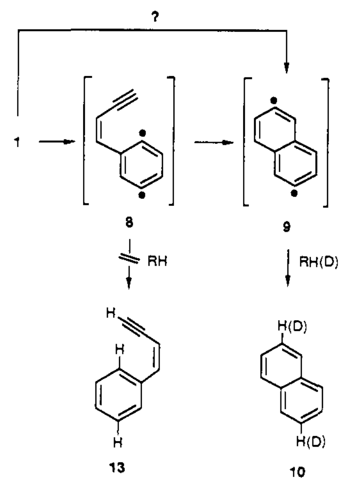
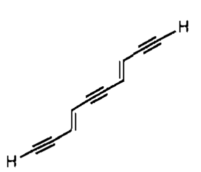
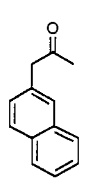
Scheme III



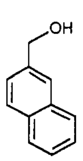
9 by hydrogen atom transfer from the acetone followed by combination of the resulting 2-naphthyl and α-acetonyl radicals. Similarly, thermolysis of **1** in methanol led to the formation of 2-naphthalenemethanol (**12**) uncontaminated with 1-naphthalenemethanol.



3



11



12

The thermolyses of *E,Z* and *E,E* dienetriynes **2** and **3** contrasted sharply with the behavior of *Z,Z* isomer **1**. No naphthalene was detected by GC in either of these reactions. Thermolysis of **2** (Scheme II) in dilute solution at 170–190 °C gave cyclized product **15**[19] (ca. 20%), in analogy to the reactivity seen for simple enediyne systems.[1-4] *E,E* isomer **3** is more stable at 170–190 °C, undergoing only slow disappearance (presumably polymerization). Heating **13**,[19] the cis isomer of **15** and potential monocyclization product of **1**, under conditions similar to those used in the thermolysis of **1** demonstrated that **13** decomposes slowly but does not form naphthalene.[20]

These data suggest that the naphthalene formed from **1** arises from 2,6-didehydronaphthalene and that this reactive intermediate has a diradical structure analogous to that of 1,4-didehydrobenzene.[1-4] Benson group equivalent calculations[21] suggest that diradical **8** has an enthalpy of formation approximately 10 kcal/mol higher than dienetriyne **1**, but that diradical **9** has an enthalpy of formation approximately *50 kcal/mol lower* than that of **1**.[22] It is of interest that monocyclized diradical **14** can be trapped to give **15** in the thermolysis of **2**, but no **13** is observed in the thermolysis of **1**. This suggests that either the 1,4-didehydrobenzene intermediate **8** cyclizes very rapidly to **9** or the cyclization of **1** to **9** is a concerted process. The cyclization of the 1,3-hexadien-5-ynyl radical to phenyl radical, analogous to the transformation of **8** to **9**, is thought to be a facile process.[23,24]

The double cycloaromatization of **1** demonstrates that arene diradicals larger than 1,4-didehydrobenzene may be accessible through appropriate poly-enyne cyclizations. This has the potential of increasing our fundamental knowledge of these unique intermediates and of widening the range of calicheamicin-type DNA-cleaving reagents to systems that have not previously been available. Further studies on systems related to **8** and **9** are in progress.

Acknowledgment. We are grateful to the National Institutes of Health for support of this research (Grant No. GM-45312), to the U.S. National Science Foundation and Natural Sciences and Engineering Research Council (Canada) for fellowships to K.N.B. and R.E.M., respectively, and to Prof. K. K. Wang (West Virginia University) for providing a preprint of his work on the intramolecular trapping of an α,3-didehydrotoluene diradical with a double bond.

Supplementary Material Available: Listings of IR, MS, ^{1}H NMR, ^{13}C NMR spectral data of all new compounds mentioned in the text, a general description of the kinetics experiments, and plots of rate data (9 pages). Ordering information is given on any current masthead page.

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(18) For a synthesis of both isomeric ketones, see: Kurz, M. E.; Baru, B.; Nguyen, P. N. *J. Org. Chem.* **1984**, *49*, 1603.

(19) Isomeric alkynes **13** and **15** were synthesized by NiCl$_2$(dppp)-catalyzed coupling of PhMgBr with (*E*)- or (*Z*)-4-chloro-1-(trimethylsilyl)-3-buten-1-yne in THF, followed by removal of the TMS groups with KF in methanol. The coupling reaction for the synthesis of **13** gave significant amounts of biphenyl. Both isomers have been prepared previously by other methods. See, for example: Eisenhuth, L.; Siegel, H.; Hopf, H. *Chem. Ber.* **1981**, *114*, 3772.

