

Might BF and BNR₂ be alternatives to CO? A theoretical quest for new ligands in organometallic chemistry

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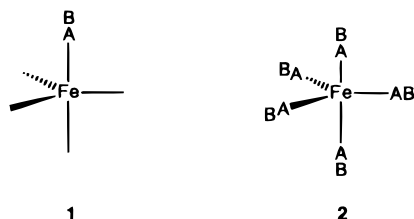
Letter

BF and BNR₂ emerge, in our DFT computations, as ideal alternatives to the CO ligand.

Carbon monoxide, CO, is ubiquitous in organometallic and coordination chemistry. It plays a key role in many catalytic processes, either as a reacting partner or as a spectator ligand.¹ Ligands isoelectronic to CO, *e.g.* N₂, NO⁺ and CN⁻, are also quite well-known in metal compounds.² But, the number of complexes with neutral isoelectronic diatomic molecules terminally ligated to transition metals is somewhat limited, mainly restricted to complexes with ligands of the type CE (E = S, Se, Te, NR, CH₂) and N₂. None of these other ligands seems to be as versatile as CO.

To find potential alternatives for the CO ligand, similar to it, and yet different, we have undertaken a nonlocal density functional theoretical (DFT) investigation at the BP86/TZ2P level on a series of 'candidate' ligands, *e.g.* SiO, BF and BNH₂, and their coordination in mono- and binuclear first-row transition metal complexes (M = Cr, Mn, Fe, Co, Ni) using the ADF program.^{3,4} Here, we report the preliminary results of our theoretical quest.

We begin our study with a careful theoretical investigation of the isoelectronic ligands AB = N₂, CO and BF, as well as their metal bonding capabilities in the model complexes Fe(CO)₄AB_{ax} (**1**, axially substituted), Fe(CO)₄AB_{eq} (equatorially substituted) and the homoleptic Fe(AB)₅ (**2**):



It is well-known that the orbital character and energetics of the frontier orbitals, *i.e.* the 5σ HOMO and the 2π LUMOs (3σ_g and 1π_g in N₂),⁵ determine the coordination capabilities of the AB molecules.⁶ The diatomic HOMO can be viewed as a slightly A–B antibonding lone-pair orbital with an sp-hybridized lobe along the z axis, which participates in the metal–ligand bond through σ donation of charge into an empty, mainly d_{z²} hybrid orbital on the Fe(CO)₄ fragment, as shown in **3**. The two A–B antibonding π* LUMOs (1π_g or 2π) are involved in π backdonation, accepting charge from d_{xz}

(**4**) and d_{yz} hybrid orbitals (**5**).

How exactly does the AB electronic structure change as we go from N₂ *via* CO to BF (see Fig. 1)? The AOs of the electropositive atom A rise in energy and become more diffuse along this series, whereas those of the electronegative atom B decrease in energy and become more compact. This leads to an energy mismatch, poorer overlaps and, therefore, to weaker A–B orbital interactions. As a consequence, the π* LUMOs, *i.e.* 2p_π(A)–2p_π(B), drop slightly in energy and become more localized on A (Fig. 1). The ligand donor orbital also becomes more localized on A and moves rather strongly to higher energy (Fig. 1). A more detailed discussion of the subtle interplay of orbital interactions behind these regularities will be given elsewhere.

These trends lead us to expect that the AB ligand's overall metal-binding ability should increase in the order N₂ < CO < BF, and that along this series the importance of σ donation should be enhanced relative to that of π backdonation. These expectations are confirmed by our further calculations. For instance, the computed Fe(CO)₄–AB bond dissociation enthalpies (for 298.15 K) of axially substituted complexes are 18.1, 42.3, 67.9 kcal mol⁻¹ for N₂, CO, BF (at the BP86/TZ2P level of DFT);⁴ the corresponding values for the equatorially substituted complexes are very much alike. A similar trend is also found for the homoleptic Fe(AB)₅ complexes.

