Inorg. Chem. **2008**, *47*, 407–409

Inorganic Chemistry
Communication

Influence of the d-Electron Count on CO Binding by Three-Coordinate $[(^tBu_2PCH_2SiMe_2)_2N]$Fe, -Co, and -Ni

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Received December 6, 2007

Reduction of (PNP)MCl [PNP = $(^tBu_2PCH_2SiMe_2)_2N$] with Mg gives three-coordinate, T-shaped (PNP)M for M = Fe($S = {}^3/_2$) and Ni. Their reactivity was tested toward CO; Ni binds one CO, but only reversibly (i.e., CO is completely lost in vacuum), and has a CO stretching frequency showing effective back-donation by Ni^I. The structure of (PNP)Ni(CO) is intermediate between planar and tetrahedral, in contrast to the planar d^8 analogue, (PNP)Co(CO). This structural reorganization on carbonylation changes the singly occupied molecular orbital from having negligible phosphorus character [no P hyperfine structure in the electron paramagnetic resonance (EPR) spectrum of (PNP)Ni] to having enough P character to have a triplet structure in the EPR spectrum of the CO. The presence of one fewer electron in (PNP)Fe (vs the Co analogue) leads to binding of two CO, and $(PNP)Fe(CO)_2$ is characterized as a spin doublet with square-pyramidal structure. Density functional theory calculations strengthen the understanding of the structural and spectroscopic changes along this d^n series ($n = 7$–9).

π donation, from a lone pair on a donor atom already bound to the metal (e.g., $R_2N \rightarrow M$), is a way to temporarily “stabilize” metal unsaturation while simultaneously enhancing the reducing power of the low-valent metal center. The Fryzuk class[1–5] of ligands $(R_2PCH_2SiMe_2)_2N^{-1}$, PNP, satisfies a number of needed criteria and offers some systematic steric tuneability via the group R. We report here the pursuit of low coordination numbers for the late elements of the first transition series, chosen in part because the 3d metals are more tolerant of one-electron redox changes than are the 4d and 5d congeners studied earlier.[6] The other major difference between 3d vs 4d and 5d metals, the occurrence of more than the minimum number of unpaired electrons, also features prominently here. The effect of sequential addition of electrons across the transition series can be most dramatic for the higher d electron counts, where empty d orbitals are becoming scarce and where the effect, on ligand binding, of *half*-filling a d orbital can be established. With the publication[7,8] of a 14-valence electron, T-shaped, three-coordinate d^8 Co^I complex, (PNP)Co, we were interested in the possibility that we could produce Fe and Ni analogues. Both would be unusual oxidation states for those metals, and each is a radical, thus beyond the domain where the 18-electron rule applies. We report here on the synthesis of (PNP)M (M = Fe and Ni) and their ability to bind CO and contrast that to the triplet ground state of (PNP)Co.

The reaction[9] of anhydrous MCl_2 (M = Fe and Ni) with ClMg(PNP) in tetrahydrofuran (THF) yields (PNP)MCl. Each of these is reduced at 22 °C in THF by magnesium powder (or by a stoichiometric amount of sodium naphthalide) to yield three-coordinate (PNP)M. This low coordination number and geometry is rare for these metals.[10–19] Neither shows ^{31}P NMR spectra in C_6D_6, due to rapid relaxation from paramagnetism of these d^7 ($S = {}^3/_2$) and d^9 species, but each shows three ^{1}H NMR signals, due to ^{t}Bu, SiMe, and CH_2 protons. None of these molecules binds the THF solvent, a

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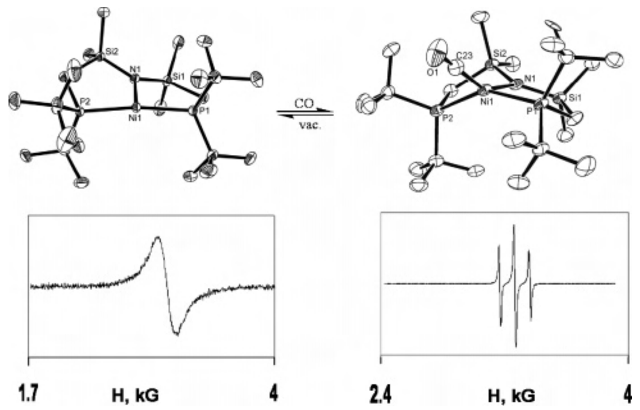

