

Correspondence

Cation Interaction with Transition Metal Carbonylates and Cyanocarbonylates

Sir:

Strongly ion-paired forms of alkali metal salts of transition metal carbonylates have been implicated as significant kinetic moderators both in intramolecular rearrangements¹ and in oxidative addition reactions of such salts.^{2,3} Conductivity measurements have been used to quantify the extent of ion-pair interactions in solution.² Infrared spectroscopy has not only served to detect the contact ion pairs⁴ but has also allowed for discerning very specific sites of cation attachment to anions possessing two or more basic, potentially interactive sites. The following are a few such examples of contact ion pairs in which the cation interaction is exterior to the coordination sphere of the transition metal. Sodium ion interacts with the equatorial group of the trigonal-bipyramidal $\text{Mn}(\text{CO})_5^-$ anion.² Sodium ion interacts with the nitrosyl oxygen of tetrahedral $\text{Fe}(\text{CO})_3\text{NO}^-$.⁵ The acyl oxygen is the ion-pair interactive site of $(\text{OC})_4\text{FeC}(\text{CH}_3)\text{O}^- \cdots \text{Na}^+$,¹ $(\text{Ph}_3\text{P})\text{Fe}(\text{CO})_3\text{C}(\text{Ph})\text{O}^- \cdots \text{Li}^+$,⁶ and $(\text{OC})_5\text{MoC}(\text{Ph})\text{O}^- \cdots \text{Li}^+$.⁷ An "equatorial" carbonyl oxygen is preferred over the "axial" CO or the hydride as the site for Na^+ contact with the pseudo-trigonal-bipyramidal $\text{H-Fe}(\text{CO})_4^-$ anion.⁸

This work defines the site of interaction of cations with cyanocarbonylates, compares the infrared probe of such interaction with analogous carbonylates, and makes a tentative statement as to comparisons of alkali cation interactions as opposed to 3A Lewis acid interactions with basic sites of carbonylate complexes and cyanocarbonylate complexes.

In diethyl ether solvent (dielectric constant $D = 4.3$), sodium salts of $\text{Fe}(\text{CO})_4\text{CN}^-$ or $\text{Mo}(\text{CO})_5\text{CN}^-$ exist predominantly in contact ion pair forms, cyanide site preference, which converts to solvent-separated ion pairs on addition of 1 equiv of 15-crown-5 or on dissolution of the salts in tetrahydrofuran ($D = 7.4$). The latter conclusion is based in two experiments. Infrared spectral patterns in these solutions indicate the cyanocarbonylates to be in symmetrical solvent fields, yet conductivity measurements in THF yield very low ion-pair dissociation constants ($K_D \approx 10^{-7} \text{ M}$).⁹ The former conclusion is based in IR frequency shift arguments that have been convincingly used to account for shifts in contact vs. solvent-separated ion pairs of many transition metal carbonylates.^{2,4,10} That is, the electron drain toward Na^+ caused by the cation's interaction with ligand CX enhances the $d_\pi(\text{M}') \rightarrow \pi^*(\text{CX} \cdots \text{Na}^+)$ back-accepting capability, thus lowering the bond order (and frequency) of that CX group relative to its bond order in a symmetrical solvent field. Simultaneously the bond orders of those CO groups, which do *not* interact with the alkali cation, are increased due to their decreased competitive ability for metal d electrons. (Differences in carbonyl stretching frequencies and/or force constants were successfully related to the extent of ion pairing in the series $\text{LMn}(\text{CO})_3\text{CO}^- \cdots \text{Na}^+$ ($\text{L} = \text{PMe}_2\text{Ph} \approx \text{PPh}_3 > \text{P}(\text{OPh})_3 > \text{CO}$) as defined by the relative amounts of contact vs. solvent-separated ion pairs.²) Thus as Table I shows, in the all-carbonyl anions the difference between $\nu(\text{CX})$ of $[\text{M}'-]\text{C}-\text{X} \cdots \text{Na}^+$ and $[\text{M}']\text{C}-\text{X} \cdots \text{Na}^+$ is -20 to -50 cm^{-1} for $\text{X} = \text{O}$ and ca. -15 cm^{-1} for $\text{X} = \text{N}$. The shifts to higher frequencies for the CO groups not interacting with Na^+ in the cation-perturbed carbonylates or cyanocarbonylates, as compared to the analogous vibrations in the same carbonylates or cyanocarbonylates in a symmetrical solvent field, range from $+1$ to $+20 \text{ cm}^{-1}$, with the shifts in general being smaller for the cyanocarbonylates. In summary,

