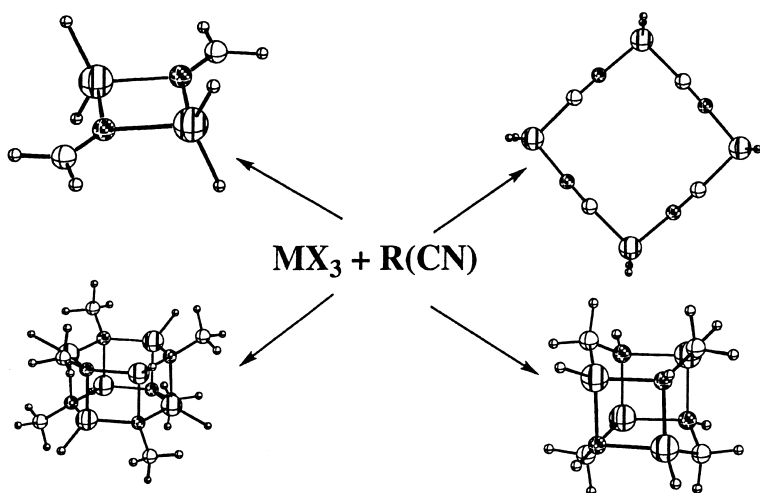Article

Fascinating Transformations of Donor−Acceptor Complexes of Group 13 Metal (Al, Ga, In) Derivatives with Nitriles and Isonitriles: From Monomeric Cyanides to Rings and Cages

Alexey Y. Timoshkin, and Henry F. Schaefer

$$\mathbf{MX_3 + R(CN)}$$

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Fascinating Transformations of Donor−Acceptor Complexes of Group 13 Metal (Al, Ga, In) Derivatives with Nitriles and Isonitriles: From Monomeric Cyanides to Rings and Cages

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Abstract: Formation of the donor−acceptor complexes of group 13 metal derivatives with nitriles and isonitriles X_3M-D (M = Al,Ga,In; X = H,Cl,CH$_3$; D = RCN, RNC; R = H,CH$_3$) and their subsequent reactions have been theoretically studied at the B3LYP/pVDZ level of theory. Although complexation with MX$_3$ stabilizes the isocyanide due to the stronger M−C donor−acceptor bond, this stabilization (20 kJ mol^{-1} at most) is not sufficient to make the isocyanide form more favorable. Relationships between the dissociation enthalpy $\Delta H°_{298}^{diss}$, charge-transfer q_{CT}, donor−acceptor bond energy E_{DA}, and the shift of the vibrational stretching mode of the CN group upon coordination $\Delta\omega_{CN}$ have been examined. For a given metal center, there is a good correlation between the *energy of the donor−acceptor bond* and the degree of a charge transfer. Prediction of the $\Delta H°_{298}^{diss}$ on the basis of the shift of CN stretching mode is possible within limited series of cyanide complexes (for the fixed M,R); in contrast, complexes of the isocyanides exhibit very poor $\Delta\omega_{CN} - \Delta H°_{298}^{diss}$ correlation. Subsequent X ligand transfer and RX elimination reactions yielding monomeric (including donor−acceptor stabilized) and variety of oligomeric cage and ring compounds with [MN]$_n$, [MC]$_n$, [MNC]$_n$ cores have been considered and corresponding to thermodynamic characteristics have been obtained for the first time. Monomeric aluminum isocyanides X$_2$AlNC are more stable compared to Al−C bonded isomers; for gallium and indium situation is reversed, in qualitative agreement with Pearson's HSAB concept. Substitution of X by CN in MX$_3$ increases the dissociation enthalpy of the MX$_2$CN−NH$_3$ complex compared to that for MX$_3$−NH$_3$, irrespective of the substituent X. Mechanisms of the initial reaction of the X transfer have been studied for the case X = R = H. The process of hydrogen transfer from the metal to the carbon atom in H$_3$M−CNH is thermodynamically favorable and is likely to be intramolecular. By contrast, intramolecular hydrogen transfer in H$_3$M−NCH has been definitely ruled out. Head-to-tail dimeric species [H$_3$M−(NC)H]$_2$ are formed exothermically and exhibit low H...H distances, which can assist in hydrogen transfer, and are likely to be the starting point for H$_2$ elimination. Elimination of H$_2$, CH$_4$, and C$_2$H$_6$ from X$_3$M−(NC)R adducts is very favorable thermodynamically; by contrast, elimination of HCl and CH$_3$Cl is highly unfavorable even if formation of oligomer species takes place. Thus, high-temperature generation of gas-phase rings and clusters has been predicted viable in the cases X = H,CH$_3$ and their presence in the reactor media should not be neglected. Moderate stability of [HMCH$_2$NH]$_4$ clusters (especially in the cases M = Ga, In) makes these species viable intermediates of gas-phase reactions. Their formation may be responsible for the carbon contamination in the course of metal organic chemical vapor deposition processes of group 13 binary nitrides.

Introduction

Despite having been known for many years, reactions of group 13 element derivatives with nitriles and isonitriles remain fascinating in their complexity. The initial reaction between group 13 Lewis acids and nitriles/isonitriles, which results in formation of the corresponding donor−acceptor complex,[1−7] is followed by reorganization processes which lead to a remarkable

diversity of products. These include a variety of cyanide species [X$_2$MCN]$_n$ (in the form of donor−acceptor stabilized monomers,[8] as well as oligomers with n = 2,[9]3,[10]4[11−13b],5,[13b]7,[9]8,[9]

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or spiral polymers[13a]), dimeric rings $[X_2MNCR_2]_2$ with M_2N_2 core,[3,14−18] products of trimerization of acetonitrile molecules,[4,5ab,19] M−N−C cyclic[16] and cage[20] compounds, and unidentified polymers.[3,19]

Despite these substantial experimental studies, the mechanisms of these transformations are not known in detail. Knowledge of the thermodynamics behind these processes is also very limited at the present time, but is expected to be important for the metal organic chemical vapor deposition (MOCVD) of high purity group 13 binary nitrides, prospective materials for high-power high-frequency electronic and optoelectronic devices.[21,22] Due to its high thermal stability, HCN is readily formed and observed during MOCVD conditions.[23] Reactions of HCN with acceptor molecules $M(CH_3)_3$ in the condensed phase result in formation of stable $[Me_2MCN]_n$ rings with metal−carbon bonds.[9−13] Analogous gas-phase intermediates may be responsible for carbon incorporation in the solid nitride. Therefore, gas-phase processes initiated by formation of donor−acceptor complexes between nitriles and group 13 element derivatives certainly require attention.

The gas phase complexes of boron derivatives with nitriles and isonitriles have been extensively studied both experimentally and theoretically.[24−26] One of the interesting features of boron trifluoride complexes with nitriles is the remarkable dependence of the donor−acceptor bond length on the aggregate state of the complex. The B−N distance shortens dramatically from 2.011 and 2.473 Å in the gas phase to 1.630 and 1.638 Å in the solid state for the BF_3−CH_3CN and BF_3−HCN complexes, respectively.[24] Therefore, results of experimental studies in condensed phases should be transferred with caution to the gas-phase processes. The gas-phase chemistry of cyanides and isocyanides of the heavier analogues of boron is not at all well-documented, and theoretical predictions for the gas-phase species thus become an important ongoing task.

In the present report, we explore theoretically reactions of the group 13 metal derivatives Al, Ga, and In with nitriles and isonitriles. To begin, the formation of donor−acceptor complexes X_3M−NCR and X_3M−CNR will be considered. Second, isomers of these complexes resulting from the migration of one or two terminal groups X from metal to carbon atom will be examined. Finally, elimination reactions leading to monomeric and oligomeric cyanide compounds $[X_2MCN]_n$ will be explored. Results obtained will be discussed in light of the influence of the metal center and substituents X, R on the thermodynamic properties of the gas-phase processes. Special attention will be

given to the identification of stable compounds with metal−carbon bonding. We present a systematic study of structure and stability of a variety of group 13 metal cyanides/isocyanides and report (for the first time) their gas-phase thermochemistry.

Computational Details

Density functional theory in the form of the B3LYP[27] functional has been employed to predict the geometries, relative energies, and vibrational frequencies of individual compounds and the thermodynamic parameters of dissociation and elimination reactions. Because considerable attention will be given to the investigation of large oligomeric species, a polarized double-ζ quality all-electron pVDZ basis set of Ahlrichs and co-workers was used for H (4s1p/2s1p), C(7s4p1d/3s2p1d), N(7s4p1d/3s2p1d), Al(10s7p1d/4s3p1d), Cl(10s7p1d/4s3p1d), Ga(14s10p5d/5s4p3d).[28] For indium, a polarized double-ζ quality all-electron basis set (18s14p9d/6s5p3d) of Godbout et al. was used.[29] All structures were fully optimized with subsequent vibrational analysis and correspond to minima on the potential energy surface. Basis set superposition error (BSSE) correction was computed by the counter-poise method.[30] Energies of the donor−acceptor bonds have been evaluated taking into account the reorganization energy of fragments and BSSE, as described in a recent report for the group 14 complexes.[31] Atomic charges were determined using Mulliken population analysis. The Gaussian 94 program package was used throughout.[32]

Computed vibrational frequencies are overestimated compared to experimental values (see, for example, Table 1s), as expected for the B3LYP level of theory. In the present report, we are primarily interested in the shift of the CN stretching mode, $\Delta\omega_{(CN)}$. Values predicted with B3LYP/pVDZ agree well with available experimental observations. Substitution of the hydrogen atom in HCN by a methyl group results in the shift of the CN stretching mode of 170 cm^{-1} (experimental value); our B3LYP/pVDZ prediction is 173 cm^{-1}. For the isonitriles, similar substitution of hydrogen by a methyl group results in a 142 cm^{-1} shift (experimental value), whereas the predicted B3LYP/pVDZ value is 137 cm^{-1}. Therefore, in the present work we used unscaled theoretical harmonic frequencies to predict shifts in the CN stretching mode.

