Insertion of a Metal Nitride into Carbon−Carbon Double Bonds

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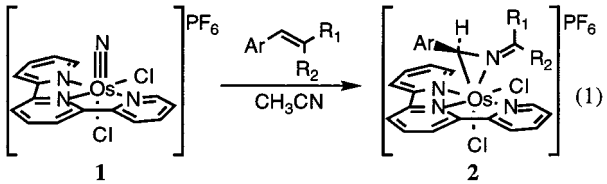
Metal nitride complexes are receiving increasing attention in reactions which form bonds to nitrogen. Reactions of electrophilic nitrido groups with reagents such as phosphines,[1] amine-*N*-oxides,[2] amines,[3] azide,[4] main group organometallics,[5] and isobenzofurans[6] have all been reported recently. Nitride compounds have also been used as starting materials for reactions with less nucleophilic reagents such as alkenes.[7] However, these reactions invariably take place only after activation of the nitride with a strong electrophile such as trifluoroacetic anhydride to form a reactive imido complex. Here I describe the direct reaction of the cationic nitrido complex *cis*-[(terpy)OsNCl$_2$]PF$_6$[8] with a variety of aryl-substituted alkenes to form η^2-azaallenium complexes. In these reactions, the alkene carbon−carbon double bond is completely ruptured, forming two new carbon−nitrogen bonds and a new metal−carbon bond. The asymmetrically bonded azaallenium adducts are formed with a high degree of regioselectivity and can be further functionalized under either oxidative or reductive conditions.

The cationic osmium(VI) nitrido complex *cis*-[(terpy)OsNCl$_2$]-PF$_6$ (**1**; terpy = 2,2′:6′,2″-terpyridine) reacts with *cis*-stilbene in acetonitrile overnight at 60 °C to give the blood-red air-stable azaallenium complex *cis*-[(terpy)OsCl$_2$(1,2-η^2-PhCH═N═CHPh)]-PF$_6$ (**2a**, eq 1).[9] *trans*-Stilbene gives the same product **2a**, albeit more slowly. The *trans* isomer of [(terpy)OsNCl$_2$]PF$_6$ also reacts with either *cis*- or *trans*-stilbene to give the same *cis* product **2a**, apparently by initial *trans* → *cis* isomerization of the nitride complex[8] followed by reaction of the *cis* nitride.



1 **2**

Ar = R$_1$ = Ph, R$_2$ = H, 66% (**2a**)
Ar = R$_1$ = 4-MeOC$_6$H$_4$, R$_2$ = H, 85% (**2b**)
Ar = Ph, R$_1$ = CH=CHPh, R$_2$ = H, 79% (**2c**)
Ar = Ph, R$_1$ = CH=CHCH=CHPh, R$_2$ = H, 61% (**2d**)
Ar = Ph, R$_1$ = CH$_3$, R$_2$ = H, 81% (**2e**)
Ar = 4-MeOC$_6$H$_4$, R$_1$ = R$_2$ = CH$_3$, 71% (**2f**)

A variety of other aryl-substituted alkenes also react with **1** to give analogous products (eq 1). *p*-Methoxy substitution of the phenyl groups increases the rate of the reaction, with dimethoxystilbene reacting ∼20 times faster than stilbene. *trans*-*β*-Methylstyrene is the most reactive alkene, with its reaction going to completion overnight at room temperature. Trisubstituted alkenes such as 1-(4-methoxyphenyl)-2-methylpropene form analogous products at rates only modestly slower than their disubstituted counterparts. Styrene and other alkenes such as norbornene or *trans*-5-decene that lack aryl substituents all react with **1** but have so far failed to yield tractable products.

The bonding in these complexes is clarified by the X-ray crystal structure of **2d**, derived from 1,6-diphenyl-1,3,5-hexatriene (Figure 1).[10] In compounds **2**, the osmium−nitrogen triple bond has inserted into one carbon−carbon double bond of the organic substrate. One carbon in the ruptured alkene in **2d** is bonded to osmium (d_{Os-C} = 2.182 (5) Å), while the other carbon forms a double bond to the coordinated nitrogen ($d_{C=N}$ = 1.293 (7) Å). The original alkene has been completely cleaved; there is no sign of residual bonding between the carbon atoms ($d_{C\cdots C}$ = 2.484 Å). The osmium is bonded in an η^2-(*C*,*N*) fashion to the new organic fragment in what may be regarded as an osmium(II) azaallenium complex or an osmium(IV) azametallacyclopropane. The metrical data of the organic fragment (C1−N1 = 1.374 Å, C1−N1−C2 = 137.5°) lie between these two extreme forms.[11] One prior example of a structurally characterized η^2-azaallenium complex, CpMo(CO)$_2$(η^2-Tol$_2$C═N═CTol$_2$), has been reported.[12] Though details are not available, the preliminary data for this complex indicate that its structure is shifted more toward the azametallacyclopropane canonical form (C−N = 1.43 Å, C−N−C = 128.3°),[13] consistent with weaker back-bonding by Os(II) than by Mo(0).

