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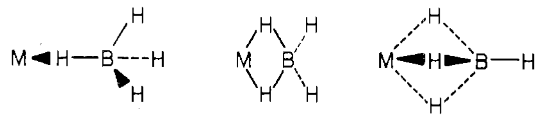
Correspondence

Some Comments on the Bonding of the Tetrahydroborate Ion to Transition Metals

AIC402705

Sir:

Because of the ambiguous ligating properties of the tetrahydroborate ion, some clarification regarding its transition metal complexes is warranted. The borohydride ion can, in principle, bind metals in several ways



monodentate I bidentate (II) tridentate (III)

Examples are known for all geometries except I. Using the filled bonding BH orbitals directed at the metal as a basis set, ligation in each case can be regarded as arising from formation of three-center, two-electron bonds using empty metal orbitals and the appropriate combinations of BH orbitals as required by the respective symmetry. Thus, in II, the tetrahydroborate ion would function as a four-electron donor.

This hypothesis was previously formulated by Marks, *et al.*,[1] by virtue of the similarity in stoichiometry between η^3-allyl complexes and their tetrahydroborate analogs. Additionally, they arrived at a corollary: "...in almost all cases, the neutral BH_4 ligand acts as a formal three-electron donor [or BH_4^- as a four-electron donor]...the mode of ligand–metal attachment (bidentate or tridentate) does not, to a first approximation, appear to affect the extent of electron donation."

The only thoroughly documented examples of III are the compounds $M(BH_4)_4$ (M = Zr, Hf), which are assigned an open-shell (16 valence electrons) configuration in ref 1 on the basis of the statement reproduced above. These species are unusually symmetric, having rigorous T_d symmetry in the crystal (by X-ray[2] and neutron[3] diffraction studies) and, reportedly, in the gas phase (by electron diffraction[4]). Under this requirement, the filled BH orbitals about the metal in $Zr(BH_4)_4$ transform as $A_1 + E + T_1 + 2\,T_2$; however, the Zr valence orbitals do not span the T_1 representation. Therefore, there exist three degenerate linear combinations of filled ligand orbitals which remain strictly nonbonding, Zr having 18 valence electrons. The situation is analogous to that proposed for $(PhC{\equiv}CPh)_3W(CO)$.[5] That is, each BH_4^- ligand contributes 4.5 bonding electrons in $Zr(BH_4)_4$, contrary to the previous suggestion.

Unfortunately, well-characterized, tridentate tetrahydroborate–transition metal complexes, having lower symmetry, are not at hand. So further testing of the proposals in ref 1 must be deferred.

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Registry No. BH_4^-, 16971-29-2.

References and Notes

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Effect of Tris(2,4-pentanedionato)chromium(III) on Carbon-13 Line Widths. Potential Dangers in Line Shape Analysis

AIC40761P

Sir:

Several years ago Gansow, Burke, and LaMar[1] and Gansow, Burke, and Vernon[2] reported that the addition of tris(2,4-pentanedionato)chromium(III), $Cr(acac)_3$, in concentrations up to 0.1 *M*, to samples used for the measurement of carbon-13 nmr spectra, especially of metal carbonyl compounds, is effective in reducing the normally long longitudinal relaxation times (T_1's), thus minimizing saturation effects and allowing more rapid collection of data. The practical advantage of this is very great and the use of $Cr(acac)_3$ has become common.[3] The particular virtue of $Cr(acac)_3$ was said to be that it has negligible effects on chemical shifts and on line widths "for $Cr(acac)_3$ concentrations up to 0.1 *M*". We wish to point out that with regard to line widths this is not entirely true and that in line shape studies of fluxional molecules intended to afford rate constants and activation parameters, serious difficulties can arise.

The recommended safe limit of 0.1 *M* $Cr(acac)_3$ was based, apparently, entirely on a study of 1.0 *M* $Fe(CO)_5$. The mole ratio of $Cr(acac)_3$:CO is thus only 0.02 when $Cr(acac)_3$ is 0.1 *M*. However, in most carbon-13 work on complex metal carbonyl compounds the concentration of the solute itself will be only *ca.* 10^{-1} *M* and if there are only one or two of each structural type of CO group, the $Cr(acac)_3$:CO ratios will be near unity. We have found in a number of cases that at the solute concentration ratios which occur under practical circumstances when $[Cr(acac)_3] \approx 0.1$ *M*, lines with intrinsic widths of about 1 Hz often have widths of 3–7 Hz or more.