For the free donor molecules, HCN and CH_3CN are predicted to be 57.2 and 93.5 kJ mol^{-1} lower in energy than HNC and CH_3NC, respectively. Taking into account zero point vibrational energy and thermal corrections, predicted standard isomerization enthalpies of HNC and CH_3NC are 56.8 and 93.9 kJ mol^{-1}, respectively. This result satisfactorily agrees with the experimental values of 61.9 ± 8.3[33] (HNC) and 99.2 ± 0.6[34] (CH_3NC) kJ mol^{-1} (for the latter compound the alternative NIST value of 89.5 ± 7.2 kJ mol^{-1} [35] is also available). The experimental heat of formation of HNC has been recently revisited,[36] and a somewhat higher isomerization enthalpy of HNC (72.8 ± 12.1 kJ mol^{-1}) was deduced using collision-induced dissociation threshold measurements and a revised proton affinity scale. The latter value has a much higher uncertainty and is likely to be overestimated

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Table 1. Selected Geometric Parameters (bond distances in Å, angles in deg) and Standard Entropies $S°_{298}$ (J mol^{-1} K^{-1}) for MX$_3$−D Donor−Acceptor Compounds, Standard Enthalpies $\Delta H°_{298}{}^{diss}$ (kJ mol^{-1}) and Entropies $\Delta S°_{298}{}^{diss}$ (J mol^{-1} K^{-1}) for the Dissociation Process: MX$_3$−D = MX$'_3$ + D; Harmonic Vibration Frequencies of CN Stretching Mode, ω(CN), cm^{-1} (unscaled) and Charge Transfer q$_{CT}$, Predicted at B3LYP/pVDZ Level of Theory

MX$_3$	donor	R(M−D)	R(C−N)	∠XMD	$S°_{298}$	$\Delta H°_{298}{}^{diss}$	$\Delta S°_{298}{}^{diss}$	ω(CN)	q$_{CT}$
AlH$_3$	HCN	2.075	1.150	98.1	282	73.3	126.5	2261	0.184
	HNC	2.130	1.163	98.3	285	86.4	126.4	2218	0.216
	CH$_3$CN	2.050	1.153	99.3	333	89.2	116.7	2429	0.216
	CH$_3$NC	2.119	1.163	99.2	336	97.4	116.1	2351	0.243
AlCl$_3$	HCN	2.036	1.148	99.9	381	89.0	133.0	2280	0.229
	HNC	2.110	1.159	99.9	385	102.2	131.4	2256	0.246
	CH$_3$CN	2.001	1.152	101.0	435	112.4	120.5	2442	0.268
	CH$_3$NC	2.090	1.159	100.8	435	118.8	122.9	2384	0.280
AlMe$_3$	HCN	2.118	1.150	98.8	421	52.1	159.0	2254	0.160
	HNC	2.176	1.164	99.6	422	59.2	160.0	2206	0.189
	CH$_3$CN	2.086	1.154	99.7	470	66.1	151.2	2422	0.192
	CH$_3$NC	2.161	1.164	100.3	474	68.7	149.3	2341	0.215
GaH$_3$	HCN	2.218	1.150	96.4	299	48.2	120.6	2255	0.169
	HNC	2.175	1.163	98.0	298	66.5	124.2	2209	0.253
	CH$_3$CN	2.176	1.154	97.6	343	60.0	118.0	2425	0.199
	CH$_3$NC	2.159	1.163	98.8	341	75.6	122.2	2344	0.282
GaCl$_3$	HCN	2.165	1.149	98.9	411	59.5	116.5	2273	0.214
	HNC	2.172	1.159	99.8	401	77.2	128.2	2251	0.288
	CH$_3$CN	2.104	1.152	100.3	455	79.6	113.4	2436	0.257
	CH$_3$NC	2.139	1.159	100.9	450	93.4	120.6	2383	0.330
GaMe$_3$	HCN	2.330	1.151	96.4	444	28.5	153.6	2245	0.138
	HNC	2.258	1.165	98.6	437	37.3	162.6	2193	0.199
	CH$_3$CN	2.261	1.155	97.5	492	38.1	147.2	2415	0.168
	CH$_3$NC	2.237	1.165	99.4	490	45.0	151.9	2331	0.226
InH$_3$	HCN	2.497	1.151	94.9	319	45.5	111.5	2250	0.149
	HNC	2.468	1.164	96.1	318	56.5	115.1	2206	0.225
	CH$_3$CN	2.444	1.155	96.2	350	55.6	121.6	2416	0.175
	CH$_3$NC	2.439	1.164	97.0	348	64.5	126.4	2341	0.253
InCl$_3$	HCN	2.403	1.150	97.5	424	69.1	120.1	2264	0.204
	HNC	2.420	1.159	98.3	426	81.2	120.5	2246	0.305
	CH$_3$CN	2.344	1.154	98.7	488	89.1	97.3	2424	0.239
	CH$_3$NC	2.379	1.159	99.5	485	98.0	102.7	2376	0.345

because high level ab initio methods predict an HNC isomerization energy of 60.2 ± 4.2 kJ mol^{-1} at the CCSD(T)/TZ2P level of theory.[37] We conclude that the B3LYP/pVDZ level of theory gives an adequate description of thermodynamic parameters and CN vibrational frequency shifts.

Results

The relationship between the processes studied is given in Figure 1. We have theoretically investigated donor−acceptor complexes of group 13 metal derivatives with nitriles X$_3$M−NCR (**Ia**) and isonitriles X$_3$M−CNR (**Ib**) (M = Al,Ga,In; X = H,Cl,CH$_3$; R = H,CH$_3$). We also considered their structural isomers obtained by the transfer of terminal groups X from the metal to the carbon atom:

Transfer of one substituent X of the nitrile adducts results in monomeric X$_2$MN=CRX (**IIa**); its complexes with ammonia and its dimer (**IIa**)$_2$ have been also considered. For the isonitrile adducts the cyclic monomers **IIb** and their ammonia complexes were considered.

Transfer of two substituents X results in monomeric XM=NCRX$_2$ (**IIIa**) for which oligomers (**IIIa**)$_{2,4,6}$, (as well as their structural isomers [X$_2$RCMNH]$_{1,2,4,6}$) were considered.

Monomeric cyclic $\overline{\text{XMCX}_2\text{NR}}$ (**IIIb**) and its oligomers (**IIIb**)$_{2,4,6}$ result from analogous transfer in the isonitrile adduct.

Finally, RX elimination products—monomeric metal isocyanides X$_2$MNC (**IVa**) and X$_2$MCN (**IVb**), their complexes with ammonia and oligomer species [X$_2$MCN]$_n$, n = 2,3,4, have been

considered. A case study of X = R = H was performed for all structures presented in Figure 1, and the influence of the terminal groups X and R was investigated in detail for structures **I**, **II**, and **IV**.

I. Donor−Acceptor Complexes MX$_3$−NCR and MX$_3$−CNR. Complexes of group 13 metal derivatives with cyanides have been extensively studied experimentally in condensed phase. Crystal structures of several nitrile[2,5,38] and isonitrile[6,39] adducts have been reported. Selected structural and thermodynamic parameters of donor−acceptor complexes are summarized in Table 1. Later in this section, we consider structural, thermodynamic, and spectral properties of these compounds in more detail.

A. Structural Changes. Predicted structural parameters for the gas-phase complexes may be compared with experimental values for the solid complexes, obtained from X-ray diffraction (Table 2). There is a reasonable agreement between theoretical and experimental data for the Me$_3$Al−NCMe adduct. Bond distances, with the exception of the donor−acceptor bond, are overestimated by about 0.02−0.05 Å. Such overestimation is not unusual for the B3LYP level of theory. In stark contrast, the theoretically predicted donor−acceptor bond distance for the gaseous adduct is considerably *shorter* compared to the experimental value obtained in the solid state. This also holds for the other cyanide and isocyanide complexes (Table 2) that were considered. Such a trend is clearly opposite to the

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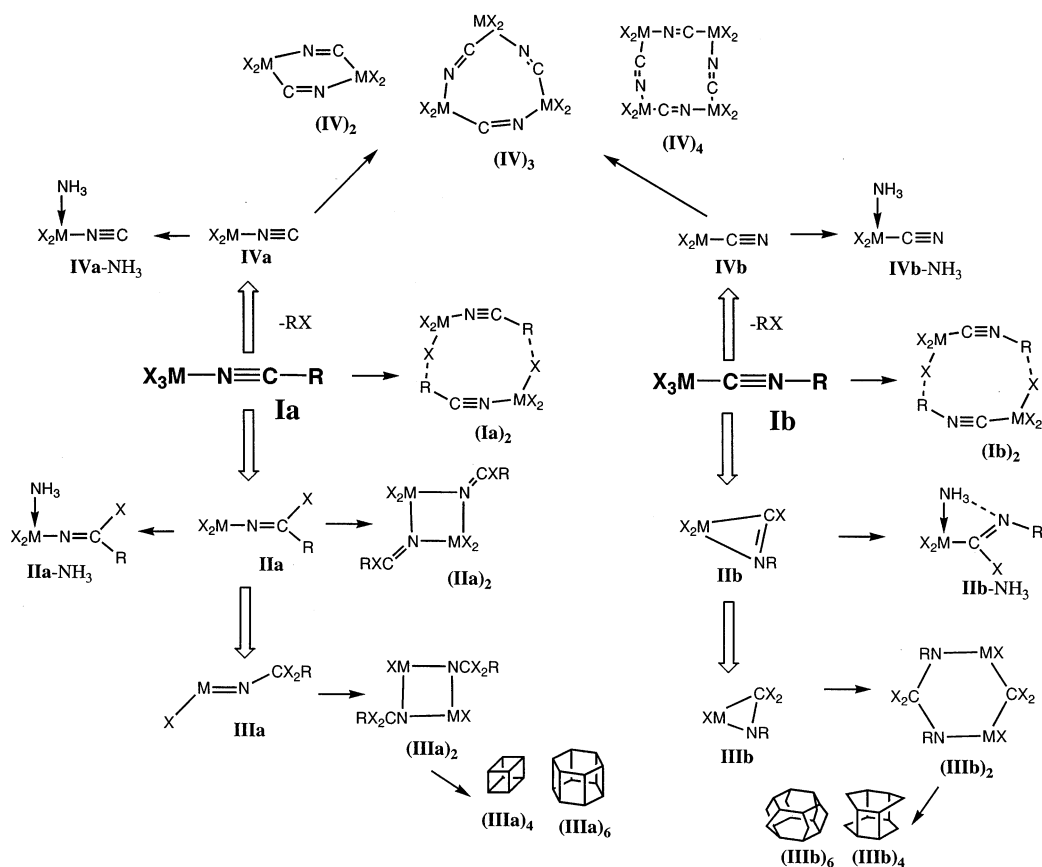
Figure 1. General scheme of the studied processes and labeling of the investigated compounds. M = Al, Ga, In; X = H, CH₃,Cl; R = H, CH₃.

Table 2. Comparison of Experimental and Theoretical Structural Parameters for Several Donor—Acceptor Complexes X₃M—D (D = NCR, CNR). All Distances in Å, All Bond Angles in Degrees, Harmonic Vibrational Frequency Shift of CN Group, $\Delta\omega$(CN), in cm^{-1} (unscaled)

parameter	Me₃AlN≡CMe exp., X-ray[5]	Me₃AlN≡CMe B3LYP/pVDZ	Mes₃GaN≡CMe exp., X-ray[2]	Me₃GaN≡CMe B3LYP/pVDZ	Cp₃AlC≡N(t-Bu) exp., X-ray[6]	Me₃AlC≡NMe B3LYP/pVDZ
r(M—D)	2.014(2)	1.901	2.207(5)	1.922	2.067(7)	1.928
r(M—X)	1.965—1.969(3)	2.019	1.988—2.014(5) (mean 2.00)	2.033	2.010 (3)	2.025
r(N—C)	1.136(3)	1.139	1.111(6)	1.141	1.152(7)	1.137
r(C—R)[b]	1.431(5)	1.454	1.475(7)	1.454	1.463(6)	1.429
∠X—M—X	115.3—116.7(1)	111.3	118.0—119.3(2)	111.0	115.2(1)	110.8
∠X—M—D	101.4(1)	107.6	94.2—101.0(2)	107.9	102.8(1)	108.1
∠M—N—C[c]	179.5(2)	180	171.2 (5)	180	180	180
∠N—C—R[d]	179.7(2)	180	178.4 (7)	180	180	180
$\Delta\omega$(CN)	42	29	32[a]	24	78	65

[a] Experimental data are given for the Me₃Ga—NCMe complex, ref 3. [b] For isonitriles, r(N—R). [c] For isonitriles, ∠ M—C—N. [d] For isonitriles, ∠ C—N—R.

remarkable shortening of the donor—acceptor bond distance in the solid-state found for BF₃—NCR systems by Leopold.[24] The increase of the M—D distance in the solid state may be dictated by the steric effect of crystal packing, for example by preventing the pyramidalization of the acceptor molecule. The linear relationship between the pyramidalization of MX₃ (X—M—D bond angle) and the M—D bond length was found for 13—15 complexes.[40] The observed decrease of the X—M—D angle in the solid state compared to the gas phase (see Table 2) leads to lengthening of the donor—acceptor bond. Thus, dramatic structural changes between the gas phase and the solid state are observed for weak "partially bonded" complexes of BF₃,[24] but are not observed for the more strongly bound complexes of its heavier analogues.

