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PERTURBATION OF METAL—METAL STRETCHING FREQUENCIES BY THE INTERACTION OF LEWIS ACIDS WITH BRIDGING CARBONYLS

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Summary

Adduct formation on the oxygen of a bridging carbonyl causes a very small perturbation of metal—metal stretching frequencies of polynuclear carbonyls. This small shift contrasts with the large change in ν(MM) when carbonyl groups are redistributed between terminal and bridging positions; therefore, using low frequency Raman spectroscopy, it is possible to infer the structural relation of C- and O-bonded adduct to the parent carbonyl. Structural inferences for $Fe_3(CO)_{12} \cdot AlBr_3$, $Ru_3(CO)_{12} \cdot AlBr_3$ and $Fe_2(CO)_9 \cdot AlBr_3$ are given.

Introduction

Recently it was shown that the metal—metal stretching frquency is significantly higher for a metal—metal bond which is carbonyl bridged than for a comparable nonbridged group, and these systematics were applied to the study of tautomeric equilibria of metal carbonyls in solution [1]. In the present work we explore the more subtle effect, on the metal—metal stretching frequencies brought about by the addition of a Lewis acid to the oxygen end of a bridging carbon monoxide. Some information on this topic has appeared in previous reports on C- and O-bonded carbon monoxide [2,3]. We were prompted to make a systematic study of this subject and to apply the results to the inference of structures for some C- and O-bonded polynuclear carbonyls. Another practical result of the present work is the finding that metal—metal stretching frequencies are observable for Lewis acid adducts of some polynuclear carbonyls even though the Raman spectra of the parent carbonyls lack discernible features in the M—M stretching region.

Experimental

Raman spectra were obtained with a backscattering illumination geometry on spinning samples in closed tubes. Details of the sample spinner, the Raman spectrometer and general techniques appear elsewhere [4,5]. Samples were prepared and handled under air-free conditions as described previously [2,6]. Concentrations of solutions were adjusted to values which are known from infrared data to produce the desired adduct [6]. Frequencies were accurately measured from the exciting line in each run using a peak finding computer routine on digital data collected at 0.17 cm^{-1} intervals. For narrow lines the peak position is located with a precision of ±0.3 cm^{-1}.

Results and discussion

For the first and second row polynuclear metal carbonyls, simple metal—metal stretching frequencies are observed in the 120—185 cm^{-1} region, and those characteristic of carbonyl bridged metal—metal bonds are observed around 200—260 cm^{-1} [7]. In the present work these two regions were investigated for compounds having bridging carbonyl oxygen bonded to Lewis acids such as CH_3^+, BCl_3, $AlEt_3$, and $AlBr_3$. While the metal—metal stretching region is fairly free of interference, attention has to be given to the possibility that deformation and rocking modes of BCl_3 [7] and $AlBr_3$ stretching modes [8—10] might be confused with M—M modes. Several lines of evidence suggest that the BCl_3 and $AlBr_3$ internal modes are not observed in the 200 cm^{-1} region under the present conditions. For example, reference to Table 1 shows that no extra bands are observed for any of the adducts beyond the number expected from the metal framework. Also the spectral data are nearly identical for $[(\eta^5\text{-}C_5H_5)Fe(CO)_4]$ adducts with either $AlBr_3$ or $Al(C_2H_5)_3$. Finally, the various $AlBr_3$ adducts display Raman bands over the range 214 to 241 cm^{-1}, which suggests that these features are not due to $AlBr_3$ modes.

To provide general information on the influence of Lewis acid addition on the M—M stretching frequencies of metal carbonyls, di-, tri- and tetra-nuclear

TABLE 1

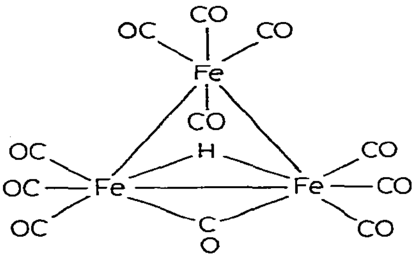
RAMAN SPECTRA IN THE METAL—METAL STRETCHING REGION

