Ab Initio Calculations on the Bonding Properties of Isonitrile and Nitrile Ligands †

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Ab initio calculations have been performed on $CNCH_3$ and $NCCH_3$ to evaluate the change in σ-donor and π-acceptor character as a function of molecular geometry. For $CNCH_3$, it is shown that as the $CNCH_3$ angle decreases, the π-acceptor character increases markedly, while the π-donor character remains essentially constant. For $NCCH_3$, calculations indicate a potential π-donor character for the ligand; a similar decrease in the $NCCH_3$ angle results in a *decrease* in π-acceptor capability. The results are discussed in the light of relevant structural, spectroscopic, and kinetic literature data.

In contrasting ways, isonitriles and nitriles form two of the most versatile groups of ligands available to the inorganic and organometallic chemist. Isonitriles form complexes with metals in both low and normal oxidation states, and within the low-valent category, the similarity to carbon monoxide in terms of both structure and reactivity may be noted. A wide variety of mixed-ligand complexes are known, and recent work has revealed an extensive array of binary uni- and polymetallic isonitrile complexes. Some of these have carbonyl analogues, but many are unique in the sense that the carbonyl analogue is unknown or unstable under normal conditions. Isonitriles exhibit a variety of bonding modes (terminal, edge-bridging, face-bridging, two-, four-, and six-electron donor) and participate in the fluxional site-exchange processes observed in metal clusters. Structural studies reveal a wide variety of co-ordination geometries ranging from linear or nearly linear with short C–N bond lengths to strongly bent conformations (CNR ~ 120°) with much longer C–N distances usually associated with edge-bridging or face-bridging isonitriles or with isonitriles in electron-rich complexes.[1]

Nitriles also form complexes with metals in both low and normal oxidation states, but in contrast to isonitriles, the synthetic utility of both uni- and poly-metallic low-valent complexes lies in the lability of the nitrile in its substitution reactions with other ligands. No zerovalent binary complexes are known, and the nitrile is invariably co-ordinated as a two-electron donor with only slight deviations from linearity being observed.

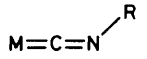
We[2] and others[3] have evaluated by calculation the effect on the bonding properties of the isonitrile ligand of conjugative R groups (R = Ph, CH_2=CH, COH, COOH, COPh, and CN). Compared with alkyl isonitriles, a substantial enhancement of the π-accepting character of the ligand is indicated, in agreement with spectroscopic results on recently prepared CNCOPh[4] and CNCN[5] complexes. We wish to report here our LCAO-MO calculations on the effect of ligand geometry (primarily that associated with the CNR angle) on the bonding properties of the isonitrile ligand, together with calculations on the isomeric nitrile ligand and a discussion of relevant spectroscopic and structural data.

Results and Discussion

The metal–ligand bonding in an organometallic complex may be described starting from a simple scheme of interactions between the metal and ligand frontier molecular orbitals (f.m.o.) (Figure 1). This f.m.o. formalism[6] has been described within the framework of a one-electron Hamiltonian (*e.g.* the so-called ' one-electron molecular orbital ' procedure[7]). Perturbation theory predicts that the energetic stabilizations δ_σ and δ_π are proportional to $S^2\sigma/\Delta E_\sigma$ and $S^2\pi/\Delta E_\pi$ where S and ΔE are the overlap integral and the energy difference between the interacting molecular orbitals respectively. In a homogeneous series of two-electron ligands, the S^2 values retain approximately the same order of magnitude and exhibit a variation which is small compared to that associated with changes in ΔE. Thus, for the same organometallic fragment, the δ_σ and δ_π stabilizations may be directly related to the energies of the ligand σ-donor and π-acceptor orbitals; the higher the ligand σ-h.o.m.o. (highest occupied molecular orbital) energy, the better the σ-donating power, while a lowering of the ligand π-l.u.m.o. (lowest unoccupied molecular orbital) improves the π-acceptor ability.