Figure 1. Carbonylation equilibrium of (PNP)Ni and observed X-band EPR spectra (25 °C, toluene) of the associated molecules, showing (lower right) coupling ($A = 97$ G) to two P for (PNP)Ni(CO).

fact confirmed by X-ray diffraction.[9] While (pincer)M species have been postulated as reactive transients for M = Rh and Ir, none has been detected,[20−23] and (PNP)Co is a triplet,[8] in contrast to expectations for its heavier congeners. Although the Fe and Ni examples, crystallized in the same way, adopt different space groups, their MP_2N cores are very similar (Figure 1).

With a d^9 configuration, (PNP)Ni is an analogue of Cu^{II}, but with reducing power. Although three-coordinate Cu^{II} is unknown, there are no known CO complexes of Cu^{II}, and even monovalent Cu has very poor back-bonding ability toward CO, as demonstrated by generally poor binding equilibrium behavior,[24] as well as by CO stretching frequencies reduced very little from that of free CO (2140 cm^{-1}). Nevertheless, CO binds to (PNP)Ni, to give an adduct whose ν_{CO} value, 1940 cm^{-1}, shows moderate back-bonding from Ni^{I}. However, removal of volatiles (including dissolved CO) from a solution of (PNP)Ni(CO) results in complete reformation of (PNP)Ni. The DFT(B3LYP) reaction energy for binding CO to (PNP)Ni is only −8.1 kcal/mol, fully consistent with a $\Delta G°$ of binding of near zero, in agreement with experiment. Crystals of the adduct can be grown from pentane, and the structure (Figure 1) shows marked contrast to the planar structure of (PNP)Co(CO). The Ni complex has a nonplanar NP_2Ni skeleton [$\angle$P−Ni−P = 149.59(4)°], with the other ligands bent in a complementary fashion [$\angle$N−Ni−C = 148.50(15)°] to produce a flattened tetrahedral coordination geometry (145° is the angle half-way between tetrahedral and planar). Note that many $CuCl_4^{2-}$ structures are similarly "intermediate".[25−27]

Consistent with its structure, the electron paramagnetic resonance (EPR) spectrum of (PNP)Ni shows three g values at 77 K with no ligand hyperfine structure resolved at both 77[9] and 298 K (Figure 1), while (PNP)Ni(CO) shows coupling (triplet structure) at low temperature, due to two equivalent P. This stark difference is explained by the character of the singly occupied molecular orbital (SOMO) of each species from DFT(B3LYP) calculations (Figure 2) at their optimized geometries: there is negligible P character in the SOMO of (PNP)Ni (nickel spin density = 0.93), while that of the CO has contributions which give a spin density at P totaling 0.11 (at Ni, 0.78). Both have amide N participation (~0.05) in the SOMO, and the SOMO of (PNP)Ni (Figure 2b) is a mainly Ni orbital directed into the open site trans to N. This forces CO binding away from that trans site, which is possible because the lowest unoccupied molecular orbital (LUMO) of (PNP)Ni (Figure 2d) is Ni p_z, attracting arriving CO out of the N_2PNi plane and able to hybridize with the in-plane occupied orbital as the PNP distorts away from planarity; this is the origin of the nonplanar structure of (PNP)Ni(CO). Nevertheless, the SOMO of the carbonyl complex is antibonding between Ni and both CO and N (Ni−N lengthens by 0.01−0.03 Å upon carbonylation), reflecting the electron excessive character of this Ni^{I} species, as well as the observed easy loss of CO. An underlying factor is d orbital contraction for Ni, which is detrimental to orbital overlap, especially π overlap.

The reaction of (PNP)Fe with CO (1 atm) in pentane gives complete conversion to a molecule characterized by X-ray diffraction[9] as $(PNP)Fe(CO)_2$; equimolar CO gives only 50% yield of $(PNP)Fe(CO)_2$. This molecule survives vacuum drying unchanged; the unobserved (PNP)Fe(CO) should be low-spin d^7, thus with an empty orbital, so binding of a second CO to Fe should be essentially irreversible. The coordination geometry of the dicarbonyl is square-pyramidal,[9] with one CO trans to an empty site and the other trans to the π-donor amide N. Binding two CO has converted (PNP)-Fe from three unpaired electrons to only one (i.e., doublet ground state). CO stretching frequencies are 1943 and 1870 cm^{-1}, whose average is below that of (PNP)Ni(CO).