The NMR spectra of the diamagnetic complexes **2** are consistent with retention of the crystallographically determined structure in solution. The two termini of the original double bond are in very different chemical environments, as judged by ^{1}H (δ 6.62 vs 8.21 ppm for **2a**) and ^{13}C (δ 44.75 vs 163.12 ppm for **2a**) NMR spectroscopy. These differences are consistent with η^2-(*C*,*N*) coordination, with the metal-bonded CH group showing upfield shifts and the iminium-like methine group shifting

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(9) Partial spectroscopic data for selected compounds (for full experimental details, see the Supporting Information): **2a**: ^{1}H NMR (CD$_3$CN) δ 5.48 (d, 8 Hz, 1H; *ortho* OsCH*Ph*); 6.49 (t, 7.5 Hz, 1H; *m*-OsCH*Ph*), 6.62 (d, 2 Hz, 1H; Os*CH*Ph), 6.72 (d, 7.5 Hz, 1H; *ortho*′ OsCH*Ph*), 7.02 (t, 7.5 Hz, 1H; *m*′-OsCH*Ph*), 7.19 (tt, 7.5, 1 Hz, 1H; *para* OsCH*Ph*), 7.32 (t, 7.5 Hz, 2H; *m*-N═CH*Ph*), 7.43 (m, 3H; *o*,*p*-N═CH*Ph*), 8.21 (d, 2 Hz, 1H; N═*CH*Ph), 9.09 (dd, 5.5, 1 Hz; terpy H-6), 9.15 (dt, 5.5, 1 Hz; terpy H-6″). ^{13}C{^{1}H} NMR (CD$_3$CN) δ 44.75 (Os*C*H), 163.12 (*C*H═N). FABMS 689 (M$^+$). **2c**: ^{1}H NMR (CD$_3$CN) δ 5.58 (br d, 8 Hz, 1H; *o*-OsCH*Ph*), 6.23 (d, 2 Hz, 1H; Os*CH*Ph), 6.62 (br t, 7.5 Hz, 1H; *m*-OsCH*Ph*), 6.68 (br d, 8 Hz, 1H; *o*′-OsCH*Ph*), 6.79 (dd, 16, 10 Hz, 1H; N═CH−*CH*═CHPh), 6.99 (br t, 8 Hz, 1H; *m*′-OsCH*Ph*), 7.23 (tt, 7.5, 1 Hz, 1H; *p*-OsCH*Ph*), 7.27 (d, 16 Hz, 1H; N═CH−CH═*CH*Ph), 7.33 (m, 3H; *m*,*p*-N═CH−CH═CH*Ph*), 7.39 (m, 2H; *o*-N═CH−CH═CH*Ph*), 7.86 (dd, 9, 2 Hz, 1H; N═*CH*−CH═CHPh), 9.12 (dd, 5, 1 Hz, 1H; terpy H-6), 9.18 (dt, 5.5, 1 Hz, 1H; terpy H-6″). ^{13}C{^{1}H} NMR (CD$_3$CN) δ 44.73 (Os*C*HPh), 122.98 (N═CH−*C*H═CHPh), 149.13 (N═CH−CH═*C*Ph), 162.99 (N═*C*H−CH═CHPh). FABMS 715 (M$^+$). **2e**: ^{1}H NMR (CD$_3$CN) δ 2.38 (dd, 5.4, 1.5 Hz, 3H; N═CHC*H*$_3$), 5.56 (br d, 7 Hz, 1H; *ortho*), 6.29 (sl br, 1H; Os*CH*Ph), 6.67 (br m, 2H, *meta*, *ortho*′), 6.96 (br t, 7 Hz, 1H; *meta*′), 7.24 (tt, 7, 1 Hz, 1H; *para*), 7.40 (qd, 5.4, 2.5 Hz, 1H; N═*CH*CH$_3$), 9.10 (ddd, 5.5, 1.5, 0.5 Hz, 1H; terpy H-6), 9.13 (ddd, 5.5, 2, 1 Hz; terpy H-6″). ^{13}C{^{1}H} NMR (CD$_3$CN) δ 23.75 (*C*H$_3$), 42.35 (Os*C*HPh), 168.57 (N═*C*HCH$_3$). FABMS: 627 (M$^+$).

