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Oxidative Addition Reactions of Bis-Aminophosphine and Bis-Phosphinite Nickel(0) Pincer Complexes

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Supporting Information

ABSTRACT: The tridentate ligands $S(CH_2CH_2NHPiPr_2)_2$ and $S(CH_2CH_2OPiPr_2)_2$ undergo C-S oxidative addition to give $(SCH_2CH_2EPiPr_2)$ -Ni $(CH_2CH_2EPiPr_2)$ (E = NH (2), O (4)). The corresponding reaction of the aminophosphine ligand HN $(CH_2CH_2NHPiPr_2)_2$ is reversible, affording access to a transient Ni(0) synthen that undergoes oxidative addition with HCl, MeI, or *o*-ClC₆H₄F to give the Ni(II) complexes [HN $(CH_2CH_2NHPiPr_2)_2$ NiR]X (R = H, X = Cl (7), PF₆ (8); R = Me, X = I (9); R = *o*-C₆H₄F, X = Cl (10)). These observations are supported via computations.



T ridentate ligand complexes have attracted great interest, as a vast array of possible variation affords uses in a broad range of applications, including sensors, switches, and catalysts.^{1,2} PCP² and PNP³ type ligands have garnered the most attention, demonstrating electronic and steric tunability, thus rendering highly reactive species stable.^{4–8} In addition, such complexes have displayed interesting reactivity, including oxidative addition of C-halogen bonds,^{7,9} C-H bond activation,⁶ N₂ activation, and homolytic cleavage of H₂.⁸ Much of this work has been described in a text.¹⁰

In seeking new systems for potential applications in catalysis, we are exploring a variety of new tridentate ligand systems. For example, we have recently developed strategies based on tridentate bis-phosphinimine ligands, demonstrating that such ligands afford both unique binding modes and the ability to access bimetallic systems.^{11–14} An alternative approach is based on the use of phosphine donor fragments derived from aminophosphines or -phosphinites. Such ligands are expected to be strongly donating, rendering the metal centers electron rich and thus potentially reactive. In this communication, we report reactions in which the ligands $D(CH_2CH_2NHP_iPr_2)_2$ (D = S, HN) are shown to undergo oxidative addition at Ni(0) to effect ligand cleavage. In the case of C-S bond activation (D =S) the formation of the resulting Ni alkyl-thiolate complex is irreversible. In contrast, for the ligand with D = NH the corresponding N-C activation is reversible, permitting access to Ni(II) products by addition of acid or an alkyl or aryl halide.

The tridentate ligand $S(CH_2CH_2NHPiPr_2)_2$ (1) is readily prepared in high yields from the corresponding diamine and $ClPiPr_2$. Subsequent reaction with Ni(COD)₂ in THF resulted in a clear orange solution from which a pale orange product (2) could be isolated in 83% yield. The ³¹P{¹H} NMR spectrum of 2 exhibited two doublets at 121.8 and 80.3 ppm with a P–P coupling constant of 270.0 Hz. These data suggest a trans disposition of inequivalent P atoms. ¹H NMR data included resonances from the ligand constituents; however, of particular note are the resonances at 1.21 and 0.97 ppm attributable to NH and NiCH₂ fragments. The corresponding ¹³C{¹H} signal for this latter group was observed as a doublet of doublets at 19.63 ppm with C–P couplings of 21.3 and 16.9 Hz. Collectively these data suggest the formulation of **2** as the Ni(II) species (SCH₂CH₂NHP*i*Pr₂)Ni(CH₂CH₂NHP*i*Pr₂) (Scheme 1). This was unambiguously confirmed by X-ray

Scheme 1. Synthesis of 2 and 4



methods (Figure 1). The pseudo-square-planar Ni center is bound to two trans phosphorus atoms and a C and an S atom. This gives rise to Ni–S, Ni–C, and Ni–P bond lengths that average 2.2019(8), 1.990(3), and 2.1750(9) Å, respectively.