(20) However, more vigorous conditions do lead to naphthalene formation. See: Becker, J.; Wentrup, C.; Katz, E.; Zeller, K. *J. Am. Chem. Soc.* **1980**, *102*, 5110. Trahanovsky, W. S.; Alexander, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 142.

(21) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976.

(22) ΔH_f's of **8** and **9** were estimated by subtraction of the H–H bond energy (104 kcal/mol) and addition of two aromatic C–H bond energies (110 kcal/mol) to the ΔH_f's of **13** and **10**, respectively.

(23) Westmoreland, P. R.; Dean, A. M.; Howard, J. B.; Longwell, J. P. *J. Phys. Chem.* **1989**, *93*, 8171 and references cited therein.

(24) Dewar, M. J. S.; Gardiner, W. C., Jr.; Frenklach, M.; Oref, I. *J. Am. Chem. Soc.* **1987**, *109*, 4456.

A New Family of 14-Vertex Hexacapped Metal Cubes with Main Group IV (14) Atoms: Synthesis and Structural-Bonding Analysis of Ni$_9$(μ_4-GeEt)$_6$(CO)$_8$ Containing a Nickel-Centered Ni$_8$(μ_4-Ge)$_6$ Cubic Cage with an Unusual Electron Count

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Our efforts to incorporate main-group elements into transition metal clusters have recently focused on group IV (14) reagents. Reactions of RSnCl$_3$ (R = Me, *n*-Bu) with [Ni$_6$(CO)$_{12}$]$^{2-}$ (**1**)[2] gave rise to a new family of icosahedral cages with main group 14 atoms, viz., the 158-electron [Ni$_{11}$(SnR)$_2$(CO)$_{18}$]$^{2-}$ dianions (R = Me, *n*-Bu) with Ni-centered 1,12-Ni$_{10}$Sn$_2$ icosahedral cages as well as their [Ni(SnRCl$_2$)$_4$(CO)]$^{2-}$ precursors with trigonal-bipyramidal d^8 Ni(II) configurations.[3]

We report herein that a similar reaction of **1** with another main group 14 organotrihalide, EtGeCl$_3$, has produced the neutral Ni$_9$(μ_4-GeEt)$_6$(CO)$_8$ (**2**) with a nickel-centered Ni$_8$ cube capped on all six faces by germylidene ligands.[4,5] Other clusters with noncentered and metal-centered M$_8$(μ_4-E)$_6$ cubic cages are known

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(1) (a) University of Wisconsin–Madison. (b) Current address: Argonne National Laboratory, Chemical Technology Division, 9700 South Cass Avenue, Argonne, IL 60439. (c) Science Institute, University of Iceland.

(2) (a) Calabrese, J. C.; Dahl, L. F.; Cavalieri, A.; Chini, P.; Longoni, G.; Martinengo, S. *J. Am. Chem. Soc.* **1974**, *96*, 2616–2618. (b) Longoni, G.; Chini, P.; Cavalieri, A. *Inorg. Chem.* **1976**, *15*, 3025–3029.

(3) Zebrowski, J. P.; Hayashi, R. K.; Dahl, L. F. Submitted for publication.

(4) A few other metal clusters with square-pyramidal μ_4-GeR ligands are known.[5]

(5) (a) Foster, S. P.; MacKay, K. M.; Nicholson, B. K. *J. Chem. Soc., Chem. Commun.* **1982**, 1156–1157. (b) Gusbeth, P.; Vahrenkamp, H. *Chem. Ber.* **1985**, *118*, 1746–1757.

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Table I. Comparison of Mean Distances for $Ni_9(\mu_4\text{-}GeEt)_6(CO)_8$ (**2**) and Other Related Clusters Containing Noncentered and M(i)-Centered $M(s)_8(\mu_4\text{-}E)_6$ Cubic Cages

