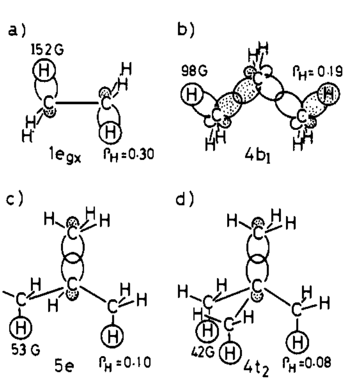

Figure 2. Unpaired electron orbitals of (a) $C_2H_6^+$, (b) $C_3H_8^+$, (c) *i*-$C_4H_{10}^+$, and (d) *neo*-$C_5H_{12}^+$.

that the observed spin density cannot be expected from the deformation associated with the Jahn–Teller active e_g CH_3 deformation vibration (ν_{11}).

When the spectrum is measured at 77 K, the three-line spectrum changes reversibly into an equally spaced seven-line spectrum with a 50.4-G splitting and a total spread unchanged from that of the 4.2-K spectrum (Figure 1b). This indicates the onset of motion, driven by a dynamic Jahn–Teller effect. Upon further warming, $C_2H_6^+$ converts into a neutral C_2H_5 radical, giving strong evidence for our assignment to $C_2H_6^+$.

The spectrum of $C_3H_8^+$ arises from two equivalent protons with coupling constants of 98 G (Figure 1c); this indicates that the $4b_1$ orbital (Figure 2b) is the highest occupied level of C_3H_8 (C_{2v}),[2] because the other orbitals, such as $6a_1$, $2b_2$ cannot give a large spin density (0.39) only on the two equivalent protons, as is observed. Upon warming, $C_3H_8^+$ loses a proton and converts into $\dot{C}H_2CH_2CH_3$ and $CH_3\dot{C}HCH_3$, the former being predominant as is expected from the spin distribution in $C_3H_8^+$.

The a_1 and a_2 orbitals of *i*-C_4H_{10} (C_{3v}) cannot give two equivalent proton couplings (53 G) as is observed (Figure 1d); so the Jahn–Teller split 5e orbital must be the highest occupied level.[2] The relatively small hyperfine coupling of *i*-$C_4H_{10}^+$ suggests that the unpaired electron is considerably localized in one of three C–C σ bonds as a result of Jahn–Teller distortion from C_{3v} to C_s symmetry. The hyperfine splitting of 53 G can be expected from the β protons in the two C–H bonds which are trans to the C–C σ-unpaired orbital as shown in Figure 2c. However, the possibility of the antibonding combination of the two C–C bonding orbitals similar to $4b_1$ in $C_3H_8^+$ cannot be excluded. Upon warming, *i*-$C_4H_{10}^+$ in SF_6 matrices converts into $\dot{C}H_2CH(CH_3)_2$ and $\dot{C}(CH_3)_3$ by proton loss, the former being predominant as is expected.

The highest occupied orbital of *neo*-C_5H_{12} (T_d) is $4t_2$.[2] *neo*-$C_5H_{12}^+$ has three equivalent protons with 42-G couplings (Figure 1e); this suggests that the unpaired electron is localized in one of the four C–C bonds as a result of Jahn–Teller distortion from T_d to C_{3v}. The $4t_2$ level of the parent molecule with T_d symmetry splits into a_1 and e states in the cation with C_{3v} symmetry, and the former is mainly confined to the C–C σ bond (Figure 2d). The 42-G coupling can be expected from the β protons (trans), one each from the three methyl groups as shown in Figure 2d. Upon warming, *neo*-$C_5H_{12}^+$ in SF_6 converts into $\dot{C}H_2C(CH_3)_3$ by proton loss while that in CCl_3F converts into $CH_2{=}C(CH_3)_2^+$ by loss of CH_4.[12] The difference may be due to cage effects in more rigid matrices.

In conclusion, small *n*-alkanes give C–H σ cations, and the spin density in the C–H σ bonds decreases with increasing carbon numbers. In branched alkanes the unpaired electron is more confined to the C–C σ bond.

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(10) G. Herzberg, Electronic Spectra and Electronic Structure of Polyatomic Molecules, Van Nostrand Reinhold, New York, 1966, p 50.

(11) I. Nakagawa and T. Simanouchi, *J. Mol. Spectrosc.*, **39**, 255 (1971).

(12) T. Shida, Y. Egawa, J. Kubodera, and T. Kato, *J. Chem. Phys.*, **73**, 5963 (1980).