In a similar fashion the ligand $S(CH_2CH_2OPiPr_2)_2$ (3) was prepared from 2,2'-thiodiethanol and was reacted with Ni(COD)₂ to give a light orange product (4) in 84% yield. Similar to the case for 2, the ³¹P{¹H} NMR spectrum of 4 showed two strongly coupled doublets as 187.00 and 152.91 ppm with a P–P coupling constant of 286 Hz. The ¹H and ¹³C{¹H} NMR spectra were also similar to those of 2, with

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Figure 1. POV-ray depictions of (a) 2 and (b) 4: C, black; S, yellow; N, aquamarine; O, red; P, orange; Ni, maroon. Hydrogen atoms are omitted for clarity.

multiplets at 1.13 and 23.12 ppm, respectively, attributed to a Ni-bound methylene fragment. Collectively these data were consistent with the formulation of 4 as the product $(SCH_2CH_2OPiPr_2)Ni(CH_2CH_2OPiPr_2)$ (Scheme 1). X-ray methods confirmed the pseudo-square-planar geometry about Ni (Figure 1). The Ni–S, Ni–C, and Ni–P bond lengths in 4 are 2.1881(4), 1.9873(15), 2.1537(4), and 2.1572(5) Å, respectively. These metric parameters are consistent with stronger Ni–P bonds and consequently slightly longer Ni–S and Ni–C bonds in 4 compared to 2.

The formation of 2 and 4 clearly result from the binding of the corresponding ligand to Ni(0) followed by oxidative addition of the S-C bonds. It is noteworthy that Yamamoto et al.¹⁵ have previously reported that the reaction of $Ni(COD)_{2}$ PEt₃, and Ph₂S proceeds to afford (Et₃P)₂Ni(SPh)Ph, while Darensbourg and co-workers have described light-induced dealkylation of sulfur in Ni(0) phosphine-thiolate complexes.¹ The noninnocence of pincer ligands in nickel complexes resulting in the cleavage of $C(sp^3)$ -heteratom bonds has recently received attention from Caulton and co-workers, who showed the cleavage of a Si-C(sp³) bond in their PNPNi system.^{17,18} However, to our knowledge this is the first intramolecular S-C cleavage affording a Ni-alkyl-thiolate derivative. It is reasonable to suggest that, in the present case, the initial interaction of the ligand with Ni(0) affords an approximately trans binding of phosphines, not unlike the the case for the known $(R_3P)_2Ni$ complexes.¹⁹ However, this geometry requires the proximity of the thioether fragment to Ni(0). This, in addition to the strong donor ability of the aminophosphine and phosphinite ligands, generates an electron-rich Ni(0) center, prompting oxidative addition of the S-C bond. Subsequent isomerization is required to generate the trans-phosphine disposition observed.

In order to probe this view of the reactions, a computational study was undertaken. Using Gaussian $03^{20,21}$ and the B3LYP-6-31g(d,p) basis set, the geometry of the three-coordinate Ni(0) species **2a** derived from the ligand **1** was optimized. The optimized geometry of this species was three-coordinate. Computation of the minimized pseudo-square-planar Ni(II),

in which S–C has undergone oxidation addition, afforded the model *cis*-2, which was computed to be 19.3 kcal/mol more stable than 2a. In considering the isomerization of *cis*-2 to *trans*-2, the tetrahedral transition state 2-TS was envisioned. Indeed, this geometry resulted in a single imaginary frequency and was found to be 7.6 kcal/mol above *cis*-2. *trans*-2 was also minimized and found to be 19.9 kcal/mol more stable than 2-TS. Thus, these calculations suggest that the observed geometry of 2 is some 31.6 kcal/mol more stable than that of a transient Ni(0) species generated from the combination of the ligand 1 and Ni(COD)₂ (Scheme 2a).

Scheme 2. Computed Energy Level Diagrams for Reactions of (a) 1 and (b) 5 with $Ni(COD)_2^a$



To further probe related systems, the analogous ligand $HN(CH_2CH_2NHPiPr_2)_2$ (5) was prepared in a conventional manner. The stoichiometric reaction of 5 with $Ni(COD)_2$ generated a red solution in THF. Monitoring this mixture by ³¹P NMR spectroscopy revealed a mixture of products that could not be separated. The major products consisted of a set of two resonances at 84.29 and 79.65 ppm which exhibited a P-P coupling constant of 10.3 Hz and a broad singlet at 65 ppm consistent with 5. In the corresponding ¹H NMR spectrum, a doublet of multiplets was observed at -1.42ppm, similar to that seen in 2 and 4, as well as resonances attributable to free COD. These data suggest similar reactivity involving C-N oxidative addition which generates inequivalent P environments. For comparative purposes computations analogous to those described above were performed for the interaction of 5 with $Ni(COD)_2$. In this case, the product of oxidation addition of a C-N bond to Ni to give cis-6 was also found to be more stable than that the corresponding Ni(0)species 6a; the difference in energy was only 12.8 kcal/mol. Isomerization of cis-6 to trans-6 requires an activation energy of 9.8 kcal/mol to reach a pseudotetrahedral transition state, 6-TS, but results in only a small gain in stability of 6.1 kcal/mol over 6a. These data support the view that the barriers to C-N activation and isomerization are low and suggest the possibility

that PNP ligands may undergo reversible C–N activation, thus accounting for the mixture of products.