cluster	CVEs	M(i)	covalent radius[a]		M(s)–M(s′)	M(i)–M(s)	M(s)–E	M(i)–E	ref
			M	E					
$Ni_8(\mu_4\text{-}PPh)_6(CO)_8$ (**3**)	120	none	1.2	1.06	2.65	2.29[b]	2.18	2.45[c]	*d*
$Ni_8(\mu_4\text{-}PPh)_6(CO)_4(PPh_3)_4$ (**4**)	120	none	1.2	1.06	2.67	2.31[b]	2.19	2.45[c]	*e*
$Ni_9(\mu_4\text{-}GeEt)_6(CO)_8$ (**2**)	124	Ni(i)	1.2	1.22	2.67	2.31	2.36	2.76	*f*
$Pd_9(\mu_4\text{-}As)_6(PPh_3)_8$ (**5**)	124	Pd(i)	1.3	1.20	3.11	2.69	2.49	2.70	*g*
$Pd_9(\mu_4\text{-}Sb)_6(PPh_3)_8$ (**6**)	124	Pd(i)	1.3	1.40	3.26	2.82	2.61	2.87	*h*
$Ni_9(\mu_4\text{-}Te)_6(PEt_3)_8$ (**7**)	130	Ni(i)	1.2	1.36	2.86	2.47	2.55	2.98	*i*

[a] Reference 16. [b] Cube center–M(s) distance. [c] Cube center–E distance. [d] Reference 6a. [e] References 6b,c. [f] This work. [g] Reference 6h. [h] Reference 6i. [i] Reference 6j.

only for M = Co, Ni, or Pd and E = main group 15 or 16 atoms.[6] Thus, **2** is the first example of a metal cube capped by main group 14 atoms. The Ni-centered **2** possesses an unusual valence electron count of 124 with four more electrons than the noncentered $Ni_8(\mu_4\text{-}P)_6$ cube in the prototype $Ni_8(\mu_4\text{-}PPh)_6(CO)_8$ (**3**)[6a] and $Ni_8(\mu_4\text{-}PPh)_6(CO)_4(PPh_3)_4$ (**4**).[6b,c] From a valence-bond viewpoint, the completely bonding Ni_8 cube in **3** and **4** possesses an electron-precise geometry with 12 skeletal electron-pair Ni–Ni bonds along the 12 cube edges.[6a,7,8]

A comparison of the structure of the 124-electron **2** with the structures of the 124-electron $Pd_9(\mu_4\text{-}E)_6(PPh_3)_8$ (E = As (**5**),[6h] Sb (**6**)[6i]) containing Pd-centered $Pd_8(\mu_4\text{-}E)_6$ cages and the 130-electron $Ni_9(\mu_4\text{-}Te)_6(PEt_3)_8$ (**7**)[6j] containing a Ni-centered $Ni_8(\mu_4\text{-}Te)_6$ cage is of interest because the high electron counts of these clusters are also not in agreement with the numbers (114, 120) predicted by general electron-counting rules.[9-11] These rules, which normally consider an interstitial atom to be an internal ligand that donates all of its valence electrons without alteration of the filled CVOs, were shown to be invalid for clusters containing icosahedral $Ni_{10}E_2$ cages (E = Sb, Sn) with interstitial Ni(i) atoms.[3,12] A major objective of the structure–bonding analysis is to determine whether geometrical variations in these metal-centered $M_8(\mu_4\text{-}E)_6$ cubic cages can be correlated with their different electron counts or whether the nature of the interstitial M(i) atom as well as the surface M(s) and E atoms and/or the metal-attached ligands play important roles. Because **2** and **5** have similar-sized E atoms and identical electron counts, a comparison of their structures is useful for assessing geometrical differences arising from congeneric replacement of first-row Ni with second-row Pd.

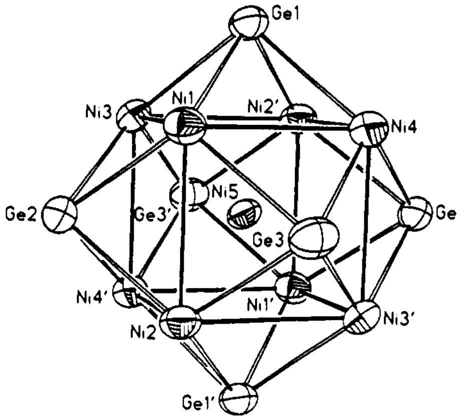

Figure 1. The Ni-centered $Ni_8(\mu_4\text{-}Ge)_6$ cubic cage of $Ni_9(\mu_4\text{-}GeEt)_6(CO)_8$ (**2**) which has crystallographic C_i-$\bar{1}$ site symmetry. This hexacapped cube of eight surface Ni(s) atoms with an interstitial Ni(i) atom experimentally conforms to O_h-$4/m\ \bar{3}\ 2/m$ symmetry. Atomic thermal ellipsoids are drawn at the 35% probability level.