Table I. CO Stretching Frequencies^a (cm^{-1}) of Cyanocarbonylate and Carbonylate Salts in Their Contact Ion-Paired^b and Solvent-Separated Ion-Paired Forms

salt ^d	solvent	$\nu(\text{CO}) (C_{3v})$			$\nu(\text{CN})$
		$A_1^{(2)}$	$A_1^{(1)}$	E	
$\text{Na}^+\text{Fe}(\text{CO})_4\text{CN}^-$	Et_2O	2041	1965	1939	2102 (65%) 2119 (35%)
$\text{Na}^+(15\text{-c-5})\text{Fe}(\text{CO})_4\text{CN}^-$	Et_2O	2040	1951	1933	2118
salt	solvent	$\nu(\text{CO}) (C_{4v})$			$\nu(\text{CN})$
		$A_1^{(2)}$	E	$A_1^{(1)}$	
$\text{Na}^+\text{Mo}(\text{CO})_5\text{CN}^-$	Et_2O	2058	1932	1907	2101 (75%) 2114 (25%)
$\text{Na}^+(15\text{-c-5})\text{Mo}(\text{CO})_5\text{CN}^-$	Et_2O	2061	1930	1903	2111
$\text{Na}^+\text{Mo}(\text{CO})_5\text{CN}^-$	THF	2061	1929	1898	2115
salt	solvent	$\nu(\text{CO}) (C_{2v})$		$\nu(\text{CO} \cdots \text{Na}^+)$	
		$A_1 + B_1$	B_2		
$\text{Na}^+\text{Mn}(\text{CO})_5^-$	Et_2O^c	1912	1883	1804	
salt	solvent	$\nu(\text{CO}) (D_{3h})$			
		A_2''	E'		
$\text{Na}^+(15\text{-c-5})\text{Mn}(\text{CO})_5^-$	THF	1894	1860		
salt	solvent	$\nu(\text{CO}) (C_g)$			$\nu(\text{CO} \cdots \text{Na}^+)$
		A	A	A'	
$\text{Na}^+\text{Mn}(\text{CO})_4\text{PPh}_3^-$	THF	1943.5	1853	1827	1774
salt	solvent	$\nu(\text{CO}) (C_{3v})$			
		A_1	A_1	E	
$\text{Na}^+(\text{HMPA})_x\text{-Mn}(\text{CO})_4\text{PPh}_3^-$	THF	1941	1845	1813	
salt	solvent	$\nu(\text{CO}) (C_s)$			$\nu(\text{CO} \cdots \text{Na}^+)$
		A	A	A'	
$\text{Na}^+\text{HFe}(\text{CO})_4^-$	THF	2003	1910	1890	1854
salt	solvent	$\nu(\text{CO}) (C_{3v})$			
		$A_1^{(2)}$	$A_1^{(1)}$	E	
$\text{PPN}^+\text{HFe}(\text{CO})_4^-$	THF	1998	1905	1876	

^a Spectra were taken in 0.1-mm sealed NaCl cells of ca. 0.01 M solutions on a Perkin-Elmer 521 infrared spectrophotometer.

^b Frequencies in italics are assigned to the contact ion species.

