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# Computational Analysis of ( $n \rightarrow \pi^*$ ) Back-Bonding in Metallylene-Isocyanide Complexes $R_2MCNR'$ ( $M = Si, Ge, Sn$ ; $R = tBu, Ph$ ; $R' = Me, tBu, Ph$ )

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## Abstract

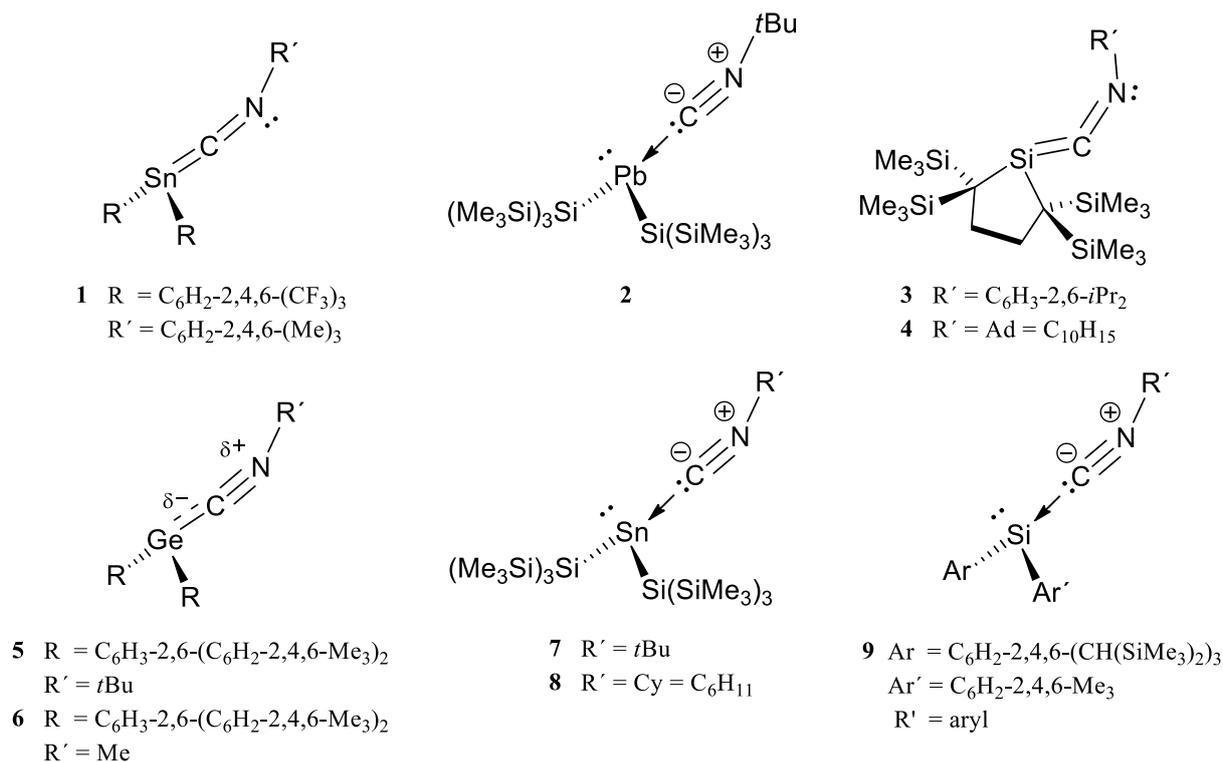
A detailed computational investigation of orbital interactions in metal-carbon bonds of metallylene-isocyanide adducts of the type  $R_2MCNR'$  ( $M = Si, Ge, Sn$ ;  $R, R' = \text{alkyl, aryl}$ ) was performed using density functional theory and different theoretical methods based on energy decomposition analysis. Similar analyses have not been carried out before for metal complexes of isocyanides even though they have for long been of common practice when investigating the metal-carbon bonds in related carbonyl complexes. The results of our work reveal that the relative importance of  $\pi$ -type back-bonding interactions in these systems increases in the sequence  $Sn < Ge \ll Si$  and, in contrast to some earlier assumptions, the  $\pi$ -component cannot be neglected for any of the systems investigated. While the fundamental ligand properties of isocyanides are very similar to those of carbonyl, there are significant variations in the magnitude of different effects observed. Most notably, when coordinated to metals, both ligands can display positive or negative shifts in their characteristic stretching frequency. However, because isocyanides are stronger  $\sigma$ -donors, the metal-induced changes in the CN bonding framework are greater than that observed for carbonyl. Consequently, isocyanides readily exhibit positive CN stretching frequency shifts even in complexes where they function as  $\pi$ -acceptors, and the sign of these shifts is alone a poor indicator of the nature of the metal-carbon interaction. On the other hand, the relative  $\pi$ -character of the metal-carbon bond in metallylene-isocyanide adducts, as judged by the natural orbitals of chemical valence as well as by partitioning the orbital interaction energy, was shown to have linear correlation with the shift in CN stretching frequency upon complex formation. The details of this correlation show that  $\pi$ -back-

donation contributions need to exceed  $100 \text{ kJ mol}^{-1}$  in order for the shift in the CN stretching frequency of metallylene-isocyanide adducts to be negative.

## Introduction

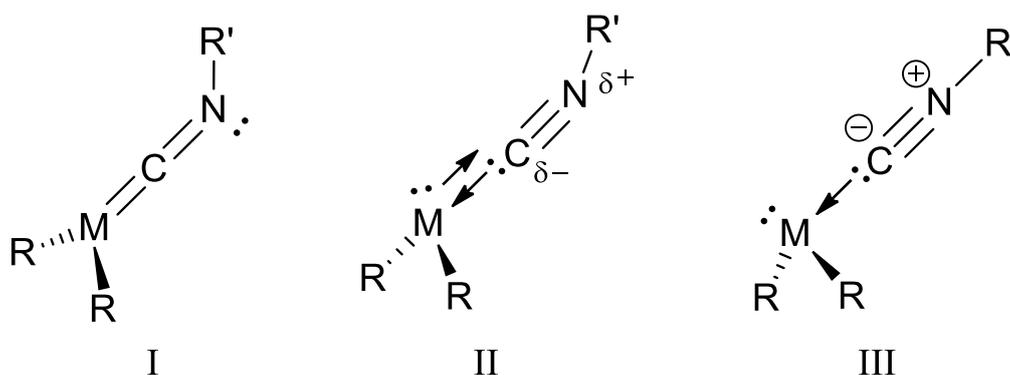
The chemistry of heavier group 14 element carbene analogues –collectively known as the metallylenes,  $R_2M$ : ( $M = Si, Ge, Sn, Pb$ )– is currently well established.<sup>1</sup> These compounds are characterized by the presence of both a non-bonded electron pair and a vacant p-orbital (oxidation state  $M^{II}$ ), which results in Lewis-amphoteric behavior. In contrast to carbenes, metallylenes retain their lone pair configuration even when  $R$  is a simple alkyl or aryl group, and therefore almost always have singlet ground states (cf. singlet and triplet carbenes).<sup>2</sup> Although the stability of metallylenes increases with the principal quantum number, the combination of a singlet ground state and a vacant p-orbital makes them extremely reactive chemical species at room temperature unless stabilized either electronically (electron withdrawing heteroatoms), kinetically (bulky peripheral substituents), or by a combination thereof. Recent advances in this field have demonstrated that even elusive acyclic silylenes can be synthesized and completely characterized through this route.<sup>3</sup>

Because of the vacant p-orbital at the heavier group 14 element, metallylenes are electrophilic and readily form complexes with typical Lewis bases. One subset of compounds which has been of particular interest over the years are complexes of metallylenes with isocyanides,  $:CNR'$ . The first member of this series to be structurally characterized in the solid state (via X-ray crystallography) was rather surprisingly a stannylene complex (**1**),<sup>4</sup> followed by the plumbylene (**2**) and silylene (**3** and **4**) adducts;<sup>5,6</sup> the crystal structures of two stable germanium isocyanides **5** and **6** were reported by us only very recently.<sup>7</sup> Lewis acid-base complexes of the general formula  $R_2MCNR'$  are of interest not only because of the nature of their metal-carbon bonding but also because of their subsequent reactivity. For example, compound **5** undergoes facile C-H bond activation to form isobutene and cyanogermane,<sup>7a</sup> whereas **6**, if allowed to stand or treated with excess methyl isocyanide, undergoes a three-fold insertion of the isocyanide into the Ge-C bond;<sup>7b</sup> C-H bond activation resulting from the reaction of a transient silylene with *tert*-butyl isocyanide has also been reported,<sup>8</sup> as are coupling reactions of isocyanides with silylenes stabilized by  $\beta$ -diketiminato ligands.<sup>9</sup> In general, metal-mediated coupling and polymerization of unsaturated organic molecules are important industrial processes,<sup>10</sup> and the synthesis of heterocycles resulting from coupling and cycloaddition reactions of isocyanides with other heteroelement unsaturated species is a widely used technique.<sup>11</sup>



During our investigations of the chemistry of the adduct **5**, it was realized that its  $\nu(\text{CN})$  stretching band is shifted to slightly lower wave number relative to the analogous stretching frequency of the free isocyanide.<sup>7a</sup> This prompted us to investigate the possibility of Ge-C  $\pi$ -bonding in **5** i.e. back-donation of electrons from the lone pair on the group 14 element to the isocyanide ligand. In agreement with our expectations, density functional theory calculations probing the characteristics of the Ge-C bond in **5** showed that the back-bonding interaction represents roughly one third of the total orbital interaction energy.<sup>7a</sup> This led us to hypothesize that back-bonding interactions in main group isocyanide adducts could be of more importance than hitherto realized.<sup>12</sup> A review of the chemical literature pertaining to complexes of the type R<sub>2</sub>MCNR' shows that their M-C bonds have been given a variety of different descriptions depending on the exact identity of M, R, and R'. For example, Grützmacher identified **1** as a stannaketenimine with a double donor-acceptor Sn=C bond,<sup>4</sup> whereas Klinkhammer found no evidence of a significant contribution from the mesomeric form R<sub>2</sub>M=C=NR' in the tin adducts **7** and **8**, or in their lead analogues.<sup>5</sup> For silylenes, the structurally characterized adducts **3** and **4** show short Si-C bonds and C-N-C bond angles significantly narrower than 180°, which led Iwamoto and Kira to describe them as silaketenimines with strong allenic character.<sup>6</sup> In contrast, Okazaki dubbed compounds **9** silylene-isocyanide Lewis acid-base complexes based primarily on NMR spectroscopic evidence.<sup>13</sup> Clearly a detailed theoretical investigation of the nature of M-C bonding

in metallylene-isocyanide adducts is required in order to elucidate to what extent the different bonding descriptions **I-III** mimic their true electronic structures. The ability of main group elements to act as both an electron donor and an acceptor is of significant current interest as numerous recent reports have shown it to lead to interesting chemistry such as the activation of small molecules like  $H_2$ ,  $NH_3$ , or  $C_2H_4$ .<sup>14</sup>



**Scheme 1.** Three possible bonding descriptions for metallylene-isocyanide adducts.

In this paper, we report a comprehensive computational analysis of bonding in metallylene-isocyanide adducts of the type  $R_2MCNR'$  ( $M = Si, Ge, Sn$ ;  $R, R' = \text{alkyl, aryl}$ ). The results of our work show that the M-C bond in these compounds contains a significant back-bonding contribution whose importance is clearly non-negligible even for stannylenes. The back-bonding contribution was quantified using different theoretical approaches and it was found to have nearly linear correlation ( $r^2 \approx 0.98$ ) with the observed change in the calculated  $\nu(CN)$  stretching band upon adduct formation. To this end, it was also necessary to explore the influence of the coordinating metal to the properties of C-N bond in isocyanides as well as to contrast this data with what is known for the analogous carbonyl systems.

