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# $^{29}Si$–$^{15}N$ Spin–Spin Coupling Constants in Silazanes

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$^{29}Si$–$^{15}N$ spin–spin coupling constants ($^1J_{SiN}$) in silazanes and cyclosilazanes were measured along with the $^{15}N$ and $^{29}Si$ chemical shifts, $^{15}N$–$^1H$ and $^{29}Si$–$^{13}C$ coupling constants, and $^{15/14}N$ isotope effects on $^{29}Si$ chemical shifts. If electronegativities of substituents at the nitrogen atom do not vary significantly, the $^{29}Si$–$^{15}N$ coupling constants can be interpreted in terms of the mean excitation energy approximation; i.e., the $^1J_{SiN}$ values reflect the s order of the Si–N bond. An increase in $^1J_{SiN}$ with the electronegativities of substituents at the Si atom and in cyclosilazanes of greater size is ascribed to enhancement of the s character of the Si–N bonds. The exocyclic Si–N bonds in cyclodisilazanes were found to be characterized by enhanced s character while the intracyclic Si–N bonds are formed mainly from the p orbitals. It was shown that the $^{29}Si$–$^{15}N$ coupling constants tend to increase and the $^{15/14}N$ isotopic shifts tend to decrease with the shortening of the Si–N bond. When substantial changes in the electronegativities of substituents at the N atom occur, the pattern of $^1J_{SiN}$ variation becomes more complex. The values of $^2J_{SiSi}$ via the nitrogen atom (2.0–2.3 Hz) and $^3J_{SiN}$ (2.8–3.1 Hz) were measured for the first time.

## Introduction

Measurements of spin–spin coupling constants make it possible to obtain information on electron distribution in molecules.[1,2] $^{29}Si$–$^{15}N$ spin–spin coupling constants ($^1J_{SiN}$) were first measured in 1973.[3] The development of polarization transfer methods (INEPT,[4] DEPT,[5] etc.) allowed their measurements under natural isotope abundance. As a result, systematic investigation of these spin–spin coupling constants and their application for structural studies became justified.[6-10] We have previously published data on $^{29}Si$–$^{15}N$ couplings for some silazanes and silazoxanes.[9] This paper is continuation of our previous investigations. Specifically, $^{29}Si$–$^{15}N$ coupling constants were measured for cyclodisilazanes along with $^{29}Si$, $^{15}N$ chemical shifts, $^{15}N$–$^1H$, $^{29}Si$–$^{13}C$, and $^{29}Si$–$^{29}Si$ coupling constants, and $^{15/14}N$ isotope effects on $^{29}Si$ chemical shifts. This enabled us to attain a more reliable interpretation of $^{29}Si$–$^{15}N$ coupling constants scarcely studied so far and to characterize in detail the structure of the investigated compounds.

## Results and Discussion

Theoretical estimations[11] and experimental data[6,10] suggest that the Fermi contact (FC) interaction provides a major contribution to $^1J_{SiN}$. This allows interpretation of $^{29}Si$–$^{15}N$ couplings in terms of analytical expressions derived by Pople and Santry for the FC term[12]

$$^1K_{SiN}{}^{FC} = \frac{4e^2h^2}{9m^2c^2}|\psi_{Si}(O)|^2|\psi_N(O)|^2\pi_{SiN} \qquad (1)$$

$$^1K_{SiN}{}^{FC} = \frac{4e^2h^2}{9m^2c^2}(\Delta E)^{-1}|\psi_{Si}(O)|^2|\psi_N(O)|^2P_{s_{Si}s_N}{}^2 \qquad (2)$$

where $^1K_{SiN}{}^{FC}$ is the reduced coupling constant ($^1K_{SiN} = 4\pi^2 \cdot {}^1J_{SiN}/h\gamma_{Si}\gamma_N$), $\pi_{SiN}$ is mutual polarizability of valence s orbitals of the Si and N atoms, and $P_{s_{Si}s_N}$ is the s order of the Si–N bond. The remaining symbols have their conventional meaning.[1,2] Since the nitrogen atom possesses an unshared electron pair, the approximation of average excitation energy (eq 2) is, in general, not valid for $^1J_{SiN}$. However, if variation in the nature of substituents at the nitrogen atom is negligible, eq 2 can be used for $^1J_{SiN}$ interpretation. For instance, a linear relation between $^1J_{SiN}$ and the Si–N bond s character has been found previously for aminosilanes,[10] which makes $^1J_{SiN}$ useful for the solution of structural problems.