One of the important features of the donor—acceptor complexes of cyanides and isocyanides is a decrease of the C—N bond distance upon complexation. This effect has been observed for boron analogues as well.[26] Our optimized C—N distances for HCN, CH₃CN, HNC, and CH₃NC are 1.155, 1.158, 1.173, and 1.174 Å, respectively. Comparison of these values with C—N distances in the complexes (Table 1) reveals a C—N bond shortening of about 0.005 Å for the nitrile donors HCN and CH₃CN. For isonitriles, bond shortening is more pronounced (mean value 0.01 Å). The most pronounced decrease of the C—N bond length is observed for the strongest Cl₃M—D complexes.

B. Dissociation Enthalpies. The dissociation enthalpies of the MX₃ complexes with nitriles range from 29 kJ mol^{-1} for GaMe₃—NCH to 112 kJ mol^{-1} for AlCl₃—NCCH₃, which is considerably lower compared to the complexes of corresponding

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acceptors with ammonia (76^{41} and 149^{42} kJ mol^{-1}, respectively). Isonitriles are stronger donors compared to nitriles. Predicted dissociation enthalpies of the metal−carbon bonded complexes are on average 12 (R = H) and 8 (R = CH$_3$) kJ mol^{-1} higher compared to those of metal-nitrogen bonded species. Thus, it is important to conclude that complex formation to some extent stabilizes the isonitrile form. As a result, relative energies of the isocyanides RNC decrease upon complex formation (Table 2s). The amount of the relative energy decrease is proportional to the difference of the M−C and M−N donor−acceptor bond energies for the given acceptor, but it does not depend on the strength of the donor−acceptor bond itself. Weak gallium complexes provide higher stabilization compared to the more strongly bound aluminum complexes. Despite the fact that metal−carbon donor−acceptor bonding is more favorable, the difference of the M−C and M−N donor−acceptor bond energies is rather small (maximal 20 kJ mol^{-1}) and is not sufficient to make the MX$_3$CNR isomers more thermodynamically stable. Complexation of CH$_3$NC with BH$_3$ results in stabilization by 55 kJ mol^{-1} (MP2/DZP level of theory).[26]

The donor ability of the molecules considered decreases in the order NH$_3$ > CH$_3$NC > CH$_3$CN > HNC > HCN. Substitution of the hydrogen by methyl group in the donor molecule increases the donor−acceptor dissociation energy by about 20 kJ mol^{-1} and 10 kJ mol^{-1} for MCl$_3$ and MH$_3$ acceptors, respectively.

C. Vibrational Frequency Shifts. As the C−N bond length is sensitive to complex formation, monitoring of the CN stretching vibrational mode is a good probe for gaining information about donor−acceptor complex formation. Shortening of the C−N bond upon complexation results in an increase of the CN stretching fundamental. As may be seen from Table 2, our predicted values of the CN shift for the gas-phase complexes are underestimated by 13 cm^{-1} compared to experimental observations in the condensed phase. In several experimental studies,[3,4,7] the acceptor ability of MX$_3$ was derived using the shift of the CN stretching vibration upon complexation. Experimental results may be compared to our theoretical predictions for the gas-phase complexes with acetonitrile (Table 3s). Despite the fact that the experimental data refer to the condensed phase PhCN complexes, and theoretical values to the gas-phase complexes of MeCN, the difference between AlCl$_3$ and AlMe$_3$ acceptors is predicted to be almost the same, both on the basis of energetic (dissociation enthalpy) and spectral (CN vibrational frequency shift) parameters. Therefore, we conclude that thermodynamic and spectral scales are in good agreement in predicting the acceptor strength order. However, as follows from the comparison of ΔH^{diss} and $\Delta\omega_{\text{(CN)}}$ values (Table 4s), such a conclusion is only valid for the given metal-donor pair.

Relationships between different parameters of acceptor ability (such as charge transfer, dissociation enthalpy, donor−acceptor bond energy, donor−acceptor bond length and CN vibrational frequency shift) will be examined in more detail for all of the donor−acceptor complexes studied in the present work (see Discussion section).

(41) Timoshkin, A. Y.; Bettinger, H. F.; Schaefer, H. F. *J. Phys. Chem. A* **2001**, *105*, 3240.
(42) Timoshkin, A. Y.; Bettinger, H. F.; Schaefer, H. F. *J. Am. Chem. Soc.* **1997**, *119*, 5668.

Table 3. Relative Energies, in kJ mol^{-1}, of Monomeric Isomers of the Donor−Acceptor Compounds **Ia** and **Ib**

X,R	M	nitrile series[b]				isonitrile series[b]			
		Ia	IIa	IIa-NH$_3$[c]	IIIa	Ib	IIb	IIb-NH$_3$[d]	IIIb
H,H	Al	0	−72.2	−184.6	45.3	0	−58.3	−192.2	−9.1
	Ga	0	−47.8	−144.3	42.0	0	−25.2	−171.2	24.2
	In	0	−22.1	−129.1	79.5	0	−27.2	−164.9	
Cl,H	Al	0	123.1		498.2				
	Ga	0	102.3		→ **IIa**[a]				
	In	0	→ **Ia**[a]		→ **Ia**[a]				
H,CH$_3$	Al	0	−40.1						
	Ga	0	−18.2						
	In	0	7.2						
Cl,CH$_3$	Al	0	162.6						
	Ga	0	→ **Ia**[a]						
	In	0	→ **Ia**[a]						

[a] → **Ia** and → **IIa** indicate that optimization of this isomer converged to structure **Ia** and **IIa**, respectively. [b] For the each series, the relative energy of the corresponding donor−acceptor complex is set to 0. [c] Relative energy with respect to **Ia** and free NH$_3$. [d] Data are given for the most stable *cis*-isomer. Relative energy with respect to **Ib** and free NH$_3$.

II. Structural Isomers of the DA Compounds.

A. Monomeric Species and Role of the Substituents X,R. Transfer of the ligand X from metal to the carbon atom is a well-known phenomenon for donor−acceptor complexes of nitriles and isonitriles. Therefore, it is of interest to compare the relative energies of the donor−acceptor complex **I** with its isomer structures, where one or two substituents X are transferred to the carbon center

$$X_3M-N\equiv CR \; (\textbf{Ia}) \rightarrow X_2M-N=CRX \; (\textbf{IIa}) \rightarrow$$
$$XM=NCRX_2 \; (\textbf{IIIa})$$

$$X_3M-C\equiv NR \; (\textbf{Ib}) \rightarrow X_2M-CX=NR \; (\textbf{IIb}) \rightarrow$$
$$\overline{XM-CX_2}NR \; (\textbf{IIIb})$$
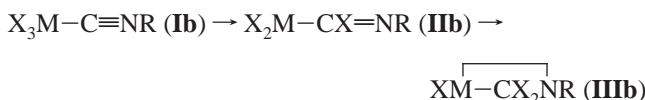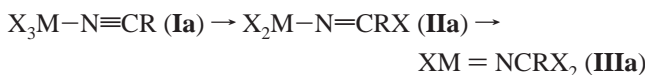
Relative energies of the monomeric isomers **I**−**III** are summarized in Table 3, and general structures of compounds are given in Figure 2.

Upon X transfer, the M−X bond is broken and the C−X bond is formed. Therefore, it is expected that favorability of the transfer process will depend on the bond energy difference. Mean M−X and C−X bond energies, summarized in Table 5s, indicate that the M−Cl bond is by 40−100 kJ mol^{-1} stronger compared to the C−Cl bond. In contrast, M−H and M−C bonds are about 80−140 kJ mol^{-1} weaker compared to C−H and C−C bonds, and hydrogen and methyl transfer is expected to be favorable, but Cl transfer is not. In agreement with these expectations, transfer of the first hydrogen is predicted to be exothermic by 20−70 kJ mol^{-1}, whereas migration of one chlorine atom is endothermic by 100−120 kJ mol^{-1} (Table 3).

However, transfer of two substituents X to the carbon atom with formation of the monomeric XMNCX$_2$R form is always endothermic, irrespective to the substituent X. In fact, transfer of two hydrogen atoms is endothermic by 40−80 kJ mol^{-1}, transfer of two chlorine atoms is very strongly (by about 500 kJ mol^{-1}) endothermic. These results point out the high unfavorability of the low coordination number (two) of the metal and nitrogen centers in **IIIa**. Coupled with the high favorability of M−Cl versus C−Cl bonding, this makes transfer of Cl

Table 4. Comparison of Experimental and Theoretical Structural Parameters for Several (**IIa**) Dimers $[X_2MN=CXR]_2$ (all distances in Å, all bond angles in degrees)[a]

parameter	$[Me_2AlN=CMe_2]_2$ exp., X-ray[15]	$[(i\text{-}Bu)_2AlN=CH(C_6H_3\text{-}2,6(CH_3)_2)]_2$ exp., X-ray[17]	$[H_2AlN=CH_2]_2$ B3LYP/pVDZ	$[Cl_2AlN=CHCl]_2$[a] B3LYP/pVDZ	$[Me_2GaN=CMe_2]_2$ exp., X-ray[44]	$[H_2GaN=CH_2]_2$ B3LYP/pVDZ	$[Cl_2GaN=CHCl]_2$[a] B3LYP/pVDZ
r(M−N)	1.925, 1.930	1.937, 1.955	1.971	1.944, 1.954 (1.942, 1.957)	1.978, 2.000	2.027	1.998, 2.012 (1.998, 2.012)
r(M−X)	1.969, 1.978	1.949, 1.986	1.591	2.113−2.116	1.965, 1.968	1.573	2.161−2.165
r(N−C)	1.273	1.248	1.268	1.260 (1.260)	1.266	1.265	1.258 (1.258)
∠N−M−N	83.7	80.6	83.4	83.4 (83.1, 83.9)	82.1	81.9	82.0 (81.7, 82.5)
∠M−N−M	96.3	96.5	96.6	96.6 (96.5)	97.9	98.1	98.0 (97.9)

[a] Data in the first row are for the *trans*-isomer, data in the second row (in parentheses) are for *cis*-isomer.
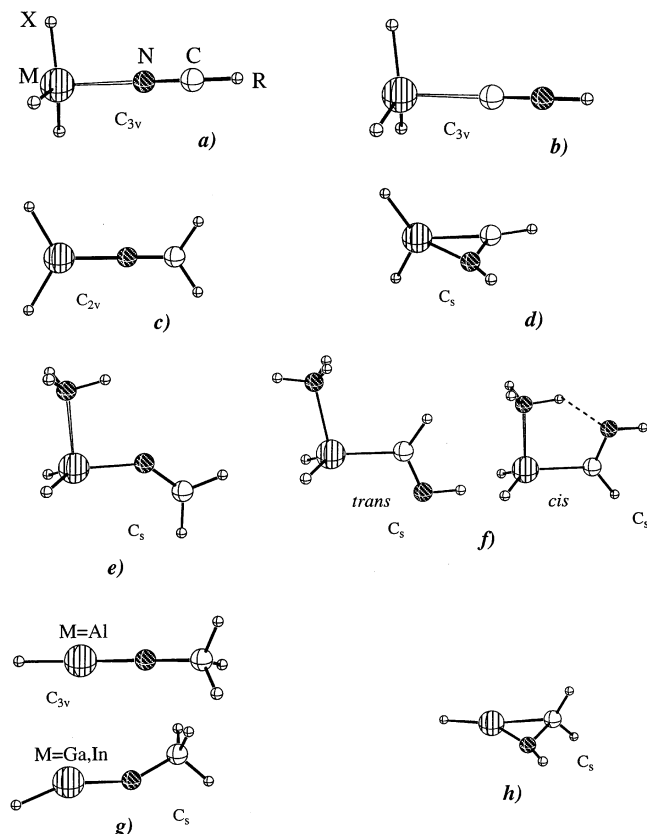

Figure 2. General structures of the monomeric **I**−**III** compounds. Donor−acceptor complexes of MX_3 with nitriles **Ia** (a) and isonitriles **Ib** (b); Monomeric **IIa** (c) and **IIb** (d) species; Donor−acceptor complexes of **IIa** with ammonia (e) and **IIb** with ammonia (f); Monomeric **IIIa** (g) and **IIIb** (h).

substituents essentially impossible: in several cases during a geometry optimization of C−Cl bonded **IIa** and **IIIa** species, a structure of the donor−acceptor complex **Ia** was obtained (Table 3). In experiments, when Me_2AlCl was reacted with $PhCH_2CN$ at 135 °C in xylene, a transfer of Me (and not Cl) was observed.[43] Therefore, Cl-substituted species will be not considered for structures **II** and **III** further.

