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Base accelerated generation of N_2 and NH_3 from an osmium nitride

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ABSTRACT

Dissolution of an $Os^{VI}{\equiv}N$ complex with non-innocent, protic, tris-chelating NNN-ligands in aqueous KOH is shown to produce nitride derived N_2 and NH_3. NH_3 production was shown to greatly increase under H_2 pressure. Most importantly, both N_2 and NH_3 generation are enhanced upon increasing [KOH]. The resulting putative complexes are trapped by in situ treatment with $K^{13}CN$ and shown to be NNN-ligated Os^{III} and Os^{II} species, in the absence and presence of H_2 respectively.

1. Introduction

Fertilizer derived from N_2 reduction to NH_3 in the Haber–Bosch process sustains food production for over 2 billion people and consumes ~2% of the world's total energy supply [1]. This process operates at high temperature and pressure utilizing heterogeneous group VIII metal (Fe or Ru) catalysts. It has become generally accepted that the key steps during catalysis are the cleavage of N_2 to generate metal-nitrides ($M{\equiv}N$) and the conversion of these $M{\equiv}N$ species to NH_3. Consequently, substantial study has been aimed at understanding these fundamental reactions [2–4]. Additionally, it is known that Na or K salts are efficient promoters in the commercial Haber–Bosch systems, which are thought to assist catalysis through the generation of strongly basic surface oxides or amides [5].

Our group has been exploring the use of acidic and basic solvents to activate homogenous metal complexes toward reactions with alkanes [6]. Recently, we have shown that homogenous Ru complexes chelated with a non-innocent, protic ligand affected CH activation at rates which *increased upon increasing [KOH]* [7]. We postulated that reversible deprotonation of the ligand generated a Ru-center which is a highly nucleophilic π-donor that can cleave CH bonds via a nucleophilic CH activation reaction (Scheme 1A). Additionally, we demonstrated that facilitation of nucleophilic M-R oxy-functionalization by hydroxide on a model complex (MTO) (Scheme 1B) is viable; suggesting that all steps of the CH functionalization reaction can be promoted by the basic media [8].

During the course of the work described above, we began to consider whether this class of catalysts could be utilized for activating other types of inert chemical bonds and recently extended this type of reactivity into the areas of catalytic C—F bond activation and hydrodefluorination [9]. Considering the strong precedent for N_2 coordination and cleavage by strong π-donor metal centers [10], and the proposed beneficial role of strongly basic oxides in the Haber process, we postulated that this class of catalyst *may* also facilitate the reduction of N_2 to NH_3. Analogous to our previous work concerning CH (and CF) bond activation (Scheme 1A), it seemed plausible that a base activated, highly nucleophilic, π-donor metal center could reversibly cleave $M{-}N_2{-}M$ complexes to generate higher energy metal-nitrides ($M{\equiv}N$, Scheme 1C). In basic media, this incipient $M{\equiv}N$ (similar to the nucleophilic M-R functionalization, Scheme 1B) could then be reduced to generate NH_3 by either promoting $M{\equiv}N$ protonation or through the activation of an added exogenous reductant (Scheme 1D). However, given the strength of the $N{\equiv}N$ bond, we anticipated that any endergonic N_2 cleavage event would require elevated temperatures to operate at any reasonable rate (>150 °C), making the identification of a suitably reactive metal complex that is stable to the harsh media quite challenging. Therefore, to begin studying this concept and the effect of basic media on a metal mediated N_2 cleavage (via the principle of microscopic reversibility, utilizing the established $M{\equiv}N$ coupling

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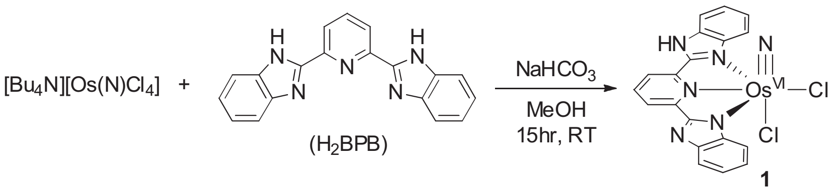
reaction initially studied by Ware and Taube) [3b] and reduction to generate NH_3, we focused on the reactivity of a model putative M≡N intermediate, to examine. Herein, we report the chemistry of an Os≡N complex with a non-innocent, protic ligand dissolved in aqueous, basic media in the presence and absence of H_2.