$M \leftarrow C{\equiv}N{-}R$

(A)



(B)

For an isonitrile, the two extremes of bonding may be associated with the resonance forms (A) and (B). The con-

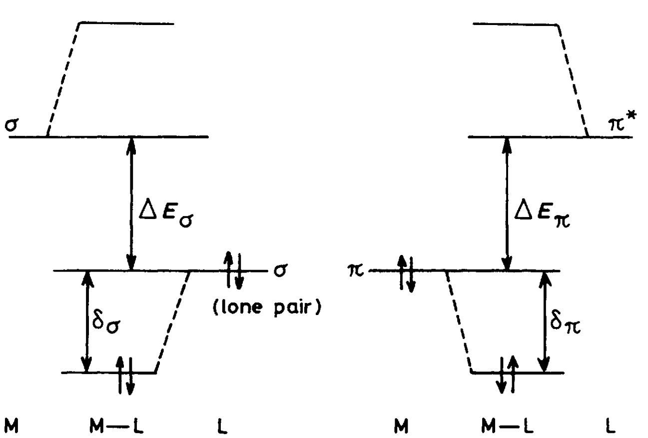


Figure 1. Frontier molecular orbital interaction diagram of a metal–ligand bond

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† *Non-S.I. unit employed*: 1 atomic unit (a.u.) = 27.210 eV (eV ≈ 1.60 × 10^{-19} J).

Table 1. *Ab initio* calculation data on CNCH$_3$, CO, and NCCH$_3$

			CNCH$_3$						CO	NCCH$_3$	
	CN bond length/Å		1.155[a]	1.16[b]	1.19[c]	1.20[d]	1.21[e]	1.24[f]	*g*	1.14[h]	1.14
	CNR or NCR/°		180	172	165	153	135	123		180	165
	Total energy/a.u.		−131.734	−131.733	−131.730	−131.724	−131.711	−131.694	−112.567	−131.760	−131.756
π^*_z	Energy/a.u.		0.215	0.212	0.202	0.196	0.185	0.169	0.217	0.158	0.214
	CX overlap population[i]		−1.00	−0.99	−0.99	−0.98	−0.98	−0.05	−1.15	−0.96	−0.96
	% terminal atom ($2p_z$)[j]		56	56	59	59	58	58	76	31	31
π^*_y	Energy/a.u.		0.215	0.209	0.194	0.175	0.144	0.122	0.158	0.217	0.227
	CX overlap population[i]		−1.00	−0.76	−0.78	−0.66	−0.49	−0.39	−1.15	−0.96	−0.87
	% terminal atom[j]	$2s$	0	0	0	1	1	0	0	0	0
		$2p_x$	0	0	0	0	0	0	0	0	0
		$2p_y$	56	46	54	57	64	70	76	31	13
		total	56	47	54	58	65	71	76	31	13
σ_{ep}	Energy/a.u.		−0.458	−0.458	−0.470	−0.478	−0.493	−0.505	−0.547	−0.547	−0.548
	CX overlap population[i]		−0.78	−0.68	−0.28	−0.30	−0.26	−0.25	−0.37	−0.37	−0.24
	% terminal atom[j]	$2s$	62	57	36	37	35	35	59	34	32
		$2p_x$	34	31	19	19	18	19	32	51	52
		$2p_y$	0	2	10	8	7	6	0	0	0
		total	96	91	65	65	60	60	91	85	84
π_z	Energy/a.u.		−0.471	−0.469	−0.460	−0.457	−0.455	−0.477	−0.636	−0.461	−0.461
	CX overlap population[i]		+0.40	+0.40	+0.40	+0.40	+0.40	+0.41	+0.38	+0.50	+0.50
	% terminal atom ($2p_z$)[j]		25	26	26	27	28	30	25	49	50
π_y	Energy/a.u.		−0.471	−0.471	−0.456	−0.453	−0.451	−0.450	−0.636	−0.461	−0.461
	CX overlap population[i]		+0.40	+0.30	−0.06	−0.02	−0.02	+0.02	+0.38	+0.50	+0.49
	% terminal atom[j]	$2s$	0	5	24	22	21	17	0	0	0
		$2p_x$	0	2	15	15	18	18	0	0	0
		$2p_y$	25	23	15	15	12	10	25	49	48
		total	25	30	54	52	51	45	25	49	48

