X-ray Crystallographic and Theoretical Comparison of $Ge[2,4,6-(CF_3)_3C_6H_2]_2$ and $Ge[N(SiMe_3)_2]_2$ as Ligands in $(Ph_3P)_2NiGeX_2$ Complexes

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A new transition metal germylene complex, $(Ph_3P)_2NiGe[2,4,6-(CF_3)_3C_6H_2]_2$ (**2**), has been synthesized and structurally characterized. The metrical parameters of complex **2** are compared and contrasted with the previously synthesized complexes $(Ph_3P)_2NiGe[N(SiMe_3)_2]_2$ (**3**) and $(Et_3P)_2PtGe[N(SiMe_3)_2]_2$ (**1**). Nonlocal BP86 density functional calculations support the presence of Ni−Ge d−p π bonding in complexes **2** and **3**.

Introduction

The extent of multiple bonding between transition metal elements and group 14 elements, and the consequence of this bonding behavior with respect to reactivity and structure, has been of intense interest to chemists for decades. This line of study was greatly encouraged by the isolation of the first metal carbenes[2] and subsequently driven by the large number of important stoichiometric and catalytic transformations in which carbenes have been observed to take part.[3] Considerable interest has also focused on the isolation, structural characterization, and reactivity of $M{=}EX_2$ (E = Si, Ge, Sn, Pb) fragments.[4] Key issues explored for these heavier congeners include the effect of stabilizing ligands bound to the group 14 element upon the magnitude of the M=E bonding interaction and M=E reactivity toward substrates. The work for the heavier congeners mirrors the seminal work exploring the stability and reactivity of carbenes that resulted in the assignment of two general classes: the alkylidene or Schrock carbene and the Fischer carbene.[2] Considerable experimental work on heteroatom effects in silylene ligands has been published.[5−10] This series of studies clearly demonstrates that M−Si bond length is not a reliable indicator of the degree of M−Si π-character.

In a recent study of platinum germylene structure and reactivity, crystallographic analysis of $(Et_3P)_2PtGe[N(SiMe_3)_2]_2$ (**1**) indicated a short Pt−Ge distance of 2.304(1) Å, 0.11−0.17 Å less than related germyl species in square-planar Pt complexes. Reaction of **1** with CO_2 and PhNO yields four-membered metallacycles reminiscent of the 2+2 type chemistry observed for carbenes.[11,12] Recent results also indicate that **1**, **2**, and **3** are photosensitive.[13] The sum of these structural and reactivity studies suggest that M−Ge π bonding may contribute significantly to the chemistry of group 10 germylenes.[14] Note that unlike the test cases utilized by Jacobsen and Ziegler in which the germylene must compete for metal back-bonding with CO ligands,[10] and the previously characterized pair of complexes $(CO)_5CrGe[CH(SiMe_3)_2]_2$ and $(CO)_5CrGe[S(2,4,6-(CH_3)_3C_6H_2]2$,[15,16] the germylene has considerably less competition for π back-bonding in the complexes of general formula $(R_3P)_2MGeX_2$ discussed in this paper. The two bis(trimethylsilyl)amide groups in the $Ge[N(SiMe_3)_2]_2$ complex may compete with the $(PPh_3)_2M$ fragment for Ge π bonding. Thus, the role of M−Ge π bonding in causing the short Pt−Ge bond distance could be minimal, especially given the results of calculations for heteroatom-stabilized platinum silylenes.[9]

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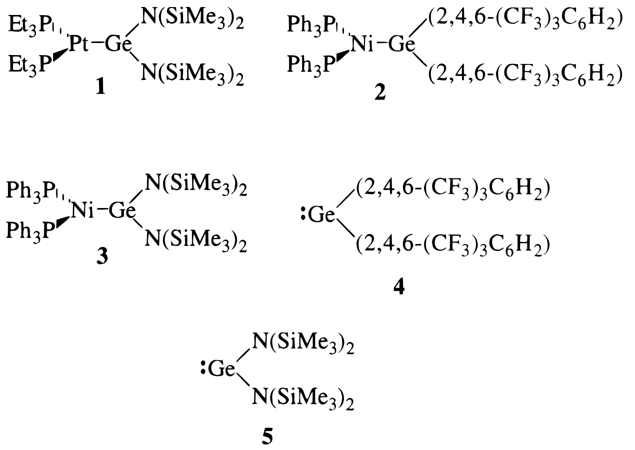

Figure 1. Germylene and metal–germylene complexes discussed herein.

