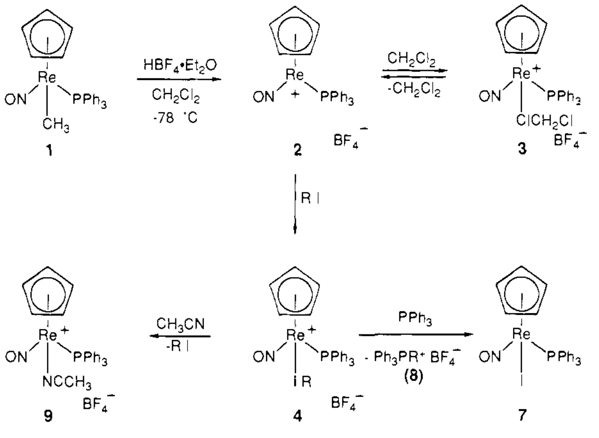
Scheme I. Synthesis and Reactions of Alkyl Iodide Complexes



a, $R = CH_3$ (67%)
b, $R = CH_2CH_3$ (70%)
c, $R = CH_2CH_2CH_3$ (87%)
d, $R = CH_2Si(CH_3)_3$ (81%)

those in $(CO)_4Re(\mu\text{-}I)_2Re(CO)_4$ and a related terminal iodide complex (2.81–2.83 Å).[8] However, the structure is not appreciably distorted along an oxidative addition reaction coordinate, as the I–Re–P and I–Re–N bond angles (91.1–97.0°) are close to idealized octahedral values (90°). Bond angles in iodonium salts $RR'I^+X^-$ are typically ca. 95°, and a short I^+/X^- "secondary bond" (2.5–3.5 Å) is usually found.[9] In contrast, the Re–I–Cl bond angle in **4d**·$(CH_2Cl_2)_{0.5}$ is 102.5 (5)°, and the BF_4^- fluorine atoms are ≥4.00 Å from the iodine. Finally, the P–Re–I–Cl torsion angle is 169°, which places the alkyl substituent in the region between the small NO and medium cyclopentadienyl ligands.

Thermal and chemical reactions of **4a–c** have been briefly studied. First, **4a-c** decompose over the course of 48 h in CD_2Cl_2 at 25 °C to give primarily the bridging halide complexes (*SS*,*RR*)-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\mu\text{-}X)(PPh_3)(NO)Re(\eta^5\text{-}C_5H_5)]^+BF_4^-$ (**5**, X = Cl,[4] 28–43%; **6**, X = I, 46–61%; assayed by ^1H and ^{31}P NMR with Ph_3SiCH_3 standard). The structure of new compound **6** was confirmed by an independent synthesis from iodide complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(I)$ (**7**)[10] and $Ag^+BF_4^-$.[11] The mechanisms of formation of **5** and **6** are under investigation.

Reactions of **4a–c** with PPh_3 (1.2 equiv, 0.04 M in $CDCl_3$, 25 °C, assayed as above) were complete within 15 min (Scheme I). Alkylation products $Ph_3PR^+BF_4^-$ (**8**, 93–86%) and iodide complex **7** (>99–95%) formed. Product identities were confirmed by ^1H and ^{31}P NMR comparison to independently prepared authentic samples (Supplementary Material). Importantly, reactions of CH_3I, CH_3CH_2I, and $CH_3CH_2CH_2I$ with PPh_3 under identical conditions were 70% complete after 4 h, and ≤10% and <2% complete after 18 h, respectively. Thus, coordinated alkyl iodides are markedly activated toward nucleophilic attack.

Reactions of **4a–c** with CH_3CN (2.0 equiv, 0.04 M in CD_2Cl_2, 25 °C, assayed as above) were complete within 24 h (Scheme I). Displacement of the alkyl iodide ligand occurred to give RI (82–72%) and acetonitrile complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NCCH_3)]^+BF_4^-$ (**9**, 87–82%).[12] Small amounts of bridging halide complexes **5** and **6** also formed. Product identities were confirmed by GLC and NMR comparison to authentic samples.

