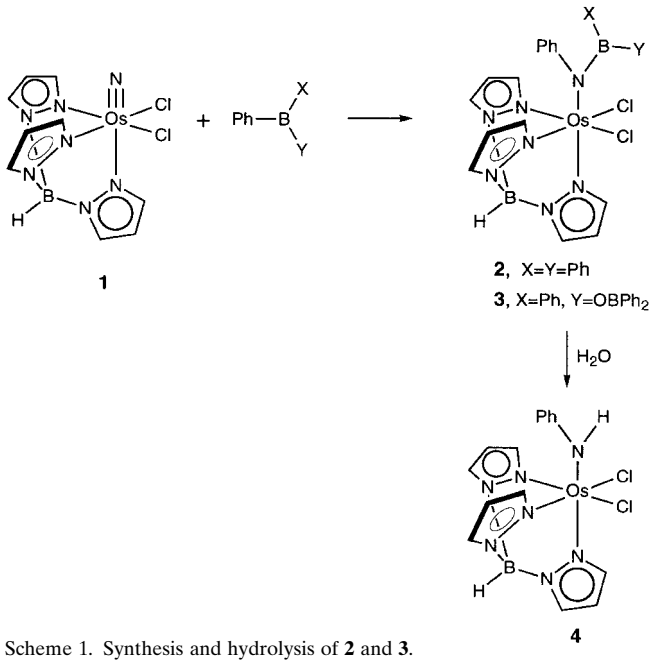
Insertion of an Osmium Nitride into Boron–Carbon Bonds**

Thomas J. Crevier and James M. Mayer*

The activation and functionalization of C–X bonds has long been a focus of transition metal chemistry. In most cases, either the carbon atom or the X group bonds directly to the metal. Here we report novel reactions that cleave aryl–boron bonds, where both the aryl and boryl groups are added to a nitrido ligand. They can formally be considered as insertions of the nitrido ligand into B–C bonds. Nitrido complexes typically react to add single electrophiles or nucleophiles to the nitrogen atom.[1] Electrophilic reactions include the alkylation of $[Os(N)R_4]^-$ to $[Os(NMe)R_4]$ by MeI,[2a] and the reversible addition of $BF_3 \cdot Et_2O$ to $[CpOs(N)R_2]$ to form $[CpOs(NBF_3)R_2]$ ($R = CH_2SiMe_3$).[2b] The addition of PPh_3 is a typical nucleophilic process, as in the conversion of $[Os(N)(tpy)Cl_2]Cl$ into $[Os(NPPh_3)(tpy)Cl_2]Cl$ (tpy = 2,2′:6′2″-terpyridine).[2c]

Reaction of the nitrido complex $[TpOs(N)Cl_2]$ (**1**; Tp = $HB(pz)_3$, hydrotris(pyrazolyl)borate)[3, 4] with one equivalent of BPh_3 rapidly gives the borylanilido compound $[TpOs\{N(Ph)BPh_2\}Cl_2]$ (**2**) in excellent yield (Scheme 1). A similar product, $[TpOs\{N(Ph)B(Ph)OBPh_2\}Cl_2]$ (**3**), is formed from the reaction of Ph_2BOBPh_2. Compound **2** reacts rapidly with atmospheric moisture in solution or in the solid state, while **3** can be handled briefly in the air. Reactions with water cleave the boron–nitrogen bond to give the known osmium(IV) anilide $[TpOs(NHPh)Cl_2]$ (**4**).[4] Hydrolysis of **2** also yields Ph_2BOBPh_2 (1/2 equiv). $PhBCl_2$ and $B(C_6F_5)_3$ appear to form similar borylanilido complexes quantitatively (as shown by ^1H and ^{19}F NMR spectroscopy), which are also converted by traces of moisture into **4** or $[TpOs\{NH(C_6F_5)\}Cl_2]$ (^1H, ^{19}F NMR). BPh_3, $PhBCl_2$, and $B(C_6F_5)_3$ react rapidly with **1**, while Ph_2BOBPh_2 reacts substantially slower. Addition of **1** (1/3 equiv) to a 1:1 mixture of BPh_3 and $B(C_6F_5)_3$ leads to the exclusive and quantitative formation of **2** (^1H and ^{19}F NMR), and aerobic workup gives **4** in good yield.