To further explore the issue of M–Ge π bonding, we have recently prepared a new species of stable, electron-withdrawing germylene, bis[2,4,6-tris(trifluoromethyl)-phenyl]germanium(II),[17] and synthesized two related nickel germylene complexes, $(Ph_3P)_2NiGe[2,4,6-(CF_3)_3C_6H_2]_2$ (**2**) and $(PPh_3)_2NiGe[N(SiMe_3)_2]_2$ (**3**),[18] to allow a direct comparison of the effects of germylene ligand substitution upon the M–Ge bond length. The set of complexes is unique because the germylenes used for complexes **2** and **3** are both stable as free molecules. Thus, direct structural comparisons can be made to $Ge[2,4,6-(CF_3)_3C_6H_2]_2$ (**4**) and $Ge[N(SiMe_3)_2]_2$ (**5**) as well. The key complexes discussed in this paper are summarized in Figure 1. In trying to assess the significance of bonding formalisms such as $M \leftarrow :GeR_2$ and $M{=}GeR_2$, crystal structures often do not provide clear guidance. Therefore, a density functional and natural bond order analysis of the bonding was also undertaken for both complexes.

Experimental Section

All procedures utilized air-free technique and dry, deoxygenated solvents.[19] $Ge[2,4,6-(CF_3)_3C_6H_2]_2$ (**4**)[17] and $Ge[N(SiMe_3)_2]_2$ (**5**)[20] were prepared according to literature procedures. $Ni(COD)_2$ was purchased from Strem Chemicals and used as received. ^1H (300 MHz), ^{19}F (282 MHz), ^{13}C (90.6 MHz), and ^{31}P (146 MHz) NMR spectra were obtained in C_6D_6 or THF-d_8 and referenced to the residual solvent protons, $CFCl_3$ in C_6D_6 at 0.0 ppm, the natural abundance ^{13}C in solvent, and external 85% H_3PO_4 in D_2O. IR spectra were taken using a Nicolet 5DXB spectrometer.

$(Ph_3P)_2NiGe[2,4,6-(CF_3)_3C_6H_2]_2$ (2). Ph_3P (207 mg, 0.788 mmol) and $[2,4,6-(CF_3)_3C_6H_2]_2$ (250 mg, 0.394 mmol) were added sequentially to a toluene solution (10 mL) of $Ni(COD)_2$ (108 mg, 0.393 mmol) at 20 °C, allowing 30 min of stirring between the additions. The solution became opaque dark red on addition of phosphine, followed by a slight darkening to burgundy when the germylene was added. The solution was stirred for an additional 60 min at 20 °C. The solvent was removed in vacuo, and the solids were allowed to vacuum-dry for 60 min for thorough removal of toluene. Sparkling, deep-burgundy microcrystals of **2** were obtained by filtration and recrystallization from hexane in two crops (385 mg, 80% yield). ^1H NMR (C_6D_6): δ 7.87 (4H, s), 7.47 (20H, m), 6.88 (10H, m). ^{19}F NMR (C_6D_6): δ −55.58 (s, 12F), −63.34 (s, 6F). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 39.61 (s). Anal. Calcd for $C_{54}H_{34}F_{18}P_2GeNi$: C, 53.2; H, 2.8. Found: C, 51.92; H, 2.97.

X-ray Data Collection, Structure Determination, and Refinement of 2. A small, deep red, irregular platelike crystal ($0.04 \times 0.10 \times 0.28$ mm) was mounted on a standard Siemens SMART CCD-based X-ray diffractometer equipped with a normal focus Mo-target X-ray tube ($\lambda = 0.710\,73$ Å) operated at 2000 W power (50 kV, 40 mA) and a LT-2 low-temperature device. The X-ray intensities were measured at 153 K; the detector was placed at a distance of 4.577 cm from the crystal. A total of 2132 frames were collected with a scan width of 0.3° in ω and an exposure time of 30 s/frame. The frames were integrated with the Siemens SAINT software package with a narrow frame algorithm. The integration of the data using a primitive monoclinic unit cell yielded a total of 55 786 reflections to a maximum 2θ value of 61°, of which 13 919 were independent and 8442 were greater then $2\sigma(I)$. The final cell constants ($a = 12.3206(1)$ Å, $b = 23.017(1)$ Å, $c = 18.0758(1)$ Å, $\beta = 104.29(1)°$, $V = 4967.33(5)$ Å^3, $Z = 4$) were based on the *xyz* centroids of the 8192 reflections above $10\sigma(I)$. Analysis of the data showed negligible decay during data collection; the data were collected for absorption using an empirical method (SADABS) with transmission coefficients ranging from 0.825 to 0.978. The structure was solved and refined (Siemens SHELXTL (5.03)) using space group $P2(1)/c$ with $Z = 4$ for the formula $C_{54}H_{34}F_{18}P_2GeNi$. All non-hydrogen atoms were refined anisotropically with the hydrogens placed in idealized positions. Final full-matrix refinement based on F^2 converged at R1 = 0.0852 and wR2 = 0.1152 (based on observed data); R1 = 0.1545 and wR2 = 0.1368 (based on all data); the largest peak in the final difference map was 1.12 e/Å^3 and was associated with Ni.