(10) Crystallographic data for **2d**·(CD$_3$)$_2$C═O: C$_{36}$H$_{27}$D$_6$Cl$_2$F$_6$N$_4$OOsP, dark red blocks grown from acetone−d_6/Et$_2$O, triclinic, space group P1, a = 11.7391 (12) Å, b = 13.2219 (10) Å, c = 14.1111 (12) Å, α = 94.154 (6)°, β = 113.610 (7)°, γ = 111.576 (7)°, V = 1803.2 (3) Å^3, Z = 2, R1 = 0.0490, wR2 = 0.0774, GOF = 1.045.

(11) Cf. d(C═N) for 1,3-ditolyl-2-azaallenium ion = 1.258 Å. Böttger, G.; Geisler, A.; Frölich, R.; Würthwein, E.-U. *J. Org. Chem.* **1997**, *62*, 6407−6411.

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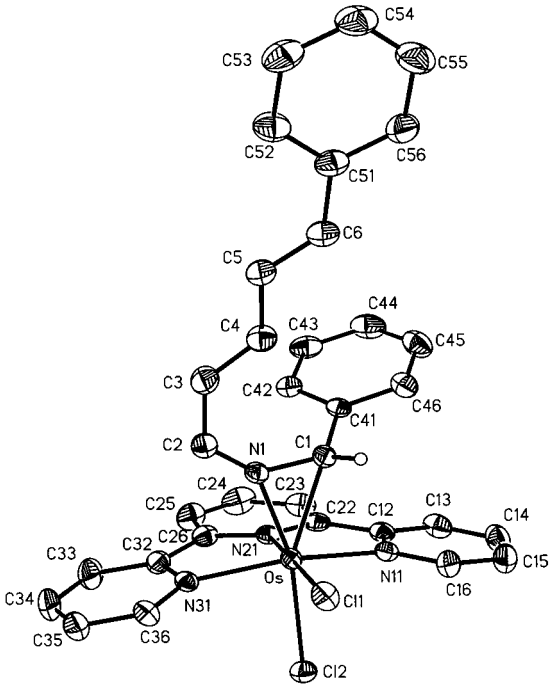

Figure 1. Thermal ellipsoid plot of the cation of *cis*-[(terpy)$OsCl_2$(1,2-η^2-PhCH═N═CHCH═CHCH═CHPh)]PF_6·$(CD_3)_2C$═O (**2d**·$(CD_3)_2$-C═O). Selected bond lengths (Å) and angles (deg): Os−N1, 2.006 (4); Os−C1, 2.182 (5); C1−N1, 1.374 (7); C2−N1, 1.293 (7); N1−Os−C1, 38.0 (2); C1−N1−C2, 137.3 (5).

downfield. The presence of two sharp sets of signals indicates that the two ends of the azaallenium group do not exchange on the NMR time scale. As in free allenes,[14] long-range proton−proton couplings are observed through the unsaturated framework ($^4J_{HH}$ = 2 Hz and $^5J_{HH}$ = 1−2 Hz in **2a**−**f**). All compounds **2** show eleven separate resonances in the ^{1}H NMR and fifteen in the $^{13}C\{^1H\}$ NMR due to the terpyridine ligands, indicating that they have C_1 symmetry in solution, consistent with static binding to one face of the C═N double bond.

The phenyl group on C-1 is held close to the terpyridine ligand, on average 3.49 Å from its least-squares plane in **2d**. As a result, exactly one aryl group in each compound **2** cannot rotate freely about the $C_{ipso}-C_{Os}$ bond and shows inequivalent *ortho* and *meta* hydrogens in the ^{1}H NMR (e.g., δ 5.48 and 6.72 *ortho*, 6.49 and 7.02 *meta* for **2a**). Slight broadening of the *ortho* and *meta* (but not *para*) resonances indicates that rotation is not quite frozen out on the NMR time scale at room temperature, with the rotation rates inversely related to the size of the substituent on the imine carbon ($k_{rot} < 3$ s^{-1} for **2a**−**b**, ≈ 18 s^{-1} for **2c**−**d**, ≈ 23 s^{-1} for **2e**). The upfield shifts suggest that this phenyl group is being held in the shielding cone of the terpyridine, consistent with retention of the crystallographically observed orientation in solution.

