

Carbon–Carbon Bond Formation from Azaallyl and Imine Couplings about Metal–Metal Bonds

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Supporting Information

ABSTRACT: Typical C–C bond-forming processes feature oxidative addition, insertion, and reductive elimination reactions. An alternative strategy toward C–C bond formation involves the generation of transient radicals that can couple at or around one or more metal centers. Generation of transient azaallyl ligands that reductively couple at CH positions possessing radical character is described. Two C–C bonds form, and the redox non-innocence of the resulting pyridine-imines may be critical to formation of a third C–C bond via dinuclear di-imine oxidative coupling. Unique metal–metal bonds are a consequence of the chelation.

Carbon–carbon bond-making is one of the most important transformations mediated by transition metals. Processes typically utilize oxidative addition, insertion, and reductive elimination sequences that directly involve metal–carbon bonds. In certain circumstances, ligands that possess radical character, perhaps due to a redox exchange with the metal, may be induced to form new C–C bonds. Recent investigations into azaallyl-based ligands, i.e., $\text{smif} = \{(2\text{-py})\text{CH}\}_2\text{N}^-$,^{1–4} suggested that C–C bonds might be constructed from coupling of the -HCNCH- backbone, whose nonbonding highest occupied molecular orbital (HOMO) possesses diradical character.

As shown in Scheme 1, treatment of metal diamides $\text{M}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{THF})_n$ ($\text{M} = \text{Cr}$ ($n = 2$),⁵ Co ($n = 1$)⁶ and $1/2[\text{Ni}(\text{NPh}_2)_2]_2$)⁷ with the bis-pyridine-imine chelate precursor $\text{Me}_2\text{C}(\text{CH}=\text{NCH}_2\text{py})_2$ afforded diamagnetic $\{\text{Me}_2\text{C}(\text{CHNCHpy})_2\text{M}\}_2$ (**1-M**; $\text{M} = \text{Cr}, \text{Co}, \text{Ni}$) dimers that feature three new C–C bonds. Coupling from positions 1, 2, and 3 of one chelate to related 2, 3, and 4 positions of the adjacent ligand render the molecules C_2 symmetric.

In an NMR tube experiment, **1-Ni** was heated to test the stability of the bicyclic ring scaffold, and demetalation, i.e., loss of “NiNCpy”, occurred to provide a diamagnetic bis-pyridine-imine complex **2-Ni**, with the ring structure intact. Complete demetalation was envisaged as a combination of amide protonation and Ni oxidation events; hence, dimethylglyoxime (dmgH_2) was employed. Exposure of **1-Ni** to 4 equiv of dmgH_2 afforded $\text{Ni}(\text{dmgH})_2$, a small amount of combustible gas, presumably H_2 (11%), and free ligand and its mono- and bis-reduction products in a 1:1:0.4 ratio. The C–C bonds appear to be produced irreversibly, and the bicyclic skeleton can be harvested.

The metal–metal bonding in each dinuclear complex is unique. In **1-Cr**, the imine $d(\text{C}–\text{N})_{\text{av}} = 1.339(3)$ Å and $\text{C}_{\text{im}}–\text{C}_{\text{py}}(\text{av})$ distance of $1.387(3)$ Å are consistent with single electron occupancy

of the pyridine-imine π^* orbital;⁸ hence, the oxidation state of each Cr is +2, and the potential for quadruple Cr–Cr bonding exists. As Figure 1 illustrates, one N_4Cr plane is rotated by $52.4(2)^\circ$ relative to the other, a staggered orientation that mitigates δ -bonding.^{9,10} From the temperature dependence of five chemical shifts,¹¹ a $\Delta E(\text{S-T})$ of $630(70)$ cm^{-1} shows that the $d(\text{Cr}–\text{Cr})$ of $2.5515(3)$ Å is best construed as representing a triple bond. Broken-symmetry (BS) calculations¹² portray anti-ferromagnetically (AF) coupled pyridine-imine ligands and AF-coupled high-spin (HS) d^4 chromous centers. While the former is reasonable, inspection of the magnetic orbitals of the BS solution suggests that the Cr–Cr interaction is best considered $(d\sigma)^2(d\pi)^4$, i.e., a long, weak, but conventional triple bond.

Imine ($1.332(3)$ Å) and $\text{C}_{\text{im}}–\text{C}_{\text{py}}$ ($1.395(4)$ Å) distances of **1-Ni** implicate a reduced pyridine-imine framework,⁸ consistent with Ni(II) centers. While configuration interactions derived from $nd/(n+1)p$ mixing are responsible for weak metal–metal bonds in $d^8–d^8$ systems in the second and third rows of the transition elements,^{13–15} the $\Delta E(3d/4p)$ is considered too great for the first row,¹⁶ yet $d(\text{Ni}–\text{Ni}) = 2.8164(6)$ Å, clearly a significant bond. The N_4Ni planes are rotated relative to one another by 58.6° , permitting d_{z^2} orbitals of each Ni(II) to slip one another, as shown by the 6.8° cant of the Ni–Ni vector relative to the central C–C bond (Figure 2). Its framework is thereby compressed similarly to **1-Cr**, with an angle between the N_4M planes of 12.6° for **1-Ni** vs 13.8° for **1-Cr**.