Computational Methods

Density functional calculations were performed using standard routines included in Spartan 5.0 (BP86/DN**) and Jaguar 3.5 (pseudospectral BP86/LACVP**).[21,22] BP86 is a nonlocal functional that employs Becke's 1988 gradient correction[23] to Slater's exchange functional,[24] and Perdew's 1986 gradient correction[25] to the Perdew–Zunger local correlation functional.[26] DN** is a numerical all-electron basis set of split-valence+polarization quality (all atoms). LACVP** is a split valence+polarization basis set that employs an effective core potential for Ni (Ne core)[27] and Ge (Ar core)[28] and uses the 6-31G** basis for all remaining atoms.[29] A singlet spin state was assumed for all molecules, and symmetry was not employed (C_1 point group). Molecular geometries were determined using crystallographic coordinates for all heavy atoms. The coordinates of hydrogen atoms in the PH_3 ligands were assigned by using Spartan to delete the atoms of the phenyl groups; this effectively replaces each phenyl group with a hydrogen lying 1.42 Å from phosphorus on the original PC_{ipso} vector. The coordinates of all other hydrogens were determined

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by a partial PM3(tm) geometry optimization (frozen coordinates for heavy atoms and PH$_3$). Calculations on "bare" germylene ligands used the same atomic coordinates derived for the nickel−germylene complexes. Natural population analyses were performed using NBO v. 4.0.[30]

Results and Discussion

As part of a previous study involving the catalytic synthesis of an amide germane, we reported the synthesis and structure of (Ph$_3$P)$_2$NiGe[N(SiMe$_3$)$_2$]$_2$ (**3**).[18] This complex exhibited a rather short Ni−Ge bond length of 2.206(1) Å, 0.064 Å less than that expected for a Ni−Ge single bond on the basis of covalent radii[31] and 0.11 Å less than a related nickel germyl bond length.[32] However, comparison to complexes such as [Cp′(CO)$_2$Mn═Ge═Mn(CO)$_2$Cp′] (Cp′ = C$_5$H$_4$Me) that have bond lengths > 0.25 Å shorter than corresponding germyls,[33,34] and consideration of counterexamples with short bonds such as the sulfur-stabilized silylenes,[9] suggested that no claims of multiple bonding should be made for a complex such as **3** without additional supporting evidence. To experimentally probe the degree of heteroatom stabilization afforded by the bis(trimethylsilylamide) groups, and the degree to which they compete with the d^{10} nickel atom for π bonding with the empty Ge p orbital, a new nickel germylene was synthesized using Ge[2,4,6-(CF$_3$)$_3$C$_6$H$_2$]$_2$ (**4**).