Hybrid Multidentate Ligands. Tridentate Amidophosphine Complexes of Nickel(II) and Palladium(II)

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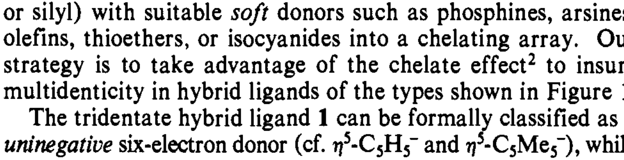
We have initiated a synthetic program to explore the coordination chemistry of a new class of potentially multidentate ligands which we call "hybrid" ligands. These hybrid ligands combine the *hard*[1] donor amido ligand (amido ≡ NR_2^-; R = alkyl, aryl, or silyl) with suitable *soft* donors such as phosphines, arsines, olefins, thioethers, or isocyanides into a chelating array. Our strategy is to take advantage of the chelate effect[2] to insure multidenticity in hybrid ligands of the types shown in Figure 1.

The tridentate hybrid ligand **1** can be formally classified as a *uninegative* six-electron donor (cf. η^5-$C_5H_5^-$ and η^5-$C_5Me_5^-$), while **2** would be similarly classified as a *uninegative* four-electron donor (cf. η^3-$C_3H_5^-$). It is anticipated that these hybrid ligands will induce new reactivity in their transition-metal derivatives over that observed in derivatives of the component monodentate donors. We report here some preliminary work with a potentially tridentate ligand of the type **1** where L is a tertiary phosphine.

The synthesis of 1,3-bis[(diphenylphosphino)methyl]tetramethyldisilazane, $(Ph_2PCH_2SiMe_2)_2NH$ (**3**), follows straightforward procedures.[3a,4] We classify this ligand as belonging to the set of *neutral*, potentially tridentate chelates represented by the nomenclature {[5,5]-P(NH)P}.[3b] As noted by Schore and others[5] in related systems, the silyl methyls of **3** appear as a doublet in the ^1H NMR spectra due to long-range coupling with phosphorus. Treatment of **3** with *n*-butyllithium in hexane generates in high yield the crystalline lithio derivative **4**,[6] Li^+{[5,5]-PNP}$^-$, which is a convenient starting material for metathetical reactions with a variety of suitable transition-metal halide derivatives, in analogy to other work with monodentate amido precursors.[7-9]



3 **4** (1)

The reaction of **4** with $NiCl_2(PR_3)_2$ (R = Ph[10a] or Me[10b]) in

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(1) Eller, P. G.; Bradley, D. C.; Hursthouse, M. B.; Meek, D. W. *Coord. Chem. Rev.* **1977**, *24*, 1.

(2) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980, p 71.

(3) (a) Fryzuk, M. D.; MacNeil, P. A., to be published. (b) Our nomenclature describes the potentially multidentate character of these ligands by indicating their charge, ring size(s), and donor atoms; thus {[5,5]-PNP}$^-$ represents a *class* of uninegative, tridentate ligands capable of forming two five-membered chelate rings utilizing one nitrogen and two phosphorus donors.

(4) **3**: colorless needles from pentane, mp 45–46 °C; ^1H NMR (ppm, C_6D_6, 60 MHz) 0.10 (d, 12, $SiCH_3$, J = 1.0 Hz), 1.36 (d, 4, PCH_2, J < 1 Hz), phenyl region not listed. Anal. Calcd for $C_{30}H_{37}NSi_2P_2$: C, 68.05; H, 6.99; N, 2.65. Found: C, 68.33; H, 7.25; N, 2.55.

(5) Schore, N. E. *J. Am. Chem. Soc.* **1979**, *101*, 7410. Grobe, J.; Heyer, G. *J. Organomet. Chem.* **1973**, *61*, 133.

(6) **4**: colorless plates from toluene–hexane, mp 120 °C dec; ^1H NMR (ppm, C_6D_6, 60 MHz) −0.05 (br s, 12, $SiCH_3$), 1.58 (br s, 4, PCH_2), phenyl region not listed. Anal. Calcd for $C_{30}H_{36}LiNSi_2P_2$: C, 67.29; H, 6.73; N, 2.61. Found: C, 67.00; H, 6.78; N, 2.48.

(7) Bradley, D. C.; Chisholm, M. H. *Acc. Chem. Res.* **1976**, *9*, 273.

(8) Cetinkaya, B.; Lappert, M. F.; Torroni, S. *J. Chem. Soc., Chem. Commun.* **1979**, 843.