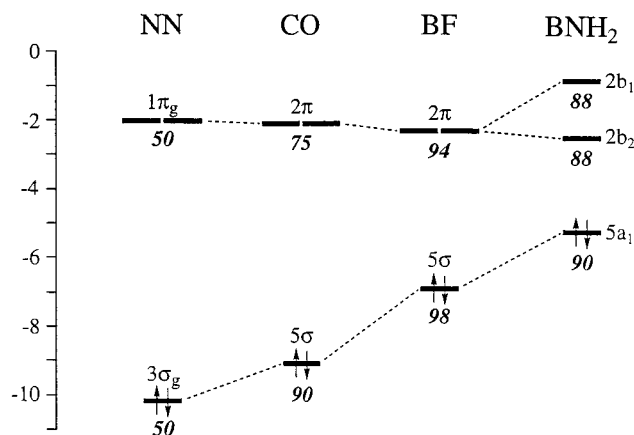
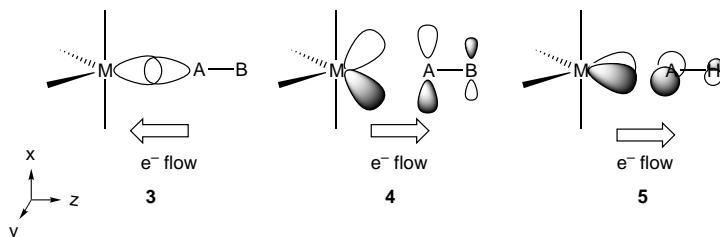


Fig. 1 Trend in HOMO and LUMO energies (in eV) of isoelectronic ligands AB. The extent (percentage over all AOs) to which each MO is centered on the more electropositive atom A is given in italics

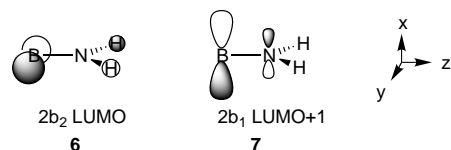
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BF does seem to be a very promising candidate for supplementing CO as a ligand. But it is a reactive molecule (its HOMO-LUMO gap is only 4.6 eV, compared to 7.0 eV for CO and 8.0 eV for N_2), and it requires special ways of generation and handling techniques.⁷ Moreover, the polar BF ligand may remain very reactive even when complexed.

How can we overcome the problem of instability of BF, ligated or not? One possibility is to build in steric bulk by substitution of the F by another group. This may be accomplished through BNR_2 , with R potentially bulky. We have explored the bonding of such a ligand with R = H and CH_3 . Here we discuss the results for the planar, C_{2v} symmetric BNH_2 . Its frontier orbital energies suggest that it has even better ligating properties than BF (Fig. 1). The $5a_1$ HOMO is higher in energy and the $2b_2$ LUMO, *i.e.* the π^* orbital lying in the molecular plane, is lower in energy.

Let's have a closer look at the $2b_1$ and $2b_2$ MOs of BNH_2 . One way to look at them is from the viewpoint of BNH_2 built up from B and NH_2 . The $2b_2$ (6) is then the 'free' $2p_y$ AO of boron (slightly perturbed by the NH_2 fragment), whereas the $2b_1$ (7) is the boron $2p_x$ AO, destabilized by the $2p_x(N)$ of NH_2 .



The smaller HOMO-LUMO gap of the free BNH_2 ligand (only 2.9 eV) suggests lesser kinetic stability. But this might be alleviated by shielding the frontier orbitals of BNR_2 through sterically more demanding substituents R. It is also important to realize that the HOMO-LUMO gap of the *free* ligand is not automatically an indicator for its inertness *after* complexation! The well-known Fischer-type carbenes,⁸ for example, have an even smaller HOMO-LUMO gap. For the (uncoordinated) archetype $C(H)OH$ we calculate a gap of only 2.2 eV. Yet, these ligands form relatively stable complexes.