The synthesis of a nickel germylene containing **4** proceeded in direct analogy to complex **3**. The general route of Fahey and Mahan to d^{10} nickel complexes, based upon addition of the free Lewis base ligands to Ni(COD)$_2$, was employed,[35] resulting in deep burgundy microcrystals of (Ph$_3$P)$_2$NiGe[2,4,6-(CF$_3$)$_3$C$_6$H$_2$]$_2$ (**2**). A single-crystal X-ray analysis of **2** confirmed that a monomeric three-coordinate nickel complex was obtained (Figure 2). The three structural parameters that provide the most information regarding the character of the Ni−Ge bonding are the Ni−Ge distance, the PNiGeN dihedral angle, and the C−Ge−C angle. The Ni−Ge bond distance of 2.1814(7) Å found for **2** is 0.025 Å shorter than that obtained for amide-stabilized **3**. By way of comparison, the Ru−Si bond in the ruthenium dimethylsilylene complex is 0.031 and 0.048 Å shorter than related sulfur-stabilized ruthenium silylenes.[5] A significant difference was also observed for the PNiGeX dihedral angle: 76.1° for **3** and 59.9° for **2**. However, given the difference in steric bulk of the ligands, and the interactions of the *ortho*-CF$_3$ groups with the germanium, the best interpretation of the 16.2° difference in angle is not readily apparent. The C−Ge−C bond angle for **2** is 104.3(2)° as compared to 99.95(10)° in the free germylene. On the basis of literature precedent,[36] this angle appears to be diagnostic of the degree of s and p character in bonds to germanium and could indirectly reveal the nature of the metal−germylene bond. The literature contains an example of a structurally characterized germanium double bond to carbon, and the C−Ge−C angle observed is 113.4°.[37] Complexes containing Ge−Ge double bonds exhibit a wide range of C−Ge−C angles (110−128°).[38,39] Structurally characterized, σ-bonded alkylmetal carbenes have C−C−C angles in the 109−112° range.[40] The C−Ge−C bond angle observed for **2** is considerably smaller than that observed for authentic complexes containing double bonds to germanium; however, the angle is appreciably larger than that observed for the free germylene despite the increased steric congestion due to the (PPh$_3$)$_2$Ni fragment. It is also interesting to note that the Ni−P distances observed for **2** of 2.1811(12) and 2.1752(12) Å are about 0.03 Å longer than the average distance observed for Ni−P bonds in Ni(PPh$_3$)$_3$ (2.147(7) Å).[41] The Ni−P distances in **3** are also somewhat greater (2.157(1) and 2.164(1) Å). The P−Ni−P

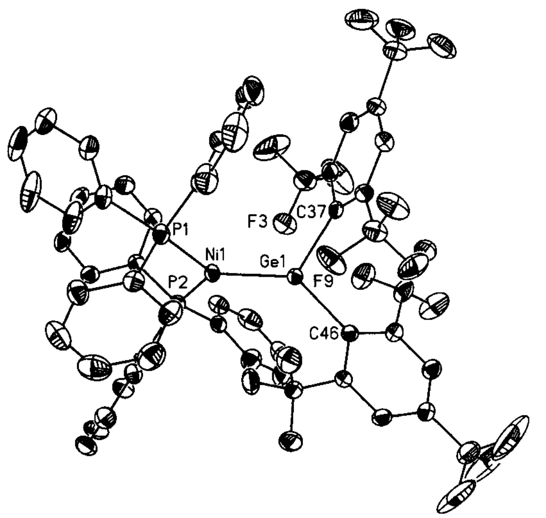

Figure 2. ORTEP diagram for **2** (50% probability). Selected bond distances (Å) and angles (deg): Ni−P1, 2.1811(12); Ni−P2, 2.1752(12); Ni−Ge, 2.1814(7); Ge−C37, 2.051(4); Ge−C46, 2.057(4); P1−Ni−P2, 118.10(5); C25−Ge−C46, 104.3(2); Ge−F3, 2.858(3); Ge−F9, 2.851(3).

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angles for **2** and **3** are 118.10(5)° and 113.81°, respectively. Another point of comparison between $Ni(PPh_3)_3$ and **2** is the interactions of the *ortho*-CH bonds of the phenyl rings. Stephan et al. noted that three close Ni−H interactions existed at 2.87, 2.74, and 2.91 Å in $Ni(PPh_3)_3$ and suggested that these may be related to the facile decomposition observed via orthometalation. **2** has two such contacts: the Ni−H12 contact of 2.748 Å and the H2−Ge contact of 3.036 Å. Indeed, the C−H bond of C2 is oriented directly over the Ni−Ge bond vector. Despite the presence of the same magnitude of Ni−H contact, **2** is observed to be quite thermally stable and well-behaved as opposed to $Ni(PPh_3)_3$, which was quite difficult to obtain in pure form, in part because of facile side-reactions.[41,42] Complex **3** also has close Ni−H and Ge−H contacts. The closest Ni−H contacts are Ni−H44B, Ni−H39C, and Ni−H30 at 2.954, 3.028, and 3.022 Å, respectively. The contacts from H44B and H39C arise from $-SiMe_3$ groups that bracket the Ni on either side of the NiP_2 plane. H30 is an *ortho*-C−H bond from one of the triphenylphosphine ligands. The closest Ge−H contacts are Ge−H2, Ge−H37C, and Ge−H43C at 3.045, 3.140, and 3.059, respectively. Unlike $Ni(PPh_3)_3$, none of the $(R_3P)_2NiGeY_2$ complexes isolated to date have exhibited a tendency to orthometalate. Apparently, germylenes **4** and **5**, as well as $Ge[CH(SiMe_3)_2]_2$, dramatically stabilize the $(Ph_3P)_2Ni$ fragment upon formation of the three-coordinate complex in a way that adding a third PPh_3 group is unable to achieve. The most obvious difference between PPh_3 and the germylenes is the presence of the empty p orbital on the germylene available for π back-bonding.