Substitution of the hydrogen by the methyl group in the donor molecule ($R=CH_3$) disfavors X transfer by about 30 kJ mol^{-1}, irrespective of the ligand X. Thus, on the basis of the results obtained, the case X = H, R = H was chosen for the further studies.

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For isonitriles, transfer of one hydrogen atom to the carbon with formation of monomeric **IIb** is exothermic by 25−60 kJ mol^{-1}. Optimization of a linear isomer resulted in a cyclic structure with trimeric ring M−C−N (Figure 2d). This compound may be considered to involve bonding of the HN=CH and MH_2 radicals with additional intramolecular donor−acceptor stabilization. It is interesting that the degree of this stabilization decreases in the series Al > Ga > In, as may be deduced from the increase of the M−C−N angle: 70.3 < 86.3 < 92.4. During an optimization of **IIIb**, the initial chain structure converged to a C_s symmetric three-membered cycle in the case of Al and Ga, in which $H_2C=NH$ is coordinated to MH via a double bond (Figure 2h). For indium, optimization of **IIIb** converged to a weakly bound InH and $NH=CH_2$. Energetically, transfer of two hydrogen atoms is slightly exothermic for Al and endothermic for Ga (Table 3).

One of the ways to stabilize monomer compounds is a donor−acceptor interaction, which prevents oligomerization processes. We considered formation of ammonia complexes for the compounds **IIa** and **IIb** for the case X = R = H. The structures of these complexes are presented in Figure 2e,f. Dissociation enthalpies of the $H_3N−H_2MN=CH_2$ complexes are 103.9, 88.1, 97.6 kJ mol^{-1} for Al, Ga, In, respectively. These values, with the exception of the In complex, are lower compared to the $H_3M−NH_3$ complexes (112, 92.1, and 83.4 kJ mol^{-1} for Al, Ga, In, respectively at the B3LYP/LANL2DZ(d,p) level of theory). The higher interaction energy of $H_2InN=CH_2$ with ammonia reflects a weaker intramolecular stabilization in free $H_2InN=CH_2$.

For complexes of **IIb**, two structures are possible (Figure 2,f)−with cis and trans orientation of the nitrogen atoms with respect to the M−C bond. In the cis isomer, additional stabilization is gained by the interaction of the nitrogen lone pair of the acceptor molecule with one of the hydrogens of the NH_3 donor molecule (N···H distances are 1.811, 1.854, and 1.866 Å for Al, Ga, In). Cis isomers also have shorter M−N donor−acceptor bond distances (by about 0.065 Å). Accordingly, the dissociation energies of the cis isomers are 40−50 kJ mol^{-1} higher compared to those of the trans structures. For the Ga compound, the trans isomer was predicted to be a transition state, whereas for Al and In it corresponds to a minimum on the PES. Dissociation enthalpies of the *cis*-complexes of **IIb** with ammonia are 124.8, 135.6, and 127.8 kJ mol^{-1}, much higher compared to the $H_3M−NH_3$ complexes. Interestingly, the order of dissociation enthalpies is Al < Ga > In for **IIa**-NH$_3$, but is Al⟨Ga⟩ In for **IIb**-NH$_3$. The gallium

Table 5. Standard Enthalpies $\Delta H^{\circ}_{298}{}^{diss}$, kJ mol^{-1} for Oligomerization Reactions of **II** and **III** (R = H) and Related Compounds

process	X	M = Al	M = Ga	M = In
X₂MNCHX = ½ [X₂MNCHX]₂, or **IIa** = ½ (**IIa**)₂	H	−120.9	−107.4	−119.0
	Cl	−131.2^f	−106.6^f	
X₂MNH₂ = ½ [X₂MNH₂]₂	H	−113.0^a	−96.1^a;−96.6^c	−105.9^a
	Me		−91.2^c	
	Cl	−131.1^a; −126.5^b	−111.8^a; −117.0^d	−121.3^a
XMNCHX₂ = ½ [XMNCHX₂]₂, or **IIIa** = ½ (**IIIa**)₂	H	−254.7	−196.4^c	−191.6
XMNH = ½ [XMNH]₂	H	−281.7^a	−227.5^a;−206.8^c	−212.8^a
	Me	277.8	−200.6^c	
	Cl	−311.9^a; −300.9^b	−245.6^a; −221.4^d	−220.3^a
½ [XMNCHX₂]₂ = ¼ [XMNCHX₂]₄, or ½(**IIIa**)₂ = ¼(**IIIa**)₄	H	−115.3	−89.7	−104.0
½ [XMNH]₂ = ¼ [XMNH]₄	H	−112.7; −115.6^e	−99.9; −98.2^e	−105.0; −109.7^e
	Me	−123.0	−97.4	−116.3
	Cl	−124.6^e	−105.9^e	−119.4^e
¼ [XMNCHX₂]₄ = ⅙ [XMNCHX₂]₆, or ¼ (**IIIa**)₄ = ⅙ (**IIIa**)₆	H	−16.7	−13.1	−9.8
¼ [XMNH]₄ = ⅙ [XMNH]₆	H	−23.4^e	−20.3; −21.3^e	−17.8^e
	Me	−22.7	−18.9	
	Cl	−26.9^e	−26.7^e	−24.2^e
IIIb = ½ (**IIIb**)₂	H	−196.6	−200.3	
½ (**IIIb**)₂ = ¼ (**IIIb**)₄	H	−115.3	−89.7	−104.0
¼ (**IIIb**)₄ = ⅙ (**IIIb**)₆	H	+4.9	+7.6	+5.3

^{a} Reference 45, B3LYP/LANL2DZ(d,p) level of theory. ^{b} Reference 42, B3LYP/DZP level of theory. ^{c} Reference 46, B3LYP/DZP level of theory. ^{d} Reference 47, B3LYP/pVDZ level of theory. ^{e} Reference 48, B3LYP/LANL2DZ(d,p) level of theory. ^{f} Data are given for the trans isomer.

complex of **IIb** with ammonia is the most stable, while the gallium complex of **IIa** with ammonia is the least stable. Comparison of the energies of the isomeric complexes **IIa**-NH₃ and **IIb**-NH₃ reveals, that **IIa**-NH₃ is 36 (Al), 12 (Ga), and 10 (In) kJ mol^{-1} lower in energy.

B. Oligomerization Reactions. Because metal and nitrogen centers in **II** and **III** have low coordination numbers, oligomerization is the anticipated process. In experimental studies, analogues of the dimeric forms **IIa** and **IIIb** were mostly observed experimentally. Reaction of AlMe₃ with MeCN at 80 °C gives the dimer [Me₂Al(NCMe₂)]₂.[14,15] Crystal structures of [Me₂AlN=CMe₂]₂[15] and [Me₂GaN=CMe₂]₂[17] have been determined and IR spectra of dimeric molecules [Me₂MN=CMe₂]₂ are reported for M = B, Al, Ga.[18] When the Et₃GaNC-*t*-Bu complex is heated, C₂H₄ is evolved and the dimeric [Et₂GaNCH-tBu]₂ product is formed. Here the C₂H₅ group of GaEt₃ is a source of hydrogen, which is transferred to the C atom of the cyano group, eliminating ethylene. This reaction pathway is common to all R₃Ga complexes, when R is a heavier homologue of CH₃.[3] Wehmschulte and Power[16] reported that reaction of primary alane [Mes*AlH₂]₂ (Mes* = C₆H₂-2,4,6-*t*-Bu₃) with nitriles proceeds with formation of intermediate complex [Mes*Al(H){μ²-N=C(H)*t*-Bu}]₂ and further heating results in ortho-metalation reactions involving the *t*-Bu group of the Mes* ligand. In the case of isonitrile, cyclic compound [Mes*AlN(*t*-Bu)CH₂]₂ with six-membered (AlNC)₂ ring is easily formed. On heating, cyclometalation product was obtained as well. Jensen[17] found that nitrile reduction by HAl(*i*-Bu)₂ proceeds at 0 °C in quantitative yield with formation of dimeric species: HAl(*i*-Bu)₂ + RCN = [(*i*-Bu)₂AlN=CHR]₂.

General structures of oligomer compounds of **II** and **III** are presented in Figure 3. Dimerization of **IIa** in case of the equivalent substituents X = R = H leads to the D_{2h} symmetric compound, and when X and R are different, two isomers are possibile, with trans (C_{2h} point group) or cis (C_{2v} point group) orientation of X atoms (Figure 3a). Optimization of the structures of these isomers was performed for X = Cl and R=H. *trans*-[Cl₂MN=CHCl]₂ was predicted to be 0.4 (Al) and

0.5 (Ga) kJ mol^{-1} lower in energy compared to *cis*-[Cl₂-MN=CHCl]₂. Note that the experimentally synthesized [(*i*-Bu)₂AlN=CH(C₆H₃-2,6(CH₃)₂)]₂ also possesses a trans orientation of 2,6 dimethylphenyl groups.[17] Comparison of the selected experimental and theoretical structural paramerters for (**IIa**)₂ is presented in Table 4. There is good agreement between experimental and theoretical data; the influence of the *cis*−*trans* orientation of Cl on the geometric parameters of the M₂N₂ ring is marginal.

Comparison of the standard enthalpies of oligomerization reactions of monomeric **II** and **III** and analogous processes is given in Table 5. Cl-substituents result in somewhat higher oligomerization enthalpies (results for other halides are similar),[48,49] whereas differences for H and CH₃ substituents are minimal. Thus, results obtained for the X = H may serve as a good estimation of the oligomerization enthalpies with organic substituents X.

