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O/C Bond Cleavage of CO_2 by Ni^I

Benjamin C. Fullmer, Hongjun Fan, Maren Pink, and Kenneth G. Caulton*

Department of Chemistry and Molecular Structure Center, Indiana University, Bloomington, Indiana 47405

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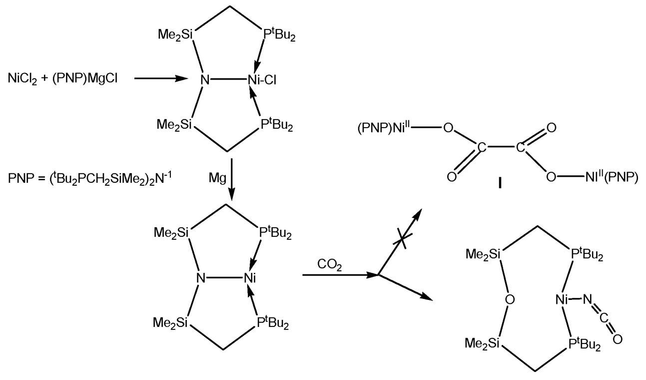
Reaction of (PNP)Ni, where PNP is $[(^tBu_2PCH_2SiMe_2)_2N]^{-1}$, with CO_2 occurs rapidly even at −60 °C to form exclusively the product of transposition of the amide N and one CO_2 oxygen: $[(^tBu_2PCH_2SiMe_2)_2O]Ni(NCO)$. DFT(B3LYP) evaluation of several candidate intermediates for breaking two Si/N and one C/O bond and forming two Si/O and one N/C bond reveal species at and below the energy of the separated particles, and establish the location of the spin densities in each.

The molecule (PNP)Ni,[1] where PNP is $[(^tBu_2PCH_2SiMe_2)_2N]^-$ is a relatively rare example[2–8] of Ni^I, with the same d^9 configuration as Cu^{II} but augmented by reducing power (Ni^{II} is a highly plausible redox product) and with a remarkably low coordination number (3) and unusual geometry (T-shaped). We were hopeful that this molecule could accomplish unusual transformations of refractory substrates and turned to CO_2,[9] precisely because Ni^I would appear to be only a one-electron reductant, and yet CO_2^- is a thermodynamically unattractive product.[10,11] The possibility that this radical anion could find metastability bound in end-on, C-bound or η^2-bound modes to $(PNP)Ni^+$ interested us, but we also anticipated a possible radical coupling reaction that would make oxalate, $C_2O_4^{2-}$ (**I**, Scheme 1), in a diamagnetic Ni complex.

Scheme 1



The reaction[12] of (PNP)Ni with excess (1 atm) CO_2 occurs to completion in time of mixing in benzene at 23 °C to give a single product (97% NMR yield). The absence of a ^{31}P NMR signal and the ^1H NMR chemical shift intensities and values of the product (54.0, 4.73, and 0.93 ppm) indicate it to be paramagnetic and to have C_{2v} symmetry. The SiMe proton chemical shift (0.9 ppm at 25 °C) obeys the Curie law (T^{-1}) over the temperature range −50 to +25 °C. The IR spectrum of the product in pentane has an absorption at 2209 cm^{-1}, which is extremely high for a C═O (double) bond, unless it is part of a cumulene (the asymmetric stretch of free O═C═O is 2349 cm^{-1}). Thus, we suspected that the product might involve a linear Ni←O═C═O structure.[13,14]

Yellow crystals (grown by slow evaporation from toluene) reveal a remarkable and unanticipated character to the reaction. The product (Figure 1) is indeed monomeric, but the ligand N and one O atom of CO_2 have been transposed, to give $[O(SiMe_2CH_2P^tBu_2)_2]Ni^I(NCO)$, containing N-bound cyanate. This explains the IR frequency because the C═O bond is strongly coupled to an N═C bond in the cumulene NCO^-. The thermodynamic driving force for this reaction is the formation of two Si−O bonds, and the resulting bis-silyl ether is too weak a donor to bind to Ni (Ni/O separation = 3.045 Å). The O atom potentially trans to N does not even lie in the $NNiP_2$ plane. The geometry at Ni in the

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* To whom correspondence should be addressed. E-mail: caulton@indiana.edu.