## Computational Details

All calculations were done within the density functional theory (DFT) formalism of electronic structure theory using the PBE0 exchange correlation functional.<sup>15</sup> The geometries of studied systems were optimized with Gaussian 09<sup>16</sup> employing def-TZVP basis sets,<sup>17</sup> relativistic large core ECP basis sets of similar valence quality were used for all In and Sn nuclei.<sup>18</sup> This particular functional-basis set combination was chosen on the basis of its good performance in our earlier analyses of the structures, reactivities and bonding in related systems.<sup>7</sup> Frequency calculations were performed for all stationary points found to ensure that they correspond to true minima on the potential energy surface as well as to determine the  $\nu(\text{CN})$  and  $\nu(\text{CO})$  stretching frequencies. Three different isocyanides were used in the calculations ( $\text{R}' = \text{Me}, t\text{Bu}, \text{Ph}$ ), while the metallylene fragment contains either an alkyl or aryl group ( $\text{R} = t\text{Bu}, \text{Ph}$ ). The  $\text{Ph}_2\text{M}$ : fragments function as model systems of the experimentally characterized metallylenes in compounds **1**, **5**, **6**, and **9**, whereas the  $t\text{Bu}_2\text{M}$ : fragments were selected on the basis of identifying and quantifying the effects of alkyl vs. aryl substitution to the characteristics of metallylene-isocyanide bonding.

The different bonding analyses were performed with the ADF 2010.01 and 2012.01 codes<sup>19</sup> using the PBE0/def-TZVP optimized geometries in together with the PBE0 functional and standard all-electron triple- $\zeta$  STO-type basis sets with two sets of polarization functions for all elements.<sup>20</sup> Scalar relativistic effects were taken into account through the zeroth order regular approximation (ZORA) as implemented in the ADF program package.<sup>21</sup> The M-C bond between metallylenes and isocyanides (complexes **19-36**) was analyzed with a modification of the constrained space orbital variation (CSOV) method<sup>22</sup> as well as with the natural orbitals of chemical valence (NOCV) theory,<sup>23</sup> both within the framework of Morokuma-Ziegler-Rauk energy decomposition analysis (EDA).<sup>24</sup> In all EDA calculations, the optimized structures of the studied complexes were divided into two fragments, metallylene and isocyanide, both in their ground state and in the geometry that they adopt in the respective complex. This fragmentation scheme was chosen because the syntheses of these adducts typically proceed via direct reaction between the respective metallylenes and isocyanides. When constraining the virtual orbital space, two additional EDA calculations were performed in which the unoccupied orbitals of the isocyanide and metallylene fragments were consecutively removed from the total orbital space, thereby allowing the quantification of donation and back-donation contributions, respectively.

## Results and Discussion

**The C-N stretching frequency as an indicator of  $\pi$ -type M-C back-bonding interactions in metal-isocyanide complexes.** The cyanide anion ( $\text{CN}^-$ ) is isoelectronic with carbon monoxide (CO), whereas the isocyanide moiety ( $\text{CNR}'$ ) is only valence isoelectronic with it. Due to their close structural and electronic relationship with each other, the ligand behavior of isocyanides finds many parallels in that of CO, and both systems can function as  $\sigma$ -donors and  $\pi$ -acceptors. However, whereas CO acts as a weak  $\sigma$ -donor and strong  $\pi$ -acceptor, isocyanides have been attributed with capabilities as strong  $\sigma$ -donors with a varying degree of  $\pi$ -acceptor nature.<sup>25</sup> Furthermore, unlike in the case of CO, the ligand properties of isocyanides can be fine-tuned by altering the identity of the terminal R'-substituent.

The synergistic donor-acceptor nature of M-C bonds in metal-carbonyl complexes is currently well-known and is therefore not reviewed herein. Equally established is the possibility to use the decrease in the carbonyl stretching frequency  $\nu(\text{CO})$  upon complex formation as an indicator of  $\pi$ -back-donation from the metal to the formally vacant  $\pi^*$ -orbital at the carbonyl, and therefore as an indirect probe of the nature of M-C bonding. While it was initially thought that the changes in CO bonding in metal carbonyl complexes would always be dominated by the  $\pi$ -acceptor properties of the ligand, it later became evident that this is not the case for all metal-carbonyl complexes imaginable. More than two hundred carbonyl complexes in which  $\pi$ -effects seem to play much smaller role in bonding –as determined by the increase in  $\nu(\text{CO})$  upon complex formation– had been characterized already at the beginning of this century.<sup>26</sup> These complexes were dubbed non-classical metal carbonyls,<sup>27</sup> and they have been under intense experimental and theoretical investigations for the last two decades.<sup>28</sup>

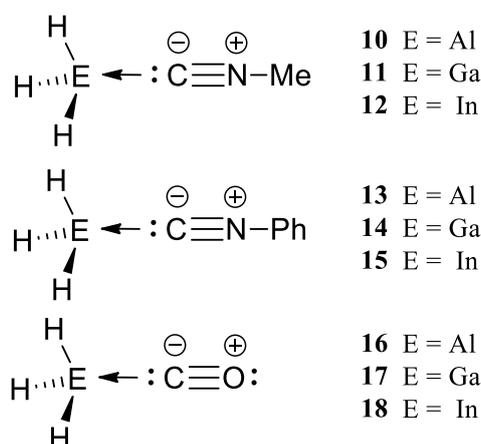
As it has been elegantly discussed by Strauss and Frenking,<sup>29</sup> the increase in  $\nu(\text{CO})$  upon complex formation can actually result from two fundamentally different situations: i) negligible  $\pi$ -back-bonding (i.e., truly non-classical bonding behavior) or ii)  $\pi$ -back-bonding that is present but is insufficient to incur lowering of  $\nu(\text{CO})$  below the reference value of  $2143\text{ cm}^{-1}$  due to dominating electrostatic and  $\sigma$ -bonding effects (i.e., classical donor-acceptor bonding behavior). Theoretical analyses have shown that when the CO ligand approaches a metal center, the C-O bond initially becomes shorter due to electrostatic induced changes in the polarization of the ligand bonding orbitals;<sup>29a</sup> the role of electrostatic effects in this process has also been discussed by other authors.<sup>30</sup> However, there is a turning point at shorter metal-carbonyl distances where the C-O bond becomes longer again. This turning point occurs at the onset of  $\pi$ -back-donation from metal to CO, and only

a small electron flow in this direction is sufficient to lengthen the carbon-oxygen bond and effectively mask all contributions from  $\sigma$ -donation and electrostatic effects. Because of the good  $\pi$ -back-donation ability of CO (which can be traced to the localization of the  $\pi^*$ -orbital of CO at the carbon end),<sup>31</sup> the vast majority (>95%) of carbonyl complexes display  $\nu(\text{CO})$  frequencies below the reference value  $2143\text{ cm}^{-1}$  determined for the free CO molecule in the gas phase.<sup>26</sup>

Returning to isocyanides, one of the first comprehensive reports of their ligand properties was published by Cotton,<sup>32</sup> in which it was demonstrated that isocyanides “have the capacity to function as good  $\sigma$ -donors alone, as  $\sigma$ -donors and good  $\pi$ -acceptors simultaneously, or to exhibit any intermediate behavior.” This conclusion was backed up by IR-spectroscopic measurements that showed characteristic  $\nu(\text{CN})$  frequency shifts depending on the type of metal employed and, consequently, the nature of the metal-carbon bond thus formed: large negative shifts were observed for zero valent metals with strong back-bonding, and equally large but positive shifts for mono- and dipositive metal ions with little or no back-bonding. At the time of publication (in 1961), the decrease in  $\nu(\text{CN})$  due to  $\pi$ -back-donation was nothing extraordinary, but the significant increase in  $\nu(\text{CN})$  in the absence of  $\pi$ -effects was in contrast with the established ligand behavior of the valence isoelectronic CO.<sup>32</sup> The ability of isocyanides to readily form stable adducts with positive metal ions (such as  $\text{Ag}^+$ ) was a clear indication of their stronger  $\sigma$ -donating ability as compared to carbonyls.<sup>33</sup> This strong  $\sigma$ -effect was taken to incur polarization of the C-N bond that further strengthens it and, consequently, leads to an increase in  $\nu(\text{CN})$ ; a similar effect was generally thought to be of little importance in carbonyl complexes due to the weak  $\sigma$ -donor ability of CO.

It is evident at this point that the description of ligand properties of carbon monoxide and isocyanides can be put on an equal footing. As discussed above,<sup>29</sup> the formation of the metal-carbon  $\sigma$ -interaction in carbonyl complexes does in fact polarize the C-O bond, which leads to non-classical changes in  $\nu(\text{CO})$  in the absence of  $\pi$ -back-donation. If  $\pi$ -contributions are possible, non-classical behavior in classical (donor-acceptor) complexes of CO can be observed, but it is often masked by even small amounts of  $\pi$ -back-donation. There should be no reason for why this discussion does not also hold for the ligand behavior of isocyanides. In other words, the *direction of the shift in  $\nu(\text{CN})$  upon complex formation should not be taken as a straightforward indication of the absence or presence of  $\pi$ -back-bonding interactions in complexes of isocyanides.* This applies even more so for the CN bond than for the CO bond because electrostatic and  $\sigma$ -type effects are significantly greater for the former than for the latter. It is interesting to note that Purcell has discussed these bonding effects in the context of CO and  $\text{CN}^-$  as early as 1969,<sup>34</sup> but this work

appears to be largely forgotten as judged by the limited number of citations it has attracted. One of the important discoveries in his theoretical work was that, while  $\sigma$ -type bonding effects play a role when  $\text{CN}^-$  ligand coordinates, an even more important source of increased stabilization comes from the direct decrease in C-N bond repulsion as a result of charge withdrawal from the carbon atom. Simply put, it is not an increase in attractive interactions within the CN triple bond but the decrease in repulsive interactions (due to reorganization of electrons within the bonding region) that drives bond strengthening. The repulsion-related mechanism was found to be of lesser importance for the isoelectronic but neutral CO, which means that in analogous non-classical complexes of CO and  $\text{CN}^-$ , the C-N bond properties are expected to be affected more by the presence of the metal and, thus, the cyanide anion should display a larger positive  $\nu(\text{CN})$  shift than the analogous carbonyl systems.