(9) Simpson, S. J.; Turner, H. W.; Andersen, R. A. *J. Am. Chem. Soc.* **1979**, *101*, 7728 and references therein.

(10) (a) Venanzi, L. M. *J. Chem. Soc.* **1958**, 719. (b) Dahl, O. *Acta Chem. Scand.* **1969**, *23*, 2342.

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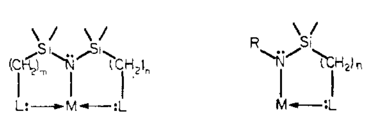
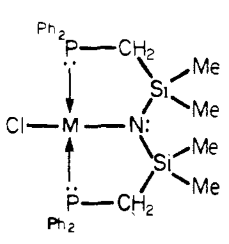


1 2

Figure 1. Hybrid tridentate (**1**) and bidentate (**2**) ligands (L ≡ soft donor ligand and M ≡ central metal atom).

THF at 0 °C produces the deep orange-brown, crystalline, *diamagnetic* nickel(II) derivative $[NiClN(SiMe_2CH_2PPh_2)_2]$ (**5**).[11]



M = Ni **5**
M = Pd **6**

This contrasts earlier work[13] using the same nickel(II) precursors and the related *monodentate* amido precursor $LiN(SiMe_3)_2$; in these cases metathesis occurred but was accompanied by reduction to generate *paramagnetic* nickel(I) derivatives, for example, $[NiN(SiMe_3)_2(PPh_3)_2]$. Diagnostic of a trans orientation of the chelating phosphines in **5** is the presence of a "virtual" triplet[12] in the ^1H NMR spectra.

The reaction of **4** with $PdCl_2(PhCN)_2$ in THF at −80 °C gives in high yield the orange, crystalline, diamagnetic palladium(II) derivative $[PdClN(SiMe_2CH_2PPh_2)_2]$ (**6**);[14] to our knowledge, this is the *first* reported[15] stable palladium amide complex. Once again, the presence of a virtual triplet[12] in the ^1H NMR spectra indicates a trans structure in solution. Previous attempts to generate palladium amides probably resulted in reduction to palladium(I) or palladium(0); indeed, if the reaction of **4** with $PdCl_2(PhCN)_2$ is carried out at ambient temperature, much insoluble residue forms and the yield of **6** is drastically reduced. Prior displacement of the benzonitrile ligands by the soft phosphine donors at low temperature may serve to stabilize the incipient palladium(II) amide bond.

In general, a linear tridentate ligand can coordinate to a transition metal in either of two limiting isomeric modes: a meridional, planar stereochemistry or a facial, pyramidal stereochemistry depending both on the flexibility of the backbone of the ligand and on the stereoelectronic requirements of the metal center. For the hybrid ligand discussed in this communication, it is not clear whether a facial coordination mode is at all possible, since, in the nickel and palladium systems described above, one would expect that the central metal atom's stereoelectronic requirements would dominate and generate the observed meridional, square-planar stereochemistry. However, we do have some evidence that suggests that the $\{[5,5]\text{-PNP}\}^-$ system is capable of a facial coordination mode. The single-crystal X-ray structure analysis of the nickel derivative[17] (**5**) (Figure 2) indicates that the planar[18] Si_2N portion of the backbone is tilted with respect to the coordination plane of the nickel complex; one silicon is calculated to lie 0.89 Å above and the other silicon 1.25 Å below the least-squares plane of the complex. Furthermore, this puckering of the two five-membered chelate rings leads to axially and equatorially disposed methyl groups on each silicon, which, if the chelate rings are fixed, should in principle be chemically distinct. The ^1H NMR spectra show these silyl methyls as a sharp *singlet* (0.01 ppm) at room temperature, indicating either rapid conformational flipping of the puckered backbone or accidental equivalence. The ^1H NMR spectrum at −80 °C shows broadened resonances and, interestingly, a *decrease* in peak intensity (by 50 ± 5%) as measured by integration vs. the residual protons solvent peak (acetone-d_6). In addition, at −80 °C, the originally deep brown solution turns *bright green* and remains clear of solids. We suggest that the paramagnetic *tetrahedral* isomer of $[NiClN(SiMe_2CH_2PPh_2)_2]$ is being stabilized at low temperature; this would account for the peak intensity decrease and broadening and also would account for the color change. Although it is tempting to suggest that the equatorial and axial sites in the puckered rings of the square-planar isomer are exchanging via a square-planar–tetrahedral equilibrium,[20] it may well be that the two processes are independent.

