# Notes

## Oxidative Azavinylidene Formation in the Reaction of 1,3-Diphenylisobenzofuran with Osmium Nitride Complexes

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### Introduction

Terminal metal nitride complexes present two complementary types of reactivity. On one hand, the uncoordinated nitrogen lone pair can act as a nucleophile, leading to Lewis acid adducts, $\mu$-nitrido complexes, or alkylation.[1] On the other hand, a growing number of studies have shown that nitrido complexes, particularly those of osmium and ruthenium, can also display electrophilic reactivity at nitrogen. Reagents as diverse as phosphines,[2] amine *N*-oxides,[3] amines,[4] azides,[5] Grignard reagents,[6] and arylboranes[7] have been reported to add to osmium(VI) nitride complexes. Below is described the reaction of the electrophilic nitrido complexes *cis*- and *trans*-[(terpy)-$OsNCl_2]^+$ (*cis*- and *trans*-**1**)[8] with 1,3-diphenylisobenzofuran to form azavinylidene complexes. This novel azavinylidene synthesis represents, formally at least, action of the nitride nitrogen as both an electrophile and a nucleophile in the formation of the new carbon−nitrogen double bond.

Azavinylidene complexes are known for transition metals ranging from group IV through group IX. They are typically prepared from precursors that already contain a carbon−nitrogen bond, although condensation of metal amides with ketones has also been used.[9] Typical synthetic methods include oxidation of coordinated amines,[10] deprotonation of organic imines,[11] reduction of oximes,[12] reductive cleavage of azines,[13] insertions of nitriles into metal−hydrogen or metal−carbon bonds,[14] protonation of nitriles,[15] addition of nucleophiles to coordinated nitriles,[16] reductive coupling of nitriles,[17] ring opening of azirines,[18] additions to vinylimido complexes,[19] and α-deprotonation of imido complexes.[20] The synthetic method described here involves formation of the nitrogen−carbon bond of the azavinylidene via a redox reaction with the metal nitride.

### Experimental Section

*cis*- and *trans*-$[(terpy)OsNCl_2]PF_6$ were prepared by the literature methods.[8] 1,3-Diphenylisobenzofuran was purchased from Aldrich. All solvents were used as received, and all manipulations were performed on the benchtop without precautions to exclude air or moisture. Reactions were carried out in the dark to avoid possible photodecomposition of the diphenylisobenzofuran. $^1H$ and $^{13}C\{^1H\}$ NMR spectra were obtained on a General Electric GN-300 NMR spectrometer at 300.49 and 75.56 MHz, respectively. IR spectra were measured on a Perkin-Elmer PARAGON 1000 FT-IR spectrometer. Fast atom bombardment mass spectra were obtained on a JEOL JMS-AX505HA mass spectrometer using 3-nitrobenzyl alcohol as a matrix. Elemental analyses were performed by M-H-W Laboratories (Phoenix, AZ).