The spin–spin coupling constants and chemical shifts of compounds studied are presented in Table I. An increase in $^1J_{SiN}$ with the electronegativities of the substituents on the Si atom in the SiR series Me < Ph < Cl < OR (compounds 1–5 and 10–12) is indicative of positive $^1J_{SiN}$ values ($^1K_{SiN} > 0$). Since variation in the electronegativities of substituents on the N atom is insignificant, it can be suggested that the increase of $^1J_{SiN}$ in this series is related to enhanced s character of the Si–N bond according to Bent's law.[13] Also, a parallel increase in the $^{29}Si$–$^{13}C$ spin–spin coupling constants supports this suggestion. No general correlation exists between these coupling constants, although, as in the case of aminosilanes,[10] such correlation can be found for compounds with identical substituents at the N atom (e.g., disilazanes 1–5 (eq 3)). Deviation from this relation occurs in the case of compound 4.

$$^1J_{SiN} = 0.31\,{}^1J_{SiC} - 4.0 \qquad r = 0.993 \qquad (3)$$

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**Table I. NMR Parameters of Silazanes**[a]

| compd | solvent | $\delta(^{15}N)$ | $\delta(^{29}Si)$ | $^1J_{NH}$ | $^1J_{SiC}$[b] | $^1J_{SiN}$ | $^1\Delta(^{15/14}N)$ | other data |
|---|---|---|---|---|---|---|---|---|
| 1[c] | acetone-$d_6$ | −354.2 | 2.1 | 69.6 | 56.2 | 13.5 | 10.7 | |
| 2 | $CDCl_3$ | −357.8 | −3.5 | 66.1 | 58.2 | 13.8 | 10.5 | $^1J_{SiC}$ = 72.2 (Ph) |
| 3 | $CDCl_3$ | −361.5 | −9.4 | 66.3 | 60.0 | 14.2 | 8.5 | $^1J_{SiC}$ = 74.6 (Ph) |
| 4[d] | $CDCl_3$ | −334.3 | 13.3 | 68.1 | 68.1 | 14.4 | 8.2 | |
| 5[d] | $CDCl_3$ | −335.7 | −11.9 | nm[e] | 69.4 | 17.4 | 5.9 | |
| 6 | $C_6D_6$ | nm | −14.6 | | 51.9 | 7.8 | 11.6 | |
| 7 | $C_6D_6$ | −255.6 | 10.9 | 64.8 | 56.7 | 6.5 | 14.3 | $\delta(^{29}Si)$ 20.9 ($OSiMe_3$)<br>$^1J_{SiC}$ = 59.5 ($OSiMe_3$) |
| 8 | $C_6D_6$ | −373.8 | −10.2 | 74.0 | 59.8 | 17.5 | 10.8 | $^1J_{SiC}$ = 74.4 (Ph) |
| 9[c] | acetone-$d_6$ | −327.3 | −15.4 | 75.0 | nm | 19.8 | nm | |
| 10 | $CDCl_3$ (endo) | −322.1 | 7.3 | | 61.9 | 7.1 | 10.5 | $^2J_{SiSi}$ = 2.2 (exo–endo) |
| | (exo) | | 6.2 | | 67.2 | 16.9 | 4.0 | |
| 11 | $C_6D_6$ (endo) | −323.8 | 3.0 | | 60.9 | 7.4 | 10.0 | $^2J_{SiSi}$ = 2.3 (exo–endo) |
| | (exo) | −363.1 | −6.7 | 72.8 | 63.9 | 17.8 | nm | $^1J_{SiN}$ = 18.4 ($NH_2$)<br>$^3J_{SiN}$ = 3.1 |
| 12 | $CDCl_3$ (endo) | −325.4 | 3.8 | | 61.2 | 7.3 | 9.5 | $^2J_{SiSi}$ = 2.0 (exo–endo) |
| | (exo) | | −8.9 | | 68.1 | 18.3 | 4.5 | |
| 13[d] | $CDCl_3$ | −347.3 | −4.6 | 69.4 | 63.0 | 15.4 | nm | |
| 14 | $CDCl_3$ ($SiMe_2$) | −347.6 | −3.1 | 69.2 | 63.1 | 16.0 | nm | |
| | ($SiPh_2$) | −351.0 | −21.7 | 70.1 | 83.8 | 18.1 | nm | $^1J_{SiN}$ = 15.3 ($SiMe_2$)<br>$^3J_{SiN}$ = 2.8 |
| 15[d] | $CDCl_3$ | −341.7 | −8.2 | 67.0 | 64.0 | 16.9 | nm | |
| 16 | $CDCl_3$ ($NSi_3$) | nm | −6.8 | nm | 64.1 | 9.8 | 8.2 | |
| | ($NSi_2$) | | | | | 14.3 | 8.7 | |