Although the similarities between  $\text{CN}^-$  and isocyanides are apparent, we chose to test whether the conclusions of Purcell would also be valid for the CO and  $\text{CNR}'$  pair. Consequently, a number of simple complexes of isocyanides and carbon monoxide with group 13 hydrides  $\text{H}_3\text{E}$  (**10-18**; E = Al, Ga, In) were investigated by theoretical calculations (PBE0/def-TZVP). The heavier group 13 hydrides are ideally suited for this study as they have no lone pairs that could partake in  $\pi$ -back-donation although hyperconjugation from E-H bonds can still take place, but is expected to be energetically insignificant. As shown in Table 1, the calculated shifts in the  $\nu(\text{CN})$  and  $\nu(\text{CO})$  frequencies upon complex formation reveal exactly the expected trend: the shift  $\Delta$  is positive for all systems studied and always greater for isocyanides (with a factor of 2-3). Furthermore, the terminal  $\text{R}'$  group in the isocyanide ligand (alkyl vs. aryl) seems to have only minor influence on the results, as is also true for the identity of the atom E. Hence, to a good zeroth-order approximation, electrostatic, steric, and  $\sigma$ -type interactions have an effect to the  $\nu(\text{CN})$  and  $\nu(\text{CO})$  frequencies that

is essentially constant for metals from the same group: 80 and 30  $\text{cm}^{-1}$  for  $\text{CNR}'$  and CO, respectively. The calculated (heterolytic) bond dissociation energies  $D_{0\text{K}}$  show rather expectedly that the dative E-C bonds are stronger with isocyanides, but these numbers cannot be directly used to estimate the relative importance of  $\sigma$ -interactions as electrostatic and steric effects also play a role; for this reason there is no correlation between  $\Delta\nu$  and  $D_{0\text{K}}$  in Table 1.

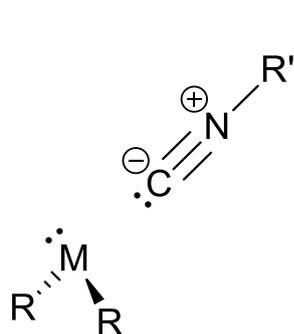
**Table 1.** Calculated Metal-Carbon Bond Dissociation Energies ( $D_{0\text{K}}$ ) and Changes in the  $\nu(\text{CN})$  and  $\nu(\text{CO})$  Stretching Bands upon Formation of Complexes **10-18**

| Complex   |                       | $D_{0\text{K}}$<br>[kJ mol <sup>-1</sup> ] | $\Delta\nu(\text{CN/CO})^a$<br>[cm <sup>-1</sup> ] |
|-----------|-----------------------|--|--|
| <b>10</b> | H <sub>3</sub> AlCNMe | 88   | 106  |
| <b>11</b> | H <sub>3</sub> GaCNMe | 81   | 86   |
| <b>12</b> | H <sub>3</sub> InCNMe | 77   | 79   |
| <b>13</b> | H <sub>3</sub> AlCNPh | 83   | 104  |
| <b>14</b> | H <sub>3</sub> GaCNPh | 77   | 84   |
| <b>15</b> | H <sub>3</sub> InCNPh | 74   | 77   |
| <b>16</b> | H <sub>3</sub> AlCO   | 30   | 56   |
| <b>17</b> | H <sub>3</sub> GaCO   | 26   | 42   |
| <b>18</b> | H <sub>3</sub> InCO   | 32   | 35   |

<sup>a</sup> Calculated stretching frequencies for the free CNMe, CNPh and CO ligands are 2276, 2235, and 2248  $\text{cm}^{-1}$ , respectively.

The above results, as well as prior theoretical work,<sup>29</sup> suggest that the change in  $\nu(\text{CN})$  (or  $\nu(\text{CO})$ ) stretching frequency upon complexation of the isocyanide (carbonyl) ligand can be divided into two opposing components which appear to be largely uncorrelated:<sup>35</sup> a positive component that depends on  $\sigma$ -donation, electrostatic and steric effects, and a negative component that depends on the amount of  $\pi$ -back-donation taking place. It is therefore the interplay of these components which determines the final, observed, shift in  $\nu(\text{CN})$  (and  $\nu(\text{CO})$ ). Because the positive component appears to be constant and markedly greater for isocyanide than for carbonyl, metal complexes of isocyanides should be ideally suited for observing non-classical  $\nu(\text{CN})$  behavior in a classical bonding situation. That is,  $\pi$ -back-bonding effects that are present but insufficient to incur lowering of  $\nu(\text{CN})$  below its reference value. Based on the existing experimental evidence for metallylene-isocyanide complexes,<sup>4-7</sup> this indeed appears to be the case even though the smallest increase in  $\nu(\text{CN})$  frequency has often been taken to indicate complete absence or negligible  $\pi$ -back-bonding. However, as shown below, a significant  $\pi$ -back-bonding component is required to be present in metallylene-isocyanide complexes in order for the effect of other bonding interactions to be cancelled and  $\nu(\text{CN})$  to decrease below the reference  $\nu(\text{CN})$  value for a free isocyanide.

**Optimized structural parameters and calculated stretching frequencies  $\nu(\text{CN})$  of model systems  $\text{R}_2\text{MCNR}'$ .** A wide variety of different metallylene-isocyanide complexes of the type  $\text{R}_2\text{MCNR}'$  was investigated in order to obtain a detailed description of M-C bonds in these compounds (**19-36**). Both alkyl- (*tert*-butyl) and aryl-substituted (phenyl) metallylenes (M = Si, Ge, Sn) were considered, whereas the coordinating isocyanide ligand employed methyl, *tert*-butyl and phenyl substituents, the last one adopting either a co-planar or perpendicular coordination with respect to the M-C-N plane.



|   |  |
|---|--|
| <b>19</b> M = Si, R = <i>t</i> Bu, R' = Me          | <b>28</b> M = Si, R = Ph, R' = Me          |
| <b>20</b> M = Si, R = <i>t</i> Bu, R' = <i>t</i> Bu | <b>29</b> M = Si, R = Ph, R' = <i>t</i> Bu |
| <b>21</b> M = Si, R = <i>t</i> Bu, R' = Ph          | <b>30</b> M = Si, R = Ph, R' = Ph          |
| <b>22</b> M = Ge, R = <i>t</i> Bu, R' = Me          | <b>31</b> M = Ge, R = Ph, R' = Me          |
| <b>23</b> M = Ge, R = <i>t</i> Bu, R' = <i>t</i> Bu | <b>32</b> M = Ge, R = Ph, R' = <i>t</i> Bu |
| <b>24</b> M = Ge, R = <i>t</i> Bu, R' = Ph          | <b>33</b> M = Ge, R = Ph, R' = Ph          |
| <b>25</b> M = Sn, R = <i>t</i> Bu, R' = Me          | <b>34</b> M = Sn, R = Ph, R' = Me          |
| <b>26</b> M = Sn, R = <i>t</i> Bu, R' = <i>t</i> Bu | <b>35</b> M = Sn, R = Ph, R' = <i>t</i> Bu |
| <b>27</b> M = Sn, R = <i>t</i> Bu, R' = Ph          | <b>36</b> M = Sn, R = Ph, R' = Ph          |

Trinquier has shown through theoretical calculations that both the singlet-triplet gap of heavier group 14 hydrides ( $:\text{MH}_2$ ) and their stability relative to the corresponding dimers ( $\text{H}_2\text{M}=\text{MH}_2$ ) increase with increasing principal quantum number.<sup>36</sup> The lone pair of silylenes has notable  $\text{sp}^2$ -character and is therefore expected to partake in back-donation interaction in complexes with isocyanides. Because silylenes are also stronger Lewis acids than corresponding germlylenes,<sup>37</sup> the formation of Si-C bond with strong ketenimine character is anticipated. On the other hand, the stannylene lone pair is of almost pure s-type, and thus should play only a relatively small role in the formation of the dative Sn-C bond. By following these assumptions, the Ge-C bonds in germylene-isocyanide complexes are predicted to display characteristics somewhere between their silylene and stannylene counterparts.

**Table 2.** Selected Optimized Structural Parameters and Calculated  $\nu(\text{CN})$  Shifts of Complexes **19-36**

|            | Complex                                   | d(M–C)<br>[Å] | d(C–N)<br>[Å] | $\angle(\text{M–C–N})$<br>[°] | $\angle(\text{C–N–R}')$<br>[°] | $\angle\theta^a$<br>[°] | $\Delta\nu(\text{CN})^b$<br>[cm <sup>-1</sup> ] |
|------------|---|---------------|---------------|-------------------------------|--------------------------------|-------------------------|---|
| <b>19</b>  | <i>t</i> Bu <sub>2</sub> SiCNMe           | 1.789         | 1.203         | 165.7                         | 129.8                          | 55.0                    | -280  |
| <b>20</b>  | <i>t</i> Bu <sub>2</sub> SiCN <i>t</i> Bu | 1.806         | 1.197         | 168.2                         | 135.6                          | 61.0                    | -235  |
| <b>21</b>  | <i>t</i> Bu <sub>2</sub> SiCNPh           | 1.786         | 1.209         | 168.0                         | 132.6                          | 56.0                    | -285  |
| <b>21'</b> | <i>t</i> Bu <sub>2</sub> SiCNPh           | 1.852         | 1.176         | 165.8                         | 173.7                          | 68.6                    | -42   |
| <b>22</b>  | <i>t</i> Bu <sub>2</sub> GeCNMe           | 2.010         | 1.166         | 165.9                         | 169.3                          | 81.0                    | -24   |
| <b>23</b>  | <i>t</i> Bu <sub>2</sub> GeCN <i>t</i> Bu | 2.019         | 1.164         | 167.4                         | 171.6                          | 82.2                    | -13   |
| <b>24</b>  | <i>t</i> Bu <sub>2</sub> GeCNPh           | 1.942         | 1.187         | 162.9                         | 145.9                          | 69.7                    | -127  |
| <b>24'</b> | <i>t</i> Bu <sub>2</sub> GeCNPh           | 1.984         | 1.171         | 163.5                         | 178.1                          | 79.0                    | -27   |
| <b>25</b>  | <i>t</i> Bu <sub>2</sub> SnCNMe           | 2.360         | 1.159         | 170.7                         | 179.1                          | 90.4                    | 23  |
| <b>26</b>  | <i>t</i> Bu <sub>2</sub> SnCN <i>t</i> Bu | 2.357         | 1.159         | 171.6                         | 179.1                          | 90.8                    | 29  |
| <b>27</b>  | <i>t</i> Bu <sub>2</sub> SnCNPh           | 2.318         | 1.165         | 164.5                         | 179.1                          | 86.7                    | -2  |
| <b>28</b>  | Ph <sub>2</sub> SiCNMe                    | 1.841         | 1.183         | 178.3                         | 142.5                          | 70.0                    | -155  |
| <b>29</b>  | Ph <sub>2</sub> SiCN <i>t</i> Bu          | 1.869         | 1.175         | 179.2                         | 151.5                          | 76.0                    | -87   |
| <b>30</b>  | Ph <sub>2</sub> SiCNPh                    | 1.826         | 1.193         | 164.9                         | 140.4                          | 63.2                    | -197  |
| <b>30'</b> | Ph <sub>2</sub> SiCNPh                    | 1.880         | 1.170         | 165.1                         | 178.9                          | 70.4                    | -8  |
| <b>31</b>  | Ph <sub>2</sub> GeCNMe                    | 2.050         | 1.160         | 175.2                         | 179.1                          | 87.1                    | 25  |
| <b>32</b>  | Ph <sub>2</sub> GeCN <i>t</i> Bu          | 2.052         | 1.160         | 179.1                         | 179.3                          | 87.1                    | 30  |
| <b>33</b>  | Ph <sub>2</sub> GeCNPh                    | 2.023         | 1.166         | 164.0                         | 179.2                          | 84.9                    | 8   |
| <b>34</b>  | Ph <sub>2</sub> SnCNMe                    | 2.395         | 1.157         | 178.8                         | 179.0                          | 93.7                    | 49  |
| <b>35</b>  | Ph <sub>2</sub> SnCN <i>t</i> Bu          | 2.390         | 1.157         | 179.0                         | 178.1                          | 94.4                    | 56  |
| <b>36</b>  | Ph <sub>2</sub> SnCNPh                    | 2.370         | 1.162         | 179.8                         | 179.0                          | 92.3                    | 35  |

<sup>a</sup> The angle between the metallylene C-M-C plane and the M-C bond vector of the coordinating isocyanide.