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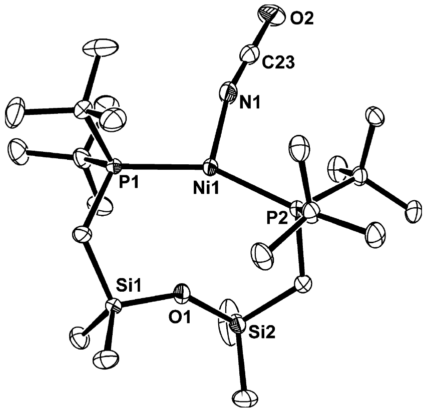

Figure 1. ORTEP drawing (50% probabilities) of the non-H atoms of [O(SiMe$_2$CH$_2$P^{t}Bu$_2$)$_2$]Ni^I(NCO), showing selected atom labeling. Unlabeled atoms are C. Selected structural parameters: Ni−N1, 1.9407(13) Å; Ni−P1, 2.2660(4) Å; Si1−O1, 1.6435(10) Å; N1−C23, 1.160(2) Å; C23−O2, 1.2070(18) Å; $\angle$P1−Ni−P2, 149.745(14)°; $\angle$N1−Ni−P1, 104.61(4)°; $\angle$C23−N1−Ni, 165.84(13)°; $\angle$N1−C23−O2, 179.68(19)°; $\angle$Si1−O1−Si2, 141.93(6)°.

product is thus unchanged, from that in (PNP)Ni, and this is a rare example of a bidentate ligand spanning trans positions. There are no agostic interactions (all Ni/C distances exceed 3.44 Å), and the linear cyanate ligand shows $\angle$Ni−N1−C23 = 165.84(13)°. The result is that the Ni oxidation state is unchanged, at Ni^I, and the reaction chemistry is that of nucleophilic amide[15–19] interacting with the electrophilic CO$_2$ carbon.

So many bonds are broken and made in this reaction that the mechanism is certainly multistep. In search of some experimental evidence on intermediates, we combined the two reagents at −80 °C in toluene, mixed quickly with minimum temperature rise, and then recorded ^{1}H NMR spectra. Already at −60 °C, the reaction has gone to completion, to give the product in Figure 1 with no detectable intermediate.

In spite of the overall lack of redox change at the metal, the need to develop more nucleophilic character at the CO$_2$ oxygen suggests possible electron transfer from Ni at an intermediate stage of the mechanism. This could then enable the poorly nucleophilic O atom of free CO$_2$ to effect nucleophilic attack on tetrahedral Si. We began a density functional theory (DFT; B3LYP) study[12] of this question (Figure 2) with a candidate intermediate that forms two new bonds (**A**), one of which (N−C) will persist in the product. This has lost its Ni−N bond, in order to have typical angles around the C sp^2 (C5 in Figure 2), and the coordination geometry at Ni is again found to be T-shaped, with an unexceptional Ni−O distance. The C5−N2 distance indicates a single bond because the amine lone pair is orthogonal to the p$_\pi$ orbital on C5. Both C5 and N2 are coplanar with their three substituents. The electronic energy of this species (Figure 2) is comparable to that of the separated molecules, and hence readily accessible, even if not *more* stable.

