Nickel(II) Complexes

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$[Ni\{N(SiMe_2CH_2PtBu_2)_2\}]^+$: Direct Observation of Transannular Si–C(sp^3) Bond Coordination**

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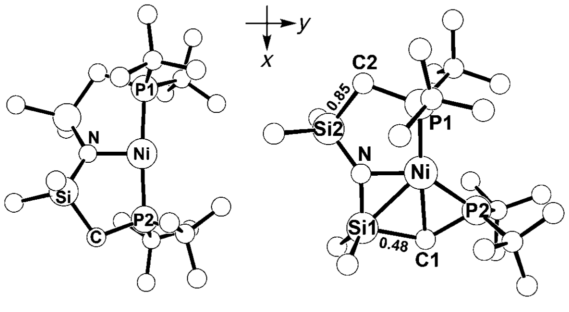
Molecules with four-coordinate d^8 metal centers adopt a planar geometry, which helps to mask their unsaturation by putting the empty orbital in the coordination plane and along the dative bonds; this arrangement places the lowest unoccupied molecular orbital (LUMO) at high energy. As it is empty, it is then less destabilizing. Geometric distortion is thus required when a nucleophile adds to such an unsaturated metal center. One solution to unmasking the Lewis acidity of such a species is to open one of the four in-plane coordination sites by ligand loss. This has been the goal of a number of efforts[1–12] to catalyze coupling of polar organic substrates. In exploring a precursor to $[(PNP)Ni]^+$ (PNP is the tridentate ligand $[(tBu_2PCH_2SiMe_2)_2N]^{-1}$), which is just such an electrophilic species, we found that halide abstraction from [(PNP)NiCl][13] with $NaBAr^F_4$ ($Ar^F = 3,5\text{-}(CF_3)_2C_6H_3$) yielded surprising results which bear on the electrophilicity of a possible T-shaped three-coordinate Ni^{II} cation.[1,4,5,7,14,15]

The product from the reaction[16] of anhydrous $[Cp^*_2Fe]B(C_6F_5)_4$ ($Cp^* = C_5Me_5$) with [(PNP)Ni][13] in THF shows several unanticipated features. The lack of a signal in the $^{31}P\{^1H\}$ NMR spectrum was especially puzzling, since the signals in the ^1H NMR spectrum were not in a chemical shift region characteristic of a paramagnetic species. Within a few hours, the solution turned highly viscous, owing to polymerization of THF.[17] In contrast, reaction of equimolar amounts of [(PNP)NiCl] and anhydrous $NaBAr^F_4$ in CH_2Cl_2 during vigorous agitation at 25 °C over a period of 1 h gives a color change from red to orange-brown. Vacuum removal of solvent, washing the solid with pentane, and vacuum removal of volatile components to solidify the resulting oil gives a product which dissolves in CD_2Cl_2 to show signals in the ^1H NMR spectrum in the normal diamagnetic chemical shift region but still no signal in the $^{31}P\{^1H\}$ NMR spectrum. The ^1H NMR spectrum shows two aryl chemical shifts, consistent with *ortho* and *para* positions of BAr^F_4, an apparent doublet for the *t*Bu group, a SiMe singlet, and a broad signal at $\delta = -0.22$ ppm for the CH_2 protons. In spite of the absence of any signal in the $^{31}P\{^1H\}$ NMR spectrum in CD_2Cl_2 at 25 °C, at −40 °C there are already two very broad signals at $\delta = 41$ and 102 ppm, and these progressively sharpen upon lowering the temperature to −50 °C. This behavior indicates that the species is diamagnetic, that it is fluxional, and that the ground-state structure has inequivalent phosphorus sites. At 25 °C, the coalescence temperature has been reached; thus, the signal is undetectably broad. Fluxionality is also the cause of the deceptively simple ^1H NMR spectrum described above, although these signals remain coalesced at −60 °C. The two ^{31}P chemical shifts are very different, suggesting very different chemical environments for the two phosphorous atoms. Spectra at −55 °C show a coupling constant $J_{PP'} = 38$ Hz. For comparison, two transoid P atoms in a $[(\eta^3\text{-PNP})M]$ complex normally show $J_{PP'} > 250$ Hz. This observed coupling rules out π coordination of one BAr^F aryl ring, which would imply one pendant, noncoordinating phosphine arm (for which $^6J_{PP'} = 0$ is expected). The ^{19}F NMR spectrum of this compound in CD_2Cl_2 shows only one signal, and only one ^{19}F NMR signal is seen if $NaBAr^F_4$ is added to the NMR sample; all of this data is consistent with a lack of interaction between $[(PNP)Ni]^+$ and the borate anion.