<sup>b</sup> Calculated stretching frequencies for the free CNMe, CN*t*Bu, and CNPh ligands are 2276, 2247, and 2235cm<sup>-1</sup>, respectively.

The most important metrical parameters of the examined metallylene-isocyanide complexes **19-36** are listed in Table 2 which reveals some interesting trends. For example, it can be seen that the stannylene adducts possess a C-N-R' angle very close to 180°, whereas most silylenes are bent (130°-152°), indicative of a ketenimine-type structure with strong sp<sup>2</sup>-character on the isocyanide nitrogen. Kira and Iwamoto have recently demonstrated that the complexes of alkyl silylenes with aryl isocyanides display conformational flexibility associated with the orientation of the N-phenyl substituent with respect to the M-C-N plane (either planar or perpendicular).<sup>6</sup> Consequently, compound **21** has another conformational isomer on its potential energy surface (denoted **21'**)

which shows, in addition to the different orientation of the N-phenyl substituent (planar for **21** and perpendicular for **21'**), a nearly linear C-N-R' moiety ( $174^\circ$ ) along with slightly longer and shorter M-C ( $1.852 \text{ \AA}$ ) and C-N ( $1.176 \text{ \AA}$ ) bonds, respectively. The energetic proximity of the two conformers ( $\Delta G = 6 \text{ kJ mol}^{-1}$ ) clearly underlines the fact that the  $\pi$ -type framework within the Si-C-N fragment is extremely adaptable as it can easily display structural features characteristic to a silaketimine (**21**) or a simple donor-acceptor adduct (**21'**). We have now observed that this adaptability is not limited to complex **21**, and that the corresponding germanium analogue **24** and the all-phenyl substituted silylene adduct **30** both exhibit it. However, for **24** the global minimum ( $\Delta G = 5 \text{ kJ mol}^{-1}$ ), has the phenyl plane in perpendicular orientation (**24'**) whereas for **30** the two conformers are energetically degenerate ( $\Delta G < 1 \text{ kJ mol}^{-1}$ ). The origin of the observed structural flexibility lies in the possibility for the N-phenyl substituent to adopt two orientations and therefore to conjugate with either the C-N double (parallel) or triple bond (perpendicular).<sup>6</sup> The reason for why only one conformer is observed for the other adducts of phenyl isocyanide (**27**, **33** and **36**) is that they show the smallest back-bonding contributions (see below) and are therefore inherently incapable of adopting a ketimine-type geometry.

The structural data for the germylene-isocyanide complexes fall between the two extremes described above for silylenes and stannylenes, though generally closer to the latter. For example, the complexes **22** and **23** with all-alkyl substituents have slightly bent C-N-R' angles ( $169^\circ$  and  $172^\circ$  degrees, respectively), while those with an aryl germylene (compounds **31** and **32**) have a more linear arrangement of atoms. This trend, which is also observed for the analogous silylenes (compounds **19** and **20** as well as **28** and **29**), can be rationalized with the electron withdrawing effect of the aryl groups in the metallylene fragment which increases the inertness of the lone pair as opposed to similar systems with alkyl substituents. With less tendency for back-bonding, the complexes employing aryl metallylenes (**28-36**) not only display more linear C-N-R' moieties but also M-C bonds that are on average  $0.05 \text{ \AA}$  longer than in the corresponding alkyl systems (**19-27**). While the Si-C bonds in silylene complexes are slightly shorter than the average Si-C single bond length of  $1.91 \text{ \AA}$  calculated from the Pyykkö single bond radii,<sup>38</sup> the corresponding M-C bonds in the studied germylene and stannylene compounds are all elongated when compared with their reference values of  $1.96 \text{ \AA}$  and  $2.15 \text{ \AA}$ , respectively. However, as pointed out by many authors and Frenking in particular,<sup>39</sup> the metal-ligand bond lengths in coordination complexes do not necessarily correlate in any straightforward manner with the bond strength or with its type.

Another structural indicator of the back-bonding ability of the metallylene lone pair is the angle  $\theta$  between the M-C bond to the coordinating isocyanide and the C-M-C plane of the

metallylene. The formally vacant p-type orbital at the metallylene center lies at a 90° angle relative to the metallylene plane, and it can thus be expected that the dative M-C bond should lie in this direction if a majority of the bonding interaction comes from donation of electrons from the isocyanide to the metallylene. With increasing back-bonding contribution from the lone pair of the metallylene to the isocyanide, the  $\theta$  angle should become smaller and therefore correlate with the characteristics of the M-C bond. The calculated values for the  $\theta$  angle are given in Table 2 and, as a whole, they display a trend similar to that inferred from the C-N-R' angles.<sup>40</sup> We also note that the  $\theta$  angles are always significantly greater than 0° (55° at minimum for **19**), which indicates that the  $\pi$ -contribution in M-C bond is never fully comparable to that in a “classical” double bond. To this end, the M-C bonds in silylene- and germylene-isocyanide adducts can be compared to that in 1-sila- and germapropadienes of West and co-workers which show nearly linear M=C=C units (172.0(3) and 159.2(2)° for Si and Ge, respectively) along with very short M=C bonds (1.693(3) and 1.783(2) Å) and small  $\theta$  angles (17.0 and 33.4°).<sup>41</sup>

The isocyanide C-N bonds are found to be the longest in silylenes for which the back-bonding contribution is expected to be the highest; the opposite is true for stannylenes. However, the C-N bond length in isocyanides changes very little upon complex formation as well as from one particular complex to another. For this reason, it is perhaps more helpful to concentrate on changes in the calculated  $\nu(\text{CN})$  stretching frequencies (see Table 2).<sup>42</sup> As discussed above, there are two components that need to be considered: electrostatic/steric/ $\sigma$ -effects and  $\pi$ -back-donation. For the group 13 complexes with no  $\pi$ -back-donation, the first component was shown to induce a roughly 80 cm<sup>-1</sup> increase in  $\nu(\text{CN})$ . If this value is used as an initial guideline for the group 14 complexes discussed herein, it becomes evident that none of the investigated metallylene-isocyanide complexes – not even stannylenes – reproduce it (maximum observed increase of 56 cm<sup>-1</sup> for **35**). This suggests that either the constant is slightly different for group 13 and 14 species, as it should be, or, that there is a varying degree of back-bonding present in all compounds **19-36** which opposes the changes to the C-N bond caused by electrostatic and  $\sigma$ -effects. As will be shown below in detail, the latter explanation is more important than the former. Table 2 also indicates that, for complexes involving silylenes, the back-bonding interaction should be the largest because the extent of their  $\nu(\text{CN})$  frequency decrease is by far the greatest. The change in  $\nu(\text{CN})$  is not nearly as large for the analogous germanium systems but it is nevertheless negative for all alkyl germylene complexes studied in this work.

Taken as a whole, the optimized structural parameters and the calculated isocyanide  $\nu(\text{CN})$  stretching frequencies not only verify the intuitively expected trend in the significance of M-C

back-bonding in complexes **19-36**, but they also demonstrate how this effect is non-negligible even for stannylenes. The ketenimine-type contributions to bonding are most evident in complex **27**, in which case the Sn-C back-donation is sufficiently large to cancel out the anticipated increase in the  $\nu(\text{CN})$  frequency (calculated  $\Delta\nu(\text{CN}) = -2 \text{ cm}^{-1}$ ). This shows that not all stannylene-isocyanide complexes should be described as simple Lewis acid-base adducts in which the flow of electrons is predominately from ligand to metallylene. The result is in line with the description given by Grützmacher for **1**,<sup>4</sup> though we will later show that this particular complex is in fact a system for which the back-bonding contribution is clearly not large. Similarly, the calculated data underline that the description of Si-C bonding in silylene-isocyanide adducts depends on the identity of the silylene substituent, but is mostly of ketenimine-type; phenyl isocyanide adducts of silylenes are a special case as they can exist in two conformers with vastly different structural characteristics but nearly equal energy.<sup>6,8</sup> In general, aryl-substituted metallylenes tend to have structures that have more donor-acceptor character than the corresponding alkyl-substituted species, although in many of the studied systems the bonding is somewhere between the formally zwitterionic and heteroallenic extremes. This is particularly true for germylene complexes which are therefore the most difficult ones to describe with classical Lewis-type structures.

**Bonding and back-bonding interactions determined using the natural orbitals of chemical valence.** Natural orbitals of chemical valence (NOCVs) are defined as eigenfunctions of the chemical valence operator from Nalewajski-Mrozek (NM) theory of valence and bond multiplicities.<sup>23</sup> The NOCVs manifest themselves in pairs with opposite but equal eigenvalues, which represent the channels through which charge density is transferred when a molecule (typically a complex) is formed from a promolecule. The promolecule is a reference system in which the bonding fragments (for example, a metal and a ligand) are placed in the final geometry of the molecule but they do not interact with each other. The eigenvalues of the valence operator describe the contribution from a particular NOCV pair to the overall valence which is defined as the total number of chemical bonds in the molecule. When analyzing the formation of coordinative bonds, NOCVs can be visually divided based on their local symmetry ( $\sigma$  or  $\pi$ ) which represent the components from donation and back-donation of electrons.

