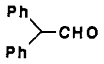
tically active epoxy silyl ether, which was readily obtained by the enantioselective epoxidation of racemic (*E*)-4-phenyl-3-buten-2-ol,[11] was smoothly rearranged under the influence of the reagent A producing the optically active, *threo*-β-siloxy aldehyde **8** exclusively (entry 5).[12]

Other selected examples in Table I concerning the epoxy alcohol rearrangement clearly indicate the effectiveness of our approach. As a whole, the facile migration of the alkyl group was observed in the case of γ,γ-disubstituted epoxy alcohols (entries 3, 4, 7, and 8). The γ-monosubstituted epoxy alcohols possessing aryl or alkenyl groups are also susceptible toward the rearrangement (entries 1, 2, 5, and 6).[13] This rearrangement is not dependent on the configuration of the β-carbon as both epoxy geraniol and epoxy nerol gave rise to the same aldol **6** as a sole isolable product (entries 3 and 4). The superiority of the reagent A over related organoaluminum reagents as well as other Lewis acids was examined with the substrate **5**. Attempted use of methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide) (MAD)[14,15] significantly retarded the rate of the rearrangement, showing the importance of the *p*-bromo substituent in the reagent A for rate acceleration of the reaction. Less bulky dimethylaluminum 4-bromo-2,6-di-*tert*-butylphenoxide lowered the yield (63%) of the reaction, while methylaluminum bis(4-bromo-2,6-diisopropylphenoxide) afforded only trace of **6**.[16] Consequently, use of two bulky 4-bromo-2,6-di-*tert*-butylphenoxy ligands in the reagent A is crucial for effecting the smooth rearrangement. It should be noted that this transformation cannot be easily accomplished by using the conventional Lewis acids. Attempted reaction of the substrate **5** with $TiCl_4$, $Ti(O\text{-}i\text{-}Pr)_4$, and $BF_3{\cdot}OEt_2$ gave none of the desired product **6**.[17]

The bulky aluminum reagent A is also applicable to the rearrangement of a variety of simple epoxides such as stilbene oxide, 1-phenylcyclohexene oxide, 2-methyl-1-undecene oxide, and the *tert*-butyldimethylsilyl ether of epoxy citronellol, providing the corresponding aldehydes **9**–**12** in 90–98% yields.[18]



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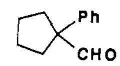

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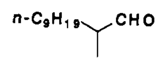
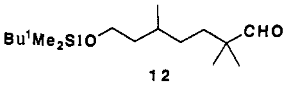


11



12

Supplementary Material Available: Experimental details and spectral data (^{1}H NMR, IR, $[\alpha]_D^{24}$, and elemental analysis) for all new compounds (7 pages). Ordering information is given on any current masthead page.

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(11) Martin, V. S.; Woodard, S. S.; Kastuki, T.; Yamada, Y.; Ikeda, M.; Sharpless, K. B. *J. Am. Chem. Soc.* **1981**, *103*, 6237.

(12) The stereostructural assignment of the aldol product **8** was determined by the correlation with the known methyl *threo*-3-hydroxy-2-phenylbutanoate (Mulzer, J.; Lammer, O. *Chem. Ber.* **1986**, *119*, 2178).

(13) Epoxy alcohols with other substitution patterns undergo no desired rearrangement. For example, the *tert*-butyldimethylsilyl ether of *trans*-2,3-epoxy-1-hexanol (γ-monosubstituted epoxy alcohol having alkyl groups) was unreactive with the reagent A after several hours at −78 ~ −20 °C and gradually decomposed at 0 °C. The *tert*-butyldimethylsilyl ether of (*E*)-2,3-epoxy-2-methyl-1-pentanol (β,β-disubstituted epoxy alcohol) gave 2-[(*tert*-butyldimethylsiloxy)methyl]-2-methylbutanal in 57% yield with migration of the ethyl group under the standard conditions.

(14) Maruoka, K.; Itoh, T.; Sakurai, M.; Nonoshita, K.; Yamamoto, H. *J. Am. Chem. Soc.* **1988**, *110*, 3588.

(15) The rearrangement of **5** to **6** was over instantaneously with the reagent A at −78 °C, while MAD requires higher reaction temperature (−20 °C for several hours).

(16) The ring-opening product, 1-(*tert*-butyldimethylsiloxy)-3,7-dimethyl-3,6-octadien-2-ol was isolated in 16% yield as a major product.

(17) With the conventional Lewis acids the isolable products presumably follow: $BF_3{\cdot}OEt_2$: 1-(*tert*-butyldimethylsilyloxy)-3,7-dimethyl-3-fluoro-6-octen-2-ol; $TiCl_4$: 2-(*tert*-butyldimethylsiloxy)-1-[2-(1-chloro-1-methylethyl)-1-methylcyclobutyl]ethanol. With $Ti(O\text{-}i\text{-}Pr)_4$, no rearrangement occurred, and the substrate **5** was recovered in more than 90% yield.