The synthesis of other alkyl halide complexes has been briefly explored. Analogous reactions of **1**, $HBF_4\cdot Et_2O$, and ethyl bromide or ethyl chloride gave ethyl halide complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(XCH_2CH_3)]^+BF_4^-$ (**10b**, X = Br; **11b**, X = Cl). This structural assignment was made on the basis of ^1H, ^{13}C, and ^{31}P NMR spectra that closely match those of **4b**. Complexes **10b** and **11b** decompose between −20 and 0 °C. Analogous pentamethylcyclopentadienyl complexes also can be prepared and will be described in a later publication.

In summary, a variety of alkyl halide complexes are now readily accessible and can be expected to exhibit a rich and useful coordination chemistry.

Acknowledgment. We thank the NSF for support of this research and the NIH for a postdoctoral fellowship (C.H.W.).

Supplementary Material Available: Tables of data for new compounds[5] and tables of crystallographic data, isotropic thermal parameters, bond lengths, bond angles, torsion angles, and anisotropic thermal parameters and a figure for **4d**·$(CH_2Cl_2)_{0.5}$ (16 pages); table of observed and calculated structure factors (34 pages). Ordering information is given on any current masthead page.

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[8] (a) Ciani, G.; D'Alfonso, G.; Freni, M.; Romiti, P.; Sironi, A. *J. Organomet. Chem.* **1979**, *170*, C15. (b) Darst, K. P.; Lenhert, P. G.; Lukehart, C. M.; Warfield, L. T. *Ibid.* **1980**, *195*, 317.

[9] (a) Khotsyanova, T. L. *Dokl. Akad. Nauk. SSSR* **1956**, *110*, 7. (b) Batchelor, R. J.; Birchall, R.; Sawyer, J. F. *Inorg. Chem.* **1986**, *25*, 1415. (c) Stang, P. J.; Surber, B. W.; Chen, Z.-C.; Roberts, K. A.; Anderson, A. G. *J. Am. Chem. Soc.* **1987**, *109*, 228.

[10] Merrifield, J. H.; Fernández, J. M.; Buhro, W. E.; Gladysz, J. A. *Inorg. Chem.* **1984**, *23*, 4022.

[11] (a) Fischer, E. O.; Moser, E. *Inorg. Synth.* **1970**, *12*, 35. (b) Symon, D. A.; Waddington, T. C. *J. Chem. Soc., Dalton Trans.* **1974**, 79.

[12] Merrifield, J. H.; Lin, G.-Y.; Kiel, W. A.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5811.

Stereoselective Formation of Conjugated Enynes via Coupling of Alkynyliodonium Tosylates and Vinylcopper Reagents

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Conjugated enynes represent an important class of aliphatic compounds. They occur in a number of natural products[1] as well as provide an attractive route for stereospecific 1,3-diene synthesis.[2] Yet outside of Stille's[3] recent, elegant report on the Pd-catalyzed direct coupling of acetylenic tin reagents with vinyl iodides and related Pd-mediated couplings,[4] few methods are available for the simple formation of stereoisomeric 1,3-enynes.[5]

The current renaissance in tricoordinate iodine chemistry[6] and the ready availability of new alkynyliodonium salts,[7] together with our recent success in the use of these species in the formation of hitherto unknown, unique, alkynyl esters,[8] led us to explore their use in coupling reactions. Herein we report the stereoselective formation of 1,3-enynes, via a new carbon–carbon bond-forming reaction, involving the direct coupling of alkynyliodonium tosylates **1** with alkenylcopper(I) reagents.

Alkynylphenyliodonium tosylates **1** are readily available in reasonable yields[8a,9] by interaction of Koser's reagent,[10] PhI-

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[1] (a) Normant, J. F.; Alexakis, A. *Synthesis* **1981**, 841. (b) Mori, K. *The Total Synthesis of Natural Products*; ApSimon, J., Ed.; Wiley: New York, 1981.