Scheme 1. Synthesis and hydrolysis of **2** and **3**.

The X-ray crystal structures of **2** and **3** (Figures 1 and 2) show isolated molecules with roughly octahedral osmium centers. The borylamido nitrogen atom is planar in both structures (sum of the angles at N = 359.2°, 359.9°). The B2–N7 distance of 1.60(2) Å in **2** corresponds to a long single bond (av B–N 1.52 Å[5]), while the Os–N7 bond is short (1.884(10) Å), indicative of multiple-bond character. In **3**, the B2–N7 distance is shorter (1.509(13) Å), and the Os–N7 distance is longer (1.937(7) Å), implying more delocalized π bonding. Consistent with the lack of B–N π bonding in **2**, the boron makes a weak fourth bond with a chloride ligand and has a roughly tetrahedral geometry. The B–Cl distance (2.078(14) Å) is the longest reported so far (av 1.822 ± 0.049 Å[6]). Complex **3** lacks a B–Cl interaction because π donation from the N and O atoms reduces the Lewis acidity of the boron atom. The structures of **2** and **3** contrast with those of other structurally characterized transition metal borylamido complexes, which involve 3d metal centers and exhibit short B–N multiple bonds and little M–N π bonding.[7]

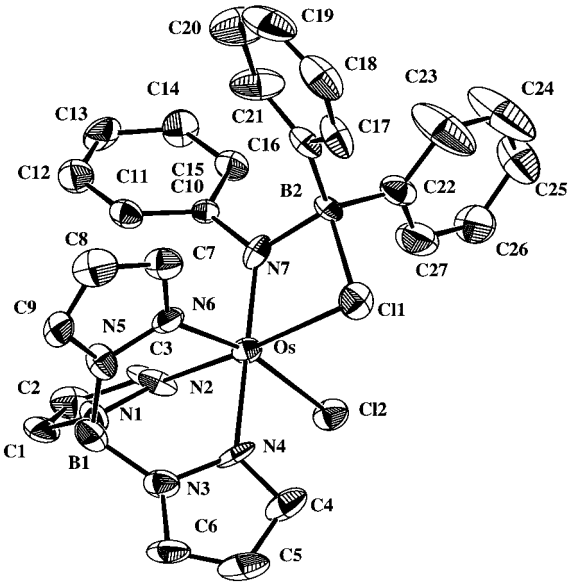


Figure 1. ORTEP diagram of the structure of **2**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Os–N7 1.884(10), Os–Cl1 2.404(3), Os–Cl2 2.354(3), N7–B2 1.600(20), B2–Cl1 2.078(14); Os-N7-B2 112.1(7).

Compounds **2** and **3** can be viewed as basic $[TpCl_2Os^{IV}{=}NPh]^-$ fragments stabilized by Lewis acidic boryl moieties. The imido fragment can be formed independently from **1** and PhMgBr or LiPh (and also yields **4** on exposure to

[*] Dr. J. Mayer, T. Crevier
Department of Chemistry, University of Washington
Box 351700, Seattle, WA 98195–1700 (USA)
Fax: (+1) 206-685-8665
E-mail: mayer@chem.washington.edu

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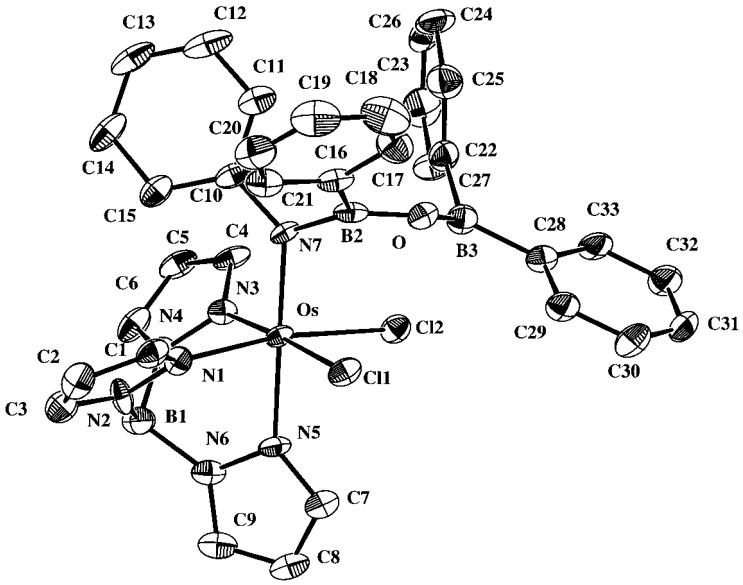