^c Another A_1 vibration is at ca. 2020 cm^{-1} ; see ref 7 for discussion. ^d 15-c-5 = 15-crown-5.

the IR data strongly suggest that the cation interactive site is at cyanide in the cyanocarbonylates. That interaction provides, however, less dramatic IR frequency shifts than those experienced in all-carbonyl anions, although the directions of shifts are precisely analogous in carbonylates and cyanocarbonylates.

This cyanide ligand interaction site preference is consistent with expectations and other observations. As Table I shows, $\nu(\text{CO})$ frequencies in cyanocarbonylates are higher than those of isoelectronic carbonylates or of the hydridocarbonylate, $\text{HFe}(\text{CO})_4^-$. The negative charge is relatively localized on the CN⁻ ligand. Furthermore adducts of $\text{CpFe}(\text{CO})_2\text{CN}$ and 3A Lewis acids are formulated $\text{CpFe}(\text{CO})_2\text{CN} \cdots \text{ER}_3$.¹¹

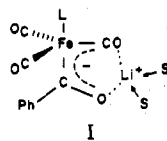
There is, however, an intriguing difference in the response of metal-bound CN stretching frequencies toward interaction with Lewis acids vs. alkali cations. Similar to the effect of a contact cation interaction on the frequency shift of CN or CO, the $[\text{M}'-]\text{C}-\text{O} \cdots \text{ER}_3$ ($\text{E} = 3\text{A}$ element, $\text{R} = \text{alkyl}$ or

halide) interaction produces a lowering of that $\nu(\text{CO})$ with a concomitant rise in $\nu(\text{CO})$ of ancillary CO groups as compared to the carbonylate or carbonyl complex in a symmetrical solvent field.¹² In marked contrast, addition of Me_3Al to $\text{Na}^+\text{Mo}(\text{CO})_5\text{CN}^-$ in THF (where the cyanocarbonylate is in a solvent-separated ion-paired form) led to an infrared spectral pattern almost identical with that of the pure cyanocarbonylate; however, $\nu(\text{CN})$ was displaced by 23 cm^{-1} to higher frequencies and the three $\nu(\text{CO})$ were displaced also to higher frequencies, by +4, +10, and +10 cm^{-1} ($A_1^{(2)}$, E, and $A_1^{(1)}$, respectively). Similarly the Lewis acid adducts $\text{CpFe}(\text{CO})_2\text{CN}\cdots\text{AlR}_3$,¹¹ $\text{CpFe}(\text{CO})_2\text{CN}\cdots\text{BR}_3$,¹¹ $\text{Fe}(\text{phen})(\text{CN}\cdots\text{BH}_3)_2$,¹³ etc. also show $\nu(\text{CN})$ values that are 30–80 cm^{-1} higher in energy than those of the free complexes; yet the remainder of the molecular fragments display electronic or vibrational properties indicative of substantial drain of electrons onto the $\text{CN}\cdots\text{ER}_3$ ligand.^{11,13}

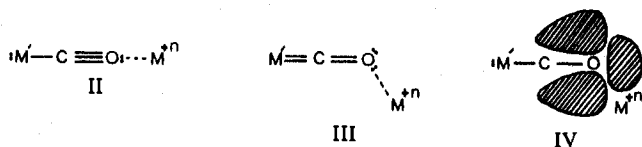
It has been noted that both the carbon and nitrogen lone pairs are actually antibonding with respect to the CN bond¹⁴ and furthermore that complexation of both lone pairs in CN^- successively by BH_3 serves to increase the $\nu(\text{CN})$ by 99 and 81 cm^{-1} , respectively.¹⁵ Carbon-end complexation of CN^- ($\nu(\text{CN})$ in $\text{KCN} = 2080\text{ cm}^{-1}$) by metal carbonyl fragments likewise increases $\nu(\text{CN})$ (Table I). However, nitrogen-end complexation by Na^+ produces a negative $\nu(\text{CN})$ shift whereas AlMe_3 interaction produces a positive $\nu(\text{CN})$ shift.