Remarkably, one upfield-shifted, nonrotating aryl group is observed in every compound **2**, indicating that the insertion reaction is completely regioselective, with an aryl group always bonded to C-1. No sign of alternate isomers with alkenyl or alkyl groups in this position can be detected when the reaction mixtures are monitored by NMR, nor is there any sign of reaction with the internal alkene of 1,6-diphenyl-1,3,5-hexatriene rather than the terminal one. The regioselectivity is clearly counter-steric, since the aryl substituent is larger than methyl or vinyl and is placed in the most crowded position in the molecule. When two different aryl groups are available, mixtures result. For example, 4-methoxystilbene gives a 4:1 mixture of the 1,2- and 2,3-isomers of *cis*-[(terpy)$OsCl_2$(PhCH═N═CHC_6H_4OMe)]PF_6. Neither **2a** nor **2b** is formed in the reaction of the monomethoxystilbene,

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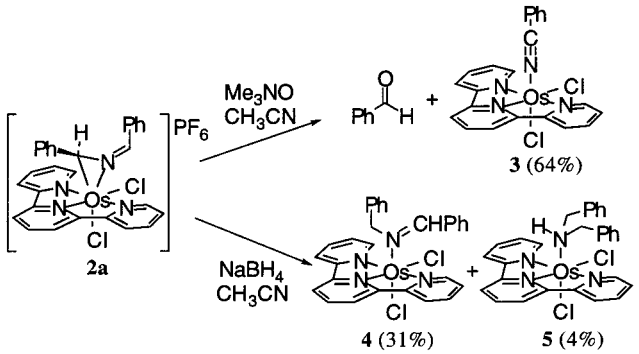
Scheme 1



confirming that formation of the azaallenium fragment is intramolecular.

The azaallenium fragments bonded to osmium retain considerable electrophilicity and can be synthetically modified by a variety of nucleophilic reagents (Scheme 1). For example, the diphenyl compound **2a** reacts with trimethylamine-*N*-oxide to split off 1 equiv of benzaldehyde (detected by ^{1}H NMR) and form the dark purple, insoluble benzonitrile complex *cis*-(terpy)$OsCl_2$(NCPh) (**3**, ν_{CN} = 2181 cm^{-1}; cf. ν_{CN} = 2204 cm^{-1} in the *trans* isomer[4]).[15] Presumably the nitrile in **3** arises by deprotonation of a cationic azavinylidene complex[16] formed after loss of benzaldehyde and trimethylamine. Curiously, the complete regioselectivity in azaallenium formation does not translate into complete regioselectivity in this reaction: the diphenylbutadiene-derived product *cis*-[(terpy)$OsCl_2$(1,2-η^2-PhCH═N═CHCH═CHPh)]PF_6 (**2c**) gives a 2:1 mixture of cinnamaldehyde and benzaldehyde on treatment with Me_3NO at room temperature. The azaallenium complexes can also be reduced. Complex **2a** reacts instantly with sodium borohydride in acetonitrile to give primarily dark blue *cis*-(terpy)-$OsCl_2$(η^1-PhCH═NCH_2Ph) (**4**) and traces of the doubly reduced violet dibenzylamine complex *cis*-(terpy)$OsCl_2$(NH[CH_2Ph]$_2$) (**5**). The ^{1}H NMR spectrum of **4** indicates that it has a mirror plane, implying that the imine is bonded only through nitrogen.

Reactions that cleave carbon−carbon double bonds are rare, due to the strength and nonpolar nature of the alkene linkage. Other reactions involving C═C bond cleavage, such as ozonolysis[17] and olefin metathesis,[18] have proven exceptionally useful in organic synthesis. Studies are in progress to further develop the reactivity of the azaallenium fragment, as well as to probe the mechanism of this remarkable transformation.

Acknowledgment. I thank Dr. Maoyu Shang for his assistance in determining the X-ray crystal structure of **2d**·$(CD_3)_2C$═O and Professor Xavier Creary for a generous gift of 1-(4-methoxyphenyl)-2-methylpropene. Financial support from the Camille and Henry Dreyfus Foundation (New Faculty Award), from a DuPont Young Professor award, and from the National Science Foundation (Grant CHE97-33321-CAREER) are gratefully acknowledged.

Supporting Information Available: Descriptions of synthetic procedures and spectroscopic data for compounds **2a**−**f** and **3**−**5**; tables of crystallographic parameters, atomic coordinates, bond lengths and angles, anisotropic thermal parameters, and hydrogen coordinates for **2d**·$(CD_3)_2C$═O (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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