Parent [a]		Adduct(s) [a]		Frequency shift (cm^{-1})
Compound	Frequency	Compound	Frequency	
$Co_2(CO)_8$ (s)	229 cm^{-1}	$Co_2(CO)_8 \cdot AlBr_3$ (s)	234 cm^{-1}	+5
$Cp_3Ni_3(CO)_2$ (b)	186	$Cp_3Ni_3(COAlEt_3)_2$ (b)	193	+7
$[Et_4N][HFe_3(CO)_{11}]$ (s)	233, 176	$HFe_3(CO)_{10}(COCH_3)$ (hp)	233, 173	
(m)	231, 172	(ac)	236, 167	
		(s)	236, 175	
$Ru_3(CO)_{12}$ (s)	186, 152	$Ru_3(CO)_{11}(COAlBr_3)$ (s)	222, 171	
$[(Cp)Fe(CO)]_4$ (s)	222	$[(Cp)Fe(COAlBr_3)]_4$ (s)	222	0
(b)	216	$[(Cp)Fe(COAlEt_3)]_4$ (b)	222	+6
		$(Cp)_4Fe_4(CO)(COAlBr_3)_3$ (s)	221	
		$(Cp)_4Fe_4(CO)_2(COAlBr_3)_2$ (s)	ca. 227	
$Fe_3(CO)_{12}$		$Fe_3(CO)_{12} \cdot AlBr_3$ (s)	ca. 241, 171	
$Fe_2(CO)_9$		$Fe_2(CO)_9 \cdot AlBr_3$ (s)	214	
$[(Cp)Fe(CO)_2]_2$		$[(Cp)Fe(CO)_2]_2 \cdot BCl_3$ (s)	236	

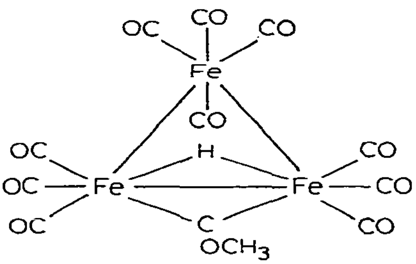
[a] s, solid; h, hexane solution; b, benzene solution; hp, heptane solution; ac, acetone solution; m, methanol solution.

metal carbonyls were studied. Two of the dinuclear systems did not provide straightforward information on the frequency perturbations brought about by Lewis acid, so the results presented at this point are confined to $Co_2(CO)_8$, and its 1 : 1 adduct with $AlBr_3$. Previous observations demonstrate that the addition of $AlBr_3$ to the oxygen of a bridging carbonyl in $Co_2(CO)_8$ has little effect on the Co—Co stretching frequency [2]. This result was confirmed by the new data, summarized in Table 1, which reveal a small, 5 cm^{-1}, increase in the M—M stretching mode upon adduct formation.

For a triangular trinuclear cluster of D_{3h} symmetry two M—M stretching bands, having A'_1 and E' symmetry, are Raman allowed. However, under resonance conditions, which may be encountered with colored polynuclear carbonyls, the spectrum is likely to be dominated by the totally symmetric mode to the exclusion of the degenerate counterpart. An example of this phenomenon is afforded by $(\eta^5\text{-}C_5H_5)_3Ni_3(CO)_2$, for which the carbonyls are triply bridged with one above and one below the triangular array of nickels. In a benzene solution only a single polarized, (and therefore symmetric) band is observed at 186 cm^{-1}, which increases by 7 cm^{-1} upon formation of the 1 : 2 adduct with triethylaluminium, Table 1 *. The observation of a single band in the adducts is consistent with the approximate D_{3h} symmetry, as indicated by infrared spectra in the CO stretching region. Here again, the small increase in metal—metal stretching frequency demonstrates a slight tightening of the metal framework upon adduct formation on triply bridged carbonyls. Another trinuclear system, $HFe_3(CO)_{11}^-$, has C_s symmetry, I [11], and therefore should yield two symmetric features, with the possibility of an additional antisymmetric M—M vibration. As shown in Table 1, only two bands are observed, both of which are polarized and are therefore attributed to preresonance enhanced symmetric modes. There is very little difference in frequency between these bands and those of $HFe_3(CO)_{10}(COCH_3)$, Table 1, which has the basic geometry of the parent anion with a methyl group attached to the bridging CO, II [12]. It is clear that the methyl carbocation does not have a large influence on the metal framework. This observation agrees with the small metal—metal frequency shifts discussed above for other systems in which electrophiles interact with bridging carbonyls.