Figure 2. ORTEP diagram of the structure of **3**. The CH_2Cl_2 solvent molecules and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Os–N7 1.937(7), Os–Cl1 2.362(2), Os–Cl2 2.372(2), N7–B2 1.509(13); Os-N7-B2 115.6(6).

moisture).[4] The reactions involve reduction of the osmium center from +VI to +IV with concomitant oxidation of a phenyl group, from formally Ph^- in BPh_3 to Ph^+ in the borylamido product. Assignment of the oxidation state Os^{IV} to the osmium centers in **2** and **3** is supported by their narrow, paramagnetically shifted ^1H NMR spectra, characteristic of d^4 octahedral Os^{IV} and Re^{III} complexes.[8] The spectra show C_s symmetry (down to $-45\,^\circ C$ for **2**), which indicates either that the B–Cl interaction in **2** is not maintained in solution or that it is cleaving rapidly on the NMR time scale.

The only previously reported reaction of a metal nitrido complex with an organoborane is the formation of the Lewis acid/base adduct $[Re(NBPh_3)(Et_2dtc)_2(PMePh_2)]$ from BPh_3 and $[Re(N)(Et_2dtc)_2(PMe_2Ph)]$ (Et_2dtc = diethyldithiocarbamate).[9] The transfer of aryl and alkyl groups from boron to nitrogen centers has previously been observed on treatment of boranes with azides or chloramines.[10] These reactions are proposed to proceed by initial adduct formation (N:→B) followed by carbon migration to a low-lying empty orbital on the nitrogen oxidant (similar to Baeyer–Villiger oxidations).[11] A similar mechanism is possible for the reactions of **1**, although the nitrido ligand has very low basicity. It is unreactive with respect to $BF_3 \cdot Et_2O$, $MeOSO_2CF_3$, and $Ph_3C^+BF_4^-$, the latter being isoelectronic and much more Lewis acidic than BPh_3. Instead, the nitrido nitrogen atom acts as an electrophile and forms adducts with PPh_3 and a N–Ph bond with the Ph^- group from PhMgBr, as noted above.[4] The observation that **1** reacts preferentially with BPh_3 rather than the much more acidic $B(C_6F_5)_3$ indicates that the reaction is not dominated by the Lewis acidity of the borane but rather also involves the nucleophilicity of the aryl group. Rate-limiting aryl transfer could occur by direct attack of the nitrido, either at the *ipso* carbon atom or at the B–C bond, or by migration in a weak borane–nitrido adduct.

Experimental Section

Manipulations were carried out under N_2 with dry degassed reagents.

2: A mixture of **1** (180.0 mg, 0.368 mmol), BPh_3 (108.0 mg, 0.446 mmol, 1.21 equiv), and benzene (10 mL) was stirred for 5 min. The solution was filtered through a glass frit, layered with hexane (60 mL), and allowed to stand overnight to yield dark orange crystals of **2** (138 mg, 52 %). ^1H NMR ($CDCl_3$): $\delta = 6.29$ (t, 2 Hz, 1 H, pz), 6.94 (d, 2 Hz, 1 H, pz), 7.47 (d, 2 Hz, 1 H, pz), 6.12 (t, 2 Hz, 2 H, pz′), 6.05 (d, 2 Hz, 2 H, pz′), 7.00 (d, 2 Hz, 2 H, pz′), 4.50 (d, 7 Hz, 2 H, *ortho*-N*Ph*), 7.26 (t, 7 Hz, 2 H, *meta*-N*Ph*), 6.90 (t, 7 Hz, 1 H, *para*-N*Ph*),7.63 (d, 7 Hz, 4 H, *ortho*-BPh_2), 7.32 (t, 7 Hz, 4 H, *meta*-BPh_2), 7.43 (t, 7 Hz, 2 H, *para*-BPh_2); elemental analysis calcd for $OsC_{27}H_{25}N_7B_2Cl_2$ (found): C 44.40 (44.03), H 3.45 (3.42), N 13.43 (13.42).