[a] Chemical shifts (δ) in ppm relative to $Me_4Si$ ($^{29}Si$) and $MeNO_2$ ($^{15}N$); spin–spin coupling constants ($J$) in Hz; isotopic shifts (Δ) in ppb. [b] For the SiMe group. [c] Reference 10. [d] Reference 8. [e] nm = not measured.

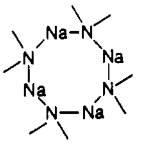
The less abrupt slope of the correlation line, as compared with the slope found for the analogous relation in aminosilanes ($^1J_{SiN} = 0.41^1J_{SiC} - 7.3$),[10] results from the lower electronegativities of substituents on the N atom in silazanes.

An increase in the electronegativities of substituents on the N atom in the NR series $SiR_3$ < H < $t$-Bu (compounds 3, 8, and 9) also a rise in $^1J_{SiN}$. At the same time, a parallel increase in $^1J_{NH}$ was observed (Table I). However, it has been shown earlier[14] that analogous changes in $^{15}N$–$^1H$ couplings are not related to changes in the hybridization of the N atom and that the quantitative relationships between $^1J_{NH}$ and N hybridization found for organic compounds in this case are not valid.[15] Similarly, $^1J_{SiN}$ changes in this series should be interpreted in terms of eq 1 and not eq 2. Hence, an increase in $^1J_{SiN}$ with the electronegativity of substituents at the N atom is related to the greater values of $\pi_{SiN}$ (eq 1) and not to a gain in the planarity of the N atom, as follows from eq 2.

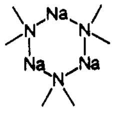
$(R_3Si)_2NH$
1: $R_3 = Me_3$
2: $R_3 = Me_2Ph$
3: $R_3 = MePh_2$
4: $R_3 = Me_2Cl$
5: $R_3 = Me_2O(SiMe_2O)_5SiMe_3$

$(Me_3Si)_2NNa$ 6
$Me_3SiNHOSiMe_3$ 7
$Ph_2MeSiNH_2$ 8
$Ph_2MeSiNH$-$t$-Bu 9

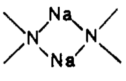
The $\pi_{SiN}$ value depends essentially on the overlap integral of the valence s orbitals of Si and N ($\beta_{SiN}$) atoms. $\beta_{SiN}$ declines with the decreasing electronegativities of substituents. Thereby, $\pi_{SiN}$ (and therefore the contribution of FC term) can drop to zero and then assume negative values. Therefore, in the presence of several electropositive substituents on the N (and Si) atom a certain departure from the common pattern is possible. This situation is characteristic of compound 6. In this case, the $^1J_{SiN}$ value (7.8 Hz) is close to that found earlier for $N(SiMe_3)_3$ (7.6 Hz).[16] However, in view of the lower electronegativity of the Na atom, one would expect a substantial drop in $^1J_{SiN}$ in compound 6. A further decrease in $^1J_{SiN}$ can take place in the case of formation of associates of the type 6a–c in solution (the tetramers 6a were found as crystals[17]). On the other hand, a substantially lower $^1J_{SiC}$ value indicates a redistribution of valence s electrons in favor of the Si–N bond whereas a considerable $^{29}Si$ upfield resonance shift (see Table I) is consistent with the high degree of $d_\pi$–$p_\pi$ conjugation in the Si–N bond (low polarity of the Si–N bond).[8,18] To intepret $^1J_{SiN}$ more definitely it is necessary to determine the sign of this coupling which is possible only for an isotopically enriched sample.