The NOCV approach in itself does not take into account the energetics involved in bond formation. The method can, however, be combined with the Morokuma-Ziegler-Rauk interaction-energy decomposition analysis (EDA),<sup>24</sup> which gives the combined ETS-NOCV method.<sup>43</sup> The (instantaneous) interaction energy  $\Delta E_{\text{int}}$  is defined as the change in energy as the molecule is formed from the promolecule. In the decomposition process, this energy is partitioned into three

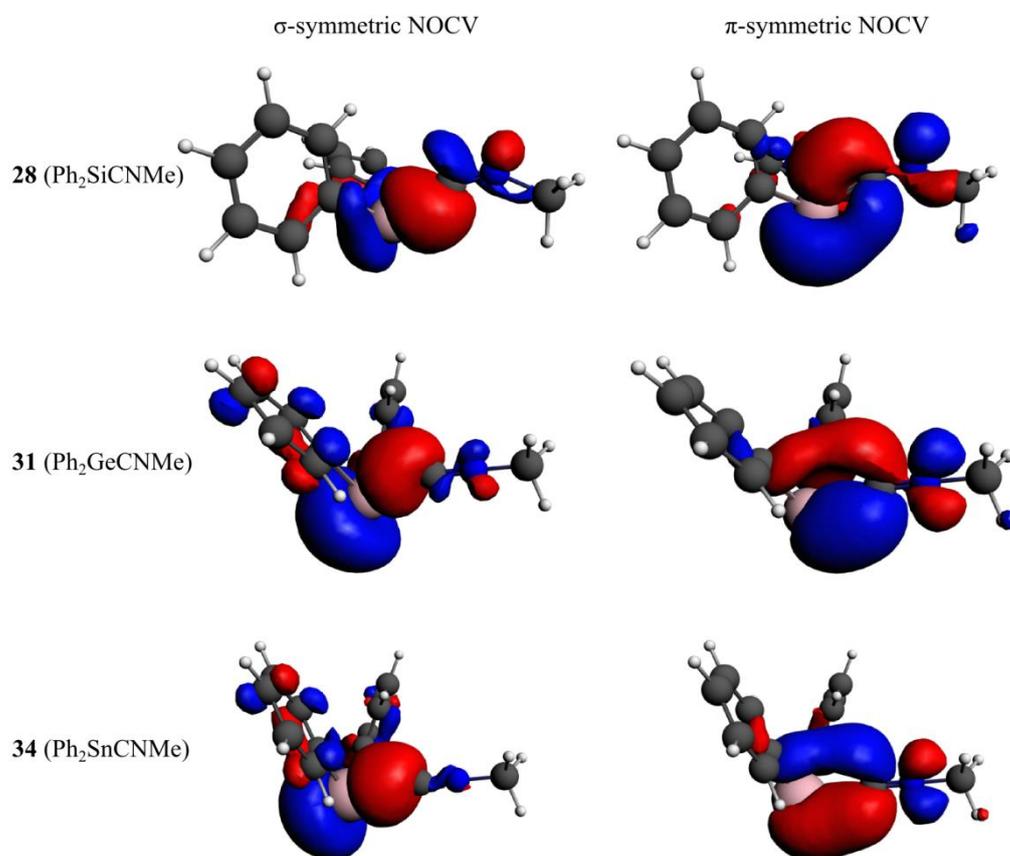
components:  $\Delta E_{\text{int}} = \Delta E_{\text{Pauli}} + \Delta E_{\text{elstat}} + \Delta E_{\text{orb}}$ . The first two terms (Pauli repulsion,  $\Delta E_{\text{Pauli}}$ , and electrostatic interaction,  $\Delta E_{\text{elstat}}$ ) consider interactions between the unperturbed electron densities of the promolecular fragments, while the last term (orbital interaction energy,  $\Delta E_{\text{orb}}$ ) considers the energy that is released when the fragment densities are allowed to mix and relax. The ETS-NOCV method allows partitioning of the orbital interaction energy to contributions from each individual NOCV. Thus, the  $\Delta E_{\text{orb}}$  term can be divided between NOCVs of given local symmetry, which in the case of a coordinative bond formation gives energies for donation and back-donation contributions.

**Table 3.** Total Orbital Interaction Energies ( $\Delta E_{\text{orb}}$ ) of Metallylene-Isocyanide Bonds in Complexes **19-36** along with the Energy Contributions ( $E_{\sigma}$  and  $E_{\pi}$ ) and Eigenvalues ( $v_{\sigma}$  and  $v_{\pi}$ ) of their Two Most Important Natural Orbitals of Chemical Valence

| Complex   | $\Delta E_{\text{orb}}$<br>[kJ mol <sup>-1</sup> ] | $E_{\sigma}$<br>[kJ mol <sup>-1</sup> ] | $E_{\pi}$<br>[kJ mol <sup>-1</sup> ] | $v_{\sigma}$ | $v_{\pi}$ |
|---|--|---|--------------------------------------|--------------|-----------|
| <b>19</b> <i>t</i> Bu <sub>2</sub> SiCNMe           | -909   | -149                                    | -697                                 | 0.473        | 1.250     |
| <b>20</b> <i>t</i> Bu <sub>2</sub> SiCN <i>t</i> Bu | -810   | -149                                    | -591                                 | 0.474        | 1.154     |
| <b>21</b> <i>t</i> Bu <sub>2</sub> SiCNPh           | -920   | -150                                    | -705                                 | 0.470        | 1.269     |
| <b>22</b> <i>t</i> Bu <sub>2</sub> GeCNMe           | -380   | -239                                    | -88                                  | 0.643        | 0.439     |
| <b>23</b> <i>t</i> Bu <sub>2</sub> GeCN <i>t</i> Bu | -369   | -241                                    | -75                                  | 0.619        | 0.418     |
| <b>24'</b> <i>t</i> Bu <sub>2</sub> GeCNPh          | -421   | -238                                    | -124                                 | 0.741        | 0.478     |
| <b>25</b> <i>t</i> Bu <sub>2</sub> SnCNMe           | -201   | -139                                    | -34                                  | 0.443        | 0.306     |
| <b>26</b> <i>t</i> Bu <sub>2</sub> SnCN <i>t</i> Bu | -204   | -144                                    | -32                                  | 0.445        | 0.288     |
| <b>27</b> <i>t</i> Bu <sub>2</sub> SnCNPh           | -229   | -122                                    | -76                                  | 0.514        | 0.388     |
| <b>28</b> Ph <sub>2</sub> SiCNMe                    | -659   | -153                                    | -443                                 | 0.496        | 0.978     |
| <b>29</b> Ph <sub>2</sub> SiCN <i>t</i> Bu          | -576   | -135                                    | -382                                 | 0.484        | 0.868     |
| <b>30</b> Ph <sub>2</sub> SiCNPh                    | -712   | -158                                    | -488                                 | 0.494        | 1.038     |
| <b>31</b> Ph <sub>2</sub> GeCNMe                    | -351   | -248                                    | -58                                  | 0.629        | 0.391     |
| <b>32</b> Ph <sub>2</sub> GeCN <i>t</i> Bu          | -347   | -250                                    | -55                                  | 0.626        | 0.371     |
| <b>33</b> Ph <sub>2</sub> GeCNPh                    | -381   | -249                                    | -83                                  | 0.662        | 0.458     |
| <b>34</b> Ph <sub>2</sub> SnCNMe                    | -189   | -141                                    | -27                                  | 0.465        | 0.252     |
| <b>35</b> Ph <sub>2</sub> SnCN <i>t</i> Bu          | -192   | -146                                    | -26                                  | 0.474        | 0.235     |
| <b>36</b> Ph <sub>2</sub> SnCNPh                    | -201   | -145                                    | -34                                  | 0.471        | 0.318     |

In order to put the analysis of M-C back-bonding interactions in on a more quantitative basis, NOCVs were determined for the metallylene-isocyanide complexes **19-36**.<sup>44, 45</sup> For all systems, a significant part (roughly 90%) of the total orbital interaction energy term originates from only two NOCV pairs, which effectively renders the individual contributions from each NOCV pair in the remaining set of orbitals negligible. Table 3 lists the energies of the two most significant

NOCV pairs along with their eigenvalues and local symmetries ( $\sigma$  or  $\pi$ , depending on whether the NOCV has a nodal plane perpendicular to the metallylene-isocyanide bond axis or if the M-C bond resides on the nodal plane, respectively). We note that the local symmetry needs to be determined through visual inspection of NOCVs because the complexes under study lack appropriate global symmetry in order for the assignment to work automatically using the symmetry properties of the orbitals; Figure 1 shows examples of the NOCVs for a selected subset of the studied complexes. Consequently, there remains a certain amount of arbitrariness involved in the process for which reason the bonding and back-bonding contributions were also determined with a different approach (see below).



**Figure 1.** The most important NOCVs visualized for adducts of methyl isocyanide with phenyl substituted silylene (**28**), germylene (**31**), and stannylene (**34**).

In silylene complexes, the most important NOCVs are clearly  $\pi$ -symmetric (see Table 3 and Figure 1). This indicates that the majority of  $\Delta E_{\text{orb}}$  in these systems (up to 77%) comes from the back-bonding interaction i.e. donation of metallylene lone pair density to the vacant  $\pi^*$ -orbital on

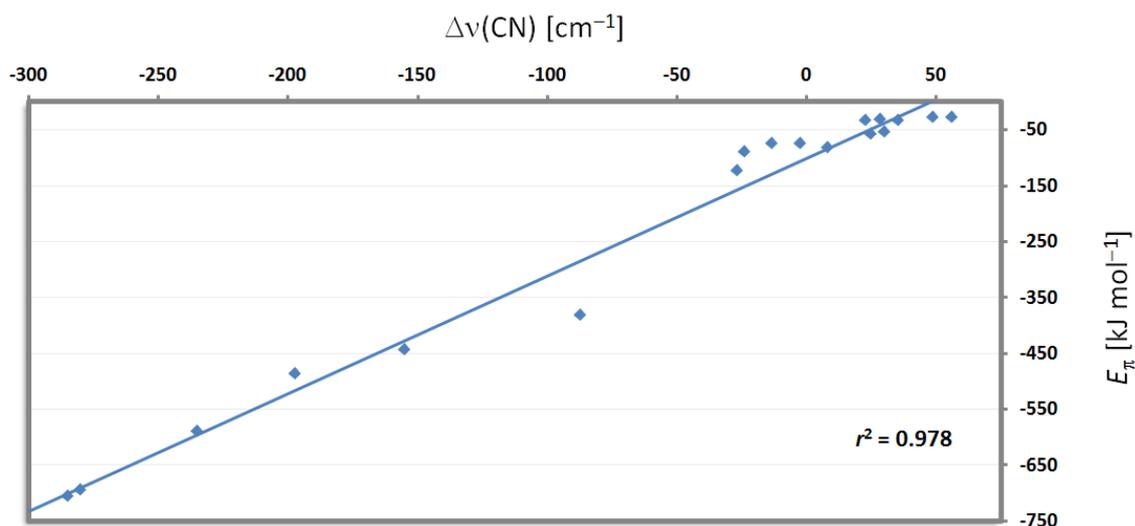
the isocyanide. The calculated back-bonding contributions are likely to be somewhat overestimated as the  $\theta$  angle between the metallylene-isocyanide bond and the metallylene plane makes the visual classification of orbitals to  $\sigma$ - and  $\pi$ -type somewhat arbitrary and only synergic contributions that mix the two symmetries are observed. However, what is evident from Table 3 and Figure 1 is that there are clearly two acceptors and donors in these systems, which gives rise to a co-operative bonding interaction with a very strong contribution from ketenimine-type metallylene-to-ligand back-donation. This is true for both alkyl- and aryl-substituted isocyanides, though the relative importance of back-donation is somewhat smaller in the latter species.

The relative importance of bonding and back-bonding interactions is reversed in stannylene complexes as compared to the analogous silylenes. Here the most important NOCV is always  $\sigma$ -symmetric and  $E_\sigma$  dominates over  $E_\pi$  with a 2:1 ratio (see Table 3 and Figure 1). Compound **27** shows the greatest percentage of  $\pi$ -type contributions to  $\Delta E_{\text{orb}}$ , 33%, which can be explained with the electron withdrawing effect of the isocyanide phenyl substituent that effectively enhances the flow of electrons from metallylene to ligand (a similar effect is seen in the germylene **24'** and, to a lesser extent, in the silylene **21**). Consequently, bonding in complexes of aryl stannylenes is for the most part  $\sigma$ -type, but  $\pi$ -type back-bonding contributions are of importance especially for alkyl stannylenes. It should also be noted that the back-bonding interaction is never completely negligible: the lowest  $\pi$ -contribution is observed for complex **35** for which it still constitutes almost 15% of the total orbital interaction energy.