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***trans*-[(terpy)OsCl$_2$(=N=C[Ph][2-PhCOC$_6$H$_4$])]PF$_6$ (*trans*-2).** *trans*-[(terpy)OsNCl$_2$]PF$_6$ (*trans*-**1**, 54.9 mg, 0.0840 mmol), 1,3-diphenylisobenzofuran (35.3 mg, 0.131 mmol, 1.55 equiv), and $CH_3CN$ (7 mL) were placed in a 20 mL screw-cap vial. After the vial was capped, the mixture was swirled to dissolve the solids and allowed to stand at room temperature for 2 days. The solvent was evaporated under reduced pressure and the residue washed several times with diethyl ether. The highly fluorescent washes, containing unreacted isobenzofuran, were discarded, and the ether-insoluble material was taken up in 3 mL of dichloromethane. The orange $CH_2Cl_2$ solution, which rapidly began depositing crystals, was layered with 3 mL of $Et_2O$. After 5 h, the glittery orange flakes were isolated by suction filtration, washed with 3 × 5 mL of $Et_2O$, and air-dried. Yield: 64.3 mg (83%). $^1$H NMR ($CD_3CN$): $\delta$ 6.76 (tt, 7.5, 1 Hz, 1H; *p*-N=C*Ph*), 6.86 (dd, 8, 1 Hz, 2H; *o*-N=C*Ph*), 7.45 (t, 7.5 Hz, 2H; *m*-N=C*Ph*), 7.52 (td, 7.5, 1.5 Hz, 1H; H-4, C$_6$*H*$_4$), 7.56 (t, 7.5 Hz, 2H; *m*-CO*Ph*), 7.61 (tt, 7.5, 1.5 Hz, 1H; *p*-CO*Ph*), 7.76 (m, 5H; H-3,5,6, C$_6$*H*$_4$ + *o*-CO*Ph*), 7.86 (td, 8, 1.5 Hz, 2H; terpy H-4,4″), 7.90 (ddd, 8, 6, 1.5 Hz, 2H; terpy H-5,5″), 8.19 (d, 8 Hz, 2H; terpy H-3′,5′), 8.31 (t, 8 Hz, 1H; terpy H-4′), 8.38 (m, 2H; terpy H-3,3″), 8.87 (m, 2H; terpy H-6,6″). $^{13}$C{$^1$H} NMR (acetone-$d_6$): $\delta$ 113.0, 124.9, 126.3, 128.1, 129.2, 129.5, 131.5, 131.7, 132.0, 132.5, 133.1, 133.7, 134.3, 134.7, 137.7, 140.3, 141.0, 144.2, 145.9, 146.0, 152.2, 161.4, 161.6, 196.4. IR (evaporated film; cm$^{-1}$): 3115, 3080, 2920 (w, $\nu_{CH}$), 1652 (s, $\nu_{C=O}$), 1600 (m), 1570 (m), 1474 (w), 1448 (s, $\nu_{C=N}$), 1315 (m), 1279 (m), 1238 (m), 1184 (w), 1159 (w), 1056 (w), 1024 (w), 936 (w), 923 (w), 919 (w), 840 (vs, $PF_6^-$), 776 (s), 750 (w), 733 (w), 719 (w), 702 (s). FABMS: *m*/*z* = 780 (M + H). Anal. Calcd for $C_{35}H_{25}Cl_2F_6N_4OOsP$: C, 45.51; H, 2.73; N, 6.07. Found: C, 45.39; H, 2.48; N, 6.22.

