ORGANOMETALLICS

Reactions of Organozinc Thiolates with Nitrosonium Ion: C-Nitroso Formation by Possible Transnitrosation

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Supporting Information



ABSTRACT: The organometallic complexes [ZnPAThEt] and [ZnPAThMes], where PATh is 2-methyl-1-[methyl-(2-pyridin-2-yl-ethyl)amino]propane-2-thiolate, were prepared and their reactions with NOBF₄ investigated. Formation of *C*-nitrosoethane and *C*-nitrosomesitylene, respectively, was established, and structural characterization of the latter by X-ray crystallography conclusively proved the dimeric nature of [MesNO]₂ in the solid state. A transnitrosation pathway for *C*-nitroso formation is proposed based on theoretical calculations.

T he importance of nitric oxide to the function of the immune, nervous, and circulatory systems has spurred interest in its chemistry¹ and that of its organic derivatives, including S-nitrosothiols,² organic nitrites, N-nitrosamines, and C-nitroso species.³ Recently, we described the reactivity of three zinc thiolate complexes (Chart 1, *a* and *b*) toward a

Chart 1. N₂S-Coordinated Zn²⁺ Complexes (a) [ZnPAThX] (X = Cl, OTf), (b) [ZnAPAThCl], (c) [ZnPAThEt], (d) [ZnPAThMes], and the S-Nitrosothiols PAThNO (e) and APAThNO (f)



variety of reactive nitrogen and oxygen species, including NO.⁴ We demonstrated S-nitrosation of the ligand upon exposure of [ZnPAThCl], [ZnPAThOTf], and [ZnAPAThCl] to NO₂(g), NOBF₄, or NO(g) and air but not to anaerobic NO(g). Analogous results had been reported for Zn^{2+} complexes containing monodentate thiolates.⁵ We also examined the behavior of the independently synthesized S-nitrosothiols

PAThNO and APAThNO in the presence of Zn^{2+} (Chart 1, *e* and *f*). Building on this work, we were interested to extend our studies to include organometallic analogues, specifically [ZnPAThEt] and [ZnPAThMes] (Chart 1, *c* and *d*), and in this report we describe their chemistry with NOBF₄.

Earlier reports and reviews⁶ describe reactions of nitrosonium ions with organometallic complexes of mercury,⁷ magnesium,⁸ tin,⁹ cadmium,¹⁰ lithium,¹¹ thallium,¹² silicon,¹³ aluminum,¹⁴ molybdenum,¹⁵ and chromium.¹⁶ The coordination chemistry of *C*-nitroso species has been explored,¹⁷ and reactions of alkylzinc complexes with nitric oxide have been exploited for nitrogen doping of ZnO films.¹⁸ Additionally, the chemistry of organozinc complexes with dioxygen, alcohols, and water has been examined,¹⁹ as well as with alkyl nitro and nitroso species.²⁰ A search of the literature did not uncover any study of the chemistry of organozinc compounds with nitrosonium ion, however, which contributed in part to the motivation for studies undertaken here.

Exposure of the protonated PAThH²¹ ligand to ZnEt₂ and ZnMes₂ afforded the desired organometallic species [ZnPAThEt] and [ZnPAThMes], respectively, in satisfactory yields. From X-ray-quality crystals the structures in Figure S1 (Supporting Information) were determined. The bond distances and angles in [ZnPAThEt] and [ZnPAThMes] are comparable to those reported for [ZnPAThMe].²²

Addition of [ZnPAThEt] to 1 equiv of NOBF₄ resulted in little change in the optical spectrum (Figure S2, Supporting Information). Similarly, little optical change occurred upon

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exposure of [ZnPAThMes] to 1 equiv of NOBF₄ (Figure S2). The headspace of the [ZnPAThEt]/NOBF₄ reaction mixture, analyzed by EI-MS, contained gaseous NO, butane, and NO₂ (Figure S3, Supporting Information) and indicated EtNO formation. EtNO is unstable and prone to decomposition along the pathway outlined in Scheme S1.²³ The presence of these gases suggests radical pathways for decomposition of [ZnPAThEt] in the presence of nitrosonium ion.

Difficulties in characterizing the nongaseous products of the $[ZnPAThEt]/NOBF_4$ reaction were overcome by examination of the related $[ZnPAThMes]/NOBF_4$ system. In this case, the C-nitrosomesitylene dimer, $[MesNO]_2$, could be isolated following treatment of [ZnPAThMes] with NOBF₄ in acetonitrile, quenching with water, and extraction into diethyl ether (Figure 1), a procedure that led to the formation of X-ray diffraction quality crystals.