The  $\pi$ -bonding contributions in germylene-isocyanide adducts show a trend similar to that seen for stannylenes. For complexes containing an aryl-substituted germylene, the most important NOCV is clearly  $\sigma$ -symmetric (see Figure 1), but the visual characterization of orbital symmetry is less straightforward for alkyl-substituted germylenes with smaller  $\theta$  angles (see above). We note that the assignment used in Table 3 is consistent with the trends in calculated  $\theta$  angles and  $\Delta\nu(\text{CN})$  shifts, and indicates  $\pi$ -contributions that account up to 30% of the  $\Delta E_{\text{orb}}$  term. Even though the absolute  $E_\pi$  energy values are significantly larger for germylenes than for stannylenes, as expected, the ratio of  $E_\pi$  and  $\Delta E_{\text{orb}}$  remains virtually unchanged between the two sets of compounds.

In Figure 2, the energy contributions from  $\pi$ -symmetric NOCVs are plotted against the calculated shifts in the  $\nu(\text{CN})$  stretching band, which reveals a very good linear correlation ( $r^2 = 0.978$ ) between the two datasets; we note that there is absolutely no correlation between  $\Delta\nu(\text{CN})$  and  $E_\sigma$  ( $r^2 = 0.082$ ). This demonstrates that changes in the  $\pi$ -bonding of the investigated complexes are largely uncoupled from all other effects, and that the importance of  $\pi$ -type contributions to metallylene-isocyanide bonding can be safely gleaned from the change in the CN stretching

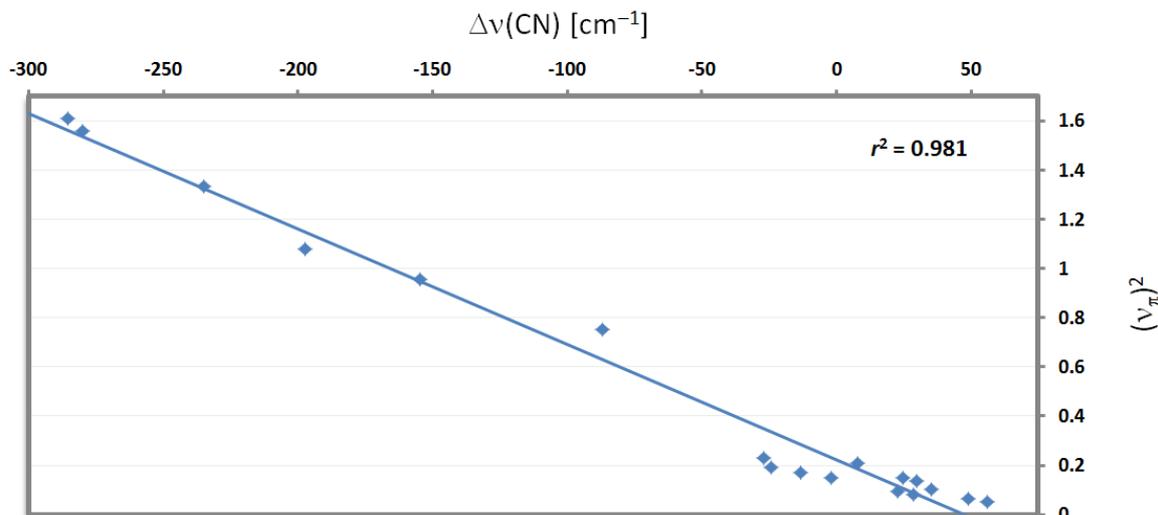
frequency. The intercept of the correlation line with the x-axis shows that the linear relationship does in fact break down to some extent for systems with sufficiently small  $E_\pi$  contributions as the change in  $\Delta\nu(\text{CN})$  is then not dominated by it (see above). Nevertheless, the constant contribution to  $\Delta\nu(\text{CN})$  can be estimated to be  $\approx 50 \text{ cm}^{-1}$ , though a system with  $E_\pi = 0$  is entirely hypothetical in the current case. The observed linear correlation also confirms the earlier assumption that the constant change to more positive wave numbers is not significantly dependent on the substituent at the isocyanide or the identity of the metal. If this were the case, linear correlation could only be observed for subsets of compounds **19-36**. Furthermore, it should be noted that the intercept of the correlation line with the y-axis shows  $\Delta\nu(\text{CN})$  to be positive even up to  $E_\pi = -97 \text{ kJ mol}^{-1}$  i.e. obtaining a negative  $\Delta\nu(\text{CN})$  requires significant  $\pi$ -back-donation to be present (cf. the behavior of CO as a ligand).



**Figure 2.** Correlation between the NOCV back-bonding contributions ( $E_\pi$ ) and the calculated shifts in the isocyanide stretching frequency ( $\Delta\nu(\text{CN})$ ) in complexes **19-36**.

Michalak and co-workers have found a similar correlation between bond multiplicities calculated using Nalewajski-Mrozek (NM) theory and changes in carbonyl  $\nu(\text{CO})$  stretching frequency in different transition-metal complexes.<sup>46</sup> It is interesting to note that the NM bond multiplicities,<sup>47</sup>  $b_{AB}$ , are closely related to NOCV eigenvalues,  $v_i$ , through the concept of overall valence  $V$ .<sup>23b</sup> In fact,  $V$  can be written either as a sum over bond multiplicities between all atomic pairs in the molecule ( $\sum_A \sum_B b_{AB}$ ) or as a sum over the squares of all NOCV eigenvalues ( $\frac{1}{2} \sum_i v_i^2$ ). Consequently, an increase in bond multiplicity increases the overall valence linearly, whereas an increase in an NOCV eigenvalue increases it geometrically. This prompted us to plot Figure 3

which shows the squared eigenvalues  $(v_\pi)^2$  against  $\Delta v(\text{CN})$  shifts. The linear relationship between the two datasets is apparent and equally good ( $r^2 = 0.981$ ) as what was obtained with  $E_\pi$ .



**Figure 3.** Correlation between the squared NOCV eigenvalues  $((v_\pi)^2)$  and the calculated shifts in the isocyanide stretching frequency  $(\Delta v(\text{CN}))$  in complexes **19-36**.

### **Bonding and back-bonding interactions determined by constraining the virtual orbital space.**

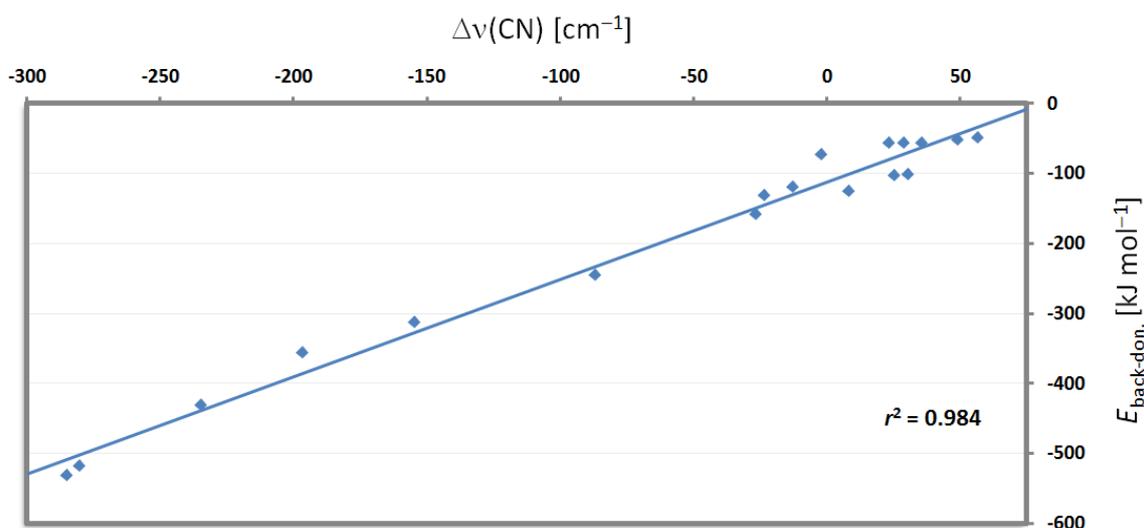
In order to avoid the visual inspection of NOCVs for obtaining the individual  $\sigma$ - and  $\pi$ -type contributions to metallylene-isocyanide bonding, we carried out EDA calculations in which the virtual orbital space of complexes **19-36** was constrained. This method offers a convenient way for partitioning the orbital interaction term for a metal-ligand bond in a coordination complex into donation and back-donation components.<sup>22</sup> The method starts with an independent optimization of the metal and ligand fragment densities, after which the final density of the complex is calculated in the basis of fragment orbitals. The calculation for the final density is then repeated, but with a reduced orbital set in which all virtual orbitals on the ligand fragment are removed. This ensures that only ligand-to-metal interactions (donation) are possible. The procedure is then repeated but this time the virtual orbitals are removed from the metal fragment in order to estimate metal-to-ligand back-donation. It should be noted that setting a constraint on the orbital space of one interacting fragments typically leads to overcompensation from the other, which means that the energies given by the two constrained calculations do not sum to the orbital interaction energy term from an unconstrained calculation.

**Table 4.** Donation ( $E_{\text{don.}}$ ) and Back-Donation ( $E_{\text{back-don.}}$ ) Energies in Metallylene-Isocyanide Complexes **19-36** as Given by Constraining the Virtual Orbital Space

|            | Complex                                   | $E_{\text{don.}}$       | $E_{\text{back-don.}}$  |
|------------|---|-------------------------|-------------------------|
|            |   | [kJ mol <sup>-1</sup> ] | [kJ mol <sup>-1</sup> ] |
| <b>19</b>  | <i>t</i> Bu <sub>2</sub> SiCNMe           | -760                    | -518                    |
| <b>20</b>  | <i>t</i> Bu <sub>2</sub> SiCN <i>t</i> Bu | -462                    | -432                    |
| <b>21</b>  | <i>t</i> Bu <sub>2</sub> SiCNPh           | -529                    | -532                    |
| <b>22</b>  | <i>t</i> Bu <sub>2</sub> GeCNMe           | -201                    | -131                    |
| <b>23</b>  | <i>t</i> Bu <sub>2</sub> GeCN <i>t</i> Bu | -198                    | -120                    |
| <b>24'</b> | <i>t</i> Bu <sub>2</sub> GeCNPh           | -217                    | -158                    |
| <b>25</b>  | <i>t</i> Bu <sub>2</sub> SnCNMe           | -98                     | -58                     |
| <b>26</b>  | <i>t</i> Bu <sub>2</sub> SnCN <i>t</i> Bu | -100                    | -58                     |
| <b>27</b>  | <i>t</i> Bu <sub>2</sub> SnCNPh           | -134                    | -74                     |
| <b>28</b>  | Ph <sub>2</sub> SiCNMe                    | -375                    | -313                    |
| <b>29</b>  | Ph <sub>2</sub> SiCN <i>t</i> Bu          | -336                    | -245                    |
| <b>30</b>  | Ph <sub>2</sub> SiCNPh                    | -403                    | -358                    |
| <b>31</b>  | Ph <sub>2</sub> GeCNMe                    | -200                    | -105                    |
| <b>32</b>  | Ph <sub>2</sub> GeCN <i>t</i> Bu          | -201                    | -100                    |
| <b>33</b>  | Ph <sub>2</sub> GeCNPh                    | -210                    | -126                    |
| <b>34</b>  | Ph <sub>2</sub> SnCNMe                    | -101                    | -51                     |
| <b>35</b>  | Ph <sub>2</sub> SnCN <i>t</i> Bu          | -104                    | -5                      |
| <b>36</b>  | Ph <sub>2</sub> SnCNPh                    | -104                    | -58                     |