Complex **2** has a number of close Ge−F contacts. The two shortest are at 2.858 Å (Ge−F3) and 2.851 Å (Ge−F9), and there are two longer range interactions at 3.002 Å (Ge−F17) and 3.058 Å (Ge−F12). These distances are all longer than the four closest contacts observed for the free germylene species of 2.566(2), 2.554(1), 2.790(2), and 2.781(2) Å.[17] Indeed, in the free germylene the two closest contacts are located directly above and below the empty p orbital, suggesting a donor−acceptor interaction between the fluorine lone pairs and the germylene.[43] In addition, the C−F bond lengths of the close contacts in the free germylene show a small but statistically significant increase of ~0.04 Å consistent with a bonding interaction, whereas none of the C−F bonds of **2** show any elongation. Calculations indicate that binding of the $(PPh_3)_2Ni$ center has served to reduce the electrophilicity of the germanium center via π back-bonding, resulting in lengthened Ge−F contacts (*vide infra*). The CF_3 contacts in **2** are unique for the germanium compounds studied to date containing the $[2,4,6\text{-}(CF_3)_3C_6H_2]-$ substituent.[17,44] This is the only case in the $[2,4,6\text{-}(CF_3)_3C_6H_2]-Ge$ system where only one of the ligands engages in short Ge−F contacts (each ~2.8 Å) with both of its CF_3 groups. The other $[2,4,6\text{-}(CF_3)_3C_6H_2]-$ substituent has leaned back and does not make any close Ge−F contacts. The Ge−C bonds in **2** are 2.057(4) and 2.051(4) Å; however the Ni−C distances are very different: 3.936(4) (Ni−C46) and 3.650(4) (Ni−C37) Å, with the shorter distance corresponding to the $[2,4,6\text{-}(CF_3)_3C_6H_2]-$ substituent with F-contacts to germanium. The Ni−F3 distance in this case is 3.286(3) Å, longer than one would expect for a contact. $(Ph_3P)_2NiGe[N(SiMe_3)_2]_2$ (**3**) shows no such asymmetry in the amide ligands.

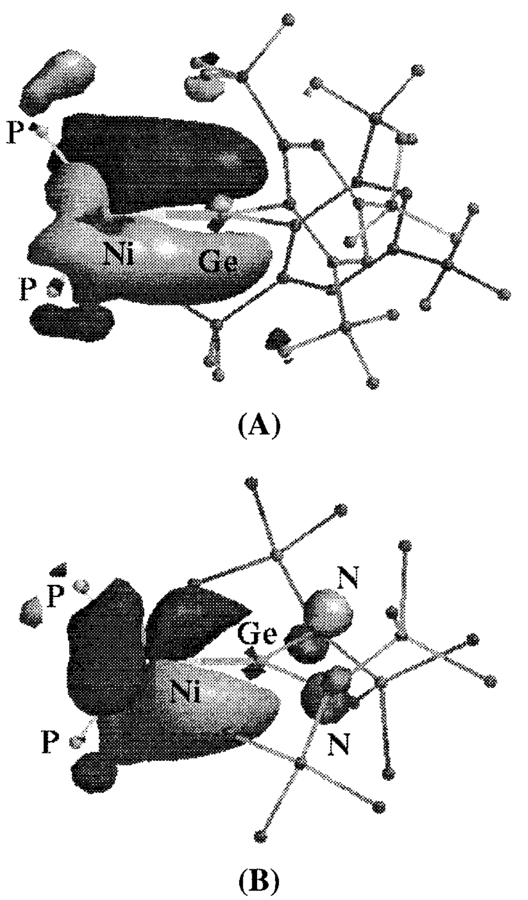

Figure 3. Ni−Ge π bond calculated for (A) $(H_3P)_2NiGe[2,4,6\text{-}(CF_3)_3C_6H]_2$ (**2H**) and (B) $(H_3P)_2NiGe[N(SiMe_3)_2]_2$ (**3H**). Coordinates from the X-ray structures of **2** and **3** were used; however the phenyl groups on phosphorus were replaced by hydrogen atoms. The calculation was at the BPDN** level as implemented by Spartan 5.0.

