**Table I.** Base Hydrolysis Rates of Coordinated Benzonitrile $M(NH_3)_5(C_6H_5CN)^{3+}$ and pK_a Values for Coordinated Benzamide, $M(NH_3)_5(C_6H_5CONH_2)^{3+}$

M	k_{OH},^{a} M^{-1} sec^{-1}	$pK_a{}^b$
Co(III)	18.2^c	1.65^d
Rh(III)	4.7	2.2
Ir(III)	2.1	2.4
Ru(III)	2.0×10^3 ^{e}	0.9^{e,f}
Free ligand	7.2×10^{-6} ^{g}	~15 or higher^h

^{a} Rate constant for eq 1 at 25.0° and $\mu = 1.0\ M$ (NaClO$_4$) unless noted. ^{b} pK_a for eq 2 at 25.0° and $\mu = 1.0\ M$ (NaClO$_4$–HClO$_4$) unless noted. ^{c} 25.6°, ref 4. ^{d} $\mu = 1.0\ M$ (LiClO$_4$–HCl). ^{e} Reference 3. ^{f} $\mu = 2.0\ M$ (NaClO$_4$–HClO$_4$). ^{g} Extrapolated from higher temperature rate data reported for 50% aqueous acetone by K. B. Wiberg, *J. Amer. Chem. Soc.,* 77, 2519 (1955). ^{h} pK_a of free ligand is uncertain; values of ~15 and >19 have been reported: R. B. Horner and C. D. Johnson in "The Chemistry of Amides," J. Zabicky, Ed., Interscience, London, 1970, Chapter 3.

mentioned above. The ir spectrum showed no ν_{CN} stretch and was comparable to that of the Ru(III) homolog,[8] [Ru-(NH₃)₅(benzamido)](ClO₄)₂ (benzamido bands at 1550 (s), 1295 (m), 1270 (s), and 700 cm⁻¹ (m–s)). These observations indicate that the course of the base hydrolysis reaction is analogous to that reported previously for nitrile complexes[2-5] of Co(III), Rh(III), and Ru(III)

$$M(NH_3)_5(C_6H_5CN)^{3+} + OH^- \rightarrow M(NH_3)_5(C_6H_5CONH)^{2+} \qquad (1)$$
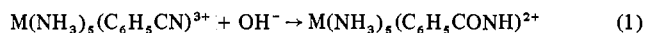
The acid–base spectral behaviors of the product solutions presumably reflect reaction of the coordinated benzamide (eq 2).

$$M(NH_3)_5(C_6H_5CONH_2)^{3+} \rightleftarrows M(NH_3)_5(C_6H_5CONH)^{2+} + H^+ \qquad (2)$$

Base hydrolysis kinetics were followed by absorbance changes at 235 nm, and linear first-order plots of ln $(A_t - A_\infty)$ vs. time were obtained. Observed rate constants were a linear function of [OH⁻] in accordance with the rate law

$$\frac{d[\text{amido complex}]}{dt} = k_{OH}[\text{nitrile complex}][OH^-] \qquad (3)$$

where k_{OH} has the values 4.7 ± 0.4 and 2.1 ± 0.2 M^{-1} sec⁻¹ for the rhodium and iridium complexes, respectively (25.0°, $\mu = 1.0$). These results are consistent with the second-order rate behavior observed with other systems.[2-5]

Examination of Table I shows that coordination to any of the 3+ metal ions markedly enhances the reactivity of benzonitrile toward base hydrolysis. This rate enhancement ranges from ~3 × 10⁵ for Ir(NH₃)₅³⁺ to ~3 × 10⁸ for Ru(NH₃)₅³⁺ and is paralleled by the dramatic enhancement in the acidities of the benzamide product coordinated to these 3+ metal ions. Given the marked differences from the free ligand reactivities the differences between the various M(III) complexes are relatively small. Of these the ruthenium(III)–benzonitrile complex is several orders of magnitude the more reactive toward base hydrolysis, a feature which has also been noted for the analogous acetonitrile complex[3] and has been attributed to the relative ability of the 4d⁵ Ru(III) center to act as a π acceptor.

It has been pointed out that when metal–ligand bond making or breaking is not a feature of the reaction of a coordinated ligand, there is little variation in rate constants over the series Co(III), Rh(III), and Ir(III).[10] This is also true for the reactions of interest here. Although the variations are small, the coordinated benzonitrile hydrolysis rates and the coordinated benzamide acidities follow the order Co(III) > Rh(III) > Ir(III) with the difference between Co(III) and Rh(III) greater in each case than between Rh(III) and Ir(III). Consideration of the M³⁺ ionic radii, Co³⁺ (0.53 Å) < Rh³⁺ (0.67 Å) < Ir³⁺ (0.73 Å),[9] supports the view that the rate

differences for the nd^6, tripositive metal–benzonitrile complexes are largely due to the relative abilities of these metal ions to stabilize the developing negative charge on the nitrile nitrogen during the rate-determining step. Certainly, other variables must play roles in the overall bonding between the reacting ligands and the respective metal centers; for example, ligand field splitting energies (therefore ligand field stabilization energies) are much larger for Ir(III) than for Co(III). However, these other variables appear not to be large contributors to the free energies of activation for the base hydrolyses of the various benzonitrile complexes thus leaving the electrostatic differences to determine the relative reactivities.

