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.

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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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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.

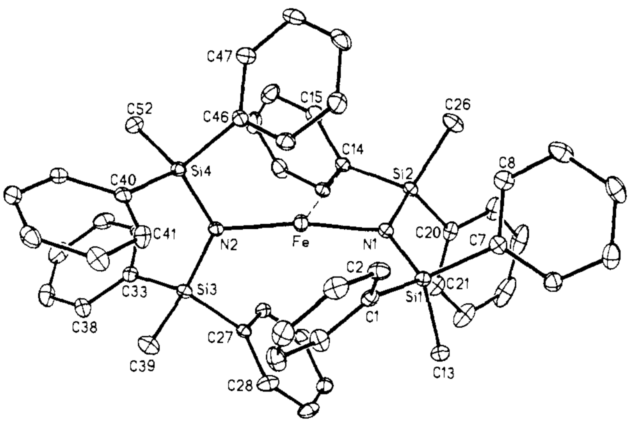

Figure 1. Computer generated plot of **1** (ellipsoids at 30% probability level). Important bond distances (Å) and angles (deg) are as follows: Fe-N(1) = 1.916 (2), Fe-N(2) = 1.918 (2), N(1)-Si(1) = 1.722 (2), N(1)-Si(2) = 1.713 (2), N(2)-Si(3) = 1.715 (2), N(2)-Si(4) = 1.717 (2), Si-C(av) = 1.877, Fe--C(14) = 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.

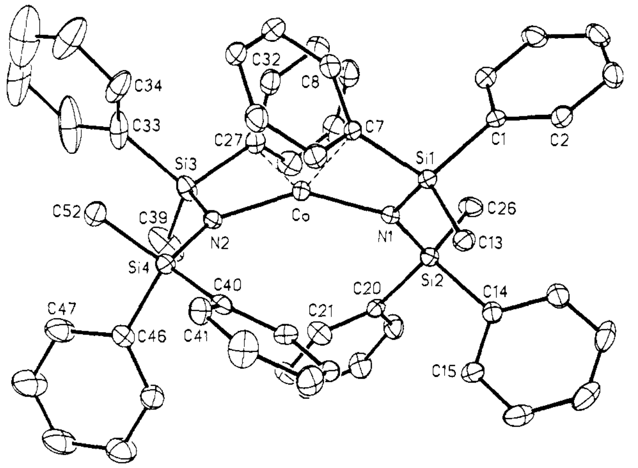

Figure 2. Computer generated plot of **2** (ellipsoids at 30% probability level). Important bond distances (Å) and angles (deg) are as follows: Co-N(1) = 1.898 (3), Co-N(2) = 1.904 (3), N(1)-Si(1) = 1.718 (4), N(1)-Si(2) = 1.725 (4), N(2)-Si(3) = 1.710 (3), N(2)-Si(4) = 1.716 (3), Si-C(av) = 1.880, Co--C(7) = 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.

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.

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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in a −20 °C freezer overnight afforded the product as very pale amber crystals; yield 1.1 g, 63%, mp = 158–160 °C (dec). In the case of cobalt, $CoCl_2$ was used to give a 65% yield of turquoise-dark green dichroic crystals; mp = 147–150 °C (with softening ca. 100 °C).

The structures of **1** and **2** were determined by X-ray crystallography[18] and are illustrated in Figures 1 and 2. Both compounds are monomeric with iron and cobalt bonded to two $-N(SiMePh_2)_2$ groups which are planar at nitrogen. Considerable deviation from the expected N–M–N linearity is apparent in the cobalt complex **2** and to a lesser degree in the iron complex **1**. Outside of d^{10} complexes and two[19] d^5, Mn(II) complexes[20,21] both **1** and **2** constitute rare instances of crystalline, two-coordinate transition-metal compounds, and they are the first such examples for the d^6 or d^7 configurations. In the iron compound the N(1)FeN(2) angle is 169.0 (1)° with an average Fe–N distance of 1.917 (2) Å, which is significantly longer than the 1.84 (2) Å seen in $Fe\{N(SiMe_3)_2\}_2$ vapor.[13] There is a rather long interaction between Fe and C(14) of about 2.7 Å and this is reflected in the assymetry of the FeN(1)Si(1) and Si(2) angles 121.9 (1)° vs 106.1 (1)°. The closest approach of any other phenyl carbons varies from about 2.96 to 3.2 Å, and any such interactions are consequently very weak. This fact is in agreement with the essentially symmetric nature of the FeN(2)Si(3) and Si(4) angles.