In an effort to understand the nature of the M−Ge bonding in greater detail, we have undertaken a computational investigation of **2** and **3** using nonlocal density functional methods. BP86/DN** calculations on $(H_3P)_2NiGe[2,4,6\text{-}(CF_3)_3C_6H_2]_2$ **(2H)** reveal molecular (Kohn−Sham) orbitals with NiGe π and π* character. The π orbital is occupied (HOMO-4) and arises from Ni−Ge d−p overlap (Figure 3a). The orbital is polarized toward Ni and contains small NiP antibonding contributions. The π* orbital is unoccupied (LUMO) and is mainly localized on Ge. These observations suggest that there is a NiGe π bond in **2H** that is highly polarized toward Ni. Interpretation of the molecular orbitals of $(H_3P)_2NiGe[N(SiMe_3)_2]_2$ **(3H)** is more difficult. Several occupied orbitals reveal out-of-plane NiGe bonding interactions, but only HOMO-4 shows simultaneous π bonding overlap above and below the NiGe axis (Figure 3b). HOMO-4 is highly polarized toward Ni and also contains small GeN antibonding contributions from p orbitals on the two N. Apparently, NiGe π bonding is

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(42) Tolman, C. A.; Seidel, W. C.; Gerlach, D. H. *J. Am. Chem. Soc.* **1972**, *94*, 2669.

(43) Shusterman, A. J.; Banaszak Holl, M. M.; Bender, J. E. Unpublished results.

(44) For other crystallographically characterized germanium compounds containing this ligand see: Bender, J. E.; Banaszak Holl, M. M.; Mitchell, A. M.; Wells, N. J.; Kampf, J. W. *Organometallics* **1998**, *17*, 5166.

Table 1. Summary of Key Metrical Parameters for Structurally Characterized Three-Coordinate Group 10 Germylene Complexes

complex	M−Ge (Å)	av M−P (Å)	av Ge−X (Å)	P−M−P (deg)	X−Ge−X (deg)	PMGeX dihedral (deg)
$(Et_3P)_2PtGe[N(SiMe_3)_2]_2$ (**1**)	2.3039(10)	2.2615(7)	1.870(5)	114.98(10)	106.3(3)	77.8
$(Ph_3P)_2NiGe[2,4,6-(CF_3)_3C_6H_2]_2$ (**2**)	2.1814(7)	2.178(4)	2.054(4)	118.10(5)	104.3(2)	59.9
$(Ph_3P)_2NiGe[N(SiMe_3)_2]_2$ (**3**)	2.2064(6)	2.160(5)	1.88(1)	113.81(4)	105.05(11)	76.1

less important in **3H** than it is in **2H**. Nevertheless, both complexes exhibit NiGe π bonding, and this may affect NiGe bond distances and mediate the photochemical and 2+2 type of reactivity previously noted in this system.[11−13]

A more definitive picture of NiGe bonding is obtained through natural bond orbital (NBO) analysis of the delocalized Kohn−Sham orbitals.[30] The orbitals are first transformed into a set of natural atomic orbitals (NAO) that provide atomic orbital populations and atomic charges and then transformed into localized natural bond orbitals (NBO) that can identify bonding interactions. Each transformation is carried out in a way that maximizes the occupancy of certain orbitals (up to two electrons) while minimizing the occupancy of others. Deviations from the ideal occupancies provide an effective measure of metal−ligand bonding.

The NAO populations for **2H** and **3H** are quite similar. The Ni atom and phosphine ligands in **2H** each carry a small positive charge, $q_{Ni} = 0.08$ (electron configuration = $d^{9.36}s^{0.54}p^{0.02}$) and $q_{PH3} = 0.08$ and 0.09, indicating net electron transfer from $(PH_3)_2Ni$ to the germylene, $q_{GeAr2} = -0.25$. The same trend is seen in **3H**, but to a lesser degree: $q_{Ni} = 0.05$ (electron configuration = $d^{9.40}s^{0.55}p^{0.02}$), $q_{PH3} = 0.04$ and 0.05, $q_{GeN2} = -0.14$. Unfortunately, these charges only define *net* electron transfer and cannot be used to describe the degree of NiGe π bonding. Separating σ and π electron transfer requires construction of natural bond orbitals.