***cis*-[(terpy)OsCl$_2$(=N=C[Ph][2-PhCOC$_6$H$_4$])]PF$_6$ (*cis*-2).** *cis*-[(terpy)OsNCl$_2$]PF$_6$ (83.3 mg, 0.127 mmol) and 1,3-diphenylisobenzofuran (50.4 mg, 0.186 mmol, 1.5 equiv) were dissolved in 10 mL of $CH_3CN$ in a 25 mL round-bottom flask. After standing at room temperature for 2 h, the solution was filtered through a plug of cotton wool. The solvent was then removed on the rotary evaporator and the residue washed several times with diethyl ether. The ether-insoluble oil was taken up in 4 mL of $CH_2Cl_2$, and the solution was layered with 1 mL of $Et_2O$. After 1 h, the orange needles that had deposited were filtered off onto a glass frit, washed with 4 mL of $CH_2Cl_2$ and then 3 × 10 mL of $Et_2O$, and air-dried to yield 111.5 mg of *cis*-**2** (95%). $^1$H NMR ($CD_3CN$): $\delta$ 6.37 (d, 7.5 Hz, 2H; *o*-N=C*Ph*), 6.39 (t, 7.5 Hz, 1H; *p*-N=C*Ph*), 6.82 (dd, 7.5, 1 Hz, 1H; H-3, C$_6$*H*$_4$), 7.35 (m, 4H; *o*- and *m*-CO*Ph*), 7.41 (td, 7.5, 1 Hz, 1H; H-5, C$_6$*H*$_4$), 7.48 (t, 7.5 Hz, 2H; *m*-N=C*Ph*), 7.53 (m, 2H; *p*-CO*Ph* + H-4, C$_6$*H*$_4$), 7.62 (dd, 7.5, 1 Hz, 1H; H-6, C$_6$*H*$_4$), 8.0−8.2 (m, 7H; terpy H-4,5,3′,4′,5′,4″,5″), 8.27 (dd, 7, 2 Hz, 2H; terpy H-3,3″), 9.13 (dd, 5, 2 Hz, 2H; terpy H-6,6″). $^{13}$C{$^1$H} NMR ($CD_3CN$): $\delta$ 109.5, 111.7, 125.0, 125.4, 127.5, 129.4, 130.6, 130.8, 132.1, 132.4, 132.7, 134.4, 134.5, 136.0, 137.5, 139.1, 140.8, 144.1, 145.6, 157.6, 160.3, 162.7, 163.1, 195.0. IR (evaporated film; cm$^{-1}$): 3080 (m, $\nu_{CH}$), 1657 (s, $\nu_{C=O}$), 1597 (s), 1568 (m), 1474 (m), 1452 (s), 1314 (m), 1274 (s), 1165 (w), 1101 (w), 1055 (w), 1026 (m), 935 (w), 911 (w), 840 (vs, $PF_6^-$), 771 (s), 749 (m), 704 (m), 656 (m), 634 (m), 558 (s). FABMS: *m*/*z* = 780 (M + H). Anal. Calcd for $C_{35}H_{25}Cl_2F_6N_4OOsP$: C, 45.51; H, 2.73; N, 6.07. Found: C, 45.36; H, 2.90; N, 6.11.

**X-ray Structure Determinations of *trans*-[(terpy)OsCl$_2$(=N=C[Ph][2-PhCOC$_6$H$_4$])]PF$_6$·CD$_3$CN (*trans*-2·CD$_3$CN) and *cis*-[(terpy)OsCl$_2$(=N=C[Ph][2-PhCOC$_6$H$_4$])]PF$_6$ (*cis*-2).** Orange plates of *trans*-**2** were deposited after slow diffusion of ether into a solution of the complex in $CD_3CN$. A 0.25 × 0.12 × 0.04 mm crystal was glued to the tip of a glass fiber in the air and examined at 20 °C on an Enraf-Nonius CAD4 diffractometer using Mo Kα radiation with a graphite monochromator ($\lambda$ = 0.710 37 Å). The crystal was monoclinic, and its unit cell was determined on the basis of 25 reflections with 13.4° < $\theta$ < 16°. A total of 7215 reflections in two octants (*hkl*, *hk*$\bar{l}$) with 2$\theta$ < 50° were collected. Crystal quality was monitored by recording three standard reflections approximately every 160 reflections measured; decay was negligible. The large size of the unit cell resulted in a small amount of overlap in reflections; this was treated by correcting the backgrounds of reflections with highly unsymmetrical backgrounds by setting both backgrounds equal to the smaller one. After corrections for absorption and for Lorentz and polarization effects, 6751 unique reflections were obtained ($R_{int}$ = 0.0405), of which 59 were suppressed during least-squares refinement due to highly negative apparent values of $F_o$. The space group was determined to be $P2_1/n$ on the basis of systematic absences. The osmium atom was located on a Patterson map, and remaining non-hydrogen atoms were found in difference Fourier syntheses. Hydrogens were placed in calculated positions. Final full-matrix least-squares refinement of $F^2$ converged at $R1$ = 0.0409 for 5093 reflections with $F_o > 4\sigma(F_o)$ and $R1$ = 0.0693 for all data (wR$_2$ = 0.1101 and 0.2232, respectively).