6a



6b



6c

An anomalously low value of $^1J_{SiN}$ (6.5 Hz) was observed for compound 7. $^1J_{NH}$ has a decreased value, too (64.8 Hz). Probably, the enhancement of nitrogen pyramidality related to a rise in electronegativity of substituent and/or the influence of the O atom unshared electron pairs on the $^1J$ values may be responsible for this phenomenon.

Investigation of $^{29}Si$–$^{15}N$ spin–spin coupling constants in cyclosilazanes 10–16 is of especial interest because it allows us to establish the dependence of $^1J_{SiN}$ on molecular geometry. It has been found earlier that $^1J_{SiN}$ declines in smaller cycles.[8] Simultaneously, a downfield shift occurs in $^{29}Si$ spectra. This phenomenon has been attributed to an increase in Si–N bond polarity in smaller cycles.[8] Decreased $^{29}Si$ shielding in the series of compounds 15, 16, 13, 14, and 10–12 is indicative of the appropriate increased polarity in intracyclic Si–N bonds along with decreased ring size and strain. A direct comparison of $^1J_{SiN}$ in cyclodisilazanes 10–12, on the other hand, and in the greater cycles 13–16, on the other, is not justified because the substituents at N differ in their electronegativity. How-

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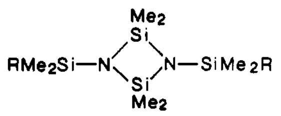
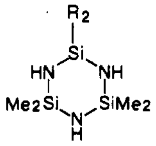
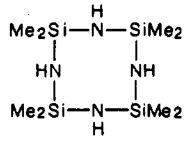


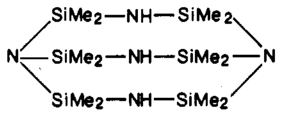
**10**: R = Cl
**11**: R = NH$_2$
**12**: R = OEt



**13**: R = Me
**14**: R = Ph



**15**



**16**

ever, in the case of compound **11** we can compare ${}^{1}J_{\mathrm{SiN}}$ for the intracyclic and exocyclic bonds. ${}^{1}J_{\mathrm{SiN}}$ in the four-membered cycle is considerably smaller (7.4 Hz) than that for the exocyclic bond Si–N (17.8 Hz). As far as electronegativities of the substituents on the respective N and Si atoms are practically equal, this indicates that the nature of Si–N bonds is significantly different, and X-ray data provide further evidence in favor of this observation (see Table II). Since ${}^{1}J_{\mathrm{SiN}}$ can be interpreted in this case by means of eq 2, the data obtained suggest that the N atom s orbitals provide a major contribution to the bonding of nitrogen with the exocyclic Si atom and that bonds in the four-membered cycle are constructed mainly from the N-atom p orbitals. The ${}^{1}J_{\mathrm{SiN}}$ values for the exocyclic Si–N bond of compounds **10**–**12** (16.9–18.3 Hz) are much higher than the values normally observed for NSi$_3$ fragments—6 Hz for N(SiH$_3$)$_3$,[1] 7.6 Hz for N(SiMe$_3$)$_3$,[16] and 9.8 Hz for compound **16**. This phenomenon also is indicative of enhanced s character of exocyclic Si–N bonds in the cyclodisilazanes **10**–**12**.

We managed for the first time to measure geminal ${}^{29}$Si–${}^{29}$Si coupling constants through the nitrogen atom in compounds **10**–**12** (2.0–2.3 Hz). These couplings usually cannot be observed due to considerable broadening of ${}^{29}$Si resonances if the silicon atom is bonded to nitrogen, as a result of fast quadrupolar relaxation of ${}^{14}$N nuclei.[19] It is interesting to note that the obtained values are comparable with the analogous couplings through the oxygen atom (1.02–4.02 Hz) measured recently in cyclosiloxanes.[8,20]

