead C-*H*), 6.71 (d, 6 Hz, 1H, C*H*═CH adj. to OCH_3), 6.78 (dd, 6, 3 Hz, 1H, CH═C*H* away from OCH_3), 8.67 (dd, 5.5, 1 Hz, 1H, terpy H-6), 8.78 (dd, 5.5, 1 Hz, 1H, terpy H-6″). FABMS: 618 (M^+).

[14] Crystallographic data for **2a**·$CDCl_3$: $C_{16}H_{18}DBCl_5N_7Os$, red plates grown from $CDCl_3$/hexane, triclinic, space group $P1$, $a = 9.584\ (2)$ Å, $b = 9.6698\ (8)$ Å, $c = 14.2881\ (8)$ Å, $\alpha = 91.938\ (5)°$, $\beta = 102.386\ (7)°$, $\gamma = 111.069\ (8)°$, $V = 1198.0\ (2)\ Å^3$, $Z = 2$, R1 = 0.0235, wR2 = 0.0591 ($I > 2\sigma(I)$), GOF = 1.038. The single and double bonds are disordered between C1−C2 (1.431(8) Å) and C3−C4 (1.435(9) Å).

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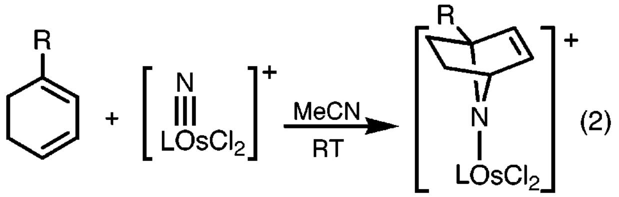
between bicyclic and normal (aromatic) amides is seen in Cr(N)(dbabh)($NRAr_F$)$_2$[11] and suggests that bicyclic amides are unusually strong π donors.

Electron-rich 1-methoxy-1,3-cyclohexadiene reacts much more rapidly with **1,** forming the C_1-symmetric bridgehead-substituted bicyclic amido complex **2b** within 6 h at 20 °C. The yield of the cycloadduct is quantitative in the presence of high concentrations of diene, but when pure **2b** is dissolved in acetonitrile, it slowly dissociates methoxycyclohexadiene and forms an equilibrium mixture of **1**, **2b**, and diene (for formation of **2b** in CD_3CN at 292 K, $K_{eq} = 481 \pm 26\ M^{-1}$). From the temperature-dependence of the equilibrium constant between 284 and 333 K, thermodynamic parameters for the cycloaddition to form **2b** have been determined to be $\Delta H° = -15.0 \pm 0.5$ kcal/mol, $\Delta S° = -39.3 \pm 1.7$ cal/mol·K.

The cationic osmium nitride complexes [(Tpm)$OsNCl_2$]PF_6 (Tpm = tris(1-pyrazolyl)methane)[17] and *cis*- and *trans*-[(terpy)$OsNCl_2$]PF_6 (terpy = 2,2′:6′,2″-terpyridine)[18] react analogously with 1,3-cyclohexadiene and 1-methoxy-1,3-cyclohexadiene (eq 2; yields determined by NMR). Although the yields are lower in the reactions of these cationic nitrides with unsubstituted cyclohexadiene, the rates are substantially faster than the corresponding rates with neutral **1**. In particular, all of the cationic nitrides react completely with methoxycyclohexadiene to give high yields of the cycloadduct in less than 20 min at room temperature. The enhanced reactivity of the cations is consistent with the nitride acting as an electrophile in these reactions.[19]



R = H (**a** series); R = OMe (**b** series):
L = Tpm: 24 hr, 15% (**3a**); 20 min, 95% (**3b**)
L = *cis*-terpy: 9 hr, 25% (**4a**);15 min, 93% (**4b**)
L = *trans*-terpy: 11 hr, 30% (**5a**);15 min, 90% (**5b**)

While the reaction appears to be reasonably general for osmium nitrides and cyclohexadienes, it has so far proved unique to this combination of reagents. Metal nitride complexes such as [$(dppe)_2$Re(N)Cl]BF_4[20] or (salen)Mn(N)[21] are inert to 1,3-cyclohexadiene even over weeks at 65 °C. Furthermore, we have not yet observed cycloadducts of osmium nitrides with any dienes other than substituted cyclohexadienes. Other cyclic dienes such as 1,3-cycloheptadiene and cyclopentadiene do not form significant amounts of diamagnetic products (the latter possibly for thermodynamic reasons, as the resulting azabicyclo[2.1.1]hexene would be highly strained).[22] Acyclic dienes have also not yet been observed to form dihydropyrrolide complexes, although some do react to give quite different products (e.g., 1,4-diphenyl-1,3-butadiene reacts with *cis*-[(terpy)$OsNCl_2$]PF_6 to give an azaallenium complex, the product of alkene cleavage).[23]

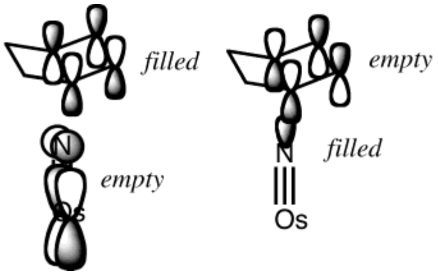


Figure 2. Possible orbital interactions in [4 + 1] cycloaddition reaction.

The pattern of reactivity in these cycloadditions, with electron-poor nitrides and electron-rich dienes reacting faster, is strongly reminiscent of the normal pattern of the Diels−Alder reaction. Likewise, the unique proclivity of cyclohexadienes to undergo cycloadditions with osmium nitrides may reflect their relatively short separation between the diene termini, a factor which is known to be very important in the Diels−Alder reaction[24] (and which might be even more important in a reaction which forms a one-atom, rather than a two-atom, bridge between those termini). A close analogy between the frontier orbitals of the osmium nitride and those of a dienophile can be drawn (Figure 2). The analogy between N≡Os and C≡O has already been noted in the literature,[25] and the well-known cheletropic extrusion of CO from 3-cyclopentenones[26] is very closely related to the microscopic reverse of the [1,4]-addition reactions described here. That there may be a mechanistic similarity, and not just a formal analogy, is made more plausible by the similarity of the activation parameters for the extrusion of 1-methoxy-1,3-cyclohexadiene from the neutral cycloadduct **2b** ($\Delta H^\ddagger = 23.7 \pm 0.4$ kcal/mol, $\Delta S^\ddagger = -0.4 \pm 1.2$ cal/mol·K, CH_3CN, 308−345 K) to those of related CO extrusions.[27] The relative insensitivity to solvent polarity of the rate of cycloreversion of **2b** (only 25% slower in CH_2Cl_2 [$\epsilon = 9$] than in CH_3CN [$\epsilon = 36$]) or of addition of 1,3-cyclohexadiene to **1** (similar rates in CD_3CN and C_6D_6) appears to preclude the presence of a zwitterionic intermediate and is more consistent with a concerted or diradical mechanism. Further studies of the mechanism of this unusual [1,4]-atom transfer process are in progress.

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Supporting Information Available: Descriptions of synthetic procedures and spectroscopic data for compounds **2**−**5** and full crystal data for **2a**·$CDCl_3$ (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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