NBO analysis of **2H** and **3H** reveals that each molecule is a strongly delocalized complex, indicating that several alternative sets of bond orbitals are possible. Given that nickel is nearly neutral, we first selected a set of bond orbitals in which each ligand carries standard bonds and lone pairs. The ligating atoms, Ge and P, each carry a single lone pair, and Ni carries five lone pairs and no metal−ligand bonds. This set of NBO allows easy identification of metal-to-ligand and ligand-to-metal electron transfer. Metal-to-ligand electron transfer is indicated by metal lone pair orbitals with "low" occupancies ($\ll$2 electrons) and outer ligand orbitals with "high" occupancies (>0 electrons). Conversely, ligand-to-metal electron transfer is indicated by ligand lone pair orbitals with low occupancies and outer metal orbitals with "high" occupancy.

Although the bonding pattern described above was arbitrarily selected, it provides a fair description of the electron density in **2H** and **3H**. 97.9% of the electron density (362.4 electrons) in **2H** is assigned to core and valence orbitals, and only 2.1% (7.6 electrons) is assigned to outer orbitals. **3H** is described even better by this set of orbitals; 98.8% of the electron density (270.7 electrons) is assigned to core and valence orbitals, and only 1.2% (3.3 electrons) is assigned to outer orbitals. The higher occupancy of outer orbitals in **2H** indicates that the diarylgermylene complex is more delocalized than the diaminogermylene complex; however, this is mainly due to different degrees of delocalization within each germylene ligand and not differences around the metal center. NBO analysis of the "bare" germylene ligands assigns 1.9% of the electron density (5.9 electrons) in the diarylgermylene (derived from **2H**) to outer orbitals, but only 0.9% of the electron density (1.8 electrons) in the diaminogermylene (derived from **3H**) to outer orbitals. This is not surprising since the benzene rings and the trifluoromethyl groups in the former are all highly delocalized.

Table 2. NBO Occupancies for 2H and 3H Assuming No Ni−Ligand Bonding Orbitals and Five Ni Lone Pair Orbitals

	orbital occupancy (electrons) and hybridization	
atom	**2H**	**3H**
Ni	1.98 (d)	1.98 (d)
	1.94 (d)	1.94 (d)
	1.93 (d)	1.92 (d)
	1.88 (d)	1.87 (d)
	1.66 (d)	1.72 (d)
	0.51 ("empty" s)	0.52 ("empty" s)
Ge	1.41 ($sp^{2.4}$)	1.51 ($sp^{1.3}$)
	0.52 ("empty" p)	0.55 ("empty" p)
P	1.74 ($sp^{2.6}$)	1.75 ($sp^{2.3}$)
P	1.73 ($sp^{2.7}$)	1.75 ($sp^{2.3}$)
N		1.76 (p)
N		1.77 (p)

The NBO occupancies in **2H** and **3H** reveal that both complexes are stabilized by nickel-to-germanium electron transfer and π back-bonding, but to a different degree (Table 2). The occupancies of the lone pair (σ donor) orbitals on the ligating atoms are relatively low ($\sim$1.5 Ge, 1.7 P), and the occupancy of the outer (σ acceptor) Ni s orbital is high ($\sim$0.5). This is consistent with partial ligand-to-metal electron transfer via σ bonds. NBO analysis also reveals a low occupancy ($\sim$1.7) Ni d orbital and a high occupancy ($\sim$0.5) "empty" Ge p orbital in each complex. These results are consistent with partial nickel-to-germanium electron transfer via π back-bonding.

We can show that NiGe π back-bonding is more effective in **2H** than in **3H** by comparing the NBO occupancies of the metal complexes with those of the "bare" ligands. The "empty" Ge p orbital in the "bare" diarylgermylene (derived from **2H**) is occupied by less than 0.01 electron. This suggests that the 0.52 electron occupying the "empty" Ge orbital in **2H** is derived almost entirely from π back-bonding. Note that this theoretical result is consistent with the experimentally observed change in the lengths of the Ge−F contacts in **4** versus **2**. Ni−Ge π back-bonding reduces Ge electrophilicity, resulting in longer Ge−F contacts. The "empty" Ge p orbital in the "bare" diaminogermylene (derived from **3H**) has an occupancy of 0.28 electrons. This means that the 0.55 electrons occupying the "empty" Ge orbital in **3H** are derived from a combination of π back-bonding and N→Ge electron transfer. Comparison of N lone pair occupancies in the "bare" germylene and in **3H** shows