Air-unstable red **2** was isolated as the only hexane-soluble product in all of our reactions of **1** with $GeEtCl_3$. In a typical reaction, the $[NMe_4]^+$ salt (2.0 g; 2.4 mmol) of **1** was suspended in 40 mL of THF, and $EtGeCl_3$ (1.0 g; 4.8 mmol) was added via syringe. The solution, which turned from red to brown when heated, was refluxed until an IR spectrum showed no further changes in the carbonyl region. After being cooled to room temperature, the solution was filtered and the supernatant brought to dryness. The resultant residue was extracted with hexane. Removal of the hexane under an N_2 stream gave microcrystalline **2** (130 mg; 12% yield, Ge). Crystalline material was characterized by spectroscopic and electrochemical measurements;[13] both the molecular configuration and composition of **2** were established from X-ray crystallography and laser desorption/Fourier transform mass spectrometry (LD/FTMS).

The structural determination[14] revealed that the molecular configuration of **2** consists of a centered $Ni_8(\mu_4\text{-}Ge)_6$ cubic cage

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(6) (a) Lower, L. D.; Dahl, L. F. *J. Am. Chem. Soc.* **1976**, *98*, 5046–5047. (b) Montag, R. A. Ph.D. Thesis, 1982, University of Wisconsin–Madison. Gavney, J. A., Jr.; Montag, R. A.; Dahl, L. F. Manuscript in preparation. (c) Fenske, D.; Basoglu, R.; Hachgenei, J.; Rogel, F. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 160–162. (d) Fenske, D.; Hachgenei, J.; Ohmer, J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 706–709. (e) Fenske, D.; Hachgenei, J.; Rogel, F. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 982–983. (f) Christou, G.; Hagen, K. S.; Bashkin, J. K.; Holm, R. H. *Inorg. Chem.* **1985**, *24*, 1010–1018. (g) Fenske, D.; Merzweiler, K.; Ohmer, J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1512–1513. (h) Fenske, D.; Fleischer, H.; Persau, C. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1665–1667. (i) Fenske, D.; Persau, C. *Z. Anorg. Allg. Chem.* **1991**, *593*, 61–68. (j) Brennan, J. G.; Siegrist, T.; Stuczynski, S. M.; Steigerwald, M. L. *J. Am. Chem. Soc.* **1989**, *111*, 9240–9241. (k) Fenske, D.; Ohmer, J.; Hachgenei, J.; Merzweiler, K. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1277–1296.

(7) An alternative treatment of the skeletal electron pair cluster bonding of $Ni_8(\mu_4\text{-}PPh)_6(CO)_8$ (**3**) was recently put forth by King,[8] who considered **3** as an "omnicapped cube" in his graph-theory scheme. King[8] proposed that this 14-vertex $Ni_8(\mu_4\text{-}P)_6$ deltahedron possessing 36 edges and 24 faces has 36 skeletal electron pairs distributed as edge-localized bonds. An analogous consideration of the entire $Ni_8(\mu_4\text{-}P)_6$ fragment as the basic unit gives rise to an electron count of 132 CVEs.

(8) King, R. B. *New J. Chem.* **1989**, *13*, 293–301.

(9) (a) Mingos, D. M. P.; Zhenyang, L. *J. Chem. Soc., Dalton Trans.* **1988**, 1657–1664 and references cited therein. (b) Mingos, D. M. P.; May, A. P. In *The Chemistry of Metal Cluster Complexes*; Shriver, D. F., Kalsy, H. D., Adams, R. D., Eds.; VCH Publishers: New York, NY, 1990; Chapter 2, pp 11–119. (c) Mingos, D. M. P.; Wales, D. J. *Introduction to Cluster Chemistry*; Prentice-Hall: Old Tappan, NJ, 1990.

(10) These predictions are consistent with EHMO calculations[11] for the hypothetical 120-electron $Ni_8(\mu_4\text{-}PH)_6(CO)_8$. The well-separated triply-degenerate HOMOs (t_{2g}), which have radial Ni(s)–Ni(s′) antibonding character, are fully occupied. The predicted 114-electron system, for which there are no examples, would correspond to the complete electron depopulation of the HOMOs.

(11) Burdett, J. K.; Miller, G. J. *J. Am. Chem. Soc.* **1987**, *109*, 4081–4091.

(12) (a) Albano, V. G.; Demartin, F.; Iapalucci, M. C.; Longoni, G.; Sironi, A.; Zanotti, V. *J. Chem. Soc., Chem. Commun.* **1990**, 547–548. (b) Albano, V. G.; Demartin, F.; Iapalucci, M. C.; Laschi, F.; Longoni, G.; Sironi, A.; Zanello, P. *J. Chem. Soc., Dalton Trans.* **1991**, 739–748.