**Table 1.** Crystallographic Data for *trans*-[(terpy)OsCl$_2$(=N=C[Ph][2-PhCOC$_6$H$_4$])]PF$_6$·CD$_3$CN (*trans*-**2**·CD$_3$CN) and *cis*-[(terpy)OsCl$_2$(=N=C[Ph][2-PhCOC$_6$H$_4$])]PF$_6$ (*cis*-**2**)

| | *trans*-**2**·CD$_3$CN | *cis*-**2** |
|---|---|---|
| empirical formula | $C_{37}H_{25}D_3Cl_2F_6N_5OOsP$ | $C_{35}H_{25}Cl_2F_6N_4OOsP$ |
| fw | 967.71 | 923.66 |
| space group | $P2_1/n$, monoclinic | $P\bar{1}$, triclinic |
| *a*, Å | 8.6941(7) | 10.6798(13) |
| *b*, Å | 32.558(4) | 11.3589(9) |
| *c*, Å | 13.696(2) | 15.655(2) |
| α, deg | 90 | 71.483(8) |
| *β*, deg | 96.098(9) | 76.942(9) |
| *γ*, deg | 90 | 79.747(8) |
| *V*, Å$^3$ | 3854.9(8) | 1742.6(3) |
| *Z* | 4 | 2 |
| $\rho_{calc}$, g cm$^{-3}$ | 1.667 | 1.760 |
| $\lambda$, Å | 0.710 73 | 0.710 73 |
| *T*, °C | 21 | 21 |
| crystal size, mm | 0.25 × 0.15 × 0.04 | 0.40 × 0.29 × 0.28 |
| $\mu$, mm$^{-1}$ | 3.554 | 3.926 |
| R1, $I > 4\sigma(I)$[a] | 0.0409 | 0.0238 |
| wR2, $I > 4\sigma(I)$[b] | 0.1001 | 0.0627 |
| GOF on $F^2$ | 1.055 | 1.095 |

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

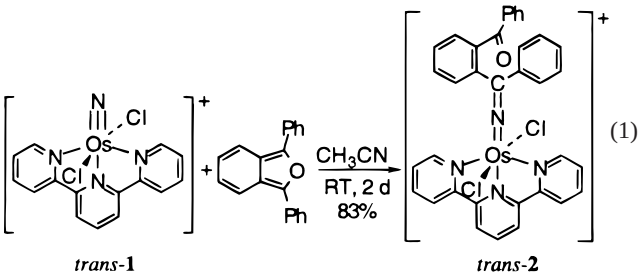
Orange blocks of *cis*-**2** formed after diffusion of benzene into a solution of the complex in acetone. A 0.40 × 0.29 × 0.28 mm orange block was treated as described for the trans isomer. A triclinic unit cell ($P\bar{1}$) was determined on the basis of 25 accurately centered reflections with 16° < $\theta$ < 17°. A total of 6369 reflections were measured (6125 unique, $R_{int}$ = 0.0255) in the hemisphere ±*h*,±*k*,−*l*. Decay was negligible. Data analysis and structure solution proceeded as described above for the trans isomer, converging at $R1$ = 0.0238 for 5884 reflections with $F_o > 4\sigma(F_o)$ and $R1$ = 0.0252 for all data (wR$_2$ = 0.0627 and 0.0637, respectively). All calculations used SHELXTL (Bruker Analytical X-ray Systems), with scattering factors and anomalous dispersion terms taken from the literature.[21] Other crystallographic details are summarized in Table 1.

## Results and Discussion

The violet osmium(VI) nitrido complex *trans*-[(terpy)OsNCl$_2$]PF$_6$[8] (*trans*-**1**; terpy = 2,2′:6′,2″-terpyridine) reacts with 1,3-diphenylisobenzofuran over the course of 1.5 days at room temperature to form the orange azavinylidene complex *trans*-[(terpy)OsCl$_2$(=N=C[Ph][2-PhCOC$_6$H$_4$])]PF$_6$ (*trans*-**2**), which can be isolated in 83% yield (eq 1). The isomeric nitrido complex *cis*-[(terpy)OsNCl$_2$]PF$_6$[8] (*cis*-**1**) reacts to give the analogous azavinylidene complex *cis*-**2** in 95% yield. The cis isomer reacts over an order of magnitude more rapidly than the trans, with the reaction going to completion in less than 1 h.