(I)



(II)

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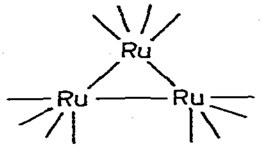
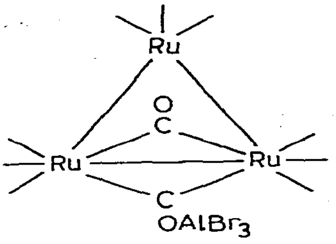
* Despite the presence of bridging carbonyls in $(\eta^5\text{-}C_5H_5)_3Ni_3(CO)_2$, this compound does not display its metal—metal stretching frequency above 200 cm^{-1} as would have been expected from the work in ref. 1. The lower observed frequency may arise from the unusual occurance of 49 valance-electrons in this triangular metal array.

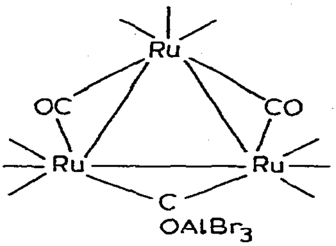
Judging from X-ray [13] and vibrational data, $Ru_3(CO)_{12}$ has idealized D_{3h} symmetry with no bridging carbonyls, III, but formation of the 1 : 1 $AlBr_3$ adduct leads to the shift of carbonyls from terminal to bridging positions, with presumed loss of 3-fold symmetry [2]. The most probably structure for this adduct is IV which is analogous to that of $Fe_3(CO)_{12}$, or V which involves CO bridges along each of the three Ru—Ru bonds.



(III)



(IV)



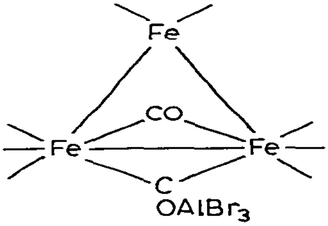
(V)

The Raman spectrum of $Ru_3(CO)_{12}$ (Table I) displays two bands below 200 cm^{-1} [14], as expected for one symmetric and one asymmetric stretch for metal—metal bonds which are unsupported by CO bridges [1]. The adduct has a prominent new feature at 222 cm^{-1} and another strong band at 171 cm^{-1}, however, owing the presence of some parent $Ru_3(CO)_{12}$ in the sample, it is not possible to rule out weak bands around 150 cm^{-1}. The pattern of frequencies and intensities for this adduct closely resemble those for the $Fe_3(CO)_{12}$ analogs, $HFe_3(CO)_{11}^-$ and $HFe_3(CO)_{10}(COCH_3)$, which suggests that the correct structure for $Ru_3(CO)_{12} \cdot AlBr_3$ is IV. Comparison with the M—M stretching modes of the carbonyl bridged and non-bridged isomers of $[(\eta^5\text{-}C_5H_5)Ru(CO)_2]_2$, 221 and 180 cm^{-1} respectively, demonstrates that the 222 cm^{-1} band of $Ru_3(CO)_{12} \cdot AlBr_3$ should be assigned to a Ru—Ru stretch for a carbonyl bridged metal—metal bond, while the 171 cm^{-1} feature is assigned for the symmetric stretch of a nonbridged Ru—Ru—Ru system, again indicating the corectness of structure IV.