[2] Zweifel, G.; Polston, N. L. *J. Am. Chem. Soc.* **1970**, *92*, 4068. Rossi, R.; Carpita, A.; Quirici, M. G.; Gandenzi, M. L. *Tetrahedron* **1982**, *38*, 361. Ulan, J. G.; Kuo, E.; Maier, W. F.; Rai, R. S.; Thomas, G. *J. Org. Chem.* **1987**, *52*, 3126. Ulan, J. G.; Maier, W. F.; Smith, D. A. *J. Org. Chem.* **1987**, *52*, 3132 and references therein.

[3] Stille, J. K.; Simpson, J. H. *J. Am. Chem. Soc.* **1987**, *109*, 2138.

[4] Heck, R. F. *Palladium Reagents in Organic Synthesis*; Academic: New York, 1985. Scott, W. J.; McMurry, J. E. *Acc. Chem. Res.*, in press.

[5] Brown, H. C.; Molander, G. A. *J. Org. Chem.* **1981**, *46*, 646. Commercon, A.; Normant, J. F.; Villieras, J. *Tetrahedron* **1980**, *36*, 1215. Hoshi, M.; Masuda, Y.; Arase, A. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2855.

[6] Moriarty, R. M.; Prakash, O. *Acc. Chem. Res.* **1986**, *19*, 244. Varvoglis, A. *Synthesis* **1983**, 709. Varvoglis, A. *Chem. Soc. Rev.* **1981**, *10*, 377. Banks, D. F. *Chem. Rev.* **1966**, *66*, 243.

[7] Koser, G. F. In *The Chemistry of Functional Groups, Supplement D*; Patai, S., Rappoport, Z., Eds.; Wiley: 1983; Chapter 25, pp 1323–24.

[8] (a) Stang, P. J.; Surber, B. W.; Chen, Z. C.; Roberts, K. A. *J. Am. Chem. Soc.* **1987**, *109*, 228. (b) Stang, P. J.; Boehshar, M.; Lin, J. *J. Am. Chem. Soc.* **1986**, *108*, 7832. (c) Stang, P. J.; Surber, B. W. *J. Am. Chem. Soc.* **1985**, *107*, 1452.

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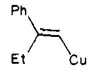
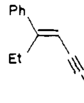
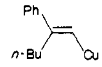
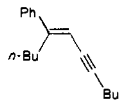
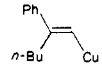
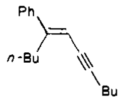
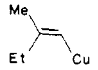
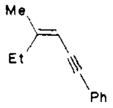
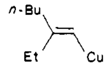
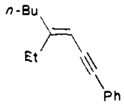
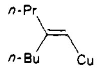
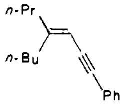
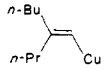
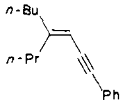
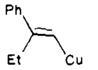
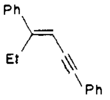
Table I. Alkynyliodonium/Vinylcopper Reagent Couplings