Purcell has provided a comprehensive discussion of the factors that influence $\nu(\text{CN})$ shifts and has suggested that, in the case of the Lewis acid adducts, the factors which would increase the $\nu(\text{CN})$ such as the removal of electrons that are formally in antibonding orbitals (i.e., the nitrogen lone pair) and kinematic coupling, counterbalance and overcome the enhanced CN π -accepting ability which would effectively decrease the $\nu(\text{CN})$.¹⁵ Evidently in the present work the electrostatic nature of the $[\text{M}'-]\text{CN}\cdots\text{M}^{n+}$ interaction allows for the π -acceptor increase to dominate changes in CN bond order.

Relevant to this line of thought is an assemblage of X-ray crystal structure analyses of alkali and alkaline earth salts of transition-metal carbonylates that establish an interesting subtle structural trend. All of the structures carried out to date of such salts have displayed an $[\text{M}'-]\text{CO}\cdots\text{M}^{n+}$ arrangement which places the M^{n+} off-linear with respect to the M–C–O linear groupage. Some examples follow ($\angle\text{C–O–M}^{n+}$): $(\text{py})_4\text{Mg}^{2+}[\text{OCMo}(\text{CO})_2\text{Cp}]_2$ (155°);¹⁶ $(\text{THF})_3\text{Al}^{3+}[\text{OCW}(\text{CO})_2\text{Cp}]_3$ ($140\text{--}163^\circ$);¹⁷ $\text{Na}_2\text{Fe}(\text{CO})_4\cdot 1.5\text{dioxane}$ (138°);¹⁸ $\text{Co}(\text{salen})_2(\text{THF})\text{Na}^+[\text{OCCo}(\text{CO})_3^-]$ (142°);¹⁹ and $(\text{THF})_4\text{V}^{2+}[\text{OCV}(\text{CO})_5^-]_2$ (168°).²⁰ In structure I, established



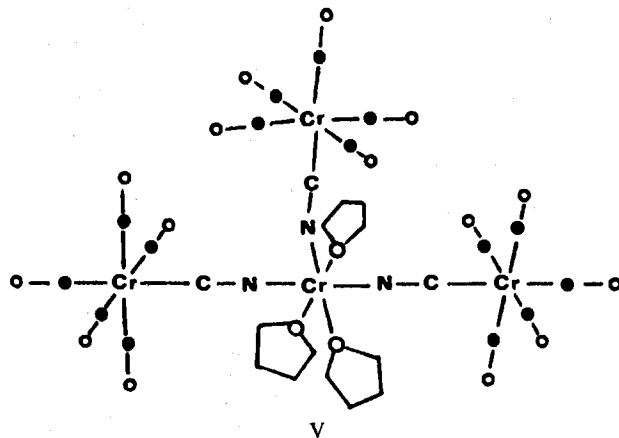
by ^{13}C NMR and $\nu(\text{CO})$ IR solution data, the off-linear interaction of Li^+ with $\text{C}=\text{O}$ was promoted by the simultaneous interaction of Li^+ with the acyl oxygen. Thus the expectation that the electrophile interaction exterior to a carbonylate anion should be with the oxygen lone pair electron density which should in turn lead to a linear arrangement as in II is not



realized in the solid state nor in at least one case in solution. The actual off-linear apparent arrangement of choice may be

thought as dependent on the relative contributions of valence bond structures II or III to the actual arrangement of electrons in the anion. A better explanation may exist in the molecular orbital description of CO electron density illustrated in IV. The drawing of IV has attempted to emphasize the fact that there is substantial π density in the region of the oxygen lone pair,²¹ thus suggesting that a rather directional electrostatic potential might be associated with cation interaction; i.e., the cation is positioned so as to interact maximally with electron density in both σ and π orbitals. Note that structure IV reinforces the expectation of lowering of $\nu(\text{CO})$ on interaction with M^{n+} in that electrons in bonding molecular orbitals are being drawn to M^{n+} , in addition to the aforementioned increase in the $d_\sigma(\text{M}') \rightarrow \pi^*(\text{CO}\cdots\text{M}^{n+})$ back-bonding.