[a] Extrapolated. [b] R. D. Adams, F. A. Cotton, and J. M. Troup, *Inorg. Chem.*, 1974, **13**, 257. [c] J. M. Bassett, D. E. Berry, G. K. Barker, M. Green, J. A. K. Howard, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1979, 1003 (equatorial). [d] As for *c* (average). [e] As for *c* (axial). [f] J. M. Bassett, G. K. Barker, M. Green, J. A. K. Howard, F. G. A. Stone, and C. Wolsey, *J. Chem. Soc., Dalton Trans.*, 1981, 219. For references to other bent isonitrile ligands, see ref. 16; B. Jovanovics, L. Manojlovic-Muir, and K. W. Muir, *J. Chem. Soc., Dalton Trans.*, 1972, 1178; J. Chatt, A. J. L. Pombiero, R. L. Richards, G. H. D. Royston, K. W. Muir, and R. Walker, *J. Chem. Soc., Chem. Commun.*, 1975, 708; S. Z. Goldberg and R. Eisenberg, *Inorg. Chem.*, 1976, **15**, 58, 158; G. K. Barker, A. M. R. Galas, M. Green, J. A. K. Howard, F. G. A. Stone, T. W. Turney, A. J. Welch, and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 1976, 256; W. E. Carroll, M. Green, A. M. R. Galas, M. Murray, T. W. Turney, A. J. Welch, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1980, 80; M. Green, J. A. K. Howard, M. Murray, J. L. Spencer, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1977, 1509; and E. Band, N. R. Pretzer, M. G. Thomas, and E. L. Muetterties, *J. Am. Chem. Soc.*, 1977, **99**, 743. [g] Interatomic Distances, Spec. Publ. No. 11, The Chemical Society, London, 1958. [h] Ref. 18. [i] X = O in the case of CO, X = N in the case of CNCH$_3$ and NCCH$_3$; based on an assumed population of two electrons. [j] Terminal atom is carbon for CO and CNCH$_3$ and nitrogen for NCCH$_3$.

tribution of (B) can be seen to increase as the CNR angle decreases, an effect which is directly linked to the importance of π-back donation from the metal to the ligand.

Ab initio LCAO-MO calculations using a double zeta basis of Gaussian type orbitals * were performed on CNCH$_3$ using (with the exception of the perfectly linear conformation) experimentally determined CNR angles and CN bond lengths (Table 1). The CNR value of 123° represents the greatest degree of bending reported to date for a two-electron donor. The bond length for the perfectly linear geometry was obtained by extrapolation.† The N–CH$_3$ distance was assigned a value of 1.45 Å for all geometries, as experimental data do not show any correlation between this bond length and the degree of bending.‡ The C–H bond length and HCH angle were assigned values of 1.0 Å and 109.5° for all geometries. The principal results concerning the h.o.m.o. and l.u.m.o. are presented in Table 1, together with previous results on CO obtained by the same method. A molecular orbital diagram for linear and bent (CNR = 123°) CNCH$_3$ is shown in Figure 2.

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* Calculations were carried out using the program HONDO (M. Dulpuis, J. Rys, and H. King, Quantum Chemistry Program Exchange, 1977, **11**, 338). In all computations, (C, N/7,3) (B. Roos and P. Siegbahn, *Theor. Chim. Acta*, 1970, **17**, 209) and (H/4) (S. Huzinga, *J. Chem. Phys.*, 1965, **42**, 1293) bases were used, contracted to (C, N/4,2) and (H/2) for double zeta calculations. The H-atom functions were scaled by a factor of 1.25.

† Bond length values for the free ligand are C≡N = 1.166 Å and N–CH$_3$ = 1.424 Å (C. C. Costain, *J. Chem. Phys.*, 1958, **29**, 864). *Ab initio* calculations on free NCCH$_3$ and CNCH$_3$ have been reported by T. K. Ha, *J. Mol. Struct.*, 1972, **11**, 185.

‡ Calculations using experimental N–CH$_3$ bond lengths change only very slightly the values given in Table 1.