The observed spectral data for compounds **2** agree with the above formulation. The reaction generates a free organic carbonyl group, as indicated by characteristic absorptions in the infrared (1657 and 1652 cm$^{-1}$ for *cis*- and *trans*-**2**, respectively; cf. $\nu$ = 1660 cm$^{-1}$ for benzophenone) and by peaks at ∼$\delta$ 195

(21) *International Tables of Crystallography*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992; Vol. C.




*trans*-**1** *trans*-**2** (1)

ppm in the $^{13}C$ NMR. The NMR resonances of **2** are sharp and unshifted, indicating that the compounds are diamagnetic. The ortho and para hydrogens of the phenyl group bonded to the azavinylidene carbon resonate in the $^{1}H$ NMR significantly upfield of the other resonances, suggesting a rather electron-rich azavinylidene ligand. The para resonance, integrating to 1H, clearly demonstrates that the $C_{2v}$ symmetry of the isobenzofuran has been lost upon reaction with the osmium nitride.

The bonding in the molecules is confirmed by X-ray diffraction studies of *trans*-**2** (Figure 1) and *cis*-**2** (Figure 2). Apart from the disposition of the chloride ligands, the two complexes are quite similar (Table 2). The azavinylidene moieties are linear (175.5(6) and 168.2(3)° for the trans and cis isomers, respectively) and have short Os═N (1.812(6), 1.806(3) Å) and C═N bonds (1.273(9), 1.264(4) Å). These features are similar to those reported for osmium(II) azavinylidene complexes[12a,b] as well as those of the isoelectronic ruthenium(IV) complex $[(bipy)(terpy)Ru(=N=CMe_2)](ClO_4)_3$.[10a] The short Os═N distance and diamagnetism of the octahedral $d^4$ complex indicate that the azavinylidene group forms a single strong $\pi$ bond, giving an overall Os−N bond order of 2. In both complexes, the orientation adopted in the crystal requires that the $\pi$ donor orbital on the azavinylidene[22] interact with an empty $d_\pi$ orbital on osmium that could otherwise be involved in back-bonding to the central pyridine of the terpyridine ligand. This orientation may be favored because of steric interactions or because of maximum favorable $\pi$ donation from the chloride ligands; the loss of back-bonding is unlikely to be significant in this relatively high-valent complex. Since twisting of the aryl groups around their bonds to C1 renders the two sides of the terpyridine ligand equivalent, the (symmetrical) NMR spectra of the complexes do not offer any information about barriers to rotation in solution. The facts that the bond to the central N21 of the terpyridine ligand is slightly longer in the trans isomer than in the cis isomer and that the Os−Cl bonds in *trans*-**2** are shorter than the Os−Cl bond trans to the azavinylidene ligand in *cis*-**2** indicate that the azavinylidene exerts a small trans influence of ∼0.03 Å (compared to a trans influence of ∼0.17 Å in the parent nitride[23]). The distortions from octahedral geometry due to constraints in the terpy ligand (relatively acute trans N11−Os−N31 angle = 159.0° (average); central Os−N21 bond shorter than outer Os−N11/N31 bonds by 0.052 Å in *trans*-**2** and 0.088 Å in *cis*-**2**) are typical (in 137 structures in the Cambridge Crystallographic Database, avg. trans angle = 155 ± 10° and average $\Delta d$ = 0.09 ± 0.05 Å).[24]

Formation of the azavinylidene ligand is presumably initiated by nucleophilic attack of isobenzofuran at the nitrogen atom of the metal nitride (Scheme 1). This is congruent with the known propensity of isobenzofurans to act as nucleophiles[25] and of the cationic nitrides **1** to react as electrophiles at nitrogen.[2b,3−5] Initiation of the reaction sequence by outer-sphere electron transfer is unlikely because the enormous difference in redox potentials of the two reagents ($E° \approx +0.75$ V vs SCE[26] for