Table 3. NBO Occupancies for 2H and 3H Assuming Two NiGe Bonding Orbitals and Four Ni Lone Pair Orbitals

	orbital occupancy (electrons), polarization, hybridization	
orbital	**2H**	**3H**
NiGe σ	1.82 32% Ni (sd$^{0.8}$)/68% Ge (sp$^{1.5}$)	1.85 32% Ni (sd$^{1.0}$)/68% Ge (sp$^{1.0}$)
NiGe σ*	0.85 68% Ni (sd$^{0.8}$)/32% Ge (sp$^{1.5}$)	0.89 68% Ni (sd$^{1.0}$)/32% Ge (sp$^{1.0}$)
NiGe π	1.94 83% Ni (d)/17% Ge (p)	1.95 86% Ni (d)/14% Ge (p)
NiGe π*	0.26 17% Ni (d)/83% Ge (p)	0.33 14% Ni (d)/86% Ge (p)

that NiGe back-bonding reduces the amount of N→Ge electron transfer in **3H**. Therefore, the difference in Ge p orbital occupancies (0.28 → 0.55 electron) represents a lower limit on the amount of NiGe electron transfer in **3H**. However, even when we allow for changes in N→Ge electron transfer, the orbital occupancies still indicate that π back-bonding is more effective in **2H** than in **3H**.

We repeated the NBO analysis with a bonding pattern in which the Ge lone pair and one Ni lone pair were replaced by two NiGe bonding orbitals (all remaining orbitals were identical to those described above). The characteristics of the NiGe bonding and antibonding orbitals are listed in Table 3. The NiGe σ bonding orbitals are polarized toward Ge. The occupancies of these orbitals are relatively low, and the occupancies of the corresponding σ* orbitals are very high, indicating weak and highly delocalized σ bonding. The hybridization of Ge in the σ bonding orbital changes substantially between **2H** (41% s) and **3H** (49% s), which is also consistent with changes in Ge lone pair hybridization obtained using the previous orbital definition (Table 2). Increasing s character in **3H** should lead to a shorter NiGe σ bond and offset the weaker π bond found in this complex (*vide infra*).

NBO analysis also finds NiGe π bonding orbitals involving NiGe d−p orbital overlap. The π orbitals are highly polarized toward Ni, consistent with the usual π back-bonding model. Interestingly, the orbital occupancies, $\pi > \sigma$ and $\pi^* \ll \sigma^*$, indicate that the π bonding electrons are localized between Ni and Ge to a much higher degree than are the σ bonding electrons. Comparison of the π orbitals of **2H** and **3H** indicates that NiGe π bonding is slightly more polarized in **3H**. The π* occupancy in **3H** is also significantly higher, indicating that π bonding is less effective in this complex.

The use of two different sets of bonding orbitals (no Ni-ligand bonds vs NiGe double bond) for NBO analysis may seem to introduce an arbitrary element into the description of NiGe bonding. However, it should be clear that both analyses agree on key points: (1) Ge acts as a σ donor/π acceptor ligand, (2) Ni acts as a σ acceptor/π donor metal, (3) the hybridization of the Ge σ donor orbital changes from “low” s-character in **2H** to “high” s-character in **3H**, and (4) NiGe π bonding is more effective in **2H**. The similarity of NiGe bond distances in **2H** and **3H** may simply reflect the different roles of σ and π bonding in the two complexes; **2H** seems to contain a weaker σ bond and a stronger π bond than **3H**. A complete description of bonding in **2H** and **3H** should also explain trends in other structural parameters, such as P−Ni−P and X−Ge−X bond angles, NiP distances, and the P−Ni−Ge−X dihedral angle. These require a more detailed analysis, however, and are beyond the scope of this paper. A detailed study of the role of π bonding in group 10 metal germylenes is in progress.[43]

Conclusions

Comparison of the bond lengths of the metal germylene complexes with related metal germyls, and with tabulated covalent radii, indicates M−Ge bond lengths ~ 0.1 Å shorter than expected for the nickel and platinum complexes. The experimental evidence suggests that some type of multiple bonding might be occurring; however no firm conclusions could be drawn based upon the experimental data alone. Nonlocal density functional calculations indicate the presence of Ni−Ge π bonds and significant amount of metal-to-germylene electron transfer for the two nickel germylenes studied. The interaction is consistent with typical metal-to-ligand π back-bonding. Additional theoretical studies are under way to assess the significance of the Ni−Ge π bonding in the observed bond length and angle changes and the relationship to the reactivity patterns observed in these three-coordinate metal−germylene systems.[43,45]

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Supporting Information Available: Crystal data for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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