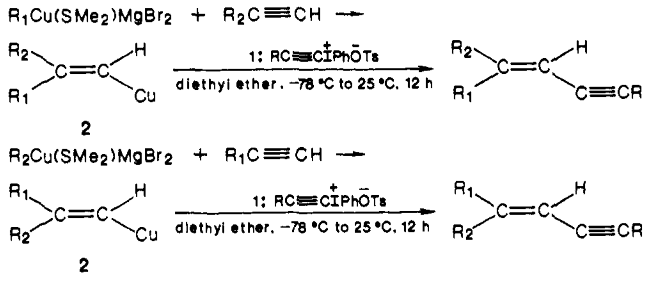
entry	alkynyliodonium salt	RCu	acetylene	alkenylcopper	enyne	yield (%)	stereoselectivity (%)
1	t-BuC≡CI$^+$PhO$^-$Ts	EtCu	PhC≡CH			79	>98[b]
2	t-BuC≡CI$^+$PhO$^-$Ts	n-BuCu	PhC≡CH			94	>98[b]
3	n-BuC≡CI$^+$PhO$^-$Ts	n-BuCu	PhC≡CH			78	>98[b]
4	PhC≡CI$^+$PhO$^-$Ts	EtCu	MeC≡CH			47	>98[b]
5	PhC≡CI$^+$PhO$^-$Ts	EtCu	n-BuC≡CH			52	>98[b]
6	PhC≡CI$^+$PhO$^-$Ts	n-BuCu	n-PrC≡CH			46	>99[c]
7	PhC≡CI$^+$PhO$^-$Ts	n-PrCu	n-BuC≡CH			48	>99[c]
8	PhC≡CI$^+$PhO$^-$Ts	EtCu	PhC≡CH			54	>98[b]

[a] Isolated yield based upon the alkynyliodonium tosylate. [b] Based[15] upon ^{1}H and ^{13}C NMR. [c] Based upon GC.

(OH)OTs, with terminal alkynes. Likewise a wide variety of alkenylcopper reagents **2** are easily made by addition of alkylcopper reagents to terminal acetylenes.[1a,11,12] This latter reaction is known[12] to occur by a regio- and stereoselective syn addition resulting in stereoisomerically pure (E)- or (Z)-alkenylcopper reagents.[1a,11,12] Addition of the solid alkynyliodonium salt **1** to the alkenylcopper reagent **2** (Scheme I) in diethyl ether at −78 °C, followed by warming to room temperature, stirring overnight, and standard workup, results in the stereoisomeric 1,3-enynes, as summarized in Table I. Products were identified by spectral means and were GC pure.[13]

As the data in Table I indicate this method affords a variety of 1,3-enynes in good yields. More importantly the reaction is highly (most likely completely)[15] stereoselective with *retention* of alkene geometry, resulting in a single geometric isomer around the olefin. What makes the method particularly attractive, as demonstrated by entries 6 and 7 and summarized in Scheme I, is that by simple choice of the order of addition of the alkylcopper reagent to the alkyne *either* geometric isomer around the olefin may be obtained in pure form.

Scheme I



Like all organocopper reactions to date[11,16] little is known about the mechanism of this new, novel coupling process. In analogy with known cuprate coupling reactions[11,16] with vinyl halides we

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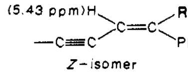
(9) Rebrovic, L.; Koser, G. F. *J. Org. Chem.* **1984**, *49*, 4700.

(10) Koser, G. F.; Wettach, R. H. *J. Org. Chem.* **1977**, *42*, 1476. Neiland, O.; Karele, B. *J. Org. Chem. USSR (Engl. Transl.)* **1970**, *6*, 889.

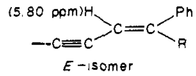
(11) Posner, G. H. *Org. React.* **1975**, *22*, 253. Posner, G. H. *An Introduction to Synthesis Using Organocopper Reagents*; Wiley: New York, 1980.

(12) Hudrlik, P. F.; Hudrlik, A. M. In *The Chemistry of the Carbon-Carbon Triple Bond*; Patai, S., Ed.; Wiley: New York, 1978; Part 1, p 233. Normant, J. F.; Cahiez, G.; Bourgain, M.; Chuit, C.; Villiêras, J. *Bull. Soc. Chim. Fr.* **1974**, 1656.

(13) All products had IR, ^{1}H and ^{13}C NMR, and mass spectra in accord with the proposed structures. In particular all enynes had a strong molecular ion in the mass spec (EI), characteristic C≡C absorption in the IR around 2195 cm^{-1}, and C≡C signals in the expected range in the ^{13}C spectra. Olefin stereochemistry was assigned by NMR and from the known stereochemistry of the vinylcuprate. For example, for t-BuC≡C—CH═C(Et)Ph the calculated, proton chemical shifts for the vinylic hydrogen, by known[14] group additives, are as follows. The experimental value in CDCl$_3$ is 5.70 ppm.