Returning to the goals of this work, with d^8 (PNP)Co-(CO) as a reference point, the addition of one electron severely inhibits the ability of (PNP)Ni to bind CO, although its apparent π basicity is sufficient to bind CO with a bond dissociation energy comparable to $T\Delta S$ (i.e., typically[28] 10−12 kcal/mol at 298 K) and with a coordination geometry intermediate between that of d^8 (planar) and d^{10} (tetrahedral). CO binding to this Ni^{I} is certainly stronger than that to any Cu^{II} complex.

Comparison[9] of (PNP)M(CO) for M = Co vs Ni shows that a planar structure should have weaker, lengthened M−N, M−CO, and M−P bonds because the σ^* orbital is occupied for Ni. This antibonding character is also suggested to be the reason why the geometry of d^9 (PNP)Ni(CO) relaxes away from planar: to hybridize $x^2 - y^2$ with 4s and 4p orbitals to prepare an empty orbital (off the N−Ni line) for

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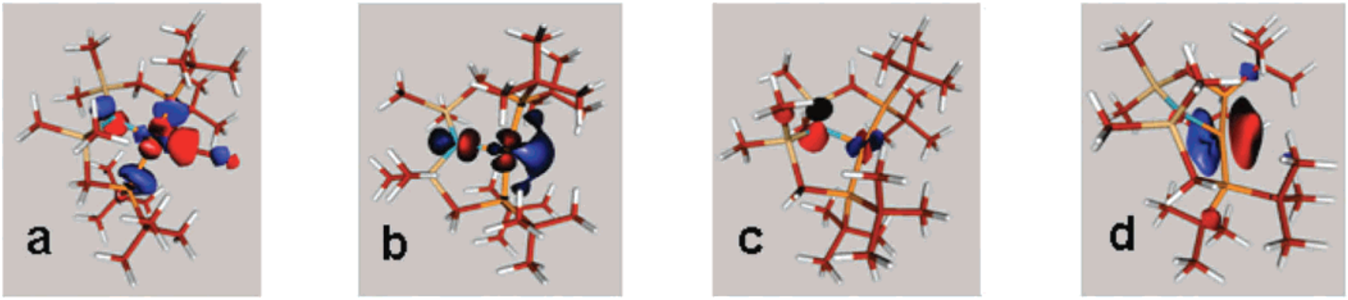

Figure 2. Frontier orbital contour plots for (a) SOMO of (PNP)Ni(CO) and (b) SOMO, (c) HOMO, and (d) LUMO of (PNP)Ni.

CO and a different SOMO. The ν(CO) value is 62 cm^{-1} higher for Ni than Co in (PNP)M(CO), showing that the earlier metal is the stronger π base. This agrees with the severe diminution of π basicity at the end of the transition series (d^9 and especially d^{10}).

For Fe, the hypothetical planar monocarbonyl thus formed can use hybrids of z^2 and 4s and 4p contributors to bind a second CO, with the SOMO directed trans to this apical CO. This may explain the unexpectedly longer Fe−C(O) distance (1.814 vs 1.738 Å) to the apical CO. A reviewer pointed out that the z^2 orbital, being singly occupied but Fe−C (apical) σ antibonding, should weaken that bond. The Fe−N distance,[9] longer than Ni−N, results from different metal-bonding radii. Decreasing from d^8 by one electron has the noteworthy effect of enabling binding of a second CO, and the resulting radical has a geometry similar to that of d^7 radicals like Mn(CO)$_5$. The absence of a *tri*carbonyl (PNP)-Fe(CO)$_3$ species again indicates that a 19-electron configuration is inferior to a 17-electron one or that binding CO to the half-filled orbital directed toward the open-coordination site in (PNP)Fe(CO)$_2$ is ineffective: a half-filled orbital is effectively blocked, even to a ligand as “powerful” as CO. Also noteworthy is that the average ν_{CO} value with the PNP ligand shows that this Fe is more electron-rich than the iron dicarbonyl[16] of the ligand PhB(CH$_2$PPh$_2$)$_3^-$.

Acknowledgment. This work was supported by the National Science Foundation under Grant CHE0544829. We thank Professor J. Telser for EPR advice.

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

IC7023764