We sought to learn how the structure of $[(PNP)Ni]^+$ can have inequivalent phosphorus donors. DFT(PBE) calculations[16] on several candidate structures revealed some surprises (Figure 1). Three-coordinated T-shaped $[(PNP)Ni]^+$ was found as both singlet and triplet states, with the singlet state (**A**) only 3.6 kcal mol^{-1} less stable than the triplet state (all energies here are electronic energies). This singlet-state energy makes this species thermally accessible for reactivity purposes. In searching for alternative minima, we obtained structure **B** (Figure 1), which lies 3.9 kcal mol^{-1} lower than the T-shaped triplet state. The seemingly unconventional struc-



A (+7.5) **B** (0.0)

Figure 1. DFT geometry-optimized structures (**A**, **B**) of singlet isomers of "$[(PNP)Ni]^{+}$" showing electronic energies in kcal mol^{-1}. Hydrogen atoms are omitted. Mayer bond orders are shown in **B**; others are Ni–C1 0.54, Ni–C2 0.02, Ni–Si1 0.19, Ni–Si2 0.01.

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tural features of this species are five-coordinate silicon and carbon. At 2.22 Å, the Ni−C1 separation is certainly short enough to indicate bonding. This finding explains the negative chemical shift for these protons, which is also found in Ni−CH_2 and Ni−CH_3 moieties. The C1−Si1 separation has lengthened by 0.16 Å compared to the other C−Si bond in this structure, and the Si1-C1-P2 angle is large (135°). The Ni-P2-C(*t*Bu) angles are all very large (122°), indicative of distortion of bonding at P2. Mayer bond orders, shown in Figure 1, support the idea that short distances involve chemical bonding: the species is a σ_{Si-C} complex.[18–22] It appears that phosphorus in this structure has moved and reoriented its lone pair to overlap better with the lobe of the empty $d_{x^2-y^2}$ orbital that lies along the y axis (*trans* to nitrogen); in doing so, it pulls both the Si atom and the CH_2 group closer to nickel, which represents donation from the Si−C bond electron density to the lobe of the nickel $d_{x^2-y^2}$ orbital directed along the x axis. Thus the phosphorus lone pair seeks out the best direction for overlap and is not simply pointed towards the metal nucleus. Symptomatic of this lone-pair orientation is the fact that P2 is nearly coplanar with the nickel center and the two *t*Bu quaternary carbon atoms. In summary, the calculated ground-state structure of singlet "$[(PNP)Ni]^+$" involves a highly activated Si−CH_2 bond (stretched to 2.07 Å from 1.91 Å for Si2−C2). The nickel center in this cation is thus highly electrophilic, and it recruits typically unreactive Si−C σ bonding density to serve as a donor. This transannular interaction of a σ bond has its precedents,[23–31] all of them in complexes of d^0 electropositive metals (Ti, Zr, lanthanides) and all showing Si−C bond lengths stretched from 1.90 to not more than 2.01 Å and none being in a ring (e.g. they are M−C($SiMe_3$)R_2).

The conclusions from this computational investigation of $[(PNP)Ni]^+$ were subsequently confirmed by an X-ray structure determination of the product $[(PNP)Ni]BAr^F_4$ crystallized from fluorobenzene (Figure 2, Scheme 1). In this structure, the Ni center shows short contacts to a CH_2 carbon atom and one Si atom, and the corresponding Si−C bond is lengthened. The unusual Ni-P-C(*t*Bu) angles from the DFT study are also confirmed, which means that the threefold axis of this phosphorous donor is not directed towards the metal center but towards the open orbital of T-shaped $[(PNP)Ni]^+$. The short contacts to the Ni center come at the expense of an unusual Ni-N-Si1 angle (89.3°). The observed fluxionality is then naturally explained by rapid reversal of the roles of the two phosphine arms at room temperature via **A** (see movie of computed motion in the Supporting Information). The small observed $J_{PP'}$ value is due to these two nuclei being far from 180° apart in **B**. A search for a transition state for this fluxional process showed it to lie 11.9 kcal mol^{-1} above the σ_{Si-C} complex **B**, consistent with the observed rate of the fluxionality. At this transition state, the Ni−C1 separation is elongated by 0.69 Å, and the P1-Ni-P2 angle has increased by 28°. It is noteworthy that this Si−C bond donation is energetically preferred to any C−H agostic donation or coordination of fluorobenzene, or to ligand *t*Bu C−H cleavage, either heterolytic (H migrating to amide N) or by oxidative addition to metal. DFT calculation showed that a *t*Bu-agostic $[(PNP)Ni]^+$ isomer is a stationary point, but it lies 5.9 kcal mol^{-1} higher in energy than **B** (Figure 1) owing to strain in getting that methyl group near (Ni−H 2.03 Å) to the nickel center, and with a large ∢(Ni-H-C) = 118.7° (i.e. very little Ni−C interaction). The Ni−N separation (Figure 2) is 0.06 Å shorter than in [(PNP)NiCl].[13]