Z-isomer



E-isomer

(14) Pretsch, E.; Seibl, J.; Simon, W.; Clere, T. *Tabellen zur Strukturaufklärung Organischer Verbindung mit Spektroskopischen Methoden*; Springer-Verlag: 1981; p H215. Pascual, C.; Meier, J.; Simons, W. *Helv. Chim. Acta* **1966**, *49*, 164. Tobey, S. W. *J. Org. Chem.* **1969**, *34*, 1281.

(15) In no case was *any* of the other isomer seen by either ^{1}H or ^{13}C NMR for all the enynes in Table I. Since both isomers were in hand for entries 6 and 7, GC showed no cross contamination of isomers. Hence these are *conservative lower* estimates on the stereoselectivity of this process. We believe that the coupling itself is 100% stereoselective and the isomer purity is controlled by the stereoselectivity of alkylcuprate additions to the terminal alkynes, known to be very high.[11,12]

(16) Jukes, A. E. *Adv. Organometallic Chem.* **1974**, *12*, 215–322.

assume that the reaction proceeds through an oxidative addition of the alkynyl species to give a Cu(III) intermediate, followed by reductive elimination and coupling.

In summary we have developed a novel, new carbon–carbon bond-forming reaction that affords stereoisomerically pure 1,1-disubstituted 1,3-enynes via the coupling of alkynyliodonium tosylates with vinylcopper reagents. The method allows the creation of a conjugated enyne with a trisubstituted olefin component with complete control of olefin geometry. We expect this simple process, complementing the known Pd-catalyzed olefin–alkyne couplings,[3,4] to be of considerable synthetic utility. Further studies delineating the full scope and limitations as well as the mechanism of this new process are underway.

Acknowledgment. This research was supported by the NCI of NIH, Grant 10RCA16903-11.

Two-Coordinate, Nonlinear, Crystalline d^6 and d^7 Complexes: Syntheses and Structures of $M\{N(SiMePh_2)_2\}_2$, M = Fe or Co

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Received August 17, 1987

The use of large amido ($-NR_2^-$) ligands has allowed the synthesis, throughout the periodic table, of a considerable number of compounds which have low coordination numbers.[2] In particular, the bis(trimethylsilyl)amido[3] and, more recently, diphenylamido[4,5] ligands have enabled many transition-metal complexes having the fairly rare coordination number three to be synthesized and structurally characterized. However, even these bulky ligands are unable to permit isolation of crystalline two-coordinate transition-metal complexes. For example, in the series $M\{N(SiMe_3)_2\}_2$, M = Mn,[6] Fe,[7] Co,[8] or Ni,[6] the crystal structures of the Mn[9,10] and Co[10] complexes reveal a dimeric structure involving bridging amido groups and three coordinate metals. Similarly, structural studies of $M(NPh_2)_2$, M = Mn,[11] Fe,[12] Co,[5] or Ni[5], show that they are also dimeric in the crystalline phase. However, electron diffraction data[13] on $M\{N(SiMe_3)_2\}_2$, M = Mn, Fe, or Co, show that they are monomeric in the vapor with a structure similar to $Zn\{N(SiMe_3)_2\}_2$.[14] In addition, earlier cryoscopic, infrared, and absorption spectral studies on $Co\{N(SiMe_3)_2\}_2$ indicated that it was monomeric in solution.[15] These data suggested to us that if the size of the amide ligand were to be increased, two-coordinate, crystalline species might result. Here, we report that the bis(diphenylmethylsilyl)amido group $-N\{SiMePh_2\}_2$ is sufficient to induce mononuclearity and enable the first X-ray crystal structures of the two-coordinate d^6 and d^7 species, $M\{N(SiMePh_2)_2\}_2$, M = Fe, **1**, or Co, **2**, to be obtained.