${}^{15/14}$N isotopic effects on ${}^{29}$Si chemical shifts (${}^{1}\Delta$) for compounds under study tend to increase with decreasing ${}^{1}J_{\mathrm{SiN}}$ (see Table I). This phenomenon can be explained by the fact that the sensitivity of ${}^{29}$Si chemical shifts to isotopic substitution increases with the p character of the Si–N bond. It appears from Tables I and II that ${}^{1}\Delta({}^{15/14}\mathrm{N})$ tends to increase and ${}^{1}J_{\mathrm{SiN}}$ tends to decrease with increasing Si–N bond length. No general correlation exists between ${}^{1}J_{\mathrm{SiN}}$ and ${}^{1}\Delta({}^{15/14}\mathrm{N})$ values; however, it can be probably found in particular cases.

**Table II. Si–N Bond Lengths in Silazanes**

| compound | SiN, Å | method of determinatn[a] | ref |
|---|---|---|---|
| **1** | 1.738 | ED | *b* |
| **6**[c] | 1.690 | X | *d* |
| **10** | 1.744 (endo)<br>1.691 (exo) | X | *e* |
| **12**[f] | 1.743 (endo)<br>1.708 (exo) | X | *g* |
| **13** | 1.728 | ED | *h* |
| **15** | 1.722 (boat)<br>1.734 (chair) | X | *i* |
| **16** | 1.749 (NSi$_2$)<br>1.749 (NSi$_3$) | X | *j* |

[a] ED stands for electron diffraction; X stands for X-ray crystal analysis. [b] Fieldberg, T. *J. Mol. Struct.* **1984**, *112*, 159. [c] Tetramer. [d] Reference 17. [e] Gurkova, S. N.; Gusev, A. I.; Alekseev, N. V.; Varezhkin, Yu. M.; Morgunova, M. M.; Zhinkin, D. Ya. *Zh. Strukt. Khim.* **1981**, *1*, 173. [f] OR = OSiMe(OSiMe$_2$)$_2$O. [g] Shklover, V. E.; Adyaasuren, P.; Kotrelev, G. V.; Zhdanova, E. A.; Svistunov, V. S.; Struchkov, Yu. T. *Zh. Strukt. Khim.* **1980**, 2, 94. [h] Rozsondai, B.; Hargittai, T.; Golubinskii, A.; Vilkov, L. V.; Mastryukov, V. S. *J. Mol. Struct.* **1975**, *28*, 339. [i] Smith, G. S.; Alexander, L. E. *Acta Crystallogr.* **1963**, *16*, 1015. [j] Shklover, V. E.; Struchkov, Yu. T.; Kotrelev, G. V.; Kazakova, V. V.; Andrianov, K. A. *Zh. Strukt. Khim.* **1979**, *20*, 96.

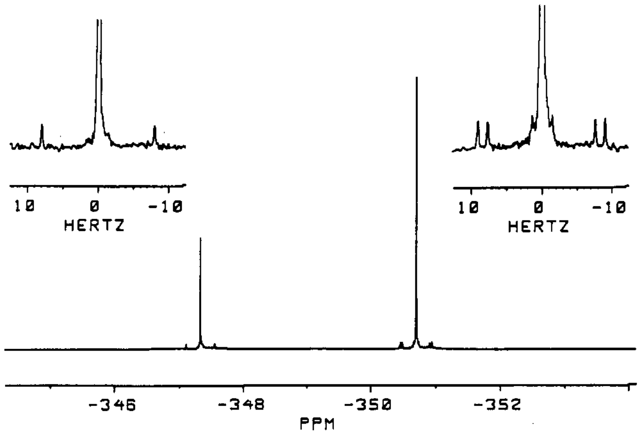


**Figure 1.** The ${}^{15}$N spectrum of compound **14** recorded at 36.5 MHz by the INEPT sequence after 3600 accumulations.