3: Prepared as above for **2** except that the mixture was stirred overnight; yield of isolated product 34 %. ^1H NMR ($CDCl_3$): $\delta = 5.96$ (t, 2 Hz, 1 H, pz), 5.73 (d, 2 Hz, 1 H, pz), 4.72 (d, 2 Hz, 1 H, pz), 6.69 (t, 2 Hz, 2 H, pz′), 6.96 (d, 2 Hz, 2 H, pz′), 4.12 (d, 2 Hz, 2 H, pz′), 9.20 (t, 7 Hz, 2 H, *Ph*), 7.70 (d, 7 Hz, 4 H, *ortho*-BPh_2), 7.47 (t, 7 Hz, 1 H, *para-Ph*), 4.10 (t, 7 Hz, 2 H, *Ph*), 1.91 (t, 7 Hz, 1 H, *para-Ph*), 1.27 (overlapping, 4 H, d), 0.89 (t, 7 Hz, 2 H, *Ph*), −4.10 (t, 7 Hz, 4 H, *meta*-BPh_2); EI-MS: *m/z*: 834 (v weak, M^+), 799 (v weak, M – Cl), 722 (weak, M – Ph – Cl), 567 (major, M^+ – PhBOBPh$_2$), 531 (major, M^+ – PhBOBPh$_2$ – Cl).

Structure analysis of **2** and **3**: Crystals were obtained by slow evaporation of solutions in CH_2Cl_2/$Me_3SiOSiMe_3$, and were immersed in oil and mounted under a stream of N_2. Data were collected on an Enraf-Nonius CAD4 diffractometer at 187 K with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Full-matrix least-squares refinement was carried out with SHELXL-93.[12] Semi-empirical absorption corrections were made with ψ scans. **2**: $OsC_{27}H_{25}N_7B_2Cl_2$, monoclinic, space group $C2/c$, $a = 21.268(4)$, $b = 9.739(2)$, $c = 28.269(5)$ Å, $\beta = 108.88^\circ$, $V = 5540(1)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.751$ g cm^{-3}, 4258 reflections, 3629 unique, 352 parameters, $R = 0.0389$, R_w(on F^2) = 0.0924, GOF = 0.945. **3** · CH_2Cl_2: $OsC_{34}H_{32}N_7OB_3Cl_4$, triclinic, space group $P\bar{1}$, $a = 11.578(3)$, $b = 12.343(5)$, $c = 15.482(5)$ Å, $\alpha = 91.31(2)$, $\beta = 110.59(2)$, $\gamma = 115.35(2)^\circ$, $V = 1832.0(11)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.666$ g cm^{-3}, 6404 reflections, 5986 unique, 445 parameters, $R = 0.0591$, R_w(on F^2) = 0.1452), GOF = 1.093. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100925. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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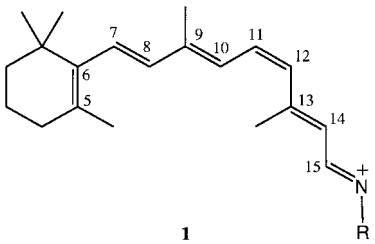
Absolute Sense of Twist of the C12 – C13 Bond of the Retinal Chromophore in Rhodopsin—Semiempirical and Nonempirical Calculations of Chiroptical Data**

Volker Buß,* Klaus Kolster, Frank Terstegen, and Rainer Vahrenhorst

The protonated Schiff base of 11-*cis*-retinal, 11-*cis*-retinal PSB (**1**), is the light-sensitive chromophore of rhodopsin, the