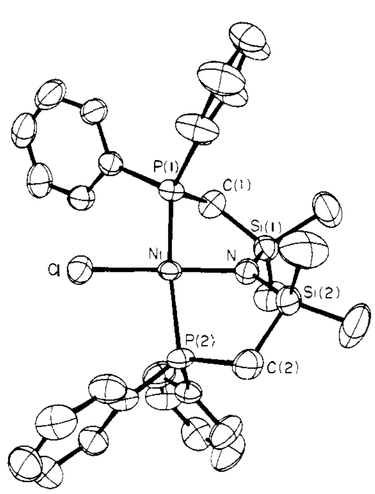


Figure 2. Molecular structure of $[NiClN(SiMe_2CH_2PPh_2)_2]$.

We are at present investigating further the coordination chemistry of the $\{[5,5]\text{-PNP}^-$ system with other group 8 metals and the early transition elements in hopes of pinning down existing stereochemical ambiguities.

Acknowledgment. We acknowledge the Department of Chemistry and the President's Emergency Research Fund for the support of this work. P.A.M. thanks the Walter C. Sumner Foundation for a Memorial Fellowship. We also thank Professor B. R. James for valuable comments on the manuscript.

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(11) **5**: deep orange-brown prisms from toluene–hexane, mp 153–155 °C; ^1H NMR (ppm, acetone-d_6, 60 MHz) 0.01 (s, 12, $SiCH_3$), 1.58 (t, 4, PCH_2, $J = 5.4$ Hz), phenyl region not listed. Anal. Calcd for $C_{30}H_{36}NSi_2P_2ClNi$: C, 57.83; H, 5.78; N, 2.25. Found: C, 57.71; H, 5.87; Ni, 2.23.

(12) Virtual coupling occurs in $AA'X_2X_2'$ systems when $J_{AA'}$ is very large. In complexes **5** and **6**, the trans phosphines are strongly coupled and results in an apparent A_2X_2 pattern for the methylene resonances. See: Brooks, P. R.; Shaw, B. L. *J. Chem. Soc. A* **1967**, 1136.

(13) Bradley, D. C.; Hursthouse, M. B.; Smallwood, R. J.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1972**, 872.

(14) **6**: orange blocks from toluene–hexane, mp 136–137 °C; contains one toluene of crystallization; ^1H NMR (ppm, acetone-d_6, 60 MHz) 0.07 (s, 12, $SiCH_3$), 1.77 (t, 4, PCH_2, $J = 6.0$ Hz), phenyl region and toluene peaks not listed. Anal. Calcd for $C_{30}H_{36}NSi_2P_2ClPd \cdot C_7H_8$: C, 58.26; H, 5.77; N, 1.83. Found: C, 58.27; H, 5.96; N, 1.81.

(15) Reference 8 states that "the only transition elements for which amides now remain unreported are Tc, Os, Ir, *Pd*, Pm, Tb, Dy, Tm, Pa, and the transuranium elements".[16]

(16) Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. "Metal and Metalloid Amdies"; Wiley: New York, 1979.

(17) Fryzuk, M. D.; MacNeil, P. A.; Secco, A. S.; Trotter, J., to be published. Unit cell, space group, and intensity data were measured on an Enraf–Nonius CAD4 diffractometer; $a = 10.091$ (3), $b = 10.224$ (3), $c = 17.237$ (4) Å; $\alpha = 81.06$ (2), $\beta = 78.51$ (2), $\gamma = 65.93$ (3)°; $Z = 2$; space group $P\bar{1}$. The nickel atom was easily located via a Patterson map, and successive difference-Fourier maps led to positioning of the rest of the atoms in the molecule. Refinement proceeded with absorption corrected data and converged at $R = 0.029$ ($R_w = 0.040$) for 5147 reflections of the 7138 collected. The mean and maximum parameter shifts on the final cycle of refinement were 0.05 and 0.30, respectively.

(18) With the exception of $[RuH(N(SiMe_3)_2)(PPh_3)_2]$,[8] all the work in the literature so far suggests that the Si_2N framework is planar due to delocalization of the nitrogen lone pair into empty silicon d orbitals.[19]

(19) Reference 2, p 125.

(20) For leading references, see: Holm, R. H. In "Dynamic Nuclear Magnetic Resonance Spectroscopy"; Jackman, L. M., Cotton, F. A., Eds.; Academic Press: New York, 1975; Chapter 9, p 328.