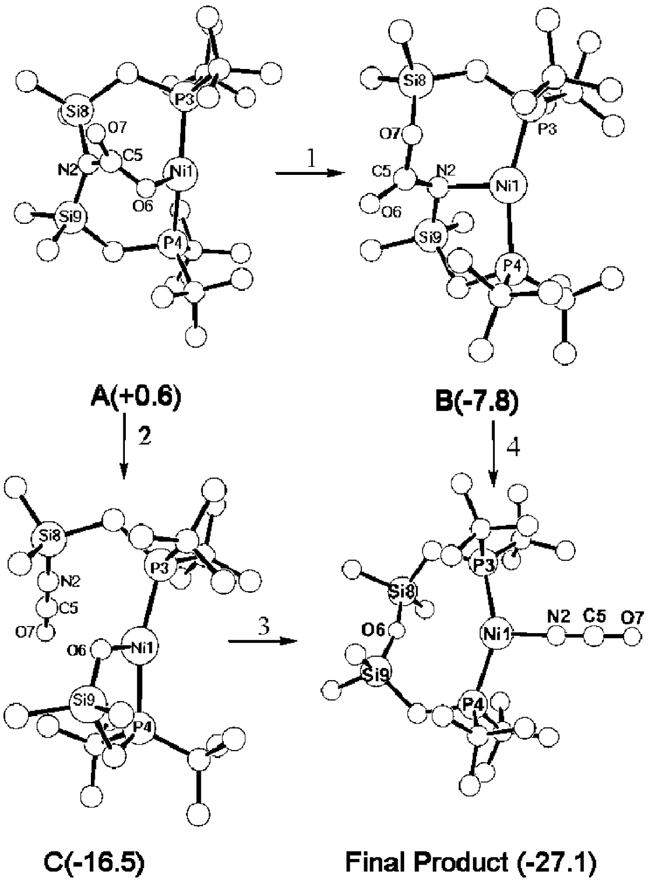

Figure 2. DFT structures and electronic energies (kcal/mol relative to separated particles (PNP)Ni and CO$_2$) of candidate intermediates and of the final product [O(SiMe$_2$CH$_2$P^{t}Bu$_2$)$_2$]NiNCO.

From **A**, it is necessary to begin forming Si−O bonds. Species **B** does this by migrating (step 1, Figure 2) one Si to O7, which forms Ni−N2 and Si8−O7 bonds and breaks Si8−N2 and O6−Ni bonds. This is silyl migration to O(sp^2) (terminal on C5). Ni in **B** is again T-shaped, C5 is planar, and N2 is pyramidal (the angle sum is 340.9°). This species is more stable than **A** by 8.4 kcal/mol.

An alternative rearrangement of **A** (step 2, Figure 2) breaks the N2−Si9 and C5−O6 bonds and forms an Si9−O6 bond (**C**); this is silyl migration to nucleophilic O(sp^3). This assembles one chelate ligand and produces a silyl cyanate, and Ni is again T-shaped. This species is more stable than **B** (16.5 kcal/mol below separated particles). Calculated bond lengths involving Ni, N, C, and O in the final product agree with the experimental ones within 0.04 Å, and angles are also satisfactorily modeled.

The spin density is 95% on Ni in all three intermediates described above, as well as in the final product, so the reaction is not driven directly by metal-to-ligand *single* electron transfer, although this more electron-rich metal (d^9) will certainly increase ligand O nucleophilicity by metal-to-ligand three- or four-electron repulsions,[20] thereby promoting silyl migrations. The fact that all Ni d orbitals, which

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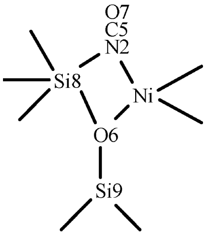
might accept π density from the silylamide N, are filled in (PNP)Ni establishes that the amide, or at least the Si_2N-Ni bond, is highly electron-rich. This nucleophilic character of late-transition-metal amides has considerable precedent.[15–19]

Conversion from **C** to the product (step 3, Figure 2) involves nucleophilic attack of O6 on Si8, perhaps via a transition state **D**. This species, even if it involves an activation energy as large as 15 kcal/mol, will be in satisfactory agreement with our low-temperature NMR observations. Alternatively, but perhaps less likely, from **B** to the product (step 4, Figure 2) involves attack of O7 on Si9. The overall reaction energy to the product is calculated as −27.1 kcal/mol. For comparison, the energy of the separated NCO radical and (linear) two-coordinate (POP)Ni^0 is so high (+60.3 kcal/mol) that this can be ruled out as a reaction intermediate (e.g., formed from intermediate **C**).



D

In summary, it is a curiosity that Ni reacts more as an amide nucleophile than as a reducing agent toward CO_2 and that *both* silyl groups of the ligand show a pronounced tendency to migrate to the same CO_2 oxygen of some reduced coordinated CO_2. The reaction is not dominated by any attempt from Ni to achieve a higher coordination number (none was found in spite of starting geometries that might have led to these) or by oxidation of Ni^I. The reaction is fast and selective for the cyanate product, and reducing equivalents remain at the metal in the product obtained. While nucleophilicity of amide N should increase for higher d electron counts, it is noteworthy that d^8 (PNP)Co[21] is recovered unchanged after 12 h at 23 °C under 1 atm of CO_2. Singlet-spin-state (PNP)NiCl is similarly unreactive.

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Supporting Information Available: Complete experimental and computational details and a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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