(13) **2** is burgundy-red in solution and dark red in the crystalline state. IR (hexane): 2014 cm^{-1}. ^1H NMR (benzene-d_6): δ 2.26 (q, C1), 1.41 (t, C2). CV (THF): irreversible oxidation at ca. 1.0 V; one reversible reduction, $E_{1/2}$ −0.74 V (vs SCE). Convincing evidence that **2** is diamagnetic is given by the sharp ^1H NMR resonances in contrast to the paramagnetically-induced broad ^1H NMR resonances observed in the 121-electron $[Ni_8(\mu_4\text{-}PPh)_6(CO)_8]^-$ (3^-)[6b] and the 119-electron $[Ni_8(\mu_4\text{-}PPh)_6(CO)_4(PPh_3)_4]^+$ (4^+).[6b]

(14) Crystals of **2** were obtained by slow vapor diffusion from hexane solution. Data were collected on a Siemens diffractometer with Mo Kα radiation. The crystal structure was determined by the use of SHELXTL PLUS. $Ni_9(GeEt)_6(CO)_8$ (fw 1362.2): monoclinic; $P2_1/n$; a = 11.113 (3) Å, b = 14.835 (5) Å, c = 11.124 (3) Å, β = 90.71 (2)°; Z = 2. $R_1(F)$ = 8.19%, $R_2(F)$ = 8.43% for 1560 reflections (−30 °C). Although a packing diagram indicated that the crystal structure approximately conforms to tetragonal $P4_2/n$ symmetry with each molecule possessing S_4-$\bar{4}$ site symmetry, a structural analysis showed that this possibility could be rejected.

(Figure 1) with terminal carbonyl ligands and ethyl substituents. Crystallographic evidence that the interstitial atom is Ni(i) rather than Ge(i) (which differ by only four electrons) was provided from separate least-squares refinements, which gave a more reasonable equivalent isotropic thermal parameter when the interstitial atom was designated as Ni(i). The central atom was unambiguously determined to be Ni(i) by LD/FTMS, which revealed the parent-ion peak and its isotopic distribution pattern as well as the fragment-ion pattern to be entirely consistent with the compound's composition.[15]

The following structural-bonding implications emerge from an examination in Table I of the mean molecular parameters in **2** and related clusters: (*1*) The closely similar geometries of **3** and **4** indicate that replacement of terminal CO with PPh_3 ligands does not markedly affect their electronic structures. (2) A consequence of each capping Ge atom in **2** having a 0.16-Å-larger covalent radius[16] than each P atom in **3** is that its Ni(s)–E distances are greater by 0.18 Å; thus, the nonbonding Ni(i)···E distances of 2.76 Å in **2** (E = Ge) are 0.3 Å larger than the corresponding cube center–E distances in **3** (E = P). It follows that the nonbonding trans P···P distances of 4.9 Å in **3** are probably too small to accommodate a Ni(i) within the $Ni_8(\mu_4\text{-}P)_6$ cage to give a cluster analogous to **7**. The unusually short eight Ni(i)–Ni(s) distances of 2.31 Å in **2** imply strong radial interactions between the Ni(i) AOs and appropriate cage Ni(s) orbitals. (3) Although **2** and **5** contain similar-sized E atoms and have the same number (124) of CVEs, their cage geometries are very different. Whereas the distances in **2** suggest that the Ni(i)-centered $Ni_8(\mu_4\text{-}Ge)_6$ cage is stabilized by both radial bonding Ni(i)–Ni(s) and tangential (edge-bridged) bonding Ni(s)–Ni(s′) interactions, those in **5** signify no edge-bridged bonding Pd(s)–Pd(s′) interactions but instead indicate that the Pd(i) is involved in radial bonding interactions with the six capping As atoms as well as with the eight Pd(s) atoms. These geometrical differences are partly attributed to the less contracted valence Pd AOs forming stronger bonding interactions at longer distances. Although similarly large bond-length differences are observed between the Pd(i)-centered $Pd_8(\mu_4\text{-}Sb)_6$ cage of the 124-electron **6** and the Ni(i)-centered $Ni_8(\mu_4\text{-}Te)_6$ cage of the 130-electron **7**,[17,18] their different electron counts prevent an unambiguous qualitative bonding analysis. (4) Both the radial bonding Ni(i)–Ni(s) and edge-bridged bonding Ni(s)–Ni(s′) interactions are presumed to be considerably smaller in **7** than in **2** on account of the 0.2-Å-longer distances in **7**. (5) From bonding considerations under O_h symmetry, it is proposed that the four "extra" electrons in the 124-electron **2** occupy an additional doubly-degenerate pair of antibonding radial MOs originating from the 3d (e_g) AOs of the interstitial Ni(i); the stronger radial interactions of the 3d (t_{2g}) Ni(i) AOs with the cage Ni(s) orbitals are presumed to produce *occupied* bonding but *empty* antibonding MOs. This structural-bonding analysis of **2** shows that general electron-counting rules[9] will need to be revised for $M_8(\mu_4\text{-}E)_6$ cubic-caged clusters containing late first-row transition metals as interstitial atoms.