Dimerization of structure **IIa** releases a considerable amount of energy (110−130 kJ mol^{-1} per mole of monomer), and therefore, the transformation of the source donor−acceptor complex **Ia** to (**IIa**)₂ is very thermodynamically favorable. Experimental results show that dimers [(*i*-Bu)₂AlN=CHR]₂ do not react with Lewis bases L (L = Et₂O, THF, Py) to form monomeric adducts (*i*-Bu)₂AlN=CHR:L,[17] in contrast to close dimeric analogues [Me₂AlN(H)SiR′₃] R′ = Ph, Et, which easily form monomeric complexes with 4-methylpyridine.[50] Comparison of the reaction enthalpies for the dimerization of **IIa** and its complex formation with ammonia (Table 6s) reveals that the dimerization process is about 20 kJ mol^{-1} more exothermic. As a result, reaction between the [H₂MN=CH₂]₂ dimers and

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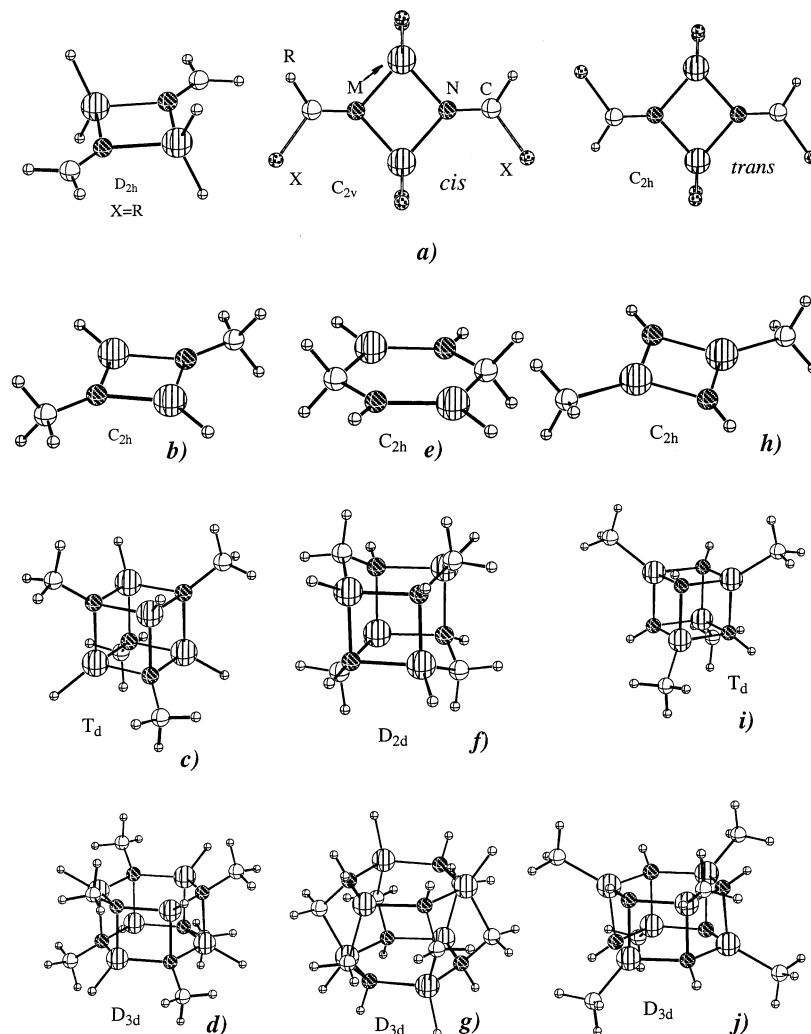
Figure 3. General structures of the oligomer compounds. Dimers of **IIa** (a); dimers (b), cubic tetramers (c) and hexamers (d) of **IIIa**; dimers (e), tetramers (f) and hexamers (g) of **IIIb**; dimers (h), tetramers (i), and hexamers (j) of $[(CH_3)_3MNH]_n$.

Table 6. Thermodynamic Parameters of the Several Gas Phase Reactions Leading to $(IIIb)_4$ (standard enthalpies and Gibbs energies of reaction are in kJ mol^{-1}, standard entropies in J mol^{-1} K^{-1}; B3LYP/pVDZ Level of Theory)

process	ΔH°_{298}	ΔS°_{298}	ΔG°_{298}	ΔG°_{500}	ΔG°_{1000}
$AlH_3 + NCH = \frac{1}{4}[HAlCH_2NH]_4$	−329.3	−296.2	−241.0	−181.3	−33.2
$AlH_3 + NMe_3 = \frac{1}{4}[HAlCH_2NH]_4 + 2CH_4$	−306.5	−10.3	−303.5	−301.4	−296.3
$Al(CH_3)_3 + NH_3 = \frac{1}{4}[HAlCH_2NH]_4 + 2CH_4$	−151.1	−86.0	−125.4	−108.1	−65.1
$GaH_3 + NCH = \frac{1}{4}[HGaCH_2NH]_4$	−255.5	−297.0	−167.0	−107.0	41.5
$GaH_3 + NMe_3 = \frac{1}{4}[HGaCH_2NH]_4 + 2CH_4$	−232.7	−11.2	−229.4	−227.1	−221.6
$Ga(CH_3)_3 + NH_3 = \frac{1}{4}[HGaCH_2NH]_4 + 2CH_4$	−113.0	−93.5	−85.2	−66.3	−19.5
$InH_3 + NCH = \frac{1}{4}[HInCH_2NH]_4$	−224.1	−251.2	−149.2	−98.5	27.1
$InH_3 + NMe_3 = \frac{1}{4}[HInCH_2NH]_4 + 2CH_4$	−201.3	34.7	−211.6	−218.6	−236.0
$In(CH_3)_3 + NH_3 = \frac{1}{4}[HInCH_2NH]_4 + 2CH_4$	−111.2	−47.9	−97.0	−87.3	−63.3

ammonia is unfavorable in terms of both enthalpy and entropy, which suggests the high stability of $[X_2MN=CXR]_2$ species even in the electron−donor solvents.

Oligomerization energies of **IIIa** fully compensate the unfavorability of the hydrogen transfer. Dimeric forms $[HMNCH_3]_2$ are still coordinationally unsaturated, which gives rise to the significant exothermicity (−90 to −115 kJ mol^{-1}) of the dimer to tetramer conversion. Formation of hexamers from tetramers is energetically favorable by 10−17 kJ mol^{-1}. $[HMNCH_3]_n$ compounds (Figure 3b,c,d) are isomers of the $[CH_3MNH]_n$ species (Figure 3h,i,j), with different arrangement of the H and CH_3 ligands. The relative energies of these isomers have a linear

correlation with the number of a methyl groups (Figure 1s), with $[HMNCH_3]_n$ compounds being less stable.

Now we turn our attention to the oligomerization reactions in the isonitrile series. Dimerization of **IIb** with formation of $[H_2MC(H)NH]_2$ was considered first, and structures which possess the planar M_2C_2 core of C_{2h} symmetry were found to be a transition state (TS) (M = Al,Ga) or a second-order stationary point (M = In). Optimization of the $(IIb)_2$ dimer under C_{2v} symmetry constraints resulted in a true minimum for Al, but the dissociation into cyclic monomeric **IIb** is *exothermic* by −44 kJ mol^{-1}. Thus, dimerization of the monomeric forms **IIb** with formation of M_2C_2 core is unfavorable.

In contrast, dimerization of monomeric forms **IIIb** is highly favorable. Reorganization of the three-membered cycles **IIIb** to six-membered cycles with the $M_2C_2N_2$ core (Figure 3e) is exothermic by about 200 kJ mol^{-1} (Table 5). Because both metal and nitrogen centers in $(IIIb)_2$ have low coordination number 3, subsequent oligomerization is also expected. Indeed, formation of D_{2d} symmetric tetramer $(IIIb)_4$ from $(IIIb)_2$ is exothermic by $90-120$ kJ mol^{-1}. The process generating D_{3d} symmetric hexamers $(IIIb)_6$ was also considered, and it was found to be both energetically and entropically unfavorable compared to $(IIIb)_4$, in contrast to the exothermic cube-hex convergence $^1/_4$ $(IIIa)_4 = {^1/_6} (IIIa)_6$. In the experiments, dimeric forms [Mes*AlCH$_2$N(t-Bu)]$_2$ with bulky t-Bu and Mes* substituents were obtained.[16] We predict that with less bulky substituents, synthesis of the tetramer cages containing M$-$C$-$N bonding pattern should also be achievable.

The tetramer and hexamers of **IIIb** [HMCH$_2$NH]$_{4,6}$ are isomers of the well-known tetrameric and hexameric species [HMNCH$_3$]$_{4,6}$ and [CH$_3$MNH]$_{4,6}$. The relationship between these forms may be seen in Figure 3. The cages [HMCH$_2$NH]$_4$ (Figure 3f) may be considered as the intermediate stage for the CH$_2$ moiety migration from the nitrogen center in [HMNCH$_3$]$_4$ (Figure 3c) to the metal center in [CH$_3$MNH]$_4$ (Figure 3i). Comparison of the relative energies of $(IIIa)_4$ and $(IIIb)_4$ tetramers show that $(IIIb)_4$ is 175 (Al), 53 (Ga) and 57 (In) kJ mol^{-1} less stable, compared to $(IIIa)_4$. This result indicates some competitiveness of the metal$-$carbon and metal-nitrogen bonding for Ga and In compounds. It is also of interest to check the stability of the [HMCH$_2$NH]$_4$ species at high-temperature conditions with respect to MH$_3$ and HCN, as well as with respect to the important source molecules used in CVD of binary nitrides. Such a comparison is presented in Table 6. As can be seen, formation of tetramers from the MH$_3$ and HCN is favorable at low temperatures. When reaction between MH$_3$ and NMe$_3$ is considered, formation of $(IIIb)_4$ is very favorable, even at high temperatures. Finally, formation of $(IIIb)_4$ in a reaction between the commercial sources of the nitride formation (M(CH$_3$)$_3$ and ammonia) is also thermodynamically favorable for all M, as the corresponding Gibbs free energy is negative even at 1000 K. We conclude that M$-$C$-$N bonded species [HMCH$_2$NH]$_4$ may be *exothermically* generated under CVD conditions. Once formed, they obstruct the CH$_4$ elimination (by trapping carbon in the form of bridging CH$_2$ groups) and, therefore, are potential intermediates, responsible for carbon contamination in nitrides.

III. RX Elimination Reactions from the Donor −Acceptor Complexes. Besides X migration, another major process upon reaction of MX$_3$ with cyanides is the RX elimination reaction (Figure 1). RX elimination from X$_3$M$-$NCR (**Ia**) and X$_3$M$-$CNR (**Ib**) formally leads to monomeric metal cyanides X$_2$MNC (**IVa**) and X$_2$MCN (**IVb**), respectively. Such species, due to the unsaturated metal and donor center, easily form oligomers (polymers). They also can form donor$-$acceptor complexes with strong donors, such as ammonia, which may prevent the oligomerization process. First, we will discuss the structures and stability of the monomeric species itself, then their complex formation with ammonia and dimerization energies. The thermodynamics of RX elimination reactions will be considered in more detail in Discussion section.

Table 7. Selected Structural Parameters and Relative Energies^a ΔE, kJ mol^{-1} for XX′MCN and XX′MNC Isomers (all bond distances in Å, all bond angles in deg; B3LYP/pVDZ level of theory)

M	X	X′	ΔE	cyanides			isocyanides		
				r(C−N)	r(M−C)	XMX′	r(N−C)	r(M−N)	XMX′
Al	Me	Me	−10	1.1639	1.9499	128.7	1.1814	1.835	129.2
	H	Me	−9.9	1.1639	1.9464	126.9	1.182	1.8275	127.7
	H	H	−9.4	1.1638	1.9463	125.5	1.1827	1.8199	126.6
	H	Cl	−8.3	1.1632	1.9346	122.1	1.183	1.8078	123.0
	Cl	Cl	−4.1	1.1626	1.9195	121.9	1.183	1.7952	122.4
Ga	Me	Me	13.2	1.1636	1.9801	131.0	1.1805	1.8953	134.6
	H	Me	14.7	1.1635	1.9698	129.4	1.1811	1.8834	132.8
	H	H	16.2	1.1634	1.9589	127.6	1.1818	1.8717	131.0
	H	Cl	19.5	1.1625	1.9437	121.3	1.1821	1.8538	124.2
	Cl	Cl	25.6	1.1616	1.9275	120.3	1.1825	1.8387	122.2
In	H	H	23.2	1.164	2.170	130.2	1.182	2.100	135.1
	Cl	Cl	32.9	1.162	2.131	118.6	1.184	2.057	121.9

^{a} ΔE denotes total energy difference between XX′MNC and XX′MCN isomers: $\Delta E = E^{tot}(XX′MNC) - E^{tot}(XX′MCN)$.