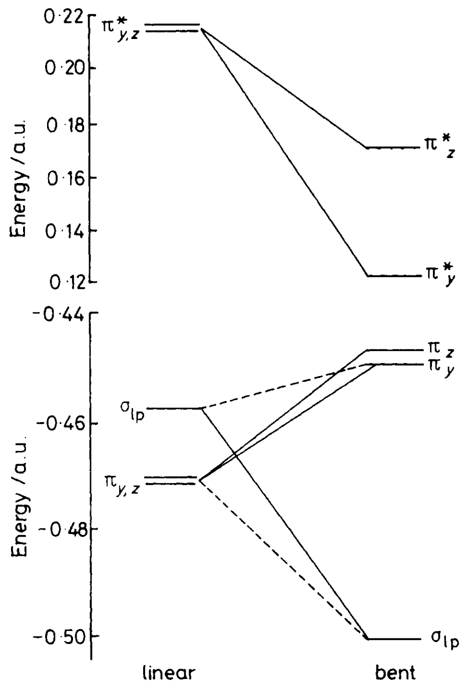
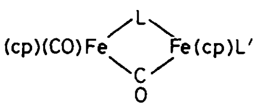
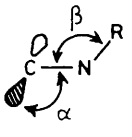


Figure 2. Molecular orbital diagram of valence orbitals of linear and bent (CNR = 123°) $CNCH_3$

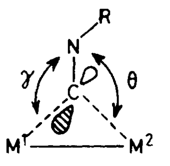
In the linear conformation, the ligand possesses almost perfect $C_{\infty v}$ symmetry. The orbital pairs π_y/π_z and π^*_y/π^*_z are degenerate, and the carbon lone pair is represented by the σ-antibonding h.o.m.o. It is conventionally accepted [1] that alkyl isonitriles are better σ-donors but poorer π-acceptors compared to carbon monoxide, and a comparison of σ_{lp} (lp = lone pair) and $\pi^*_{y,z}$ energies of linear $CNCH_3$ with CO is consistent with this statement.* Bending of the isonitrile in the *x*–*y* plane lowers the symmetry, lifts the degeneracy of the π and π* orbitals, and results in a mixing of the $2p_y$ orbitals with σ-type atomic orbitals. When $CNCH_3$ is strongly bent, the mixing between the occupied orbitals labelled ‘ π_y ’ and ‘ σ_{lp} ’ implies that both must be considered as σ-donors. Interaction of such a molecular orbital with the metal will be greatest when its energy is highest and when the coefficients of the $2p_x$ and $2s$ carbon atomic orbitals are greatest. In energy terms, therefore, ‘ π_y ’ may be regarded as the principal donor orbital in strongly bent cases, even though it retains a substantial $2p_y$(C) character and the ‘ σ_{lp} ’ orbital is mainly $2p_x$(C) and $2s$(C) in nature. As the degree of bending decreases (increasing CNR angle), the ‘ π_y ’ and ‘ σ_{ep} ’ orbitals approach one another in energy and cross over at a CNR angle of approximately 165°. The σ-donor ability of the isonitrile probably changes little with the degree of bending. For the strongly bent case (CNR = 123°) the ‘ π_y ’ orbital is only 0.008 a.u. higher in energy than the ‘ σ_{lp} ’ orbital of the linear case, and this small increase in energy may in any case be offset by the great decrease in localization of this orbital on the terminal carbon.



(C)
cis or *trans*



(D)



(E)

	M^1C/Å	M^2C/Å	γ/°	θ/°
trans-$[Fe_2(cp)_2(CO)_2(\mu\text{-}CNPh)_2]$	1.915(3)	1.944(3)	137.4(2)	140.9(2)
cis-$[Fe_2(cp)_2(CO)_2(\mu\text{-}CNMe)_2]$	1.917(7)	1.948(7)	137.2(6)	140.7(5)
	1.937(7)	1.947(7)	136.5(5)	140.7(5)

The major energy change associated with bending is a stabilization of the π^*_y orbital to such an extent that it loses its antibonding character between the carbon and hydrogens of the methyl group. It takes a certain $2s$(N) and $2p$(N) character, but in contrast to ‘ π_y ’, remains purely $2p_y$ on the terminal carbon, and its localization on this atom increases greatly. On bending, stabilizations of the π^*_z and π_z orbitals are also observed; these moderate changes in energy are a direct consequence of the elongation of the C–N bond.† The π-accepting character of the isonitrile is thus substantially increased, due principally to the stabilization of the π^*_y orbital; indeed, bending CNR to less than 140° lowers the energy of this orbital below that of the π* levels of carbon monoxide.