2. Experimental

2.1. General

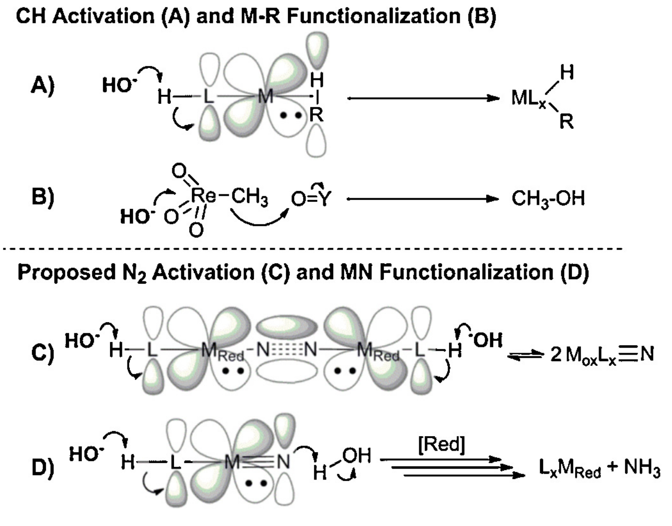
All air and water sensitive procedures were carried out either in an MBraun inert atmosphere glove box, a custom built polycarbonate wetbox under argon, or using standard Schlenk techniques under argon. Anhydrous methanol was purchased from Alfa Aesar and used without further purification. All deuterated solvents (Cambridge Isotopes) and 40% KOD/D_2O (Sigma–Aldrich) were used as received. The KOD/D_2O solutions were prepared by dilution of 40% KOD/D_2O with D_2O to the desired concentration. OsO_4 was purchased from Electron Microscopy Sciences, $(NH_4)_2OsCl_6$ was purchased from Alfa Aesar, and all other chemicals were purchased from Alfa Aesar, Sigma–Aldrich, or Acros Chemical. Synthesis of 2,6-bis(benzimidazoyl)pyridine (BPB) [11], $[Bu_4N][OsNCl_4]$ [12] and $[Bu_4N][Os^{15}NCl_4]$ [12] were prepared using a previously published methods. NMR spectra were obtained on a Bruker Digital Avance III 400 (400.132 MHz for ^1H and 100.623 MHz for ^{13}C) spectrometer. All chemical shifts are reported in units of ppm and referenced to the residual protonated solvent. FTIR was performed on a PerkinElmer Spectrum One FT-IR Spectrometer equipped with a UATR with a ZnSe crystal top-plate. Gas measurements were analyzed with a Shimadzu GC-MS QP2010S equipped with an Agilent GasPro or HP-MoleSieve column. Electrochemical measurements were made using a BAS Inc. Epsilon in a standard 3-cell electrochemical cell with a glassy carbon working electrode and solutions were purged with Ar prior to experiments. All potentials are reported vs NHE and were determined in 10 mM solutions in DMA (0.5 M TBAH) using ferrocene ($E_{1/2} = 0.55$ V) as an in situ calibration standard. All high-resolution mass spectra were obtained by the Mass Spectrometry Laboratory at the University of Illinois at Urbana-Champaign on a Q-Tof Ultima mass spectrometer. Elemental Analysis was performed by Columbia Analytical Services of Tucson, Arizona.