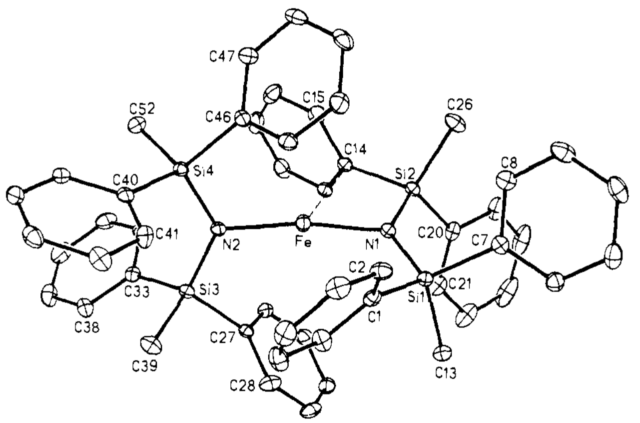

Figure 1. Computer generated plot of **1** (ellipsoids at 30% probability level). Important bond distances (Å) and angles (deg) are as follows: Fe–N(1) = 1.916 (2), Fe–N(2) = 1.918 (2), N(1)–Si(1) = 1.722 (2), N(1)–Si(2) = 1.713 (2), N(2)–Si(3) = 1.715 (2), N(2)–Si(4) = 1.717 (2), Si–C(av) = 1.877, Fe--C(14) = 2.695 (5), N(1)–Fe–N(2) = 169.0 (1), Fe–N(1)–Si(1) = 121.9 (1), Fe–N(1)–Si(2) = 106.1 (1), Si(1)–N(1)–Si(2) = 131.8 (1), Fe–N(2)–Si(3) = 117.8 (1), Fe–N(2)–Si(4) = 115.0 (1), Si(3)–N(2)–Si(4) = 127.1 (1), dihedral angle between NSi_2 planes 76.1.

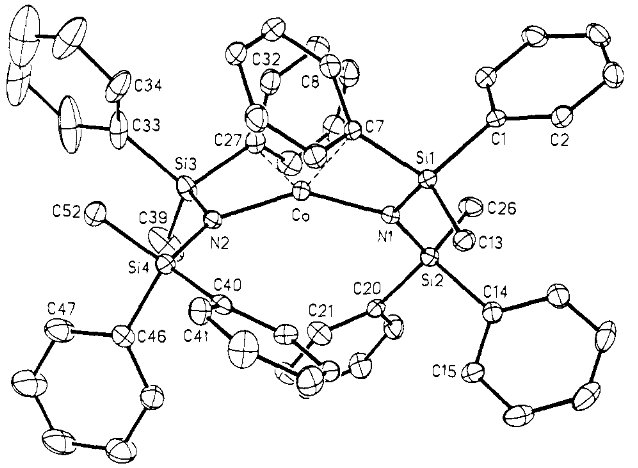

Figure 2. Computer generated plot of **2** (ellipsoids at 30% probability level). Important bond distances (Å) and angles (deg) are as follows: Co–N(1) = 1.898 (3), Co–N(2) = 1.904 (3), N(1)–Si(1) = 1.718 (4), N(1)–Si(2) = 1.725 (4), N(2)–Si(3) = 1.710 (3), N(2)–Si(4) = 1.716 (3), Si–C(av) = 1.880, Co--C(7) = 2.588 (7), Co--C(27) = 2.584 (7), N(1)–Co–N(2) = 147.0 (1), Co–N(1)–Si(1) = 103.8 (2), Co–N(1)–Si(2) = 130.7 (2), Si(1)–N(1)–Si(2) = 125.5 (2), Co–N(2)–Si(3) = 103.0 (2), Co–N(2)–Si(4) = 130.2 (2), Si(3)–N(2)–Si(4) = 126.7 (2), dihedral angle between NSi_2 planes 64.0.