To probe this possibility further, mixtures of 5 and $Ni(COD)_2$ were subsequently reacted with NEt_3HCl to give an orange solid (7) in 87% yield (Figure 2). The ³¹P{¹H} NMR



Figure 2. Synthesis of 7-10 and POV-ray depictions of the cations of 7/8 and 10.

spectrum of 7 revealed a single resonance at 80.00 ppm, while the ¹H NMR exhibited a triplet resonance at -20.90 ppm with a P-H coupling of 81.2 Hz attributable to a Ni hydride. Collectively the NMR data were consistent with the formulation of 7 as the diamagnetic Ni(II) complex [HN- $(CH_2CH_2NHPiPr_2)_2NiH$]Cl. While simple anion exchange affords the species [HN(CH₂CH₂NHP*i*Pr₂)₂NiH]PF₆ (8), 8 can be prepared directly from the reaction of $[NH_4][PF_6]$ with the Ni(0) mixture. In a similar fashion, addition of MeI to a mixture of 5 and Ni(COD)₂ afforded the analogous Ni(II) species [HN(CH₂CH₂NHP*i*Pr₂)₂NiMe]I (9) in 79% yield. This species exhibited a single ³¹P signal at 72.4 ppm, while the ¹H NMR triplet at -0.79 ppm, which showed a P-H coupling of 10.8 Hz, was consistent with the presence of a Ni-Me fragment. Previous work in our group has shown that the addition of o-ClC₆H₄F to a mixture of Ni(0) and tridentate phosphinimine ligands yields the nickel aryl complex.^{11,12} In an experiment akin to those, the addition of o-ClC₆H₄F to the Ni(0) mixture led to the isolation of [HN- $(CH_2CH_2NHPiPr_2)_2Ni(o-C_6H_4F)]Cl$ (10) in 86% yield. The 19 F NMR spectrum of 10 shows resonances at -84.11 and -84.23 ppm, while the ³¹P{¹H} NMR spectra gave rise to signals at 70.58 and 69.53 ppm. These data, together with analogous ¹H NMR data were consistent with the presence of a 50:50 mixture of the two conformational isomers, attributable to the relative orientation of the o-F and the NH fragments.

The formulations of 8 and 10 were confirmed via a crystallographic study (see the Supporting Information). Each of these compounds exhibited the expected pseudo-square-

planar geometries, with the ligand **3** acting as a tridentate chelate. Thus, it appears that the low energy barrier to the reversibility of the ligand N–C oxidative addition in **6a** generating *cis*-**6**/*trans*-**6** provides access to the Ni(0) species **6a**. This species is irreversibly oxidized to give the Ni(II) species **7–10**. Consistent with this view are computations which suggest that the reaction of the Ni(0) species **6a** with *o*-ClC₆H₄F to give the Ni aryl Cl complex **10** is thermodynamically downhill by 40.9 kcal/mol.

While the oxidation of Ni(0) to Ni(II) hydrides, alkyls, or aryls is well documented in the literature, $^{16,22-25}$ the present reactions of **5** with Ni(COD)₂ illustrate examples where reversible oxidative addition of a ligand, combined with oxidative addition of HX, RX, or ArX, permit access to the more thermodynamically stable Ni(II) products, in which the tridentate nature of the ligand is retained.

In summary, tridentate bis-aminophosphine and bis-aminophosphinite ligands 1 and 3 undergo oxidative addition with Ni(0). In the case of these thioether ligands, the C–S cleavage is irreversible, providing unique Ni(II) alkyl-thiolate complexes. In contrast, the analogous pathway for the corresponding C–N cleavage of the amine-based ligand **5** is inferred to be reversible, allowing the Ni(0) synthons to provide a convenient route to Ni(II) cations via oxidative additions. The chemistry of transition-metal complexes of these electron-rich tridentate ligands continues to be the subject of study in our laboratories.

ASSOCIATED CONTENT

Supporting Information

Figures, tables, and CIF files giving synthetic, experimental, and crystallographic details. 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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