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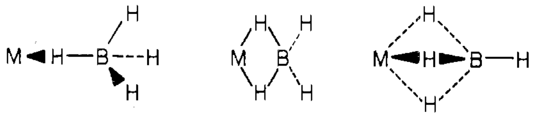
Correspondence

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.

Acknowledgment. This work was supported by the National Science Foundation (Grant GP 737334X).

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

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Received April 23, 1974

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.

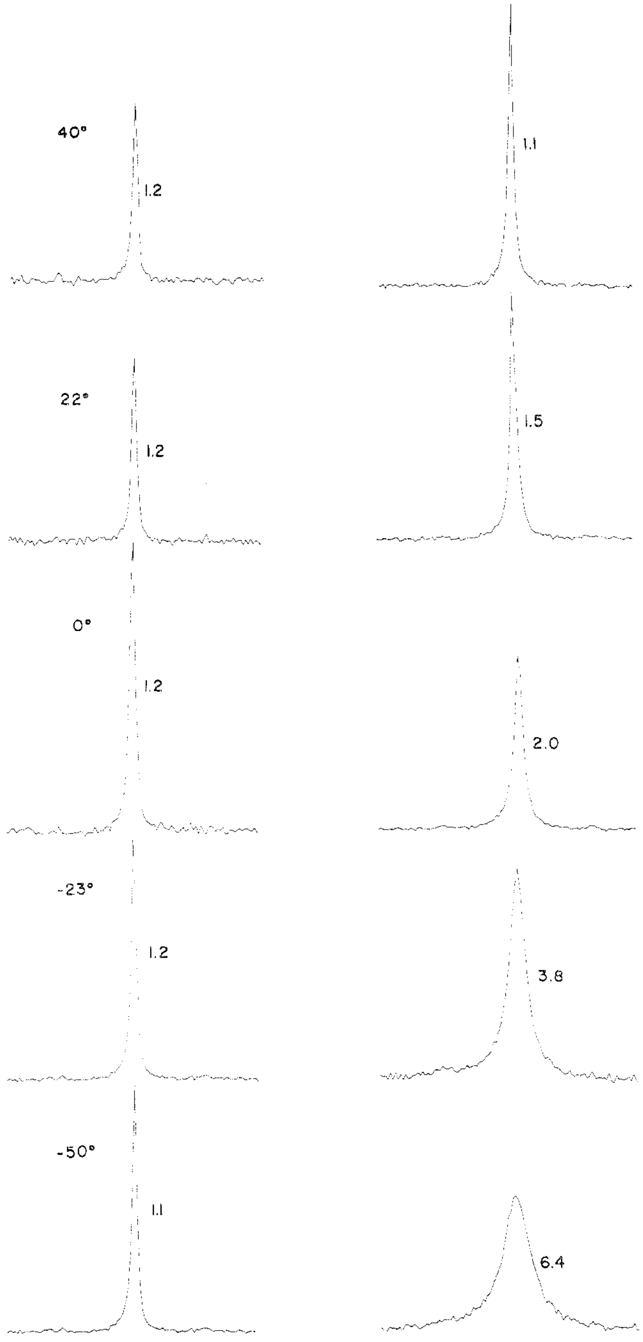

Figure 1.

Errors of this magnitude can have a serious effect on the evaluation of the rates of exchange and hence on the activation parameters.

We have found also that the effect of Cr(acac)$_3$ on line widths is markedly temperature dependent in some cases, as the following example shows.

A sample of $C_5H_5Fe(CO)_2I$ (Strem Chemicals) was enriched to *ca.* 48% in ^{13}CO using an apparatus similar to that described by Angelici[4] and then purified by chromatography on alumina followed by recrystallization from CH_2Cl_2–hexane.[5] Cr(acac)$_3$ was obtained commercially and recrystallized from benzene. A 5:1 THF–toluene-*d*$_8$ solution containing 0.20 *M* $C_5H_5Fe(CO)_2I$ and 0.0026 *M* Cr(acac)$_3$ was prepared and ^{13}C nmr spectra were collected at several temperatures from −50 to +40°. Sufficient Cr(acac)$_3$ was then added to increase its concentration to 0.079 *M* and another series of spectra were collected. The spectra were recorded on a JEOL PFT 100/Nicolet 1080 Fourier-transform spectrometer at 25.036 MHz with a tilt angle of 49° and repetition rate of 2.2 sec. In all spectra 256 pulses were accumulated at a 4000-Hz sweep width and expanded to 100-Hz width in the region of the carbonyl resonance giving a plot scale of 0.26 Hz/mm with a digital resolution of 0.5 Hz.

Some representative spectra are shown in Figure 1. The number beside each peak gives its width as half-height ($W_{1/2}$) in hertz. The series of spectra at the left, taken with 0.0026 *M* Cr(acac)$_3$ added, exhibit no significant variation in peak width at half-height (1.2 Hz). In contrast the spectra on the right, taken with 0.079 *M* Cr(acac)$_3$ added, display line widths which vary smoothly, though nonlinearly, with temperature from 6.4 Hz at −50° to 1.1 Hz at +40°. Inspection of the nmr tube at −50° revealed no evidence of any precipitated solid, nor was there any evidence for decomposition. Similar results were obtained from a 0.25 *M* solution of $C_5H_5Fe(CO)_2I$ in CD_2Cl_2–CH_2Cl_2 using Cr(acac)$_3$ concentrations varying between 0.0001 and 0.080 *M*.

The accurate calculation of rates and of activation parameters for exchange processes observable on the nmr time scale requires knowledge of the line widths of the resonances in the absence of exchange. In practice line widths are often measured at several temperatures below the slow-exchange limit and assumed to be constant through the intermediate-exchange region. We have performed a series of calculations to assess the effect of Cr(acac)$_3$-induced variations in line width on the calculated rates for a simple two-site carbonyl-exchange process and have found the calculated rate constants to be as much as two orders of magnitude too large in the portions of the exchange region above coalesence.

We conclude that great care must be taken to keep the Cr(acac)$_3$:substrate mole ratio as low as possible whenever temperature-dependent features of metal carbonyl type molecules are studied by ^{13}C nmr. There is probably no concentration of Cr(acac)$_3$ which is ideal for all substrates. However, our results suggest that a Cr(acac)$_3$:substrate mole ratio of 1:100 should minimize the effect of Cr(acac)$_3$ on carbonyl line widths while still providing significant signal enhancement.

Registry No. Cr(acac)$_3$, 13681-88-4.

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Received November 4, 1974