The question then arises as to whether a substantial difference exists for the isoelectronic CN^- ligand. An off-linear placement of the cation would yield an interaction involving electron density from the π -bonding orbital of CN, consistent with the observed frequency shift and providing a reasonable escape from the 3A Lewis acid/alkali cation dichotomous effect on $\nu(\text{CN})$, i.e., assuming the Lewis acid covalent interaction to be linear. Countering this argument, however, are electron density calculations which have shown that there is much less π density in the exterior region of the cyanide and that the nitrogen lone pair density extends much further along the CN axis²² (or is more available²³) than does the oxygen lone pair density in CO. These data would tempt one to conclude that the $[\text{M}'-]\text{CN}\cdots\text{M}^{n+}$ interaction has less of a likelihood of taking advantage of an electrostatic potential made up of both π and lone-pair orbitals and in fact has a much better chance of being linear than bent. In fact, there is a predominant linearity of the $\text{Cr}^{3+}\cdots\text{NC}$ linkages in V^{24} and



also with the geometry of $\text{M}'\text{—C}\equiv\text{N}\cdots\text{M}^{n+}$ of cyanide complexes of the Prussian blue type²⁵ as well as the Hofmann clathrates.^{26,27} To be sure, the polymeric nature of the latter binary cyanides imposes a rigidity and high symmetry which might dictate linearity of the CN bridge; however, compound V has the potential for flexibility or deviation from linearity, as is seen for the analogous $(\text{THF})_4\text{V}^{2+}[(\text{OC})\text{V}(\text{CO})_5^-]_2$ salt,²⁰ yet maintains linearity on the whole.

In the absence of X-ray structural data on an alkali or alkaline earth salt of a cyanocarbonylate,²⁸ further speculation on the linear/nonlinear electrostatic arrangement and its ultimate effect on $\nu(\text{CN})$ is premature. The aim of this correspondence has been to point out that the directions of $\nu(\text{CX})$ frequency shifts are not necessarily compatible in all cases of acid/base interactions. The nature of the interaction (electrostatic vs. covalent) may determine not only magnitudes but directions of shifts, and the geometry of the interaction could provide the ultimate reason for seemingly anomalous behaviors.

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Registry No. $\text{Na}^+\text{Fe}(\text{CO})_4\text{CN}^-$, 70982-66-0; $\text{Na}^+(15\text{-c-5})\text{Fe}(\text{CO})_4\text{CN}^-$, 70982-67-1; $\text{Na}^+\text{Mo}(\text{CO})_3\text{CN}^-$, 15040-37-6; $\text{Na}^+(15\text{-c-5})\text{Mo}(\text{CO})_3\text{CN}^-$, 70982-65-9; $\text{Na}^+\text{Mn}(\text{CO})_5$, 13859-41-1; $\text{Na}^+(15\text{-c-5})\text{Mn}(\text{CO})_5^-$, 59890-72-1; $\text{Na}^+\text{Mn}(\text{CO})_4\text{PPh}_3^-$, 19457-74-0; $\text{Na}^+\text{HFe}(\text{CO})_4^-$, 53558-55-7; $\text{PPN}^+\text{HFe}(\text{CO})_4^-$, 56791-54-9.