A. Metal Cyanides XX′MCN and Isocyanides XX′MNC (X,X′ = H,CH$_3$,Cl). Monomeric cyanides and isocyanides of group 13 metal derivatives are scarcely studied. The recently synthesized gallium tricyanide Ga(CN)$_3$ has an ionic structure in the solid state with coordination number 6 on gallium.[8] The experimental gas-phase reactions of atomic group 13 metals with HCN resulted in the formation of monocyanides MCN and MNC.[51] According to theoretical predictions at the BP86 level of theory, the stability of MNC forms is decreased in the order B > Al > Ga > In > Tl, and for thallium, the form TlCN was predicted to became more stable. A DFT study of the relative stability of group 13 tricyanides M(CN)$_3$ revealed that tricyanides are more stable for Ga and In, while for Al the triisocyanide form is preferable.[52] In another recent theoretical study, Sung[53] compared energies of RCN and RNC bonded structures for 23 different R groups using the B3LYP/6$-$33+G(2d,p)// HF/6-31+G* level of theory. He found that only with highly electropositive groups (Li, MgH, Na, AlH$_2$, BeH) does the isocyanide form becomes more stable.

In the present report, the investigation of the influence of metal M and substituents X,X′ on the relative stability of cyanides XX′MCN and isocyanides XX′MNC has been carried out. The results obtained are summarized in Table 7. Consideration of the atomization energies reveals that the relative energy $\Delta E = E^{tot}(RNC) - E^{tot}(RCN)$ is determined by the differences in the R$-$C and R$-$N bond dissociation energies: $\Delta E = E^{dis}(R-CN) - E^{dis}(R-NC)$. On the basis of relative energies listed in Tables 2s and 7, the following trend is obtained: CH$_3$ > H > X$_2$In > X$_2$Ga > X$_2$Al. For all X$_2$Al substituents, the RNC form (i.e., X$_2$AlNC) becomes the most stable, irrespective of the nature of the substituent X. This indicates that Al$-$N bonding is preferable compared to Al$-$C bonding, whereas for Ga and In the situation is reversed and the X$_2$MCN isomer is the most stable.

Trends in ΔE with changing substituent X are less pronounced. The relative stability of X$_2$MNC forms decreases slightly with the increasing electronegativity of the terminal group X both for Al and Ga: CH$_3$ < H < CN < Cl. This conclusion agrees well with "electropositivity" statement of Sung.[53]

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Table 8. Structural and Thermodynamic Parameters of $X_2MCN-NH_3$ and $X_2MNC-NH_3$ Donor–Acceptor Complexes (all bond distances in Å, all bond angles in deg, standard enthalpies $\Delta H^{\circ}{}_{298}{}^{diss}$ in kJ mol^{-1}, and entropies $\Delta S^{\circ}{}_{298}{}^{diss}$ in J mol^{-1} K^{-1}; harmonic vibration frequency shift of CN stretching mode, $\Delta\omega$(CN), cm^{-1} (unscaled) and charge transfer q_{CT}, predicted at B3LYP/pVDZ level of theory)

M	X	r(C–N)	r(M–(CN))	r(M–NH$_3$)	XMX	$\Delta H^{\circ}{}_{298}{}^{diss}$	$\Delta S^{\circ}{}_{298}{}^{diss}$	q_{CT}	$\Delta\omega$(CN)
				cyanides					
Al	H	1.1641	1.980	2.066	121.6	150.3	132.1	0.287	−4
Al	Cl	1.1630	1.951	2.030	117.8	172.7	129.5	0.306	−5
Al	Me	1.1643	1.992	2.081	114.2	131.7	154.5	0.275	−4
Ga	H	1.1636	1.991	2.151	123.9	122.0	128.8	0.294	−1
Ga	Cl	1.1620	1.958	2.095	117.2	145.3	132.9	0.325	−4
Ga	Me	1.1640	2.007	2.177	124.5	101.6	138.0	0.277	−2
In	H	1.1640	2.197	2.378	127.0	114.4	120.4	0.281	−2
In	Cl	1.1626	2.154	2.325	117.5	145.4	124.9	0.321	−2
				isocyanides					
Al	H	1.1790	1.861	2.062	122.3	146.9	129.0	0.282	21
Al	Cl	1.1800	1.831	2.022	118.2	174.3	133.5	0.303	15
Al	Me	1.1787	1.873	2.076	122.4	130.1	145.0	0.272	15
Ga	H	1.1782	1.915	2.144	126.3	120.7	124.1	0.295	21
Ga	Cl	1.1794	1.875	2.083	118.4	149.6	132.3	0.331	17
Ga	Me	1.1781	1.933	2.168	127.2	101.4	133.8	0.279	14
In	H	1.1796	2.144	2.369	130.6	118.8	123.6	0.278	14
In	Cl	1.181	2.089	2.312	119.9	150.9	126.6	0.328	15

Trends in ΔE are closely related to the reorganization effects and correlated with XMX angle deformation and with the electronegativity of the terminal group X. For aluminum compounds this trend is less pronounced than for Ga. Note also that going from Me to Cl, the CN distance in RCN is decreasing, while in RNC it is increasing both for Al and Ga (Table 7). The overall changes in the C–N bond length are symbiotic with the relative energies of the isomers (Figure 2s).

We have also examined the so-called bond length–bond order relationship for the X_2MNC and X_2MCN species. Previously, a correlation between the XMY bond angle and donor–acceptor bond length M–Y was observed for the series of X_3M-YH_3 adducts for the fixed donor–acceptor pairs M,Y.[40] Now we test this relationship for the planar group 13 species. Because structures with different substituents X,X′ were considered, the influence of the M–N or M–C bond length on the value of the X–M–X′ angle was monitored (Figure 3s). Due to the planarity of the molecule, this single parameter reflects overall changes of XMY and X′MY angles. There is a satisfactory correlation between X–M–X′ angle and M–Y bond length for the each donor–acceptor pair M,Y. Correlation coefficients are 0.93–0.95 for Al–N, Ga–N, Ga–C, and 0.77 for Al–C pairs. Thus, a bond length – bond angle relationship holds for the planar group 13 derivatives as well.

B. Complexes of Metal Cyanides X_2MCN and Isocyanides X_2MNC with Ammonia. Major structural and thermodynamic parameters of these complexes are presented in Table 8. Complexation with ammonia lowers the energy differences between the X_2MCN and M_2MNC isomers. Comparison of the CN stretching vibration shift in the complexes relative to free $X_2M(CN)$ shows, that in the case of the cyanides, the only minor decrease (by 1–5 cm^{-1}) is observed upon complexation with ammonia. In contrast, for isocyanides, the CN stretching mode is increased by 14–21 cm^{-1}, indicating a stabilization of the CN bond. Thus, whereas complexation with ammonia slightly destabilize CN bonding in nitriles, it stabilizes CN bonding in isonitriles, leading to a lowering of the relative energies of isomers.

It is also of interest to compare the acceptor ability of MX_2CN with respect to that of MX_3. Compared to the Cl_3GaNH_3 complex with a dissociation enthalpy of 137 kJ mol^{-1} (B3LYP/

pVDZ),[47] the predicted dissociation enthalpies of the Cl_2Ga-$NC-NH_3$ and $Cl_2GaCN-NH_3$ complexes are 145 and 150 kJ mol^{-1}, respectively. Thus, substitution of the Cl atom by the CN group leads to an *increase* of the Lewis acidity of the acceptor by 13 kJ mol^{-1}. Note, that substitution of Cl by F leads to an increase of the dissociation enthalpy of the $GaFCl_2-$ ammonia complex by only 10 kJ mol^{-1} (B3LYP/6−3111++G** level of theory).[54] Compared to Me_3GaNH_3 (dissociation enthalpy 76 kJ mol^{-1}),[41] dissociation enthalpies of the Me_2-$GaNC-NH_3$ and $Me_2GaCN-NH_3$ complexes are increased by 25 kJ mol^{-1}. Thus, the following order of the acceptor ability of the MX_3 species may be deduced (see data for Ga complexes in Table 7s)

$$CN > F > Cl > Br > I > H > Me$$

Thus, is important to conclude that inclusion of the cyano group into the acceptor molecule always *increases* its acceptor ability.

C. $[X_2MNC]_n$ Rings: Oligomerization Processes. Oligomerization of unsaturated monomer X_2MCN species leads to $[X_2MNC]_n$ oligtomer species, which have been known since 1963 (tetrameric $[Me_2AlCN]_4$ and $[Me_2GaCN]_4$).[11] The indium analogue $[Me_2InCN]_x$, structurally characterized in 1993, exists as a polymer with a spiral structure in the solid state.[13a] The analogous gallium compound is tetrameric, it can be purified by sublimation at 90 °C/0.01 Torr.[11] In mass spectroscopy (MS) experiments, mostly trimeric units have been observed for Ga and In, and no presence of tetramers was evidenced.[12] In stark contrast, for the Al compound the tetramer has almost the same intensity (99%) as the trimer (100%, highest peak). The product of partial dissociation $[(CH_3)_2MCNM(CH_3)_2]^+$ has a relatively high intensity for all metals M. The first crystal structure of oligomeric cyanides was determined in 1995 by Uhl and co-workers.[10] Trimeric $[\{(Me_3Si)_2CH\}_2AlCN]_3$ was produced in a 26% yield by reaction of isonitrile t-BuNC with R_2AlAlR_2; $R = (Me_3Si)_2CH$. Predicted structural parameters for the C_{3h} symmetric $[Me_2AlCN]_3$ are in good agreement with experimental findings for $[\{(Me_3Si)_2CH\}_2AlCN]_3$. The mean experimental C–N distance 1.164 Å agrees very well with B3LYP/pVDZ result of 1.163 Å. The predicted highly inequivalent

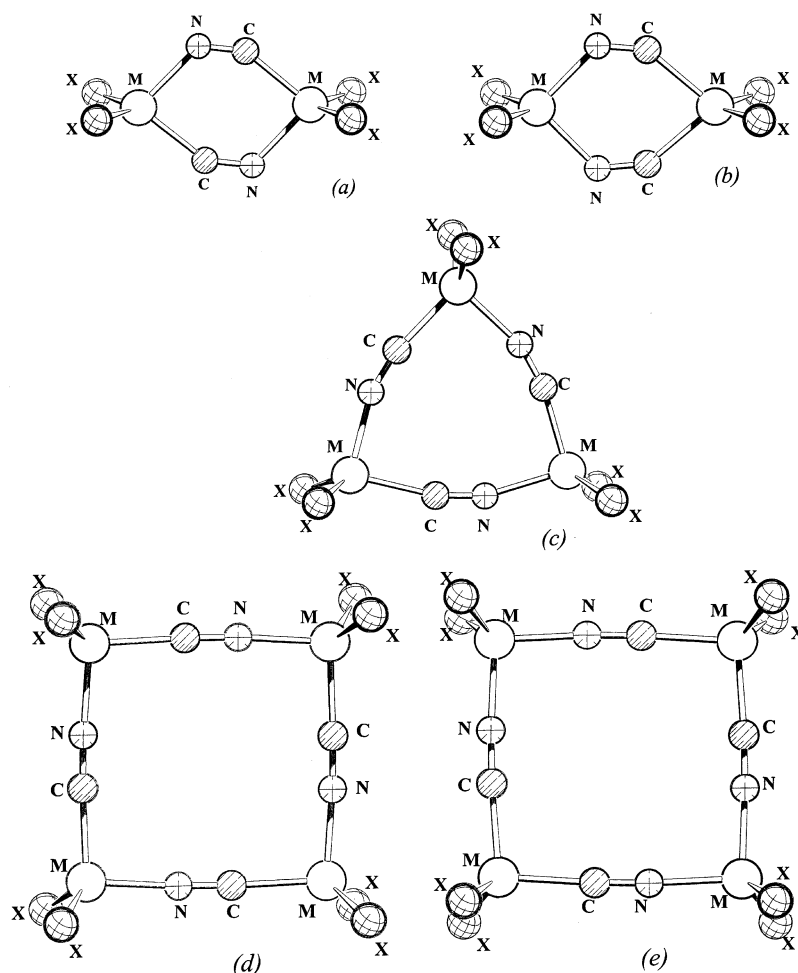(54) Ogawa, A.; Fujimoto, H. *Inorg. Chem.* **2002**, *41*, 4888.