Figure 1. Thermal ellipsoid plot of the *C*-nitrosomesitylene dimer, shown at 50% probability. The major component of the disordered molecule is shown. Hydrogen atoms have been omitted for clarity.

C-Nitrosomesitylene exists as a dimer in the solid state, with the two monomer units linked by an N–N bond (Figure 1). The distance between these symmetry-equivalent nitrogen atoms is 1.3248(15) Å. This value matches the 1.32 Å average N-N bond distance in dimeric C-nitrosoaryl compounds in the Cambridge Structural Database (CSD)²⁴ and is comparable to the 1.33 Å N-N average bond distance of C-nitrosoaryl species tabulated in reviewed work.²⁵ The monomer units are crystallographically related by an inversion center, located at the center of the N–N bond. The planar N(O)N(O) moiety in [MesNO]₂ subtends an angle of 73.70° with respect to the plane of the mesityl groups. This nearly perpendicular orientation prevents unfavorable steric interactions of the N(O)N(O) fragment with the methyl groups of mesitylene. The nitrogen atom of the nitroso group has an idealized trigonal environment, with angles of 121.44(15), 119.82(14), and 118.71(9)° at nitrogen. The N1-C1 and N1-O1 distances are 1.4615(12) and 1.263(3) Å, respectively, and are comparable to values of 1.44 and 1.26 Å for the N-C and N-O average bond lengths in C-nitrosoaryl species.^{24,25} The Cnitrosomesitylene dimer exhibits whole molecule disorder in the crystal lattice (Figure S4, Supporting Information), with the mesitylene moiety of the minor component tilting at an angle of 10.78° relative to the mesitylene moiety of the major component. The minor component accounts for $\sim 15\%$ of the electron density. The atomic displacement parameters for the atoms of the two components of the disorder were constrained to be equivalent in order to facilitate refinement of the structure.

The C-nitrosomesitylene dimer, $[MesNO]_2$, was isolated in 63% yield from the $[ZnPAThMes]/NOBF_4$ mixture after 2 h of reaction time. This yield is comparable to the reported 78%

recovery of [MesNO]₂ from the direct nitrosation of mesitylene with NOBF₄.²⁶ The comparable yield and shorter reaction time for the [ZnPAThMes]/NOBF₄ chemistry compared to the direct nitrosation of mesitylene by nitrosonium ion lead us to conclude that nitrosation is facilitated by mesitylene binding to Zn^{2+} .

Long-standing discussions in the literature regarding the structural properties of C-nitrosomesitylene in the solid state²⁷ are resolved with our determination of the [MesNO]₂ crystal structure. Historically, differences in color between C-nitroso compounds in solution and in the solid state generated interest in such species. The differences in color were attributed to monomer/dimer equilibria, which drew attention to the structural properties. In 1924, Ingold and Piggott proposed a ring structure for $[MesNO]_2$.²⁸ This hypothesis was revised in the 1930s to describe [MesNO]₂ as the N-N bonded dimer that we have crystallographically characterized in the present work.²⁷ Fenimore structurally characterized tribromonitrosobenzene in 1950, and he simultaneously reported the unit cell parameters of C-nitrosomesitylene.²⁹ He found that tribromonitrosobenzene exists as a dimer in the solid state, with the individual monomer units bound together through their nitrogen atoms. No interaction between the oxygen atoms of the monomers existed. In 1956, Nakamoto and Rundle used IR spectroscopy to conclude that nitrosomesitylene is a dimer in the solid state.³⁰ The structural characteristics of [MesNO]₂ described in this work conclusively confirm the dimeric structure of C-nitrosomesitylene in the solid state.

In pursuit of the zinc-containing products of the [ZnPAThMes]/NOBF₄ reaction, we combined a stoichiometric quantity of NOBF₄ with [ZnPAThMes] in a 2:1 MeCN:CH₂Cl₂ solvent mixture. Subsequent workup led to the isolation of crystalline [ZnPAThCl] (Figure S5, Supporting Information). This complex crystallized with a space group and unit cell parameters comparable to previously reported values.³¹ A ¹H NMR spectroscopic experiment revealed complete conversion of the coordinated mesitylene anion to C-nitrosomesitylene and ~60% conversion to [ZnPAThCl] (Figure S6, Supporting Information). The presence of additional species in the reaction mixture precluded kinetic analyses and mechanistic studies of the [ZnPAThMes]/NOBF₄ reaction.