The complexes **1** and **2** were synthesized in a straightforward manner in high yield. In the case of **1**, a suspension of $FeBr_2$ (0.43 g, 2 mmol) in Et_2O (20 mL) cooled in an ice bath was treated dropwise with an Et_2O (20 mL) solution of $LiN(SiMePh_2)_2$ formed from $HN(SiMePh_2)_2$[16,17] (1.64 g, 4 mmol) and *n*-BuLi (2.5 mL of 1.6 M solution in hexanes). Stirring for 3 h at ambient temperature gave a brown solution from which the volatiles were then removed under reduced pressure. The residue was redissolved in toluene (15 mL) and filtered. The volume of the yellow-brown solution was halved under reduced pressure, and *n*-hexane (~5 mL) was added until incipient crystallization occurred. Cooling

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[1] Fellow of the A. P. Sloan Foundation 1985–1987.

[2] Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. *Metal and Metalloid Amides*; Ellis Horwood: Chichester, England, 1980. Bradley, D. C.; Chisholm, M. H. *Acc. Chem. Res.* **1976**, *9*, 273. Bradley, D. C. *Chem. Br.* **1975**, *11*, 393. Eller, P. G.; Bradley, D. C.; Hursthouse, M. B.; Meek, D. W. *Coord. Chem. Revs.* **1977**, *24*, 1.

[3] Harris, D. H.; Lappert, M. F. *J. Organomet. Chem. Libr.* **1976**, *2*, 13. Bradley, D. C.; Copperthwaite, R. G. *Inorg. Synth.* **1978**, *18*, 112.

[4] Frölich, H. O.; Märkisch, V. *Z. Chem.* **1975**, *15*, 276. Brito, V.; Frölich, H. O.; Müller, B. *Z. Chem.* **1979**, *19*, 28. Frölich, H. O.; Römhild, W. *Z. Chem.* **1979**, *19*, 414. Frölich, H. O.; Römhild, W. *Z. Chem.* **1980**, *20*, 154.

[5] Hope, H.; Olmstead, M. M.; Murray, B. D.; Power, P. P. *J. Am. Chem. Soc.* **1985**, *107*, 712.

[6] Bürger, H.; Wannagat, U. *Monatsh. Chem.* **1964**, *95*, 1099. Horvath, B.; Möseler, R.; Horvath, E. G. *Z. Anorg. Allg. Chem.* **1978**, *450*, 165.

[7] Andersen, R. A., personal communication.

[8] Bürger, H.; Wannagat, U. *Monatsh. Chem.* **1963**, *94*, 1007.

[9] Bradley, D. C.; Hursthouse, M. B.; Malik, K. M. A.; Moseler, R. *Transition. Met. Chem.* (*Weinheim, Ger.*) **1978**, *3*, 253.

[10] Murray, B. D.; Power, P. P. *Inorg. Chem.* **1984**, *23*, 4584.

[11] Bartlett, R. A.; Odink, D.; Power, P. P., unpublished results.

[12] Olmstead, M. M.; Power, P. P., unpublished results.

[13] Andersen, R. A.; Green, J. C.; Lappert, M. F.; Leung, W.-P.; Faegai, K.; Haaland, A.; Rypdal, K. *Acta Chem. Scand.*, submitted for publication.

[14] Haaland, A.; Hedberg, K.; Power, P. P. *Inorg. Chem.* **1984**, *23*, 1972.

[15] Bradley, D. C.; Fisher, K. J. *J. Am. Chem. Soc.* **1971**, *93*, 2058.

[16] Andrianov, K. A.; Kononov, A. M.; Makanova, N. N. *Zh. Obshch. Khim.* **1966**, *36*, 895.

[17] The structure of $HN(SiMePh_2)_2$ was solved by X-ray diffraction. It is planar at nitrogen with a wide SiNSi angle of 131.6 (1)° and N–Si bond distances of 1.720 (2) Å. Dias, H. V. R.; Power, P. P., unpublished results.

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