Figure 4. General structures of [X$_2$MCN]$_n$ oligomer compounds. C_{2h} (a) and C_{2v} (b) symmetric dimers, trimers (c) and C_{4h} (d) and D_{2h} (e) symmetric tetramers.

Al−N (1.969 Å) and Al−C (2.088 Å) distances reflect the stronger Al−N bonding, compared to Al−C. The average theoretical value for the Al−(N/C) bond of 2.029 Å agrees well with the experimental mean value of 2.022 Å. The experimental Al−(N/C)−(N/C) angles are 161.9−167.0°, with the predicted Al−N−C values being 164.5° and Al−C−N 166.6°. In the mass spectrometer the monomer fragment M$^+$−CH$_3$ has the highest intensity, and the trimeric form 3M$^+$−C(SiMe$_3$)$_2$ was detected with an intensity of 2%. The dimeric species 2M$^+$−CH$_3$ (2%) and 2M$^+$−CH(SiMe$_3$)$_2$ (13%) have also been observed, indicating partial dissociation under MS conditions.

The general structures of the [X$_2$MCN]$_n$ oligomers ($n = 2-4$) are presented in Figure 4. Dimerization of X$_2$MCN and X$_2$-MNC molecules lead to formation of cyclic compounds with six-membered M,N,C-containing rings. Two isomer structures for the dimer is possible: with equivalent metal centers, possessing N,C coordinated cyanogroups (C_{2h} point group), and inequivalent M(N,N) and M(C,C) coordinated metal atoms (C_{2v} point group). Both isomers are found to be minima on the PES and exhibit strictly planar cycles. The absolute energy difference between these C_{2h} and C_{2v} symmetric isomers is less than 1 kJ mol^{-1}. C_{2v} symmetric X$_2$M(NC)$_2$MX$_2$ isomers are more stable, with the exception of M = Al X = Cl, for which the C_{2h} structure was found to be preferable. For the tetramers, similar arrangement of the cyanogroups leads to C_{4h} or D_{2h} symmetric structures with planar cycles. Both isomers are minima on the

Table 9. Subsequent Oligomerization Enthalpies (kJ mol^{-1}) of X$_2$MNC Compounds[a]

M	X	monomer = $^1/_2$ dimer	$^1/_2$ dimer = $^1/_3$ trimer	$^1/_3$ trimer = $^1/_4$ tetramer
Al	H	−87.2	−55.7	−9.9
	Me	−77.1	−52.5	−8.6
	Cl	−91.4	−59.4	−9.4
Ga	H	−84.8	−48.3	−9.3
	Me	−72.3	−43.7	−7.6
	Cl	−83.0	−53.4	−8.5
In	H	−103.8	−35.3	−5.2
	Cl	−110.2	−42.0	−5.8

[a] For dimeric and tetrameric species data are given for the most stable isomer.

PES and, are very close in energy (within 1 kJ mol^{-1}), as was the case for the dimeric species.

Thermodynamic parameters for the association processes are presented in Table 9. Subsequent oligomerization enthalpies only slightly depend on the different substituents X, in agreement with our findings for the oligomerization of structures **II** and **III**. Formation of tetramers is very favorable energetically even at high (1000 K) temperatures. It is of interest to compare the thermodynamics of the oligomerization process with formation of [X$_2$MCN]$_4$ and complex formation of X$_2$MCN with ammonia. Data are summarized in Table 8s. For X = Cl, the cleavage of tetramer by ammonia is exothermic. In contrast, formation of tetramer is predicted to be slightly more exothermic compared
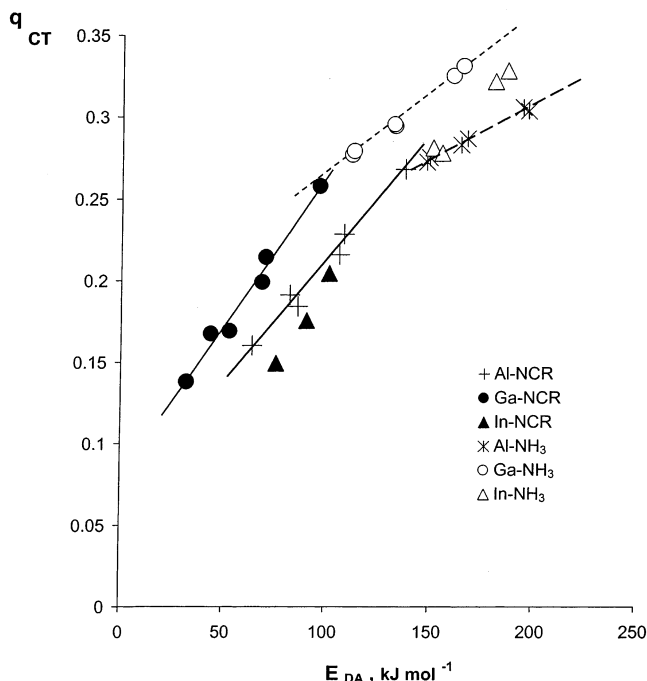
Figure 5. Relationship between the energy of the donor−acceptor bond and charge transfer for donor−acceptor complexes with N-donor ligands.

to complexation in case of $X = H, CH_3$, but the difference in the reaction enthalpies is not large (5−16 kJ mol^{-1}). Therefore, for $X = H, CH_3$ tetramers are predicted to be stable compared to reaction with NH_3, but may dissociate on reaction with stronger donors. In fact, in experimental studies, $[Me_2AlCN]_4$ and $[Me_2GaCN]_2$ absorb four molecules of NMe_3 "which doubtless competes with cyanide groups in coordination with metal".[11]

Discussion

I. Relationship between $\Delta\omega(CN)$, q_{CT}, $\Delta H°_{298}^{diss}$, E_{DA}. Data obtained in the present study allows one to examine general relationships between the shift of the C−N stretching mode, dissociation energy of the complex and charge transfer. In our previous research, it was shown that for the series of metal halide complexes MX_3 (M = Al, Ga, In; X = F, Cl, Br, I) with simple group 15 donors YH_3 (Y = N,P,As) there is no correlation between the degree of charge transfer and the dissociation enthalpy of the complex.[40] When we examine relationship of the q_{CT} and $\Delta H°_{298}^{diss}$ for the complexes studied in the present work, we see no general $q_{CT} - \Delta H°_{298}^{diss}$ correlation. However, for each acceptor center (Al, Ga, In) there is some proportionality between the charge transfer and the dissociation enthalpy (Figure 4s). Another parameter, the shift of the C−N stretching mode upon coordination, should be more sensitive to the charge transfer. Indeed, there is a very nice correlation for each nitrogen-containing *donor* molecule (HCN and CH_3CN), but the relationship for the carbon-coordinated donors is very poor (Figure 5s). Finally, there is a mediocre correlation between the shift of the CN and the dissociation enthalpy of the complex (Figure 6s). According to the data in Table 4s, standard enthalpies and the shift of the CN stretching mode are consistent and indeed can be used as a qualitative measure of the strength of the complex for the fixed metal atom M and different substituents X (Me < H < Cl), or for the fixed substituent X and different metal centers (Al > Ga ≤ In). All of these trends
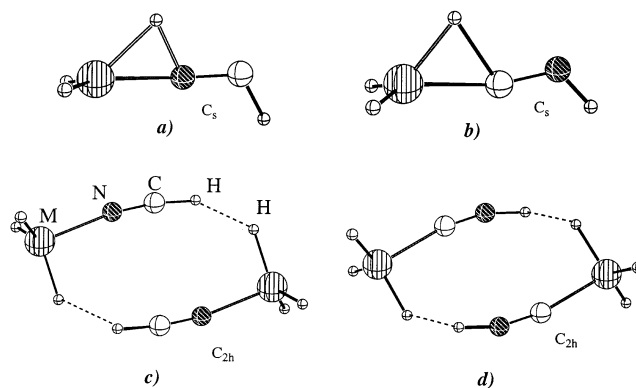

Figure 6. Structures of intramolecular transition states for hydrogen transfer in donor−acceptor complexes **TSa** (a) and **TSb** (b) and structures of dimers of the donor−acceptor complexes $(\mathbf{Ia})_2$ (c) and $(\mathbf{Ib})_2$ (d).

Table 10. Relative Energies (kJ mol^{-1}) of Initial Transition States for the monomolecular H transfer

		nitrile series				isonitrile series	
	Ia	TSa	H$_2$MNHCH	IIa	Ib	TSb	IIb
Al	0	203.0	104.1	−72.2	0	70.6	−58.3
Ga	0	225.3	109.4	−47.8	0	82.3	−25.2
In	0	236.2	118.6	−22.1	0	96.7	−27.2

are in good agreement with the available experimental data. The shift of the coordinated CNR group is more than the analogous shift of coordinated NCR, indicating bigger changes upon complexation, which agrees with the higher dissociation energies of the MX_3-CNR complexes. However, when data for all acceptor molecules are taken into consideration, there is a poor correlation between $\Delta H°_{298}^{diss}$ and $\Delta\omega(CN)$ (Figure 6s). In fact, the shifts for all $GaCl_3$ complexes are always higher than for the AlH_3 complexes, but the dissociation energies of the $GaCl_3$ complexes are always lower compared to dissociation energies of the AlH_3 complexes with the same donor molecule (Table 1). Therefore, the qualitative correlation between $\Delta H°_{298}^{diss}$ and $\Delta\omega$ (CN) is found to be valid only for relative acceptor ability (fixed M,D) and cannot be simply generalized for the entire set of data.

The energy of the donor−acceptor bond E_{DA} was estimated taking into account the reorganization energies of the fragments and a BSSE correction.[31] BSSE corrections and reorganization energies were computed for all donor−acceptor complexes considered. Data obtained are given in Table 9s for complexes of MX_3 with nitriles/isonitriles and in Table 10s for complexes of $X_2M(CN)$ with ammonia. The results indicate that the distortion energy of the donor fragment is no more than 1.5 kJ mol^{-1}, and the distortion energy of the acceptor molecules varies from 4.4 to 29 kJ mol^{-1}. Total BSSE corrections range from 8 to 20 kJ mol^{-1}. Both distortion energy and BSSE are maximal for Cl-containing acceptors.

We have also examined the relationship between the E_{DA} and the degree of charge transfer (Figure 5). Taking into account reorganization energies and correcting for the BSSE error significantly improves the $q_{CT} - \Delta H°_{298}^{diss}$ correlation. Note, that correlations for NH_3 and NCR donors are different. A nice correlation holds only for the fixed metal and fixed donor centers (Figure 7S in the Supporting Information).