Structural and spectroscopic data on a series of closely related complexes of structure (C) provide support for these conclusions. Detailed molecular orbital descriptions of the bonding have been made; [9,10] particularly, the isolobal nature of cp^- (η^5-cyclopentadienyl) and $(CO)_3$ may be noted, and these compounds may be related to the M_2L_{10} bridged complexes treated in great detail by Hoffmann and co-workers.[11] The bonding feature of interest in such compounds involves an overlap which is effectively in the $M_2(\mu\text{-}CO)_2$ plane between π*CO orbitals and metal frontier orbitals. In compounds of type (C) which contain a strongly bent isonitrile in position L it is always found that the R group lies approximately in the $Fe_2(\mu\text{-}L)_2$ plane, thus maximizing the interaction of the energetically favoured π^*_y orbital of the bent isonitrile with the appropriate metal orbitals.

Secondly, the directionality of the ‘ π_y ’ donor orbital of the bent isonitrile may be considered. In contrast to the h.o.m.o. of CO and linear $CNCH_3$, this orbital is not collinear, but is tilted as shown in structure (D). In general, α > β and α becomes smaller as β becomes smaller. The ‘ σ_{lp} ’ orbital

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* Based on calculated orbital populations for $[MnL_6]^+$ (L = CO or CNMe) (A. C. Sarapu and R. F. Fenske, *Inorg. Chem.*, 1975, **14**, 247) and $[Ni(CO)_3L]$ (L = CO or CNMe),[8] a reverse order of σ-donor ability is indicated (CO > CNMe). It is not immediately clear whether the results are strongly influenced by either the method of calculation or the metal fragment chosen, as in the latter calculation the order of π-acceptor ability is also reversed (CNMe > CO). Our overlap integral calculations [2] between the σ-h.o.m.o. and π*-l.u.m.o. of CO, CS, and a variety of CNR ligands and either various 3*d* functions of Cr or simple Gaussian functions of different exponents (0.6—0.2) are in agreement with the hypothesis that δ_σ and δ_π are primarily a function of the energies of the ligand h.o.m.o. and l.u.m.o.

† Elongation of the C≡N bond while retaining the linear $CNCH_3$ conformation results in similar energy changes of the π and π* degenerate orbitals. A slight stabilization of σ_{ep} also occurs on elongation.[3]

Table 2. Selected i.r.[a] and n.m.r.[b] data for complexes of type [(cp)(CO)Fe(μ-CO)(μ-L)Fe(L′)(cp)]

Complex	L	L′	ν_{CO}	δ_{CO}	ν_{CS}	δ_{CS}	ν_{CN}	δ_{CN}	Ref.
(1) [$Fe_2(cp)_2(CO)_4$]	CO	CO	1 797	272.9					*c*
(2) [$Fe_2(cp)_2(CO)_3\{P(OEt)_3\}$]	CO	$P(OEt)_3$	1 750	282.2					*c*
(3) [$Fe_2(cp)_2(CO)_3(CNMe)$]	CO	CNMe	1 774	278.8			2 110	158.4	*d*
(4) [$Fe_2(cp)_2(CO)_3(\mu$-CNMe)]	CNMe	CO	1 802	272.6			1 737	246.6	*d*
(5) [$Fe_2(cp)_2(CO)_3(CS)$]	CS	CO	1 811	267.2	1 130	378.3			*e*
(6) [$Fe_2(cp)_2(CO)_2(CS)(PEt_3)$]	CS	PEt_3	1 760	278.3	1 102	396.6			*f*

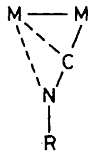
[a] Bridging CO only; ν in cm^{-1}. [b] δ in p.p.m. from $SiMe_4$. [c] D. C. Harris, A. Rosenberg, and J. D. Roberts, *J. Chem. Soc.*, *Dalton Trans.*, 1974, 2398. [d] J. A. S. Howell and A. J. Rowan, *J. Chem. Soc.*, *Dalton Trans.*, 1980, 503 Note that the terminal and bridged isomers are in equilibrium in solution. [e] M. H. Quick and R. J. Angelici, *J. Organomet. Chem.*, 1978, **160**, 231. [f] M. H. Quick and R. J. Angelici, *Inorg. Chem.*, 1981, **20**, 1123.

is tilted in the *opposite* direction, but only to a very small extent even when β is small. Absolute values for α and β have little quantitative meaning as they probably depend on the atomic base chosen.

