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

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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. Ligands isoelectronic to CO, e.g. N₂, NO⁺ and CN⁻, are also quite well-known in metal compounds. 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, CH₃) 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. 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)₅ABₙ₋₅ (1, axially substituted), Fe(CO)₅ABₙₓ (equatorially substituted) and the homoleptic Fe(AB)₂ (2):

- It is well-known that the orbital character and energetics of the frontier orbitals, i.e. the 5r HOMO and the 2r LUMOs (3σ and 1π in N₂), determine the coordination capabilities of the AB molecules. 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 hybrid orbital on the Fe(CO)₅ fragment, as shown in 3. The two A–B antibonding π* LUMOs (1π* or 2n) are involved in π backdonation, accepting charge from dₓz.

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. 2p₂(A)–2p₂(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(AB)₂–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/TZP level of DFT); the corresponding values for the equatorially substituted complexes are very much alike. A similar trend is also found for the homoleptic Fe(AB)₂ complexes.

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\begin{align*}
  &\text{NN} &\text{CO} &\text{BF} &\text{BNH₂} \\
  1\pi_σ &50 &75 &94 &88 \\
  2\pi &5 &9 &98 &88 \\
  3\sigma &50 &75 &98 &88 \\
\end{align*}
\]

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.

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 N₂), and it requires special ways of generating CO as a ligand. But it is a reactive molecule (its reaction and handling techniques.

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 BNR₂ with R potentially bulky. We have explored the bonding of such a ligand with R = H and CH₃. Here we discuss the results for the planar, C₂ᵥ, symmetric BNH₂. Its frontier orbital energies suggest that it has even better ligating properties than BF (Fig. 1). The 5a₁ HOMO is higher in energy and the 2bₗ LUMO, i.e. the π* orbital lying in the molecular plane, is lower in energy.

Let's have a closer look at the 2b₂ and 2bₗ MOs of BNH₂. One way to look at them is from the viewpoint of BNH₁ built up from B and NH₂. The 2b₂ (6) is then the 'free' 2pₓ AO of boron (slightly perturbed by the NH₂ fragment), whereas the 2bₗ (7) is the boron 2pᵧ AO, destabilized by the 2pᵧ(N) of NH₂.

The smaller HOMO-LUMO gap of the free BNH₂ ligand (only 2.9 eV) suggests lesser kinetic stability. But this might be alleviated by shielding the frontier orbitals of BNR₂ 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.

BNH₂ is isoelectronic with the well-known vinylidene ligand CCH₂, which forms stable, isolable complexes. 9 We have analysed the frontier orbitals of CCH₂, to see how they differ from those of BNH₂. The CCH₂ 3a₁ HOMO (83%) and 2bₗ 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 CCH₂ frontier orbitals is, however, very similar to those of BNH₂ (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 BNH₂ ligand makes it potentially more reactive (more sensitive, e.g. toward nucleophilic attack).

There is also some experimental evidence, which indicates that BNR₂ may be a realistic ligand. 10 In 1970, Schmid, Petz and Nöth synthesized the thermolabile compound Fe(CO)₃BNR₂ with R = CH₃ and C₆H₅, and, very recently, Braunschweig and Wagner 10 reported the first X-ray structure of a complex containing the BNH(CH₃)₂ ligand, the binuclear Mn₂[3(C₆H₅)₂(CO)₃BN(CH₃)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 BNH₂ 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)₅AB are reproduced in all the other first-row transition metal complexes (see Table 1). Both ligands bind well but the M—BF bond is almost 1.5—2 times stronger. And BNH₂ binds even better than BF. The Cr(CO)₅—ABₐ bond dissociation energy, for example, increases from 41.8 to 62.1 to 72.1 kcal mol⁻¹ along CO, BF and BNH₂. An analysis of the M—AB binding 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. Mn₃Cr₂(CO)₈—AB (AB = BF, BNH₂). The detailed results will be reported elsewhere.

We conclude that the BNR₂ 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 BNR₂ remains.

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References

4 The Fe(CO)$_3$AB and Fe(AB)$_3$ 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-$\zeta$ 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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