Table 4 lists the  $\sigma$ -donation (ligand-to-metallylene) and  $\pi$ -back-donation (metallylene-to-ligand) energies as obtained from constraining the virtual orbital space. The data reproduce most of the trends discussed in the context of NOCVs analyses. For example, the degree of back-donation clearly decreases with increasing principal quantum number, and it is always greater in alkyl-substituted metallylenes than in their aryl analogues. For the majority of stannylenes and germylenes, the  $\sigma$ : $\pi$  ratio is close to 2:1, with the exception of alkyl germylenes for which the relative importance of back-bonding interactions is greater; again, complexes containing phenyl isocyanide have the lowest  $\sigma$ : $\pi$  ratios due to the electron withdrawing nature of the substituent. However, the data in Tables 3 and 4 show vastly different values for  $\sigma$ -type bonding contributions in silylenes: although the  $\pi$ -contributions are roughly comparable between the two datasets, restricting the virtual orbital space gives energies for  $\sigma$ -donation which are from 200 kJ mol<sup>-1</sup> to 600 kJ mol<sup>-1</sup> greater than those obtained with the NOCV analysis! This discrepancy is a direct result from constraining the orbital space, which leads to overcompensation effects (see above). In order to calculate the energy for  $\sigma$ -donation, the virtual orbitals of the ligand are removed from the

employed basis. This creates a very high energy bonding situation for all silylenes with bent geometries, and the system adapts to the set constraint through all interactions possible to lower the total energy. Consequently, the “error” arising from orbital space restriction should be the greatest when estimating  $\sigma$ -type contributions in silylenes; for calculating the  $\pi$ -contribution, the situation is much better as the virtual orbitals are removed from the metallylene fragment and not from the ligand. This kind of overcompensation is inherent to the method and it is clearly the greatest for compound **19**, for which the sum of  $\sigma$ - and  $\pi$ -type contributions exceeds  $\Delta E_{\text{orb}}$  by a clear margin (see Tables 3 and 4).



**Figure 4.** Correlation between the back-donation energies obtained through orbital space restriction ( $E_{\text{back-don.}}$ ) and the calculated shifts in the isocyanide stretching frequency ( $\Delta\nu(\text{CN})$ ) in complexes **19-36**.

Despite the complications arising from constraining the virtual orbital space via orbital deletion procedure, the back-donation contributions listed in Table 4 show a remarkably good linear correlation ( $r^2 = 0.984$ ) when plotted against  $\Delta\nu(\text{CN})$  in Figure 4. In fact, the correlation is equally good as when plotting  $\Delta\nu(\text{CN})$  against energies and eigenvalues of NOCVs (c.f. Figures 2 and 3). The only difference is the intercept of the correlation line with the y-axis that now is at  $\Delta\nu(\text{CN}) = 75 \text{ cm}^{-1}$  (cf.  $50 \text{ cm}^{-1}$  in Figure 2). These findings further support the notion that the  $\pi$ -type component of the metallylene-isocyanide bond is directly coupled to the  $\text{CN}^*$  orbital at isocyanide and functions independently of the  $\sigma$ -framework and electrostatic/steric. Consequently, the relative importance of back-bonding effects can be gleaned from the calculated  $\Delta\nu(\text{CN})$  values with reasonable accuracy. This allows us to use any one of Figures 2-4 as a predictor of the nature of

metallylene-isocyanide bonding in different complexes of the type  $R_2MCNR'$  as long as the calculated shift in CN stretching frequency is known. In the following, the data obtained in this section for the model systems **19-36** will be used to inspect the bonding in metallylene-isocyanide adducts whose structures have been reported in the literature.

**The amount of  $\pi$ -back-bonding in structurally characterized metallylene-isocyanide adducts.**

In order to obtain an estimate of how well the established correlation lines in Figures 2-4 work in practice, the structures of silaketenimines **3** and **4** were optimized with the same density functional-basis set combination, after which their fundamental frequencies were determined and compared to that of the free isocyanide.<sup>6</sup> By using the correlation line in Figure 2, the calculated  $\Delta\nu(\text{CN})$  values of  $-161$  and  $-302\text{ cm}^{-1}$  yield  $E_\pi$  values of  $-440$  and  $-737\text{ kJ mol}^{-1}$  for **3** and **4**, respectively. This means that the compound **4** has by far the strongest Si-C  $\pi$ -interaction found in the current work and that complex **3** has a Si-C bond that is similar to those in the model systems of phenyl substituted silylene. When carrying out the explicit NOCV analyses for **3** and **4**, the values thus obtained are  $-536$  and  $-780\text{ kJ mol}^{-1}$ . As seen, the match between the predicted and calculated numbers is remarkably good for compound **4** but only qualitative for **3**. In any case, the correlation line works surprisingly well for both **3** and **4** considering that they contain cyclic silylenes which were not included within the set of model compounds examined.

Yet another test case for the established correlation line is the germylene-isocyanide adduct **5**, synthesized and characterized by us only recently.<sup>7a</sup> The calculated  $\Delta\nu(\text{CN})$  value of  $-13\text{ cm}^{-1}$  yields  $E_\pi = -128\text{ kJ mol}^{-1}$ ; the NOCV analysis gives  $-84\text{ kJ mol}^{-1}$ , again in good agreement with the prediction. The last case to be considered is the stannylene-isocyanide adduct **1** that is to some extent an extreme system as its linear geometry suggests little or no  $\pi$ -type interactions.<sup>4</sup> In agreement with this assumption, geometry optimization and subsequent frequency calculation gave  $\Delta\nu(\text{CN}) = 61\text{ cm}^{-1}$ . This value is in fact slightly greater than what was observed for any of the systems in the set of model compounds. Consequently, the correlation line cannot be used directly, but a prediction of  $-25\text{ kJ mol}^{-1}$  is obtained from the  $\Delta\nu(\text{CN})$  values calculated for the adducts of phenyl substituted stannylenes (complexes **34-36**). In excellent agreement, the NOCV analysis gives  $E_\pi = -30\text{ kJ mol}^{-1}$ , which also sets the limit for minimum amount of  $\pi$ -contributions in metallylene-isocyanide adducts examined herein (see Table 3).

## Conclusions

The most important conclusions of this work can be summarized as follows:

- i) The fundamental ligand properties of isocyanides and carbon monoxide are very similar, while variation appears in the magnitude of the individual effects exhibited. This is true also from the point of view that, within a metal complex, both ligands can display  $\nu(\text{CN})$  and  $\nu(\text{CO})$  shifts that are either positive or negative. However, because isocyanides are stronger  $\sigma$ -donors than carbon monoxide, the changes in CN bonding framework due to electrostatic and  $\sigma$ -effects, as well as due to decreased electron pair repulsion, are greater. Consequently, isocyanides are more likely to exhibit positive  $\nu(\text{CN})$  shifts even in metal complexes where the metal-carbon bond can be described with a dual donor-acceptor model. In contrast, carbonyl systems typically display increased, non-classical,  $\nu(\text{CO})$  shifts because of the absence of  $\pi$ -back-bonding contributions. This means that the shift of  $\nu(\text{CN})$  to higher values upon complex formation is a much poorer indicator of the absence of  $\pi$ -type back-bonding effects than what a similar change in  $\nu(\text{CO})$  implies.
- ii) The  $\nu(\text{CN})$  shifts in metallylene-isocyanide complexes were found exhibit linear correlation with three different theoretical measures of metal-carbon  $\pi$ -back-donation: the energies and squared eigenvalues of natural orbitals of chemical valence as well as the energies of  $\pi$ -back-donation determined with constraining the virtual orbital space through orbital deletion procedure. The theoretical analyses univocally showed that  $\pi$ -back-bonding is present in all complexes studied and it ranges from 15 to 80% of the total orbital interaction energy in the energy decomposition analysis. The conducted correlation analyses further showed that the  $\pi$ -back-bonding contribution needs to be close to 100 kJ mol<sup>-1</sup> in order for the  $\nu(\text{CN})$  shift in metallylene-isocyanide complexes to be negative. The established correlation lines can be used to obtain semi-quantitative estimates of  $\pi$ -interactions in metallylene-isocyanide complexes once the  $\nu(\text{CN})$  shift has been determined.
- iii) Detailed analyses of metallylene-isocyanide bonding using structural, spectroscopic, and energetic arguments showed that the M-C bonds (M = Si, Ge, Sn) in these systems

contain a varying degree of  $\pi$ -type back-donation contributions. The flow of electrons from the metallylene to the ligand is clearly the most significant for silylene complexes whose electronic structures are therefore closest to the ketenimine-type Lewis-structure **I**. However, the angle between the M-C bond and the metallylene plane is always significantly greater than  $0^\circ$ , which means that the Si-C bonds in silylene-isocyanide adducts differ greatly from Si=C bonds in classical double bonded systems such as 1-silapropadienes. The stannylene-isocyanide adducts reside at the opposite end of the observed spectrum with M-C bonds that are predominately of  $\sigma$ -type and electronic structures that are closest to the zwitterionic donor-acceptor formulation **III**. However, the use of Lewis-structure **III** is obviously an oversimplification, especially for complexes of alkyl stannylenes, because  $\pi$ -type back-donation interactions can constitute up to one third of the total orbital interaction term in these systems. The germylene-isocyanide adducts fall in between the two extremes set by silylenes and stannylenes. Hence, to a good approximation, the extended-Lewis formulation **II** is the best simplified representation of their electronic structure.

## Associated Content

**Supporting Information** Optimized geometries of the studied complexes as well as full results from energy decomposition analysis. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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**Notes** The authors declare no competing financial interest.