BNH_2 is isoelectronic with the well-known vinylidene ligand CCH_2 , which forms stable, isolable complexes.⁹ We have analysed the frontier orbitals of CCH_2 to see how they differ from those of BNH_2 . The CCH_2 $3a_1$ HOMO (83%) and $2b_2$ LUMO (80%) are somewhat less localized on the terminal atom, in line with the reduced electronegativity difference

between the two main group atoms. The appearance of the CCH_2 frontier orbitals is, however, very similar to those of BNH_2 (see above), and we compute a nearly identical HOMO-LUMO gap of 3.0 eV. This suggests similar coordination properties for the two ligands. But still the higher polarity of the BNH_2 ligand makes it potentially more reactive (more sensitive, *e.g.* toward nucleophilic attack).

There is also some experimental evidence, which indicates that BNR_2 may be a realistic ligand.¹⁰ In 1970, Schmid, Petz and Nöth^{10a} synthesized the thermolabile compound $Fe(CO)_4BNR_2$ with R = CH_3 and C_2H_5 , and, very recently, Braunschweig and Wagner^{10b} reported the first X-ray structure of a complex containing the $BN(CH_3)_2$ ligand, the binuclear $Mn_2(C_5H_5)_2(CO)_4BN(CH_3)_2$.

To test the validity of our qualitative considerations, we have carried out an extensive study in which we compare the metal-binding of CO, BF and BNH_2 in mononuclear (axially) substituted, hexa- (Cr, Mn^+), penta- (Fe, Co^+) and tetra-coordinate (Ni) as well as in binuclear (Fe, Mn) transition metal carbonyl complexes at the BP86/TZP level.^{3,4} The trends found for CO and BF in $Fe(CO)_4AB$ are reproduced in all the other first-row transition metal complexes (see Table 1). Both ligands bind well but the $M-BF$ bond is actually 1.5–2 times stronger. And BNH_2 binds even better than BF. The $Cr(CO)_5-AB_{ax}$ bond dissociation energy, for example, increases from 41.8 *via* 62.1 to 72.1 kcal mol⁻¹ along CO, BF and BNH_2 . An analysis of the $M-AB$ bonding mechanism furthermore shows that along this series of ligands σ donation becomes increasingly important leading to a build-up of positive charge on the ligand. The balance between σ donation and π backdonation is restored in binuclear metal complexes, *e.g.* $Mn_2Cp_2(CO)_4-AB$ ($AB = BF, BNH_2$). The detailed results will be reported elsewhere.

We conclude that the BNR_2 entity should be a superb ligand and may well be a good supplement to CO in the design of catalytically active transition metal complexes. BF and other ligands (SiO, BO^-) have very interesting properties, too, but they do not contain the potential structural features (*i.e.* substituents R) that with clever synthetic design might shield their reactive frontier orbitals. The problem of generating a good precursor to BNR_2 remains.

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Table 1 BP86/TZP metal complex—ligand, $[M]-AB$, bond dissociation energies (in kcal mol⁻¹) and, in parentheses, ligand A—B bond lengths (in Å)

Compound	Ligand AB		
	CO	BF	BNH_2
AB	— (1.138)	— (1.272)	— (1.380)
$Cr(CO)_5-AB$	41.8 (1.155)	62.1 (1.281)	72.1 (1.379)
$Mn(CO)_5-AB^+$	44.2 (1.141)	71.4 (1.259)	94.4 (1.354)
$Fe(CO)_4-AB_{ax}$	48.4 (1.156)	73.8 (1.275)	87.7 (1.378)
$Co(CO)_4-AB_{ax}^+$	37.3 (1.139)	70.6 (1.251)	98.6 (1.346)
$Ni(CO)_3-AB$	28.2 (1.151)	45.3 (1.274)	52.7 (1.384)

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- 4 The Fe(CO)₄AB and Fe(AB)₅ calculations were done with two basis sets: TZ2P (reported in the text) and TZP (in Table 1). The other systems (Table 1) were computed with the TZP basis set only. TZ2P is a triple- ζ basis set of Slater-type orbitals (STOs) augmented with a set of 4p functions on Cr, Mn, Fe, Co and Ni, and a set of 3d and 4f polarization functions on main group atoms (2p and 3d on H). The TZP basis contains only one set of polarization functions per atom. The values reported in the text for the iron complexes are bond dissociation enthalpies, including zero point energies, thermal energy and PV corrections. The comparative values in the table are bond dissociation energies.
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