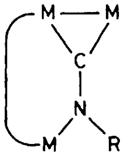
Thus, in the overlap of 'π_y' with *acceptor* metal orbitals [type (E)], either an inequality in the metal–carbon bond lengths [$M^1C < M^2C$] or a reorientation of the ligand to equalize overlap such that $\gamma < \theta$ is expected. Such deviations are in fact observed in the two most precise crystal structures reported of derivatives of this type [type (E)].[12,13] Although the M^1C–M^2C differences in *cis*-[$Fe_2(cp)_2(CO)_2(\mu$-CNMe$)_2$] (cp = η^5-C_5H_5) approach those found for the parent dimer *cis*-[$Fe_2(cp)_2(CO)_4$] [14] there is less ambiguity in a comparison of the M^1C–M^2C value of *trans*-[$Fe_2(cp)_2(CO)_2(\mu$-CNPh$)_2$] with that of *trans*-[$Fe_2(cp)_2(CO)_4$].[15] There seems no ambiguity in the bond angles, as in *trans*-[$Fe_2(cp)_2(CO)_4$], $\gamma = \theta$ and in the *cis* isomer, γ and θ differ by less than one degree.

Thirdly, calculations on [$Fe_2(cp)_2(CO)_4$] and related compounds [9,11] indicate that although CO σ-donation is probably roughly comparable in bridging and terminal positions, population of the π*CO orbitals is much more significant in the bridging carbonyl. Therefore it is expected that spectroscopic properties associated with the bridging CO (particularly C–O stretching frequency or ^{13}C chemical shift) might provide a relative guide to the σ-donor and π-accepting properties of substituting ligands. Representative data on complexes of interest are detailed in Table 2. Substitution by the strongly σ-donating $P(OEt)_3$ ligand [complex (2)] results in a *decrease* in ν_{CO} and an *increase* in δ_{CO} consistent with increased back donation into the $M_2(\mu$-CO$)_2$ system. A similar, although smaller, shift is observed on substitution of a terminal carbonyl by linear CNMe [complex (3)] consistent again with a stronger σ-donor but weaker π-acceptor character. In contrast, however, substitution of a *bent* CNMe ligand into a bridging position [complex (4)] results in an *increase* in ν_{CO} and a small *decrease* in δ_{CO}. These changes are smaller, but in the same direction are those observed on substitution of a bridging CO by CS [complex (5)], which is conventionally accepted as a stronger π-accepting ligand compared to CO.* The change in frequency and chemical shift of *both* CO and CS on substitution of a terminal CO by a strongly electron donating PEt_3 group [complex (6)] may be noted.

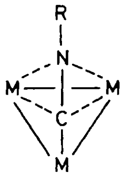
Two final points may be noted. (*a*) Bridging isonitriles exhibit fluxional behaviour involving a 'windscreen wiper' motion of the R group which may be rapid on the n.m.r. time-scale even at low temperature.[16] This is thought to proceed *via* nitrogen inversion involving a linear transition state; thus, Figure 2 may provide a qualitative picture of the ligand molecular orbital changes during this process. (*b*) Isonitriles may function as both four- and six-electron donors.



(F)



(G)



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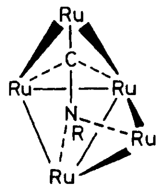

(I)

Structural types (F) [17] and (G) [18] have been observed for the four-electron donor situation, while six-electron donors have been found in the bonding schemes represented by (H) [19] and (I).[20]

In all cases, the isonitrile is substantially bent (CNR = 117—137°) and the C–N bond is quite elongated (1.23—1.38 Å). The presence of the three donor orbitals 'π_y', 'σ_{lp}', and 'π_z' of appropriate symmetry may be noted, but any further quantitative discussion is not meaningful in the absence of calculations on these complexes as a whole.