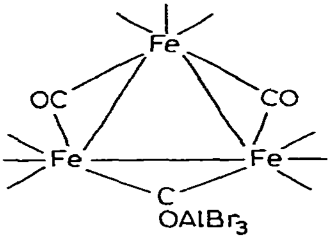
A series of adducts was investigated for the tetrahedral metal cluster compound, $[(\eta^5\text{-}C_5H_5)Fe(CO)]_4$, Table 1. In the parent compound, each carbonyl bridges three iron atoms, [15] and the compound is known to display a single resonance enhanced metal stretching mode in the Raman spectrum [16]. Solution data reveal a small increase, 6 cm^{-1}, in the totally symmetric stretching mode upon the formation of $[(\eta^5\text{-}C_5H_5)Fe(COAlEt_3)]_4$. For solid samples, there is no perceptible shift upon formation of 1 : 4 adduct with aluminum bromide, and the 1 : 2 and 1 : 3 adducts with aluminum bromide show very little shift from metal breathing mode of the parent. It is clear from these results that the metal—metal stretching region is not a useful tool for deducing the distribution of Lewis acids among bridging carbonyls, but the $Ru_3(CO)_{12} \cdot AlBr_3$ example shows that Raman spectroscopy can be highly sensitive to the Lewis acid induced tautomerism of carbonyl groups. Judging from the present results, the general expectation is either a small increase or little change in the metal—metal stretching frequencies when Lewis acids add to either double or triple metal bridging carbonyls and the general bonding implication of these findings is that the addition of a Lewis acid strengthens the metal bridging carbonyl framework in some cases, but the effect is small providing that carbonyl rearrangement is not induced by the Lewis acid.

The remaining systems to be discussed in this paper display a very interesting difference in M—M intensity between the parent carbonyl and the Lewis acid adduct. It has been noted in the literature that $Fe_2(CO)_9$, $Fe_3(CO)_{12}$, and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ do not display peaks assignable to Fe—Fe stretching vibrations [1,4]. This was confirmed in the present work using a variety of excitation lines from 676.4 to 457.9 nm. However, upon adduct formation, these compounds appear to display Fe—Fe stretching around 200 cm^{-1}, Table 1. Since for the parent carbonyls there is no sign of the M—M stretch, for a broad range of laser excitation frequencies, it appears unlikely that the low intensity of the M—M stretch can be attributed to interference in the pre-resonance enhancement, because a frequency dispersion is expected in the interference effects [17]. Furthermore, the compounds do not undergo large color changes upon adduct formation, and the Raman intensities of the M—M modes for the adducts fall off smoothly with increasing excitation wavelength so we are inclined to reject an explanation for the appearance of M—M stretches in the adducts which is based on large changes in the electronic spectra leading to large resonance enhancement. One possible explanation for the lack of observable bands in certain polynuclear carbonyls is the existence of high damping of these modes, whereas the observation of ν(MM) for the adducts might result from a large reduction in damping. Another possibility is that the M—M stretch is strongly coupled to another low frequency symmetric mode, perhaps a CMC deformation, to yield an intense in-phase feature outside the M—M stretching region, and a weak out of phase feature in the M—M stretch region. In this case adduct formation might perturb the form of the normal modes and regain some intensity in the M—M stretching region.

The solid sample of $Fe_3(CO)_{12} \cdot AlBr_3$ yields a spectrum which is a quite similar spectrum to that of $HFe_3(CO)_{11}^-$ and/or $HFe_3(CO)_{10}(COCH_3)$; namely, it shows two peaks at 241 and 171 cm^{-1} (514.5 nm excitation). The probable structure for 1 : 1 adduct $Fe_3(CO)_{12} \cdot AlBr_3$ is either VI or VII. Owing to the similarity of this spectrum with that of $HFe(CO)_{11}^-$ and $HFe_3(CO)_{10}(COCH_3)$, Fig. 1, both of which have structures analogous to VI, structure VI is preferred. One also may argue from the observation of one of the bands, 241 cm^{-1}, at a frequency typical of a carbonyl bridged metal—metal stretch, and the other at 171 cm^{-1} which is typical of an unsupported M—M bond that structure VI is preferred to VII.