Registry No. Rh(NH₃)₅(C₆H₅CN)³⁺, 46343-55-9; Ir(NH₃)₅-(C₆H₅CN)³⁺, 53783-43-0; Rh(NH₃)₅(C₆H₅CONH₂)³⁺, 53702-61-7; Ir(NH₃)₅(C₆H₅CONH₂)³⁺, 53783-44-1.

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Absolute Integrated Infrared Intensities of the Carbonyl and Thiocarbonyl Stretching Modes in η^5-C₅H₅Mn(CO)₂(CS)[1]

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Following the discovery of the first transition metal–thiocarbonyl complex by Baird and Wilkinson in 1966,[2] there has been considerable interest in the comparative bonding properties of the CO and CS ligands. Molecular orbital calculations,[3] photoelectron spectroscopy measurements,[4] and various other physiochemical data[5] suggest that CS is both a better σ-donor and a better π-acceptor ligand than CO. The utility of absolute integrated infrared intensity measurements is assessing the extent of π-electronic delocalization in the CO and N₂ groups of transition metal carbonyls and transition metal–dinitrogen complexes has now been well established.[6-18] We report here the results of the first intensity study for a CS stretching vibration in a transition metal–thiocarbonyl complex, viz., η^5-C₅H₅Mn(CO)₂(CS). This complex is particularly interesting because it is possible to make a direct comparison of the π-electronic properties of CO and CS in the same complex on the basis of the absolute infrared intensities of the CO and CS stretching modes.

Table I. Infrared Frequencies (cm⁻¹), Absolute Intensities, and Group Dipole Moment Derivatives for the CO and CS Stretching Vibrations in η^5-C$_5$H$_5$Mn(CO)$_2$(CS) and Related Complexes

| Compd | $\nu(CO)^a$ | | $\nu(CS)^a$ | $I_s{}^b$ | $I_a{}^b$ | $I_{CS}{}^b$ | μ_s' | μ_a' | $\mu'(MnCS)$ | μ_s'/μ_a' |
	A'	A''								
η^5-C$_5$H$_5$Mn(CO)$_2$(CS)	2009.7	1956.9	1263.8	11.5	15.4	13.8	9.04	10.1	11.0	0.90
η^5-C$_5$H$_5$Mn(CO)$_2$(SbPh$_3$)^c	1934	1874		10.2	11.3		8.51	8.65		0.99
η^5-C$_5$H$_5$Mn(CO)$_2$(C$_7$H$_8$)^c	1963	1903		8.90	11.6		7.95	8.77		0.91
η^5-C$_5$H$_5$Mn(CO)$_3{}^c$	2024	1939		7.02	21.9		8.77	10.4		0.84

^{a} In CS$_2$ solution. The half-bandwidths, $\Delta\nu^a{}_{1/2}$, for η^5-C$_5$H$_5$Mn(CO)$_2$(CS) are as follows: ν(CO) A', 7.0 cm⁻¹; A'', 8.7 cm⁻¹; ν(CS), 9.5 cm⁻¹. ^{b} In units of 10⁴ l. mol⁻¹ cm⁻². Average standard deviation ±0.2. ^{c} Data from ref 13.

Experimental Section

A pure sample of η^5-C$_5$H$_5$Mn(CO)$_2$(CS) was prepared from η^5-C$_5$H$_5$Mn(CO)$_3$ (a gift from Ethyl Corp.) by the literature method.[19]

Infrared spectra were recorded on a Perkin-Elmer Model 337 double-beam grating spectrophotometer coupled to a Sargent-Welch Model SRLG linear absorbance recorder using the maximum frequency expansion possible (8 cm⁻¹/in.). The CO and CS frequencies were calibrated against the 2147.08-cm⁻¹ peak of CO gas and the 1601.4-cm⁻¹ peak of polystyrene film; the precision of the frequencies is ±0.5 cm⁻¹. The spectral slit width used was ∼2.5 cm⁻¹.

The absolute integrated absorption intensities were determined by the Russell–Thompson extrapolation method.[20] The measurements were made on fresh solutions prepared from six individually weighed samples of η^5-C$_5$H$_5$Mn(CO)$_2$(CS) dissolved in CS$_2$ (concentration range: (8–16) × 10⁻³ M). The areas under the absorption bands were determined by the weighing method and were reproducible to within ±1%. No wing corrections were made. The data were analyzed by the linear least-squares method on an IBM 36/75 computer.