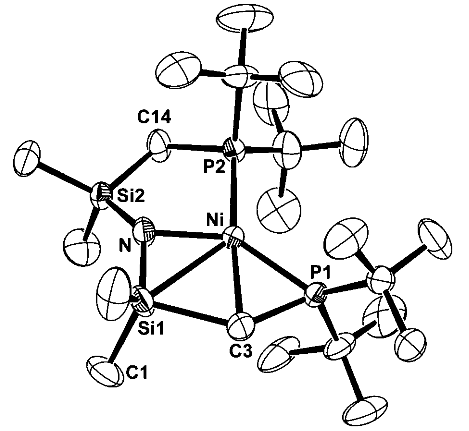
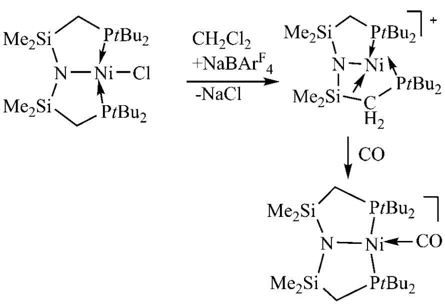


Figure 2. ORTEP view of the structure of $[(PNP)Ni]^+$ as its $BAr^F{}_4^-$ salt. Thermal ellipsoids are set at 50% probability; hydrogen atoms are omitted for clarity. Unlabeled atoms are carbon. Selected structural parameters: Ni–N 1.866(2) Å, Ni–P1 2.1201(8), Ni–P2 2.23(2), Ni–C3 2.158(3), Ni–Si1 2.494(2), Ni–Si2 3.135(1), Si2–C14 1.854(6), Si1–C3 2.069(4), C3–P1 1.840(3), C14–P2 1.818(17); P1-Ni-P2, 124.6(6), Si1-N-Ni 89.27(13), Si2-N-Ni 122.81(14), N-Si1-C3 103.92(16), P1-C3-Si1 135.50(18).



Scheme 1.

To evaluate the electrophilicity of this nickel center and the reactivity of the unusual ground-state structure, we added CO to $[(PNP)Ni]BAr^F_4$. Consistent with the fast fluxionality passing through species **A**, this reaction occurs in the time of mixing in CD_2Cl_2, with bleaching from orange-brown to pale yellow, to give a species identified as $[(PNP)Ni(CO)]^+$. This compound shows ^1H and $^{31}P\{^1H\}$ NMR spectra consistent with C_{2v} symmetry, hence the compound is planar and four-coordinate. The IR spectrum of this product shows a stretching frequency at 2044 cm^{-1}, consistent with[32] a carbonyl complex with minimal back-bonding (compare to 2036 in d^0 $[Cp^*_2Hf(H)_2(CO)]$,[33] 2119 in $[(imine)_3Cu(CO)]^+$,[34] or 1940 cm^{-1} in $[(PNP)Ni(CO)]$[13]), and also showing the ready ability of the complex to reverse the donation of the Si−C bond to nickel.

In T-shaped $[(PNP)Ni]^+$, the amide nitrogen lone pair finds no empty d orbital of suitable symmetry in which to relieve the electrophilicity of the Ni^{II} center. The LUMO is $d_{x^2-y^2}$, which then leaves only the (relatively improbable) ligand σ-bond electron density in the molecular plane to donate, as observed in the unusual calculated structure and subsequently established experimentally. For comparison, the isoelectronic molecule [(PNP)Co][35] persists in the T-shaped geometry, because the ground state for [(PNP)Co], in spite of its even electron count, is a triplet with a large (21 kcal mol^{-1}) S–T gap; there is no empty orbital to attract the Si–C bond, in contrast to the nickel(II) analogue. The spin state is apparently influential here, and it is controlled by larger d-orbital splitting for the divalent metal than for Co^{I}. This idea is supported by our geometry optimization of triplet [(PNP)Ni]$^+$ beginning at a geometry in which both the Si atom and the CH_2 carbon atom are within bonding distance of the nickel center; this arrangement optimized to the T-shaped triplet discussed above. Likewise, d^9 [(PNP)Ni][13] has no completely empty $d_{x^2-y^2}$ orbital to coordinate the Si–CH_2 bond, and in fact this molecule shows no such structure. The present work suggests[12,36] that d^8 T-shaped cations (e.g. Pd^{II} or Au^{III}) will in general have exceptional structures and perhaps reactivities, including binding even very weak nucleophiles.

CCDC-689289 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

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