(VI)



(VII)

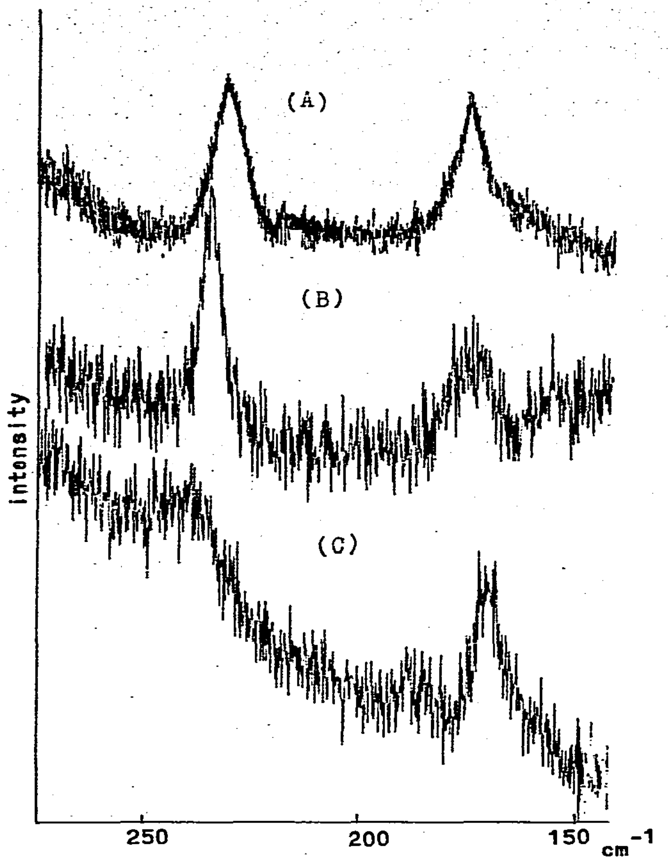
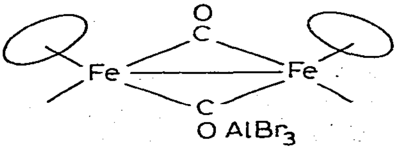


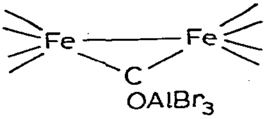
Fig. 1. Raman spectra of solid: (A) $[Et_4N][HFe_3(CO)_{11}]$, (B) $HFe_3(CO)_{10}(COCH_3)$, and (C) $Fe_3(CO)_{12} \cdot AlBr_3$.

A structural study on 1 : 1 adduct of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ with BCl_3 by infrared spectroscopy has shown that the double carbonyl bridging arrangement is conserved on adduct formation, VIII [2]. Unlike the parent carbonyl, the adduct displays a strong Raman peak in the M—M stretching region at 236 cm^{-1} for a solid sample. This frequency is quite reasonable for the double carbonyl bridging structure VIII. For example $[(\eta^5\text{-}C_5H_5)Ru(CO)_2]_2$, which has the double carbonyl bridging structure, shows a strong peak at 217 cm^{-1} for a solid sample [1].



VIII (plus *trans*)

Raman measurement of $Fe_2(CO)_9 \cdot AlBr_3$ display a peak at 214 cm^{-1} for a solid sample even though the parent compound lacks an observable Fe—Fe stretch. This frequency is significantly lower than that of $HFe_2(CO)_8^-$ (255 cm^{-1} for solid sample) [1], which has two bridging carbonyls and one bridging hydrogen, or that of the carbonyl bridged isomer of $Fe_2(CO)_8^{2-}$ (222 cm^{-1} in DMF) [1]. The low value for the Fe—Fe stretch in $Fe_2(CO)_9 \cdot AlBr_3$ might arise from a rearrangement of the triple carbonyl bridge of the parent carbonyl to a single carbonyl bridge in the adduct as shown in IX.



(IX)

As was documented in the first part of this paper, a very small change in the metal—metal stretching frequency is associated with adduct formation on bridging carbonyls, providing the original carbonyl arrangement around metal atoms is not changed upon adduct formation. Therefore, it is possible to employ the M—M stretching frequencies observed for the adducts $Fe_3(CO)_{12} \cdot AlBr_3$ and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2 \cdot BCl_3$ to infer Fe—Fe stretching frequencies around 240 and 170 cm^{-1} for the symmetric modes of $Fe_3(CO)_{12}$ and 235 cm^{-1} for $[(\eta^5\text{-}C_5H_5)Fe_2(CO)_2]_2$. In the case of $Fe_2(CO)_9$, it appears that the original carbonyl arrangement is disturbed by adduct formation; so the Fe—Fe stretch of the parent carbonyl cannot be estimated from data on this adduct.

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