2.2. Synthesis of (HBPB)Os(N)Cl_2 (**1**)



(1)

A variation of a published procedure [13] was utilized to synthesize **1**: To a 30 mL amberized vial equipped with a stirbar, $[Bu_4N][OsNCl_4]$ (2.37 g, 4.01 mmol, 1.25 eq.), 2,6-bis(benzimidazoyl)pyridine (1.00 g, 3.21 mmol), $NaHCO_3$ (0.07 g, 0.8 mmol, 0.25 eq.) and anhydrous MeOH (25 mL) was added and stirred for 15 h. The solvent was removed under reduced pressure and redissolved in anhydrous THF (50 mL). The residue was washed with anhydrous THF (3× 30 mL) and the solvent was removed under reduced pressure. To the resulting residue, anhydrous MeOH (75 mL) was added and the orange solid was filtered. The solid was washed successively with MeOH (3× 25 mL) and ether (3× 25 mL). The resulting orange solid was placed under high vacuum at 100 °C overnight to remove residual solvent to yield a deep red product (60–70% yield). ^1H NMR (400 MHz, d^7-DMF): δ(ppm) 8.87 (t, 1H, $j = 7.8$ Hz), 8.57 (dt, 2H, $j = 8.1$ Hz, 0.8 Hz), 8.55 (d, 2H, 7.8 Hz), 7.93 (dt, 2H, $j = 8.1$ Hz, 0.8 Hz), 7.50 (ddd, 2H, $j = 8.2$ Hz, 7.1 Hz, 1.2 Hz), 7.38 (ddd, 2H, $j = 8.2$ Hz, 7.1 Hz, 1.2 Hz). $^{13}C\{^1H\}$ NMR (400 MHz, d^7-DMF): δ(ppm) 164.1, 152.5, 147.9, 147.9, 147.0, 125.0, 123.1, 121.3, 120.8, 115.8. HRMS (ESI): Calculated for $C_{19}H_{11}ClN_6Os$ (M-Cl) 551.0427, found 551.0417. Elemental Analysis: Calculated for $C_{19}H_{12}Cl_2N_6OOs$: C, 38.98; H, 2.07; N, 14.35. Found: C, 38.72; H, 2.33; N, 14.03. FTIR (ZnSe) in cm^{-1} = ν(Os≡^{15}N) 1099 (vs). UV–vis (DMF) [λ_{max} nm]: 317, 430.

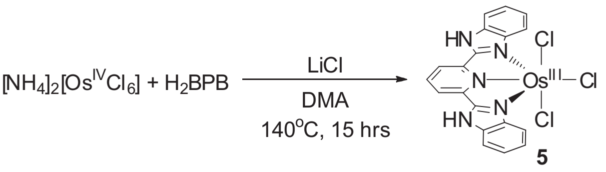


Scheme 1. The conceptual extension of base enhanced metal complex nucleophilicity from (A) CH activation and (B) M–R functionalization to (C) N_2 activation and (D) M≡N functionalization.

2.2.1. Synthesis of (HBPB)Os(^{15}N)Cl_2 (**^{15}N-1**)

This was prepared by the same method starting with $[Bu_4N][Os^{15}NCl_4]$. HRMS (ESI): Calculated for $C_{19}H_{13}ClN_5{}^{15}NOs$ (M-Cl) 552.0397, found 552.0392. Elemental Analysis: Calculated for $C_{19}H_{12}Cl_2N_5{}^{15}NOOs$: C, 38.91; H, 2.06; N, 14.50. Found: C, 39.22; H, 2.03; N, 14.31. FTIR (ZnSe) in cm^{-1} = ν(Os≡^{15}N) 1063 (vs). UV–vis (DMF) [λ_{max} nm]: 317, 430.

2.3. Synthesis of (H_2BPB)OsCl_3 (**5**)



(2)

To a 50 mL Schlenk flask equipped with a reflux condenser and vacuum adapter, $(NH_4)_2OsCl_6$ (2.00 g, 4.56 mmol), 2,6-bis(benzimidazoyl)pyridine (1.42 g, 4.56 mmol, 1 eq.), LiCl (0.58 g,