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photoreceptor that is responsible for dim-light vision of vertebrates. Photochemical isomerization of **1** to the all-*trans* isomer triggers the visual transduction process, which eventually results in the excitation of the visual nerve and the liberation of all-*trans*-retinal from the protein.[1] To understand this process on a molecular basis, the conformation of the retinal chromophore and its interaction with neighboring groups inside the protein-binding pocket have been studied by a variety of methods, mostly spectroscopic and including circular dichroism (CD) spectroscopy.[2]

All retinals are chiral (point group C_1), a consequence of the distorted geometry about the C6 – C7 bond of the β-ionone ring. In addition, steric hindrance from the C13 methyl group may cause the C13 – N16 fragment in **1** to rotate about the C12 – C13 bond into a more stable geometry. In the absence of other sources of chirality, retinal conformations in which the dihedral angles are twisted in the opposite direction are enantiomers and cannot be distinguished. In the chiral environment of the protein pocket, discrimination between the enantiomers takes place and the chromophore becomes optically active, leading to two well-resolved positive CD absorptions in the visible (480 nm) and near-UV (340 nm) region. These absorptions are called the α and the β band, respectively.[3] It has long been assumed, on the basis of spectroscopic studies of conformationally locked retinal analogues,[4] that the α- and β-bands derive their rotatory strengths from the twist about the C12 – C13 and the C6 – C7 bonds, respectively.

Recently, in a study of artificial pigments formed from bovin opsin with several 11,12-dihydroretinal derivatives, the absolute sense of twist of the C12 – C13 bond was derived from CD exciton chirality theory,[5] a method that cannot be applied to the native chromophores with their through-conjugated π systems. In view of the importance of the absolute configuration of the retinal chromophore for modeling the binding site in rhodopsin, we computed the chiroptical properties of 11-*cis*-12-s-*trans*-retinal PSB directly with the best methodologies available. The results prove that a positive long-wavelength CD absorption of this compound corresponds to a positive twist about the C12 – C13 s-*trans* bond.

The starting point for every calculation of chiroptical properties is a reliable three-dimensional molecular structure. The only known crystal structure of a retinal PSB has an all-*trans*-configured chromophore, including *trans* C11 – C12 and C6 – C7 bonds.[6] This configuration corresponds to the dark-adapted state of bacteriorhodopsin[7] but not to rhodopsin, in which the conformation is twisted 6-s-*cis*-11-*cis*-12-s-*trans*. The crystal structure of 11-*cis*-retinal is of no use either as the chromophore is twisted from 12-s-*cis*.[8] Computational resources are now sufficient to treat molecules as large as retinal in a rigorous manner. We have recently reported the completely optimized geometry of *N*-methyl-11-*cis*-12-s-*trans*-retinal PSB (**1**, R = Me) employing ab initio (RHF/6-31G**) and density functional theory (DFT) methodologies (B3LYP/6-31G**).[9] According to these calculations the whole chromophore is planar except for the C6 – C7 dihedral angle. This structure agrees with results of other calculations of comparable sophistication,[10] and with the exception of the rotation about the C12 – C13 bond, is our basis for the calculation of chiroptical properties.

From resonance Raman spectroscopy[11] it is known that the C12 – C13 bond is twisted significantly from s-*trans* as a consequence of steric and/or electronic interactions with the protein environment, a factor that we have not taken into account in our calculations. We arbitrarily assigned values of $+160^\circ$ and -160° to this dihedral angle (180° corresponds to a planar s-*trans* conformation) and have combined each of these with the two possible orientations of the cyclohexene ring. Calculations of the excited states of these geometries were performed with three different theoretical models: CNDO/S including configuration interaction of 100 singly excited states (model 1); the nonempirical method CIS from the GAUSSIAN 94 package[12] using the same basis set as for the

[*] Prof. Dr. V. Buß, Dr. K. Kolster, Dipl.-Chem. F. Terstegen, Dipl.-Chem. R. Vahrenhorst
Fachgebiet Theoretische Chemie der Universität-GH Duisburg
D-47048 Duisburg (Germany)
Fax: (+49) 203-379-2772
E-mail: theobuss@uni-duisburg.de

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