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## References

- (1) Mizuhata, Y.; Sasamori, T.; Tokitoh, N. *Chem. Rev.* **2009**, *109*, 3479.
- (2) For metallylenes with a triplet ground state, see: (a) Jiang, P.; Gaspar, P. P. *J. Am. Chem. Soc.* **2001**, *123*, 8622. (b) Sekiguchi, A.; Tanaka, T.; Ichinohe, M.; Akiyama, K.; Tero-Kubota, S. *J. Am. Chem. Soc.* **2003**, *125*, 4962. (c) Sekiguchi, A.; Tanaka, T.; Ichinohe, M.; Akiyama, K.; Gaspar, P. P. *J. Am. Chem. Soc.* **2008**, *130*, 426.
- (3) (a) Protchenko, A. V.; Birjkumar, K. H.; Dange, D.; Schwarz, A. D.; Vidovic, D.; Jones, C.; Kaltsoyannis, N.; Mountford, P.; Aldridge, S. *J. Am. Chem. Soc.* **2012**, *134*, 6500. (b) Rekken, B. D.; Brown, T. M.; Fettinger, J. C.; Tuononen, H. M.; Power, P. P. *J. Am. Chem. Soc.* **2012**, *134*, 6504. (c) West, R. *Nature* **2012**, *485*, 49. (d) Driess, M. *Nat. Chem.* **2012**, *4*, 525.
- (4) Grützmacher, H.; Freitag, S.; Herbst-Irmer, R.; Sheldrick, G. S. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 437.
- (5) Klinkhammer, K. *Polyhedron*, **2002**, *21*, 587.
- (6) Abe, T.; Iwamoto, T.; Kabuto, C.; Kira, M. *J. Am. Chem. Soc.* **2006**, *128*, 4228.
- (7) (a) Brown, Z. D.; Vasko, P.; Fettinger, J. C.; Tuononen, H. M.; Power, P. P. *J. Am. Chem. Soc.* **2012**, *134*, 4045. (b) Brown, Z. D.; Vasko, P.; Erickson, J. D.; Fettinger, J. C.; Tuononen, H. M.; Power, P. P. *J. Am. Chem. Soc.* **2013**, *135*, 6257.
- (8) Takeda, N.; Kajiwara, T.; Suzuki, H.; Okazaki, R.; Tokitoh, N. *Chem. Eur. J.* **2003**, *9*, 3530.
- (9) Xiong, Y.; Yao, S.; Driess, M. *Chem. Eur. J.* **2009**, *15*, 8542.
- (10) (a) Sugimoto, M.; Ito, Y. *Adv. Polym. Sci.* **2004**, *171*, 77. (b) Marcilly, C. *J. Catal.* **2003**, *216*, 47. (c) Malpass, D. *Introduction to Industrial Polyethylene*; Wiley-Scrivener: Hoboken/Salem, 2010; (d) Millich, F. *Macromol. Rev.* **1980**, *15*, 207.
- (11) Frühauf, H.-W. *Chem. Rev.* **1997**, *97*, 523.
- (12) The digermene-isocyanide adducts  $[\text{Ar}^{\text{iPr}^4}\text{GeGeAr}^{\text{iPr}^4}](\text{CNR})_n$  ( $\text{R} = t\text{Bu}$ ,  $n = 1$ ;  $\text{R} = \text{Mes}$ ,  $n = 2$ ;  $\text{Ar}^{\text{iPr}^4} = \text{C}_6\text{H}_3\text{-}2,6\text{-}(\text{C}_6\text{H}_3\text{-}2,6\text{-iPr}_2)_2$ ) [see: (a) Cui, C. M.; Olmstead, M. M.; Fettinger, J. C.; Spikes, G. H.; Power, P. P. *J. Am. Chem. Soc.* **2005**, *127*, 17530. (b) Spikes, G. H.; Power, P. P. *Chem. Commun.* **2007**, 85.] have been reported to have lower  $\nu(\text{CN})$  stretching frequencies than their tin analogues [see: (c) Peng, Y.; Wang, X.; Fettinger, J. C.; Power, P. P. *Chem. Commun.* **2010**, 46, 943.].
- (13) Takeda, N.; Suzuki, H.; Tokitoh, N.; Okazaki, R. *J. Am. Chem. Soc.* **1997**, *119*, 1456.
- (14) (a) Stephan, D. W.; Erker, G. *Angew. Chem. Int. Ed.* **2010**, *49*, 46. (b) Power, P. P. *Acc. Chem. Res.* **2011**, *44*, 627. (c) Martin, D.; Soleilhavoup, M.; Bertrand, G. *Chem. Sci.* **2011**, *2*, 389.
- (15) (a) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865. (b) Perdew, J. P.; Ernzerhof, M.; Burke, K. *J. Chem. Phys.* **1996**, *105*, 9982. (c) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1997**, *78*, 1396. (d) Adamo, C.; Barone, V. *J. Chem. Phys.* **1999**, *110*, 615.
- (16) Gaussian 09, Revision A.1, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.
- (17) Schaefer, A.; Huber, C.; Ahlrichs, R. *J. Chem. Phys.* **1994**, *100*, 5829.
- (18) Bergner, A.; Dolg, M.; Kuechle, W.; Stoll, H.; Preuss, H. *Mol. Phys.* **1993**, *80*, 1431.

- 
- (19) ADF2010.01 and ADF2012.01, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, <http://www.scm.com>.
- (20) van Lenthe, E.; Baerends, E. J. *J. Comp. Chem.* **2003**, *24*, 1142
- (21) (a) van Lenthe, E.; Baerends, E. J.; Snijders, J. G. *J. Chem. Phys.* **1993**, *99*, 4597. (b) van Lenthe, E.; Baerends, E. J.; Snijders, J. G. *J. Chem. Phys.* **1994**, *101*, 9783. (c) van Lenthe, E.; Ehlers, A. E.; Baerends, E. J. *J. Chem. Phys.* **1999**, *110*, 8943.
- (22) (a) Bagus, B. S.; Hermann, K.; Bauschlicher, C. W. Jr. *J. Chem. Phys.* **1984**, *80*, 4378. (b) Bagus, P. S.; Illas, F. *J. Chem. Phys.* **1992**, *96*, 8962.
- (23) (a) Mitoraj, M.; Michalak, A. *J. Mol. Model.* **2007**, *13*, 347. (b) Michalak, A.; Mitoraj, M.; Ziegler, T. *J. Phys. Chem. A* **2008**, *112*, 1933. (c) Radón, M. *Theor. Chem. Acc.* **2008**, *120*, 337.
- (24) (a) Morokuma, K. *J. Chem. Phys.* **1971**, *55*, 1236. (b) Kitaura, K.; Morokuma, K. *Int. J. Quantum. Chem.* **1976**, *10*, 325. (c) Ziegler, T.; Rauk, A. *Theoret. Chim. Acta* **1977**, *46*, 1.
- (25) Malatesta, L.; Bonati, F. *Isocyanide Complexes of Metals*, Wiley, New York, 1969. (b) Vogler, A. in *Isonitrile chemistry*, Ugi, I. (Ed), Academic Press, New York, 1971, 217.
- (26) (a) Strauss, S. H. *J. Chem. Soc., Dalton Trans.* **2000**, 1. (b) Hocking, R. K.; Hambley, T. W. *Chem. Commun.* **2003**, 1516.
- (27) For very early work in this area, see: (a) Hurlburt, P. K.; Rack, J. J.; Dec, S. F.; Anderson, O. P.; Stauss, S. H. *Inorg. Chem.* **1993**, *32*, 373. (b) Hurlburt, P. K.; Rackla, J. J.; Luck, J. S.; Dec, S. F.; Webb, J. D.; Anderson, O. P.; Strauss, S. H. *J. Am. Chem. Soc.* **1994**, *116*, 10003.
- (28) (a) Lupinetti, A. J.; Strauss, S. H.; Frenking, G. in *Prog. Inorg. Chem.* Vol. 49, Karlin, K. D. (Ed), Wiley, New York, 2001, 1. (b) Aubke, F.; Wang, C. *Coord. Chem. Rev.* **1994**, *137*, 483.
- (29) (a) Lupinetti, A. J.; Fau, S.; Frenking, G.; Strauss, S. H. *J. Phys. Chem. A* **1997**, *101*, 9551. (b) Lupinetti, A. J.; Frenking, G.; Strauss, S. H. *Angew. Chem., Int. Ed., Engl.* **1998**, *37*, 2113.
- (30) (a) Tiana, D.; Francisco, E.; Blanco, M. A.; Macchi, P.; Sironi, A.; Pendás, A. M. *J. Chem. Theory Comput.* **2010**, *6*, 1064. (b) Goldman, A. S.; Krogh-Jespersen, K. *J. Am. Chem. Soc.* **1996**, *118*, 12159.
- (31) For a recent study combining photoelectronic spectroscopy and theoretical calculations, see: Csonka, I. P.; Szepes, L.; Modelli, A. *J. Mass. Spectrom.* **2004**, *39*, 1456.
- (32) Cotton F. A.; Zingales, F. *J. Am. Chem. Soc.* **1961**, *83*, 351.
- (33) In fact, the analogous carbonyl complexes, such as  $[\text{Ag}(\text{CO})_2]^+$ , were not characterized until 1994, which marked the beginning of the era of non-classical carbonyls. See Ref. 27b.
- (34) Purcell, K. F. *J. Am. Chem. Soc.* **1969**, *91*, 3487.
- (35) For example, the changes in  $\nu(\text{CO})$  depend more on the effective charge of the species that the carbonyl ligand coordinates to, and not on the extensiveness of the  $\sigma$ -donation taking place. This positive component is therefore largely independent of orbital interactions, whereas the negative component is induced by  $\pi$ -back-donation which is inherently an orbital effect. See Ref. 30 for a more thorough discussion.
- (36) Trinquier, G. *J. Am. Chem. Soc.* **1990**, *112*, 2130.
- (37) Kostina, S. S.; Singh, T.; Leigh, W. J. *Organometallics* **2012**, *31*, 3755.
- (38) Pyykkö, P.; Michiko A. *Chem. Eur. J.* **2009**, *15*, 186.
- (39) For a review, see: Frenking, G.; Wichmann, K.; Fröhlich, N.; Loschen, C.; Lein, M.; Frunzke, J.; Rayón, V. M. *Coord. Chem. Rev.* **2009**, 238-239, 55.
- (40) Though not explicitly shown, we note that both  $\angle(\text{C-N-R}')$  and  $\angle\theta$  values show a reasonable linear correlation with the calculated  $\Delta\nu(\text{CN})$  values ( $r^2 = 0.955$  and  $0.977$ , respectively), which fully supports the conclusions of back-bonding in the examined complexes. In contrast, there is no correlation between the calculated  $d(\text{M-C})$  and  $\Delta\nu(\text{CN})$  values ( $r^2 = 0.677$ ).
- (41) (a) Trommer, M.; Miracle, G. E.; Eichler, B. E.; Powell, D. R.; West, R. *Organometallics* **1997**, *16*, 5737. (b) Eichler, B. E.; Powell, D. R.; West, R. *Organometallics* **1998**, *17*, 2147.

- 
- (42) As expected, there is a very good linear correlation ( $r^2 = 0.985$ ) between the calculated  $d(\text{C-N})$  and  $\Delta\nu(\text{CN})$  values. However, the data for  $\Delta\nu(\text{CN})$  is preferred in the subsequent analyses as trends in it are easier to see due to the much wider range of numeric values.
- (43) Mitoraj, M. P.; Michalak, A.; Ziegler, T. *J. Chem. Theory Comput.* **2009**, *5*, 962.
- (44) To this end it was necessary to perform a full energy decomposition analysis of the different metallylene-isocyanide interactions. Details of these results will not be discussed herein as the emphasis of the current work is in analysis of the key orbital interactions. A summary of the calculated data is however given in the Supporting Information.
- (45) We note that the isomers **21** and **24'** were used in the EDA calculations as they are the ones lowest in energy. For **30**, the two isomers **30** and **30'** are degenerate and only the isomer **30** was included in the analyses.
- (46) Michalak, A.; DeKock, R. L.; Ziegler, T. *J. Phys. Chem. A* **2008**, *112*, 7256.
- (47) (a) Nalewajski, R. F.; Mrozek, J. *Int. J. Quantum Chem.* **1994**, *51*, 187. (b) Nalewajski, R. F.; Formosinho, S. J.; Varandas, A. J. C.; Mrozek, J. *Int. J. Quantum Chem.* **1994**, *52*, 1153. (c) Nalewajski, R. F.; Mrozek, J. *Int. J. Quantum Chem.* **1996**, *57*, 377. (d) Nalewajski, R. F.; Mrozek, J.; Mazur, G. *Can. J. Chem.* **1996**, *74*, 1121. (e) Nalewajski, R. F.; Mrozek, J.; Michalak, A. *Int. J. Quantum Chem.* **1997**, *61*, 589. (f) Nalewajski, R. F.; Mrozek, J.; Michalak, A. *Polish J. Chem.* **1998**, *72*, 1779.