Figure 3 is a truncated orbital diagram of **1-Ni** obtained from a BS[1,1] calculation.¹² Due to σ/π mixing, the antibonding character of the $(d_{z^2}–d_{z^2})$ orbital (i.e., Ni(2)), is sufficiently nullified that a Ni–Ni bond exists; its primary component is the $(d_{z^2}+d_{z^2})$ orbital (Ni(5)). A set of py π^b orbitals (red) is intermingled with Ni-based $d\pi^b$ (Ni(6), Ni(7)), $d\pi^*$ (Ni(3), Ni(4)), $d\delta^b$ (Ni(9)), and $d\delta^*$ (Ni(8)) orbitals, and an amide-based set (green) is close to the HOMO of the system. The pair of electrons in the pyridine-imine π^* orbitals is depicted by BS[1,1] as an AF-coupled pair of α and β spins (blue); a closed-shell singlet solution is calculated to be 3.2 kcal/mol higher in energy.

Preparation of **1-Co** was predicated on the idea that a $d^7–d^7$ configuration akin to the $d^8–d^8$ electronic structure of **1-Ni** would lack significant M–M σ^* character, but its $d(\text{Co}–\text{Co})$ of $2.9111(7)$ Å belies this logic, although its Mayer bond order¹⁷ of 0.1221 is slightly greater than that of **1-Ni** (0.1018; cf. 0.4095 for **1-Cr**). Its imine ($1.316(3)$ Å) and $\text{C}_{\text{im}}–\text{C}_{\text{py}}$ ($1.408(3)$ Å)

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Scheme 1

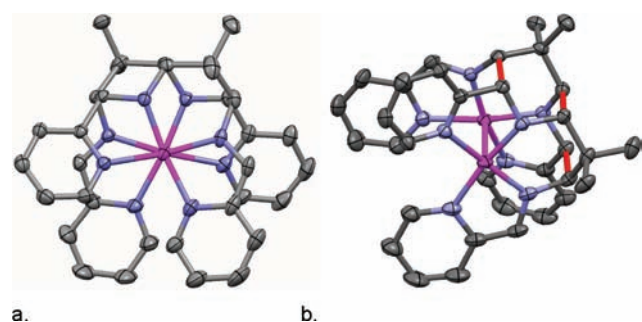
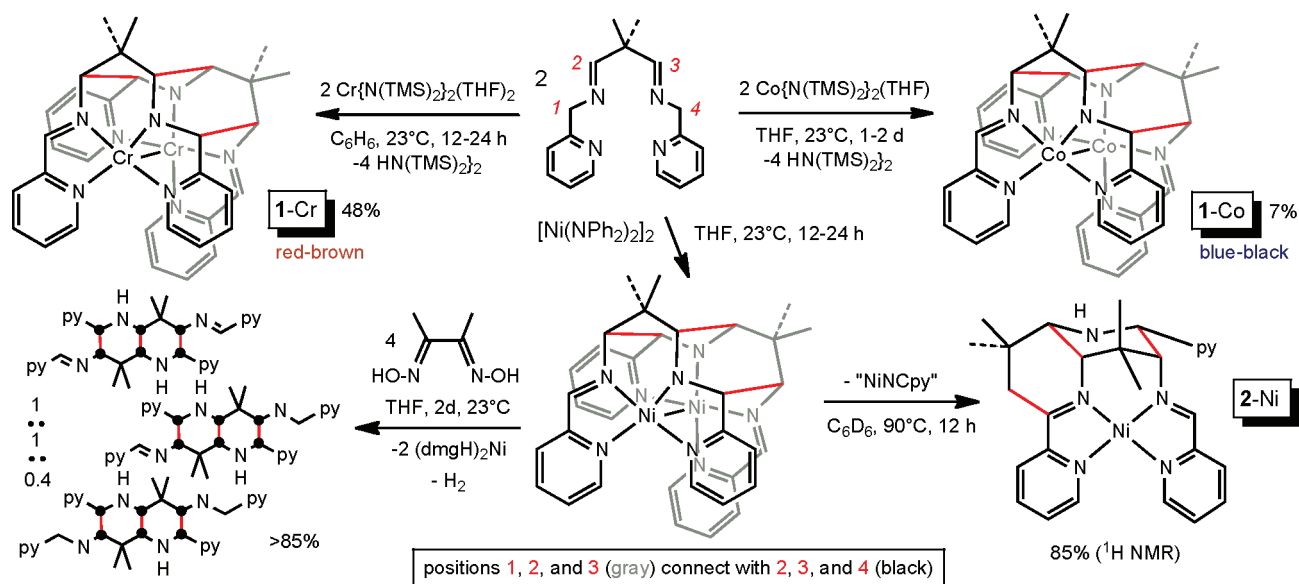