Results and Discussion

X-Ray crystallographic data have now been reported for several η^5-C$_5$H$_5$Mn(CO)$_2$L complexes where L = CO,[21] PPh$_3$,[22] SO$_2$,[23] C$_7$H$_8$.[24] The results indicate that η^5-C$_5$H$_5$Mn(CO)$_2$(CS) may be considered as pseudooctahedral with the CS group located cis to the carbonyls and the C$_5$H$_5^-$ ligand located trans to the carbonyls and the CS group. Also, the OC–Mn–CO and OC–Mn–CS angles may be assumed to be 92°. The local symmetry of the Mn(CO)$_2$(CS) moiety is C_s for which two ir-active CO stretching modes (A' + A'') and one ir-active CS stretching mode (A') are expected. The ir spectrum of the complex is in accord with this with two well-resolved bands being observed in the CO stretching region at 2009.7 (A') and 1956.9 (A'') and one solitary band in the CS stretching region at 1263.8 cm⁻¹. The measured absolute intensities of these three bands are given in Table I.

Darensbourg[12] has shown that the absolute intensities of the symmetric (A') and antisymmetric (A'') CO stretching modes, I_s and I_a, in cis-dicarbonyl compounds are related to the MCO dipole moment derivatives, μ_s' and μ_a', and geometrical factors through the equations

$$\mu_s' = \sqrt{I_s}/(0.540 \cos\theta) \tag{1}$$

$$\mu_a' = \sqrt{I_a}/(0.540 \sin\theta) \tag{2}$$

where 2θ is the angle between the two MCO vectors and I_s and I_a are the measured intensities × 10⁻⁴. The μ_s' and μ_a' values for η^5-C$_5$H$_5$Mn(CO)$_2$(CS) shown in Table I were calculated from I_s and I_a assuming θ = 46°. For comparative purposes, intensity and dipole moment derivative data for η^5-C$_5$H$_5$Mn(CO)$_2$L (L = SbPh$_3$, C$_7$H$_8$, CO)[13] have been included in Table I.

From previous studies on the CO intensities of cis-dicarbonyl compounds such as η^5-C$_5$H$_5$Mn(CO)$_2$L[13] and η^5-C$_5$H$_5$Fe-(CO)$_2$L,[12] it has been concluded that the ratio μ_s'/μ_a' is a measure of the vibronic contributions to μ_s'. The value of this ratio for η^5-C$_5$H$_5$Mn(CO)$_2$(CS) is 0.90 which compares closely with the values found for various η^5-C$_5$H$_5$Mn(CO)$_2$L de-

rivatives where L is a group Va donor ligand or an olefin (0.91–1.01).[13] A constant value of μ_s'/μ_a' has also been reported for some η^5-C$_5$H$_5$Fe(CO)$_2$L complexes where L = Cl, I, CN, and SnCl$_3$.[12] These constant values have been attributed to the C$_5$H$_5^-$ ligand trans to the carbonyls leveling the influence of the π-bonding ligands (L) cis to the carbonyls on vibronic contributions to μ_s'.[13] Presumably, this is also the case here for the CS ligand in η^5-C$_5$H$_5$Mn(CO)$_2$(CS).

The μ_s' and μ_a' values for η^5-C$_5$H$_5$Mn(CO)$_2$(CS) are comparable to those found for related η^5-C$_5$H$_5$Mn(CO)$_2$L complexes[13] and many other substituted metal carbonyls; e.g., see ref 6, 8, and 12. However, the μ'(MnCS) value (11.0)[25] is significantly greater than the μ'(MnCO) values and this may be taken as direct evidence for the greater π-acceptor ability of CS compared to that of CO. Consequently, absolute infrared intensity measurements are completely in accord with the results mentioned earlier of many other studies on transition metal thiocarbonyls. It is anticipated that with the increasing number of transition metal thiocarbonyls now being prepared, the absolute intensities of the CS stretching vibrations in these complexes will become the focus of considerable attention in the near future.

Registry No. η^5-C$_5$H$_5$Mn(CO)$_2$(CS), 31741-76-1.

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CS group (0.1144). This calculation assumes that ν(CS) is a "pure" vibration which strictly speaking is probably not true owing to coupling with the A' CO stretching mode and some of the low-frequency vibrations. In any event, the conclusion reached here concerning the π-acceptor ability of the CS ligand should not be altered radically because the net result would be an even greater CS intensity than that actually measured and so an even greater difference between μ'(MnCS) and the other dipole moment derivatives being considered.

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)
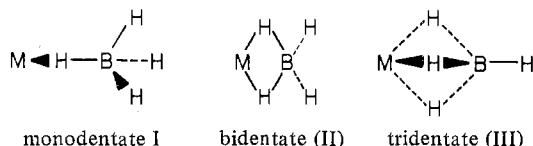
Examples are known for all geometries except I. Using the filled bonding BH orbitals directed at the metal as a basis set, ligation in each case can be regarded as arising from formation of three-center, two-electron bonds using empty metal orbitals and the appropriate combinations of BH orbitals as 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 BH₄ ligand acts as a formal three-electron donor [or BH₄⁻ 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(BH₄)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(BH₄)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≡CPh)₃W(CO).[5] That is, each BH₄⁻ ligand contributes 4.5 bonding electrons in Zr(BH₄)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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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.