Finally, we may consider the bonding properties of the isomeric $NCCH_3$ ligand. In contrast to isonitriles, complexed nitriles in general exhibit little bending (NCR = 170—180°) with no obvious correlation between the degree of bending and the C–N bond length,[21] which is more affected by the nature of the metal to which the nitrile is bound.[22]

Calculations have been performed on both linear and bent (NCR = 165°) $NCCH_3$ geometries using bond lengths (N–C = 1.14 and C–C = 1.45 Å) taken from the structures of $VOCl_3$·NCR (R = Ph, Me, or CH_2Ph).[23] Analogous bond lengths in both uni-[24] and poly-metallic [25] low-valent complexes show only small deviations from these values.

These results are summarized in Table 1. A comparison of h.o.m.o. and l.u.m.o. energies with those of linear $CNCH_3$ shows that the nitrile is a poorer σ-donor, identical in energy to CO. Although the π* orbitals of $NCCH_3$ are close in energy to those of $CNCH_3$, their small degree of localization on the terminal nitrogen indicates only a mediocre π-acceptor character. In contrast, the strong localization of the π-bonding orbitals on the two atoms of the C≡N bond implies a certain *π-donor* character for this ligand. This π-donor character may

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* Calculated h.o.m.o. and l.u.m.o. energies for CS by the method used here are −0.460 a.u. and +0.077 a.u. respectively.[2]

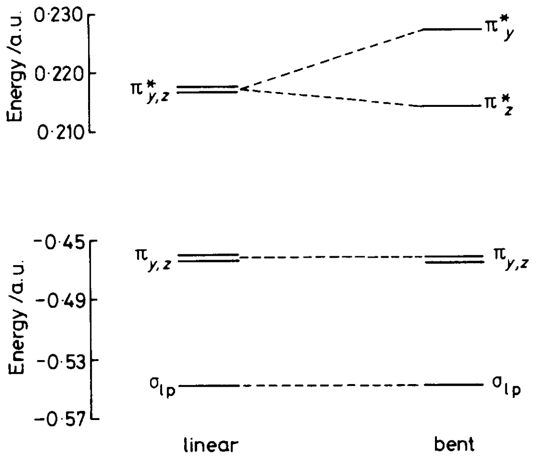

Figure 3. Molecular orbital diagram of valence orbitals of linear and bent (NCR = 165°) $NCCH_3$

be linked to frequent observations of deviations from linearity in M–N–C angles.[21] Such deviations allow the π orbitals to augment to a greater or lesser degree the M–NCR σ bond, and this interpretation is not inconsistent with that suggested previously of a partial sp^2 hybridization of the nitrogen.[26]

The effect of bending on the energy of the $NCCH_3$ valence orbitals is shown in Figure 3. In contrast to $CNCH_3$, the π^*_y orbital is destabilized by bending, which is accompanied by a loss in localisation on the terminal nitrogen to the benefit of the methyl group. The π^*_y orbital thus loses partially its acceptor character, and the overall acceptor character of the ligand decreases as none of the other orbitals changes appreciably in energy.

The expected π-donor character of $NCCH_3$ is consistent with kinetic work on carbonyl substitution by nitriles. Substitution of $[M(CO)_6]$ to give $[M(CO)_5L]$ (M = Cr, Mo, or W) generally proceeds *via* a two-term rate law of the form rate = $k_1[M(CO)_6] + k_2[M(CO)_6][L]$ corresponding to competing 'd' and 'I_a' pathways; k_1 thus reflects rate-determining CO dissociation and is ligand independent, while k_2 is related to the I_a process and in general reflects the nucleophilicity of the ligand. Measured values of k_2 place $NCCH_3$ on a level with PPh_3.[27] Most interestingly, further substitution of $[M(CO)_5(NCCH_3)]$ to give *cis*-$[M(CO)_4(NCCH_3)_2]$ and *fac*-$[M(CO)_3(NCCH_3)_3]$ is substantially faster than the initial monosubstitution. Labilization of CO in $[Mn(CO)_5(NCCH_3)]^+$ has also been reported.[28] Brown and co-workers [29] have provided qualitative and semi-quantitative molecular orbital considerations which show that in a monosubstituted $[M(CO)_5L]$ species, substantial labilization of the carbonyls *cis* to L will result with ligands which are weak σ-donors but substantial π-donors, and which are weak π-acceptors. These seem precisely the properties which our calculations would associate with $CNCH_3$.

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