Figure 1. Molecular views of **1-Cr**: (a) down the Cr–Cr bond showing the torsion angle of 52.4° between the N_4Cr planes, and (b) angled view highlighting the three new intraligand C–C bonds (red).

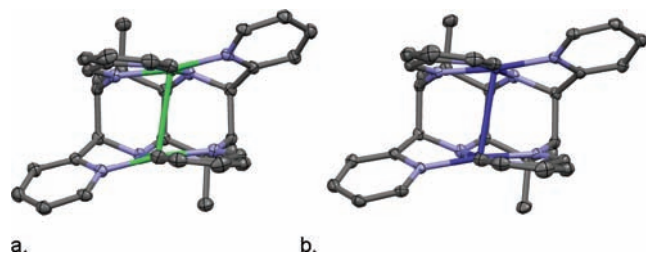


Figure 2. Molecular views of **1-Ni** (a) and **1-Co** (b) showing the cant of the M–M bond relative to the mid-C–C bond (dihedral $\angle\text{MCCM} = 1\text{-Ni}$, 6.8° ; 1-Co , 4.8° ; 1-Cr , 2.0°). The angle between the N_4M planes is 12.6° for 1-Ni , and 17.2° for 1-Co (13.8° for 1-Cr), and the torsion angle between the planes is 59.7° for 1-Ni and 58.6° for 1-Co .

distances fall within the range of monoreduced pyridine-imine functionalities, suggesting that metal centers are $\text{Co}(\text{II})$.

Calculations revealed an orbital diagram similar to that of **1-Ni** with the $(d_{z^2}-d_{z^2}) \sigma^*$ -orbital filled, but the BS approach was unnecessary, as the pyridine-imine π^* orbital had substantial cobalt character (16%). In **1-Co**, d- and ligand-based orbitals are

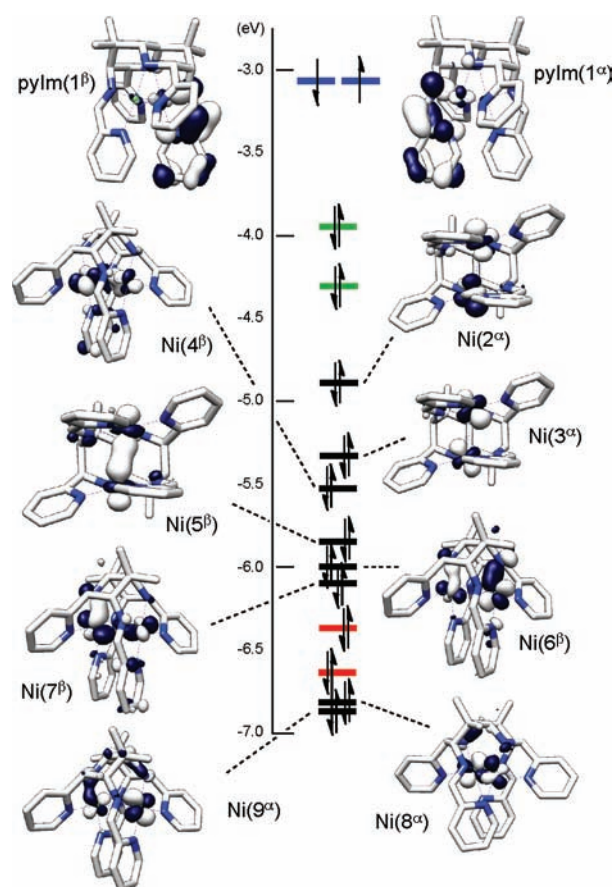
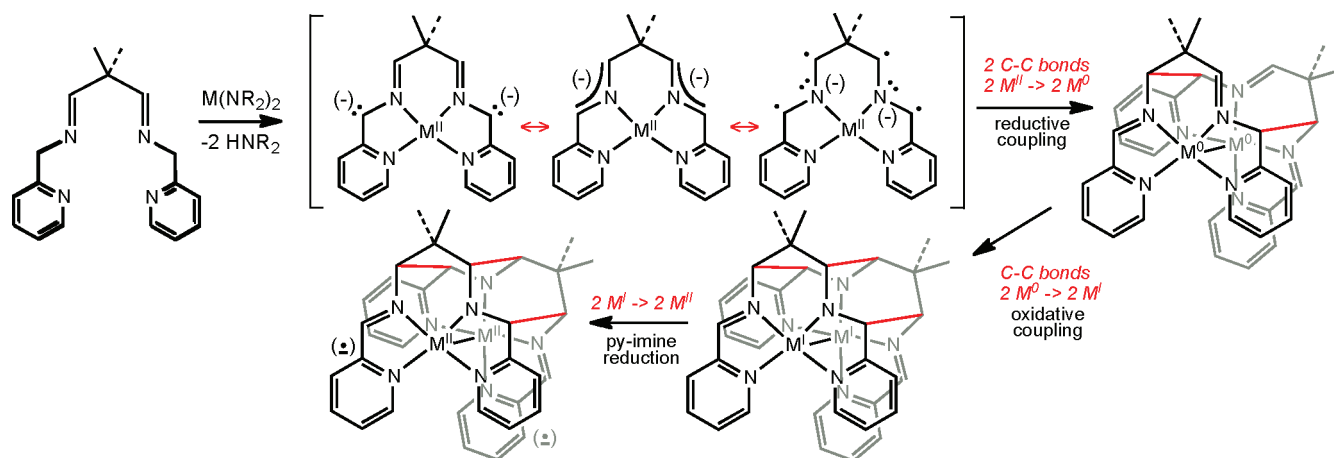