Work is in progress to characterize other compounds from reactions of **1** with $EtGeCl_3$; these include the $[Ni_{11}(GeEt)_2(CO)_{18}]^{2-}$ dianion, which has a nickel-centered icosahedral $Ni_{10}Ge_2$ cage, and the trigonal-bipyramidal Ni(II) $[Ni(GeEtCl_2)_4(CO)]^{2-}$ complex. Fenske–Hall MO calculations are also being carried out[19,20] as operational tests of the bonding interpretations presented herein.

Acknowledgment. This research was supported by the National Science Foundation. We thank Mr. Jackson Ma (UW–Madison) for obtaining NMR spectra. We gratefully acknowledge EXTREL FTMS (6414 Schroeder Road, Madison, WI 53711) for the use of a FTMS-2000 spectrometer.

Supplementary Material Available: A figure showing a mass spectrum of **2** and tables listing atomic parameters, interatomic distances, and bond angles of **2** (7 pages); listing of structure factor amplitudes of **2** (11 pages). Ordering information is given on any current masthead page.

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[15] Mass spectra were obtained with an EXTREL FTMS-2000 Fourier transform mass spectrometer equipped with an infrared CO_2 laser. For experimental details, see: (a) Bjarnason, A.; DesEnfants, R. E., II; Barr, M. E.; Dahl, L. F. *Organometallics* **1990**, *9*, 657–661. (b) Bjarnason, A. *Rapid Commun. Mass Spectrom.* **1989**, *3*, 373–376.

[16] (a) Huheey, J. E. *Inorganic Chemistry: Principles of Structure and Reactivity*, 3rd ed.; Harper and Row: New York, 1983; pp 258–259. (b) Porterfield, W. W. *Inorganic Chemistry: A Unified Approach*; Addison-Wesley: Reading, MA, 1984; p 168.

[17] An EHMO treatment[18] of the corresponding hypothetical 130-electron $[Ni_9(\mu_4\text{-}Te)_6(H)_8]^{8-}$ under O_h symmetry gave triply-degenerate HOMOs (t_{2g}) containing four electrons with closely spaced (<0.1 eV) doubly-degenerate LUMOs (e_g).

[18] Wheeler, R. A. *J. Am. Chem. Soc.* **1990**, *112*, 8737–8741; **1991**, *113*, 4046.

[19] The indicated diamagnetism[13] of **2** is completely consistent with the results of preliminary Fenske–Hall MO calculations[20] for the 124-electron $Ni_9(\mu_4\text{-}GeH)_6(CO)_8$ (in which H atoms are substituted for Et substituents). The filled doubly-degenerate HOMOs are well-separated (ca. 2.9 eV) from the triply-degenerate LUMOs.

[20] Spencer, B.; Gavney, J. A., Jr.; Dahl, L. F. Unpublished results.

Organoyttrium-Catalyzed Cyclization of Substituted 1,5- and 1,6-Dienes

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Cyclization of dienes, diynes, and enynes promoted by various organometallics represents an extremely powerful means to convert simple, readily accessible substrates to more complex organic molecules.[2] Our interest in utilizing lanthanide reagents for stereoselective organic transformations[3] has prompted us to explore employment of organolanthanide and group 3 organometallic catalysts for selective carbon–carbon bond formation. In this initial effort we report the first use of organoyttrium catalysts in reductive cyclization reactions of 1,5- and 1,6-dienes.

In related work, unsaturated organotitaniums undergo intramolecular olefin insertion,[4] and organoscandiums have been reported to promote cyclization of simple, unfunctionalized 1,5- and 1,6-dienes.[5] However, the former process is not catalytic, and stereochemical issues, functional group compatibility,[6] and a facile catalyst synthesis were not addressed in the latter study. More

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