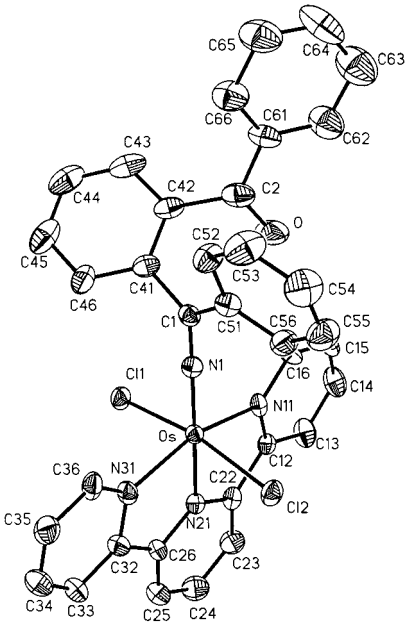



**Figure 1.** Molecular structure of the cation of *trans*-$[(terpy)OsCl_2(=N=C[Ph][2\text{-}PhCOC_6H_4])]PF_6 \cdot CD_3CN$ (*trans*-**2**·$CD_3CN$), with thermal ellipsoids shown at the 30% probability level.

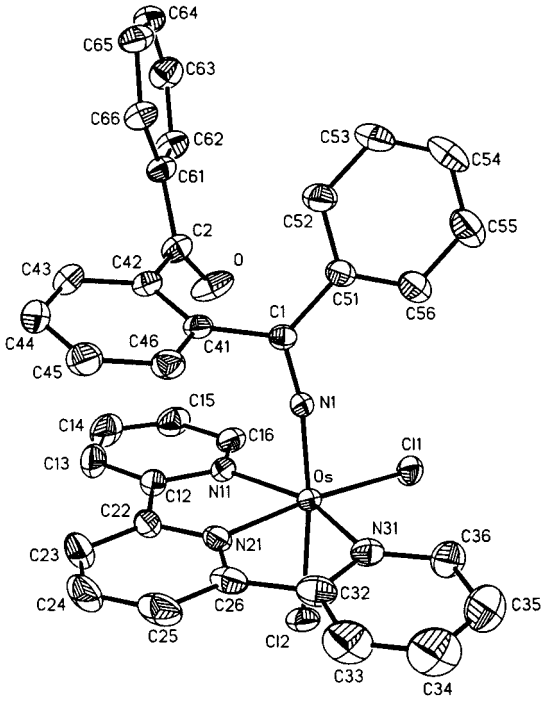



**Figure 2.** Molecular structure of the cation of *cis*-$[(terpy)OsCl_2(=N=C[Ph][2\text{-}PhCOC_6H_4])]PF_6$ (*cis*-**2**), with thermal ellipsoids shown at the 30% probability level.

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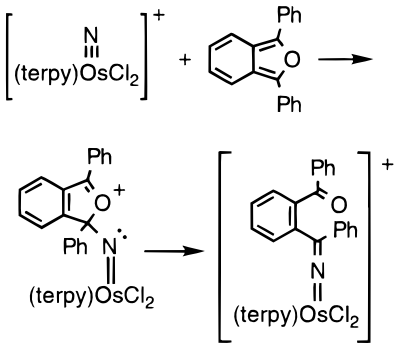
**Table 2.** Selected Bond Distances (Å) and Angles (deg) for *trans*-[(terpy)$OsCl_2$(=N=C[Ph][2-$PhCOC_6H_4$])]$PF_6$·$CD_3CN$ (*trans*-**2**·$CD_3CN$) and *cis*-[(terpy)$OsCl_2$(=N=C[Ph][2-$PhCOC_6H_4$])]$PF_6$ (*cis*-**2**)