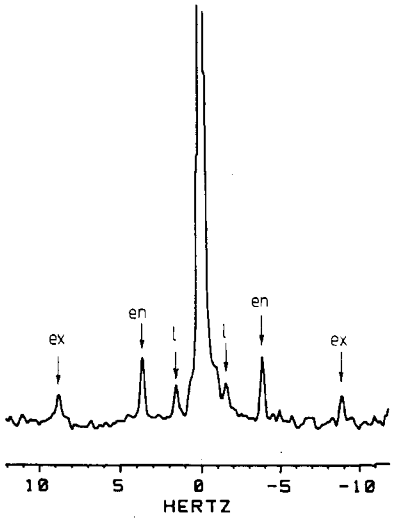


**Figure 2.** ${}^{29}$Si satellites in the ${}^{15}$N spectrum of compound **11** for the endocyclic nitrogen atom. The spectrum was recorded at 36.5 MHz by the INEPT sequence assuming the ${}^{15}$N–${}^{1}$H coupling to the SiMe protons of 1.5 Hz (number of scans, 9200). Designations: ex, exo; en, endo; l, long range.

## Experimental Section

**General Comments.** All measurements were performed on a Bruker WM-360 spectrometer at 71.5 (${}^{29}$Si) and 36.5 (${}^{15}$N) MHz and 303 K using ca. 20–50% solutions and 10-mm sample tubes. Acetone-$d_6$, CDCl$_3$, and C$_6$D$_6$ were dried over 4-Å molecular sieves and used as solvents and internal ${}^{2}$H lock materials.

${}^{29}$Si–${}^{13}$C coupling constants, ${}^{15}$N and ${}^{29}$Si chemical shifts, and ${}^{15/14}$N isotope effects were measured simultaneously with ${}^{1}J_{\mathrm{SiN}}$ measurements. Chemical shifts were referred to external MeNO$_2$ (${}^{15}$N) or Me$_4$Si (${}^{29}$Si). ${}^{15}$N–${}^{1}$H coupling constants were measured in ${}^{15}$N spectra by the basic DEPT pulse sequence.[5]

**Measurement of ${}^{29}$Si–${}^{15}$N Coupling Constants.** All ${}^{29}$Si–${}^{15}$N coupling constants were measured at the natural abundance of

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isotopes. The measurements of $^1J_{\mathrm{SiN}}$ in the case of compounds **1–9** and for the exocyclic Si–N bonds of compounds **10** and **12** posed no problems. With use of polarization transfer from protons, $^{15}$N satellites were observed in the $^{29}$Si spectra under "near ultrahigh resolution" conditions (instrumental broadening of 0.02–0.1 Hz) after 50–100 scans, which corresponds to 2–5 min of accumulation. Their detection was significantly facilitated by the broadening of the central line due to the partially relaxed scalar $^{29}$Si–$^{14}$N coupling,[19] the $^{15}$N satellites remaining narrow. As has been found earlier,[10] the DEPT sequence is favored in such conditions because of a substantial decrease in the intensity of the central line but not of the $^{15}$N satellites.

At low $^1J_{\mathrm{SiN}}$ values the broadening of the central line in the $^{29}$Si spectra was negligible (compounds **6** and **7** and the intracyclic Si atom in compounds **10–12**), hence complicating $^1J_{\mathrm{SiN}}$ measurements.[9] In these cases, $^{29}$Si–$^{15}$N coupling constants were measured by ultrahigh resolution methodology,[21] as described earlier.[22] This enabled, for the first time, the measurement of geminal $^{29}$Si–$^{29}$Si coupling constants via the nitrogen atom in compounds **10–12** (see Table I) as well as the observation of $^{15}$N satellites in the $^{29}$Si spectra of compounds even with two nitrogen atoms at Si (compound **16** and the intracyclic Si atom in compounds **10–12**). In the latter case the $^{15}$N satellites are also broadened due to partially relaxed scalar $^{29}$Si–$^{14}$N coupling in the $^{15}$N–$^{29}$Si–$^{14}$N fragment. At higher $^1J_{\mathrm{SiN}}$ values this broadening was too large to observe the $^{15}$N satellites (compounds **13–15** and the exocyclic Si atom in compound **12**). In these cases $^1J_{\mathrm{SiN}}$ were measured in $^{15}$N spectra.