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The Transition State for Octahedral Substitution and the Interpretation of Volumes of Activation: The Role of Nonlabile Ligands

Sir:

In recent years, the most important innovations in understanding of the mechanism of octahedral substitution have followed from analysis of pressure dependence and volumes

Table I. Rates of Dissociative Water Loss from Representative Complexes at 25 °C

complex ^a	log [k (s ⁻¹)]	complex ^a	log [k (s ⁻¹)]
$\text{Ni}(\text{OH}_2)_6^{2+}$	4.5	$\text{Co}(\text{OH}_2)_6^{2+}$	6.4
$\text{Ni}(\text{OH}_2)_5\text{Cl}^+$	5.1	$\text{Co}(\text{OH}_2)_5\text{NH}_3^{2+}$	7.2
$\text{Ni}(\text{NH}_3)_3(\text{OH}_2)_3^{2+}$	6.4	$\text{Mn}(\text{OH}_2)_6^{2+}$	6.8
$\text{Ni}(\text{en})_2(\text{OH}_2)_2^{2+}$	6.5	$\text{Mn}(\text{phen})(\text{OH}_2)_4^{2+}$	7.1
$\text{Ni}(\text{bpy})_2(\text{OH}_2)_2^{2+}$	4.8	$\text{Fe}(\text{OH}_2)_6^{3+}$	4.3
$\text{Ni}(\text{EDTA})\text{OH}_2^-$	5.8	$\text{Fe}(\text{OH}_2)_3\text{Cl}_3$	5.3

^a Ligand abbreviations: en, ethylenediamine; bpy, bipyridine; EDTA, ethylenediaminetetraacetic acid; phen, 1,10-phenanthroline.

of activation (ΔV^\ddagger). Notably, the negative value of ΔV^\ddagger (which is, in addition, pressure independent) associated with a process like water exchange at a Cr(III) center is crucial to the recognition of the associative contribution to this activation process.¹ After the realization of the significance of the ΔV^\ddagger results, information documenting the more traditional test of associative character—rate sensitivity to the nature of the entering group²—was reported.¹ Interestingly, this last test has not received universal assent.³ The sensitivity of reactions at Cr(III) centers to nucleophilicity seems to be qualitatively different from that observed in highly associative reactions like those at Pt(II) centers. This is despite the fact that the observed activation volumes are quite negative and that the slopes of linear free energy relationships are those predicted by a theory of strongly associative substitution derived from a one-dimensional potential function by German and Dogonadze (see ref 1 and papers cited therein).

It seems likely that there is an additional variable which has not yet been fully evaluated. A clue to the problem can be found in the focus of the discussion which has surrounded octahedral substitution. The discussion concentrates on the *leaving* and *entering* ligands.² (The bonds to these ligands are the ones considered in defining the terms associative and dissociative and in the one-dimensional theory of Dogonadze and German.) However, it was clear to Pearson⁴ that well-documented examples of *dissociative* reaction occur with activation energies well *below* (much less than half) *the bond dissociation energies!* The other factor is the stabilization of the transition state afforded by the remaining five ligands which are not either the leaving or the entering ones. In Table I, we collect evidence which shows that the remaining five ligands do have a very significant effect on the rate of dissociative substitution reactions. The observed effect is one in which ligands of greater σ -donor power stabilize the center of reduced coordination number as one would expect.

In order to interpret the important data coming from ΔV^\ddagger measurements, it is desirable to evaluate the contribution of the nonlabile ligands to volume change. We begin with the dissociative reaction. As one ligand is lost, the remaining five must strengthen bonds. This will lead to two contributions to the volume of activation which are negative. These are (i) compression of the bonds which reduce the volume of the primary coordination sphere and (ii) collapse of the solvent onto this contracted primary coordination sphere. In a dissociative substitution process, these two negative contributions will be balanced by a major positive contribution from the transfer of the leaving group from the first to the second coordination sphere. The most clearly documented case of dissociative substitution occurs in complexes of Co(III) where correlations based on all of ΔG^\ddagger , ΔH^\ddagger , ΔS^\ddagger , and ΔV^\ddagger point clearly to the completeness of the dissociation of the leaving group in the transition state and the lack of bonding to the entering group.¹ In a representative reaction, the water-exchange process of $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$, the value of ΔV^\ddagger is 1.2 mL mol⁻¹ for a reaction with, of course, a ΔV° of zero.¹ This modest positive value suggests that the negative terms ap-