| | *trans*-**2** | *cis*-**2** |
|---|---|---|
| Os−N1 | 1.812(6) | 1.806(3) |
| Os−N21 | 2.028(7) | 1.991(3) |
| Os−N11 | 2.078(6) | 2.090(3) |
| Os−N31 | 2.081(6) | 2.069(3) |
| Os−Cl1 | 2.341(2) | 2.3571(10) |
| Os−Cl2 | 2.331(2) | 2.3688(10) |
| N1−C1 | 1.273(9) | 1.264(4) |
| N1−Os−N21 | 178.1(2) | 91.38(12) |
| N1−Os−N11 | 99.9(3) | 88.53(12) |
| N21−Os−N11 | 79.6(3) | 80.03(13) |
| N1−Os−N31 | 101.6(3) | 94.90(13) |
| N21−Os−N31 | 78.8(3) | 79.71(14) |
| N11−Os−N31 | 158.5(3) | 159.52(13) |
| N1−Os−Cl2 | 98.8(2) | 173.35(9) |
| N21−Os−Cl2 | 83.1(2) | 83.33(9) |
| N11−Os−Cl2 | 88.9(2) | 86.59(9) |
| N31−Os−Cl2 | 88.3(2) | 88.14(9) |
| N1−Os−Cl1 | 95.1(2) | 95.84(9) |
| N21−Os−Cl1 | 83.1(2) | 172.67(9) |
| N11−Os−Cl1 | 89.3(2) | 98.87(9) |
| N31−Os−Cl1 | 88.4(2) | 100.84(10) |
| Cl2−Os−Cl1 | 166.14(8) | 89.38(4) |
| C1−N1−Os | 175.5(6) | 168.2(3) |
| N1−C1−C51 | 121.7(7) | 120.9(3) |
| N1−C1−C41 | 116.8(7) | 115.7(3) |

**Scheme 1**




1,3-diphenylisobenzofuran and $E° \approx -0.36$ V vs SCE[27] for $[(terpy)OsNCl_2]^+$) makes one-electron transfer too endoergic to account for the observed rates. Formation of the first carbon−nitrogen bond restores the aromaticity of the benzene ring of the isobenzofuran and generates a superb leaving group, a diaryl ketone. Its departure allows the lone pair on nitrogen to form the second carbon−nitrogen bond. It should be noted that free organic nitrenes have also been observed to react with 1,3-diphenylisobenzofuran to give imines of 2-benzoylbenzophenone in a reaction presumed to involve initial aziridination.[28] Initial aziridination by **1** prior to formation of the open structure shown in Scheme 1 cannot be ruled out but seems unlikely in view of the lack of precedent for aziridine formation from nitrido complexes and the unusual reactivity of the isobenzofuran. In contrast to the reactions of free nitrenes, which react readily with a variety of furans,[28] *trans*-**1** does not react with furan, 2,5-dimethylfuran, or vinylene carbonate, even upon heating at 65 °C for several days.

Thus, azavinylidene formation appears to take place by initial action of the nitride as an electrophile, followed by the action of the (newly electron-rich) nitrogen as a nucleophile. This pattern of successive electrophilic/nucleophilic reactivity seems to be typical of electrophilic osmium nitrido complexes. A very close analogy exists for the reaction of **1** with the nucleophilic oxidant $Me_3NO$,[3] which presumably involves initial bond formation between oxygen and the nitride followed by expulsion of $Me_3N$ concurrent with formation of the nitrosyl N−O multiple bond. The reaction of **1** with azide[5] is likely analogous, and the Grignard addition/protonation sequence used to make amides from nitrides[6] also exhibits this sequence. The only other example where azavinylidene complexes have been prepared from nitrides uses a two-step sequence in which the order of reactivity is reversed. Shapley has prepared a methyleneamido complex of osmium by initial methylation of $CpOsN(CH_2SiMe_3)_2$[29] followed by deprotonation of the resulting cationic methylimido complex.[30] The possibility of still other sequences—for example, reactions where nucleophilic and electrophilic bond-forming steps are concerted—is currently being explored.

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**Supporting Information Available:** Tables listing crystallographic parameters, atomic coordinates, bond lengths and angles, anisotropic thermal parameters, and hydrogen coordinates and *U*(eq) values for *trans*-**2**·$CD_3CN$ and *cis*-**2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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