With the proton attached to the N atom (compounds **13–16**) the INEPT method allows one to observed $^{29}$Si satellites in $^{15}$N spectra after 2000–4000 scans (1–2 h of accumulation). If several peaks are present in the $^{15}$N spectra of silazanes, the $^{29}$Si satellites can facilitate their assignment (see Figure 1). In the absence of NH protons, long-range $^{15}$N–$^1$H coupling to the SiMe protons of 1–1.5 Hz was assumed for the INEPT sequence[9] permitting observation of $^{29}$Si satellites after 6–12 h of accumulation (Figure 2). For the first time, long-range couplings $^{29}$Si–$^{15}$N were observed in $^{15}$N spectra (Figures 1 and 2).

**Registry No.** **1**, 999-97-3; **2**, 3449-26-1; **3**, 7453-26-1; **4**, 3449-24-9; **5**, 114691-61-1; **6**, 1070-89-9; **7**, 22737-37-7; **8**, 7482-02-2; **9**, 91308-43-9; **10**, 2329-10-4; **11**, 13270-82-1; **12**, 13270-86-5; **13**, 1009-93-4; **14**, 50781-21-0; **15**, 1020-84-4; **16**, 63374-38-9.

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# Studies on Olefin-Coordinating Transition-Metal Carbene Complexes. 15.[†] Novel Reaction of (Limonene)tricarbonyliron with Nucleophiles: Synthesis, Spectra, and Crystal and Molecular Structure of Several Carbene and Isomerized Carbene Complexes Therefrom

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Reaction of (limonene)tricarbonyliron (1) with aryllithium reagents, ArLi (Ar = $C_6H_5$, *p*-, *o*-$CH_3C_6H_4$, *p*-$CH_3OC_6H_4$, *p*-$CF_3C_6H_4$), in ether at low temperature afforded acylmetalate intermediates. Subsequent alkylation with $Et_3OBF_4$ in aqueous solution at 0 °C gave five new complexes, $(\eta^4\text{-}C_{10}H_{16})(CO)_2FeC(OC_2H_5)Ar$ (**4**, Ar = *o*-$CH_3C_6H_4$) and $(\eta^3\text{-}C_{10}H_{16})(CO)_2FeC(OC_2H_5)Ar$ (**2**, Ar = $C_6H_5$; **3**, Ar = *p*-$CH_3C_6H_4$; **5**, Ar = *p*-$CH_3OC_6H_4$; **6**, Ar = *p*-$CF_3C_6H_4$). The structures of two of the new compounds have been determined by X-ray diffraction analyses. Complexes **3** and **4** crystallize in the monoclinic system: space group $P2_1/c$ with $a$ = 14.188 (3) Å, $b$ = 9.157 (2) Å, $c$ = 16.269 (3) Å, $\beta$ = 106.22 (2)°, $V$ = 2029.5 (8) Å$^3$, $Z$ = 4, $D_{\mathrm{calcd}}$ = 1.30 g/cm$^3$, $R$ = 0.0318, and $R_w$ = 0.0306 for 1728 reflections with $F_o \geq 3\sigma(F_o)$ for **3**; space group $P2_1/a$ with $a$ = 7.795 (5) Å, $b$ = 26.677 (13) Å, $c$ = 9.989 (5) Å, $\beta$ = 93.19 (4)°, $V$ = 2047.0 (17) Å$^3$, $Z$ = 4, $D_{\mathrm{calcd}}$ = 1.27 g/cm$^3$, $R$ = 0.0847, and $R_w$ = 0.0616 for 1755 reflections with $F_o \geq 3\sigma(F_o)$ for **4**.

## Introduction

In recent years, the syntheses and characterizations of olefin-coordinating transition-metal carbene complexes have been of interest in this laboratory.[2-7] In extension of our research, we found that polyolefin ligated carbonyliron compounds reacted with aryllithium reagents to give acylmetalate intermediates that could be alkylated with $Et_3OBF_4$ to give variety of products. For example, the reaction of (butadiene)- and (isoprene)tricarbonyliron, where the olefin ligands are a straight-chain and a branched-chain conjugated diene, gave a series of novel isomerized olefin-coordinated carbene complexes,[2,3] while in the case of (cyclooctatetraene)-, (cycloheptatriene)-, and (1,3-cyclohexadiene)-, and (norbornadiene)tricarbonyliron a series of novel diallyliron complexes were obtained.[4-7] In the present work, we attempt a similar reaction with (limonene)tricarbonyliron (1),[8] where the limonene is

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