II. Mechanisms of Initial Transformations. The mechanisms of the transformations considered are expected to be

important in light of the use of MX_3 halides as catalysts in organic synthesis. Thus, Al(III) complexes catalyze the enantioselective addition of HCN to imines,[55] but the mechanism of this transformation is not understood. Due to time limitations, only the mechanisms of the initial reactions will be considered. First, we will consider hydrogen transfer within the donor–acceptor complexes **Ia**. A transition state (TS) for the monomolecular process (**Ia** → **IIa**) has been found, and it lies 200–240 kJ mol^{-1} higher in energy. Therefore, formation of the $[X_2MN=CXR]_2$ dimers via intramoleculer transfer of X and subsequent dimerization of the product presents considerable energy difficulties. Yet this process easily occurs at 0 °C in toluene solution.[17] Therefore, on the basis of the experimental observations, a high lying TS should be ruled out. Instead, X transfer may occur between two DA complexes of **Ia** with formation of a dimer $(\mathbf{Ia})_2$ as a transition state (Figure 1). Initial dimer formation is exothermic by −22 kJ mol^{-1} (per mole of monomer), but entropically unfavorable (by −64 J mol K^{-1}). At 298 K the Gibbs energy of the dimerization process is −2.8 kJ mol^{-1}; this result is in agreement with crystallographic studies, which found "head-to-tail" packing of the $Me_3AlNCMe$ molecules in the unit cell.[38] The entropy factor makes dimerization unfavorable at temperatures higher that 340 K. Another possible mechanism, which relies on the excess of MX_3 as a catalyst, was proposed in several experimental studies.[16,56,57]

In contrast to the nitrile series, in isonitriles the hydrogens are transferred to the carbon, which is directly bonded to the metal. Therefore, there is a marked decrease in the transition state energies for the monomolecular hydrogen transfer **Ib** → **IIb** (TS energy is less than 100 kJ mol^{-1}), and formation of the product is exothermic (Table 10). In both series, the order Al < Ga < In is observed for the energy of the TS.

Dimerization of the isonitrile complexes H_3M-CNH was also considered for comparison; C_{2h} symmetric structures, which are minima on the PES, were obtained and are presented in Figure 6. Dimerization enthalpies are −35, −28, and −34 kJ mol^{-1} (per mole of monomer) for Al, Ga, and In, respectively. These dimers possess even shorter H...H intermolecular contacts: 1.417 Å, compared to 1.753 Å for the corresponding H_3AlNCH dimer. The optimized structure of the H_3AlNCH dimer clearly reflects the initial formation of two H_2 molecules: compared to the monomer donor–acceptor complex, in the dimer the C−H bonds and Al−H bonds are elongated by 0.023 and 0.03 Å, respectively. Simultaneously, the H−C−N angle decreases from 180.0° to 171.5°, and the H...H separation is 1.753 Å. There is also a significant H−C−N angle deformation: H−C−N 171.5°; C−N−H 162.2°. These dramatic structural changes occur exothermically and can greatly reduce the energy required for the hydrogen elimination. It is interesting that the experiment reaction of Me_2AlH with HCN in benzene at 0 °C resulted in rapid H_2 (and not CH_4 !) evolution,[9] which suggests that the observed H...H intermolecular contacts in dimers may play a role in the elimination reactions at low temperatures.

III. Comparison of the Thermodynamics of Elimination, Dissociation, and Oligomerization Processes in the Gas Phase. Theoretical enthalpies of RX elimination with formation of monomeric and oligomeric forms $(\mathbf{IV})_n$ are given in Table

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Table 11. Comparison of the Thermodynamic Parameters of Gas Phase Reactions 1–4 (standard enthalpies ΔH^0_{298} and standard Gibbs energies ΔG^0_T are in kJ mol^{-1}, standard entropies of the reaction are in J mol^{-1} K^{-1})

process	ΔH^0_{298}	ΔS^0_{298}	ΔG^0_{298}	ΔG^0_{500}	ΔG^0_{1000}
		X = H;R = H			
M = Al					
(1)	73.3	126.5	35.6	10.1	−53.2
(2)	−182.0	−98.3	−152.7	−132.9	−83.7
(3)	−142.1	−9.3	−139.3	−137.5	−132.8
(4)	−194.9	−164.5	−145.9	−112.7	−30.4
M = Ga					
(1)	48.2	120.6	12.2	−12.1	−72.4
(2)	−143.1	−101.0	−113.0	−92.6	−42.1
(3)	−110.6	−13.5	−106.5	−103.9	−97.1
(4)	−170.3	−171.7	−119.1	−84.4	1.4
M = In					
(1)	69.1	120.1	33.3	9.0	−51.0
(2)	−129.8	−103.6	−98.9	−78.0	−26.2
(3)	−104.9	−18.6	−99.4	−95.6	−86.3
(4)	−167.7	−178.5	−114.5	−78.5	10.7
		X = Cl;R = H			
M = Al					
(1)	89.0	133.0	49.4	22.5	−43.9
(2)	−131.2	−104.7	−100.0	−78.8	−26.5
(3)	16.5	13.2	12.5	9.8	3.2
M = Ga					
(1)	59.4	125.5	22.0	−3.4	−66.1
(2)	−106.6	−100.5	−76.7	−56.4	−6.1
(3)	19.9	7.2	17.7	16.3	12.7

11s. RX elimination reactions from the donor–acceptor complexes strongly depend on the nature of the substituent X, and, taking into account subsequent oligomerization of the products, are highly exothermic in the case of X = H, CH_3 and endothermic for X = Cl, reflecting the higher stability of the metal-Cl bonds. HCl and CH_3Cl elimination from X_3MNCR adducts is predicted highly unfavorable even if formation of oligomer species takes place.

Comparison of the different reaction pathways of the donor–acceptor complexes will be carried out by considering the Gibbs free energies of the major reactions. On the basis of the previous discussion, four major processes have been identified:

(1) $X_3MNCR = X_3M + NCR$ (dissociation of the complex)

(2) $X_3MNCR = {}^1/_2 [X_2MNCXR]_2$ (X transfer with dimerization following)

(3) $X_3MNCR = {}^1/_4 [X_2MNC]_4 + RX$ (elimination of RX with subsequent tetramerization)

(4) $X_3MNCR = {}^1/_4 [XMCX_2NR]_4$ (transfer of two X with formation of the M−C−N core and tetramerization following)

We will not discuss the process of rearrangement in which two X moieties are transferred to the carbon atom to form $[XMNCX_2R]_n$ oligomers (structures $(\mathbf{IIIa})_n$), because experimental attempts at such transformation have failed.[14] Thermodynamic parameters for processes (1–4) are summarized in Table 11. At low temperatures, process (2) − generation of the dimers $[X_2MNCXR]_2$ $(\mathbf{IIa})_2$ − is the most favorable. The Gibbs energy for this process at 298 K is negative both for X = H and X = Cl substituents. For X = H, formation of an M−C−N bonded cage is also favorable. As the temperature increases, unfavorable entropy change disfavors processes (2) and (4) and favors processes (1) and (3). In the case of R = H, process (3) of H_2 elimination with formation of $[X_2MCN]_4$ tetramer becomes the most favorable for all M at T = 500 K, and is still dominant at T = 1000 K. For X = Cl, elimination of HCl is

unfavorable for all M at all temperatures, and dissociation of the adduct into components prevails at 1000 K. Thus, thermodynamic analysis shows that formation of dimers $(\mathbf{IIa})_2$ and tetramers $(\mathbf{IV})_4$ as major products of reactions between X_3M and NCR is expected at low and high temperatures, respectively. Although the dimers $(\mathbf{IIa})_2$ are predicted to be stable with respect to interaction with donor molecules, cleavage of tetrameric rings $(\mathbf{IV})_4$ is expected to proceed with donors stronger than ammonia.

Conclusions

Reactions of group 13 metal derivatives MX_3 with nitriles/isonitriles R(CN) result in exothermic formation of the corresponding donor−acceptor complex. The acceptor ability of MX_3 decreases in the order Cl > H > CH_3; Al > Ga ≤ In; the donor ability of R(CN) decreases in the order CH_3NC > CH_3CN > HNC > HCN. Irrespective of the acceptor molecule, complexation with MX_3 to some extent stabilizes the isonitrile form due to the higher M−C donor−acceptor bond energy. Prediction of the $\Delta H°_{298}{}^{diss}$ on the basis of the shift of CN stretching mode is possible within limited series of cyanide complexes (for the fixed M,R); in contrast, complexes of the isocyanides exhibit very poor $\Delta\omega_{CN}$ − $\Delta H°_{298}{}^{diss}$ correlation. The correlation between the energy of the donor−acceptor bond and the degree of a charge transfer is very good for a given metal-donor pair, but cannot be simply generalized for the entire set of data.

Migration of the terminal group X from metal to carbon center in MX_3-(CN)R is determined by the difference between the metal-X and carbon-X bond energies and the coordination number on the metal. Transfer of one hydrogen or methyl group is predicted to be exothermic; in contrast, Cl transfer is highly endothermic. Stabilization of coordinationally unsaturated products of X transfer is achieved via oligomerization or via donor−acceptor interaction with Lewis bases. Dimerization processes are dominant for the X_2MNCHX species, while X_2MCXNH monomers are stabilized by intramolecular donor−acceptor interactions. Transfer of *two* substituents X from metal to carbon center is always endothermic, irrespective of the substituent X. However, oligomerization processes of $HMNCH_3$ and $HMCH_2$-NH fully compensate this unfavorability. The relative energies of $[HMN(CH_3)]_n$ with respect to their isomers $[(CH_3)MNH]_n$ depend linearly on the number of methyl groups n.

RX elimination reactions from the donor−acceptor complexes strongly depend on the nature of the substituents X, and, taking into account subsequent oligomerization of the products, are highly exothermic in the case of X = H,CH_3 and endothermic for X = Cl. Monomeric aluminum isocyanides X_2AlNC are more stable compared to Al−C bonded isomers; for gallium and indium situation is reversed and cyanide forms are more

stable. Substitution of X by CN in MX_3 increases the dissociation enthalpy of the X_2MCN−NH_3 complex compared to that for MX_3−NH_3, irrespective of the substituent X. Thus, inclusion of the cyano group into the acceptor molecule MX_3 always *increases* its acceptor ability.

Mechanisms of the initial reactions of X transfer in MX_3−(NC)R have been studied for the case X = R = H. Intramolecular hydrogen transfer has been definitely ruled out for nitrile adducts. Complexes MX_3−(NC)R exothermically form 'head-to-tail' dimers, which exhibit short H...H intramolecular distances and possess activated nitrile and isonitrile molecules. These dimers are likely to be intermediates toward both X transfer and RX elimination processes and may play a key role in catalytic activity of group 13 derivatives.

Comparison of the thermodynamic parameters of subsequent oligomerization reactions shows that oligomerization enthalpies of the halide containing species are slightly more exothermic, whereas differences for H and CH_3 substituents are minimal. Thus, results obtained for the systems with X = H, which are most amenable to theoretical studies, may serve as a good models for the organometallic systems.

Analysis of predicted thermodynamic parameters shows that major products of the reaction of MX_3 with nitriles/isonitriles are dimers $[X_2MNCRX]_2$ and tetramers $[X_2MCN]_4$, at low and high temperatures, respectively. Although $[X_2MNCRX]_2$ dimers are predicted to be thermodynamically stable toward reactions with Lewis bases, $[X_2MCN]_4$ rings may be cleaved by donors stronger than ammonia. Tetrameric M−C−N bonded $[HMCH_2$-NH]_4$ cages may be exothermically generated in the gas phase under MOCVD conditions, and are potential intermediates, responsible for carbon contamination in nitrides.

Supporting Information Available: A listing of experimental and theoretical vibrational frequencies for the donor molecules; tabulated $\Delta H°_{298}{}^{diss}$ − $\Delta\omega(CN)$ data, BSSE, reorganization, and donor−acceptor bond energies of the studied complexes (19 pages, print/PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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