In contrast to **1** the central angle, 147.0 (1)°, in the cobalt complex **2** displays much more deviation from linearity. This appears to be a result of the interaction between the metal center and a phenyl ring from each $-N(SiMePh_2)_2$ group as shown by the distances CoC(7) = 2.588 (7) Å and Co–C(27) = 2.584 (7) Å. These interactions are supported by the large asymmetries (≈27°) in the CoNSi angles which are 103.4 (2)° (av) for CoNSi (1 and 3) and 130.5 (2)° (av) for CoNSi (2 and 4); however, detailed examination of the Si–N and C–C distances within the $-N(SiMePh_2)_2$ groups reveal little or no differences which would support the observed distortions. Although the metal centers are electron deficient, a fact which encourages the aromatic ring–metal interaction, there is no ready qualitative explanation for the structural differences between **1** and **2**. Quite possibly, the NMN angle is a "soft" one and even relatively weak interactions elsewhere in the molecule or, perhaps, crystal packing forces can effect large changes in this parameter.

The absorption spectra of both **1** and **2** were recorded in toluene at ambient temperature. The spectrum of **1** is almost featureless in the 400 → 800-nm region with slow rise in absorption toward the UV. A very weak shoulder at 560 nm (17 900 cm^{-1}) is apparent. The spectrum of the cobalt compound **2** displays three absorptions at 526 nm (19 010 cm^{-1}, $\epsilon = 70$), 634 nm (15 770 cm^{-1}, $\epsilon = 125$), and 802 nm (12 470, $\epsilon = 50$). If a linear, two-coordinate geometry is assumed for **2**, then these bands can be assigned[22] to the ${}^4\Sigma_g \rightarrow {}^4\Pi_g(P)$, ${}^4\Sigma_g \rightarrow {}^4\Sigma_g(P)$, and ${}^4\Sigma_g \rightarrow {}^4\Delta_g(F)$ transitions. However, a structural assignment on this basis is not possible, because the three observed bands are also consistent[23] with an approximate trigonal planar (as in a dimer) or a C_{2v} geometry as seen in the X-ray structure. The spectrum of **2** is, in fact, similar to that of solid $Co\{N(SiMe_3)_2\}_2$, which is a dimer, and $CoCl_2$ vapor, which is a linear monomer. Little can be said about the spectrum of **1**, except that within the scan range 300–850 nm it is similar to that of $FeCl_2$ vapor.[24]

It is planned to synthesize other metal (Cr, Mn, Ni) derivatives so that further conclusions may more readily be drawn. In addition, detailed ^1H NMR and magnetic studies on these interesting, two-coordinated species are currently underway.

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Supplementary Material Available: Summary data collection and refinement, tables of atom coordinates, thermal parameters, bond distances and angles, and hydrogen coordinates (15 pages). Ordering information is given on any current masthead page.

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[18] Crystal data with Mo Kα (λ = 0.71069 Å) radiation at 130 K: **1**, $C_{52}H_{52}FeN_2Si_4$, a = 10.928 (3) Å, b = 15.337 (5) Å, c = 26.855 (7) Å, β = 91.75 (2)°, Z = 4, monoclinic, space group, $P2_1/c$, R = 0.039; **2**, $C_{52}H_{52}CoN_2Si_4$, a = 13.436 (3) Å, b = 10.570 (2) Å, c = 32.807 (16) Å, β = 99.06 (2)°, Z = 4, monoclinic $P2_1/c$, R = 0.049.

[19] There are now four mononuclear Mn(II) species which are known to be two-coordinate at or near ambient temperature. Two of these involve X-ray structures of solids[20,21] and two are diffraction studies of the vapors of $Mn\{N(SiMe_3)_2\}_2$[13] and $Mn(CH_2\text{-}t\text{-}Bu)_2$. Andersen, R. A.; Haaland, A.; Rypdal, K.; Volden, H. V. *J. Chem. Soc., Chem. Commun.* **1985**, 1807.

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A Synthetic Peptide Binds 16 Base Pairs of A,T Double Helical DNA

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One approach to the design of synthetic sequence specific DNA binding molecules that bind large sequences of double helical DNA is to couple together DNA binding domains of similar or diverse base pairs specificities.[1] The DNA binding domains should be linked together in a way that allows simultaneous binding of the units to contiguous DNA sequences.

Netropsin and distamycin are crescent-shaped di- and tripeptides containing two and three *N*-methylpyrrolecarboxamides, respectively. These natural products bind in the minor groove of B-DNA with a strong preference for A,T sequences.[2–6] X-ray analysis of the complex formed between netropsin and the duplex, 5′-CGCGAATTCGCG-3′, revealed that netropsin sits in the center of the minor groove of the DNA. Each of the three amide groups of netropsin forms bifurcated hydrogen bonds between adjacent adenine N3 or thymine O2 atoms on opposite strands of the helix.[4] We have previously shown that analogues of distamycin with four to six *N*-methylpyrrolecarboxamides (P4, P5, P6) bind six to eight base pairs of A,T DNA, respectively.[7,8] Recognition of larger sequences of A,T DNA sites by synthetic

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[8] The finding that n amides affords binding site recognition of size of $n + 1$ base pairs is consistent with the analysis of the netropsin:DNA duplex.[4]

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