We hypothesize that the nitrosation reaction takes place as outlined in Scheme S2, in which formation of [MesNO]₂ generates an unstable [ZnPATh]⁺ cation that abstracts chloride from methylene chloride. The presence of the poorly coordinating tetrafluoroborate anion appears inadequate to stabilize [ZnPATh]⁺. Similarly, previous attempts to recrystallize the triflate salt [ZnPAThOTf] from methylene chloride solutions resulted in isolation of [ZnPAThCI].³²

Our prior work on the interaction of S-nitrosothiols with Zn^{2+} complexes⁴ prompted us to consider the possibility that C-nitroso compounds might form in the reaction of [ZnPAThR] (R = Et, Mes) with NO⁺ through transient S-nitrosothiol formation. In particular, we wondered whether NO⁺ attack on [ZnPAThR] (R = Et, Mes) might initially occur at the sulfur atom of the PATh ligand, with subsequent C-nitroso formation following transnitrosation chemistry.

We used theory to probe aspects of the nitrosation reaction. In particular, we were interested to determine whether the initial site of nitrosation in the organometallic [ZnPAThR] complexes would be the metal-bound carbon atom or at sulfur, with *C*-nitroso formation occurring following transnitrosation. Theoretical calculations were performed to examine the atomic

orbital contribution to the HOMO of [ZnPAThEt] (Figure 2 and Figures S7 and S8 in the Supporting Information).



Figure 2. Highest occupied molecular orbital for [ZnPAThEt], calculated in the gas phase and visualized at an electron density isovalue of 0.06.

Comparison of natural atomic charges for [ZnPAThEt] reveals that partial negative charge density accumulates at both the sulfur and coordinated carbon atoms (Table S8). The contribution of the carbon atom to the HOMO increases with increasing solvent polarity (Figure S8), whereas the sulfur atom consistently makes a significant contribution to the HOMO, regardless of solvation. It is possible that C-nitroso formation might occur via transnitrosation following initial NO⁺ attack on the sulfur atom of [ZnPAThR] (R = Et, Mes) to form an Snitrosothiol, which then transfers NO⁺ to a coordinated carbon to generate the C-nitroso products (Scheme 1). Such a reaction pathway is supported by transition state and intrinsic reaction coordinate (IRC) theoretical calculations (Figure S9). A transition state for the attack of NO⁺ at the sulfur atom of [ZnPAThEt] was characterized by theoretical methods, and IRC analysis revealed that the formation of zinc-coordinated Snitrosothiol constitutes a feasible reaction pathway. Further experimental studies are required to investigate this possibility.

To summarize, exposure of [ZnPAThEt] to NOBF₄ led to formation of EtNO. When the analogous NOBF₄ reaction was performed with [ZnPAThMes], we were able to to trap *C*nitrosomesitylene as a stable product, which was isolated and characterized as a dimer in the solid state. When the [ZnPAThMes]/NOBF₄ reaction was performed in a 2:1 mixture of CH₃CN:CH₂Cl₂, the zinc-containing product isolated was [ZnPAThCl]. This result suggests that chloride abstraction may be effected by a transiently formed [ZnPATh]⁺ cation. Theoretical calculations were performed to analyze the character of the [ZnPAThEt] HOMO. The results of these calculations suggest possible attack by NO⁺ on [ZnPAThR] (R = Et, Mes) at sulfur, with *C*-nitroso formation by subsequent transnitrosation.

ASSOCIATED CONTENT

S Supporting Information

Experimental methods; thermal ellipsoid plots, crystallographic tables, and an analysis of structural properties for [ZnPAThEt] and [ZnPAThMes]; optical spectra of [ZnPAThEt] and [ZnPAThMes] reactions with NOBF₄; EI-MS data for the analysis of the headspace of the [ZnPAThEt]/NOBF₄ reaction; a depiction of thermal ellipsoid plots at 50% probability for [MesNO]₂, showing whole molecule disorder; crystallographic tables for [MesNO]₂; a thermal ellipsoid plot of [ZnPAThCl]; ¹H NMR spectra for the spectroscopic yield experiment for the [ZnPAThMes]/NOBF₄ reaction; a discussion of the formation and decomposition of EtNO; a proposed reaction pathway for the nitrosation of [ZnPAThMes]; a summary of computational results; a comparison of the HOMOs for the S.R and R.S configurations of [ZnPAThEt]; tables comparing experimentally and computationally determined structural parameters: a comparison of the effects of solvation on charge distribution and the composition of the HOMO of [ZnPAThEt]; an intrinsic reaction coordinate describing the interaction of [ZnPAThEt] with NO⁺; and XYZ matrices for all computationally determined species. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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Scheme 1. Possible Reaction Pathway for C-Nitroso Formation via Inter- or Intramolecular Transnitrosation in the Reaction of [ZnPAThR] (R = Et, Mes) with NO⁺



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