Figure 3. Calculated (BS[1,1]) orbital energies of **1-Ni**: black levels are Ni d-based (>80% Ni character, either an α or β orbital is shown); blue levels are py-imine π^* (pyIm); green and red levels (orbitals not shown) are N-amide and pyridine π^* , respectively.

difficult to distinguish due to greater metal–ligand mixing (i.e., greater covalency) as compared to **1-Ni**. Descriptions of **1-Co** as

Scheme 2



Co(I)–Co(I) or Co(II)–Co(II) appear to be equally satisfactory. The ^1H NMR chemical shift dispersion for 1-Co (δ 0.84–13.60; see Supporting Information), while T-independent, is greater than that of 1-Ni (δ 1.22–7.35 (broad)); low-lying paramagnetic states that are not readily thermally accessible may be present in both species.

The cant of the M–M bond and torsion angles (Figure 2) of 1-Co and 1-Ni are similar, but the angle between the N_4M planes is more compressed for 1-Ni (12.6° vs 17.2° for 1-Co). The distance between *ortho*-pyridine-imine positions is 2.979 Å for 1-Ni vs 3.131 Å for 1-Co (3.128 Å for 1-Cr). If the pyridine-imine radical character is subtly greater for 1-Ni, this favorable interaction, which is well within the sum of van der Waals radii (3.4 Å), might explain the greater compression for 1-Ni. A related π^* -interaction has been claimed in a family of diimino-semiquinolate zirconium halide complexes.¹⁸

Scheme 2 illustrates a plausible sequence of events leading to the formation of the three C–C bonds in 1-M (M = Cr, Co, Ni), in which six relative stereocenters are set. Each dibasic $\text{M}(\text{NR}_2)_2$ starting material can be construed as doubly deprotonating the chelate precursor to form a pseudo-square-planar complex containing two azaallyl subunits. By analogy with *smif*, the HOMO of each azaallyl is essentially comprised of two p-orbitals on the carbons adjacent to the nitrogen, and its character can be considered nonbonding, with valid ionic (e.g., $-\text{HC}=\text{N}-\text{CH}^-$) or “singlet diradical” (e.g., $-\text{HC}^{\cdot}-\text{N}-\text{C}^{\cdot}\text{H}$) depictions. Radical coupling from 1 and 3 positions (Scheme 1) of the chelate to 2 and 4 positions of one on another metal center generates two C–C bonds. Alternatively, the attack of two azaallyl carbanions on corresponding electrophilic sites of other chelates forms the bonds. In the process, a $2e^-$ reduction at each metal occurs, and these M^0 centers are now capable of oxidatively coupling the imines derived from the prior reaction to provide two M^{I} centers. For Cr, Ni, and possibly Co, reduction of the py-imine units to radical anions affords M^{II} cores. Naturally, the order of these events and the possibility that redox non-innocence of the py-imine units triggers C–C bond formation^{19–21} in some or all of the steps remain under consideration.

The potential to form unusual organic frameworks via C–C coupling reactions that can be construed as radical in character is illustrated by the reactions shown. Attempts to catalyze the C–C bond-forming events are ongoing, as well as the design of different frameworks toward new and more useful (e.g., remove CMe_2) ring constructions.

■ ASSOCIATED CONTENT

S Supporting Information. Experimental and analytical information on 1-M and 2-Ni and CIF files on 1-M (M = Cr, Co, Ni). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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