(18) Attempted rearrangement of *tert*-butyldimethylsilyl ether of epoxy citronellol with $BF_3{\cdot}OEt_2$ resulted in formation of a number of deteriorated reaction products.

Nickel-Catalyzed Intramolecular [4 + 2] Dienyne Cycloadditions: An Efficient New Method for the Synthesis of Polycycles Containing Cyclohexa-1,4-dienes

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Received March 21, 1989

The low reactivity of unactivated alkynes as dienophilic reagents has proven to be a major limitation of the Diels–Alder reaction.[1] In order to circumvent the forcing and often deleterious thermal conditions required for [4 + 2] cycloadditions involving such alkynes,[1] several imaginative alternatives employing alkyne equivalents have been developed.[2] Utilization of these equivalents in formal dienyne cycloadditions normally requires pre- and post-cyclization substrate modifications, thereby representing only an indirect solution to this reactivity dilemma. As an alternative to the use of alkyne equivalents, titanium-,[3] iron-,[4] and rhodium-[5]mediated intermolecular dienyne cycloadditions have been examined. Although the application of these catalysts to intramolecular cycloadditions has not been investigated, these direct approaches have been limited by product aromatization or isomerization, competing oligomerizations, modest yields, extended reaction times, and/or a lack of established generality. The capability of nickel(0) to catalyze C–C bond formation between two dienes[6] and the advantages of this process in complex molecule total synthesis[7] prompted our examination of nickel catalysts for dienyne cycloadditions. This investigation has led to the development of the first nickel(0) catalyst system which provides a practical, direct, and mild dienyne cycloaddition approach to 1,4-cyclohexadiene-containing polycycles.

Illustrative of the efficacy of this method, *treatment of the sorbic acid derived dienyne* **1**[8] (Table I) *with 10 mol % Ni(COD)$_2$ and*

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(1) This limitation was initially treated by Sauer (Sauer, J. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 211) and is reinforced in recent reviews on the Diels–Alder reaction: Ciganik, E. *Org. React.* **1984**, *32*, 1. Fallis, A. G. *Can. J. Chem.* **1984**, *62*, 183. Taber, D. F. *Intramolecular Diels–Alder and Ene Reactions*; Springer-Verlag: Berlin, 1984. Brieger, G.; Bennett, J. N. *Chem. Rev.* **1980**, *80*, 63. The problems attending thermal dienyne cycloadditions have limited the number of examples of this process in synthesis. For some recent examples which provide calibration on the thermal requirements for such reactions, see: (a) Shea, K. J.; Burke, L. D. *J. Org. Chem.* **1988**, *53*, 318. (b) Kanematsu, K.; Hayakawa, K.; Yodo, M.; Ohsuki, S. *J. Am. Chem. Soc.* **1984**, *106*, 6735. (c) Liu Z.-Y.; Zhou, X.-R.; Wu, Z.-M. *J. Chem. Soc., Chem. Commun.* **1987**, 1868. (d) Cyclization involving a deca-7,9-dien-1-yne was found to require 150 °C, 72 h, 89% (Trost, B. M. Stanford University, personal communication, 1988). (e) Cyclizations involving nona-6,8-dien-1-ynes were found to require 150 °C, 5 h, 65–68% (Roush, W. R. Indiana University, personal communication, 1988).

(2) For a general review, see: (a) De Lucchi, O.; Modena, G. *Tetrahedron* **1984**, *40*, 2585. Recent examples of acetylene or general alkyne equivalents include the following: (trimethylsilyl)vinyl sulfone (Carr, R. C. V.; Paquette, L. A. *J. Am. Chem. Soc.* **1980**, *102*, 853), ethynyl sulfone (Davis, A. P.; Whitham, G. H. *J. Chem. Soc., Chem. Commun.* **1980**, 639), vinyl sulfoxide (Paquette, L. A.; Moerck, R. E.; Harirchian, B.; Magnus, P. D. *J. Am. Chem. Soc.* **1978**, *100*, 1597), (*E*)- or (*Z*)-1,2-bis(phenylsulfonyl)ethylene (De Lucchi, O.; Lucchini, V.; Pasquato, L.; Modena, G. *J. Org. Chem.* **1984**, *49*, 596), maleic anhydride (Westberg, H. H.; Dauben, H. J. *Tetrahedron Lett.* **1968**, 5123) and 1,4-benzodithiin-1,1,4,4-tetraoxide (Nakayama, J.; Nakamura, Y.; Hoshino, M. *Heterocycles* **1985**, *23*, 1119).

(3) Mach, K.; Antropiusova, H.; Petrusova, L.; Turecek, F.; Hanus, V. *J. Organomet. Chem.* **1985**, *289*, 331.

(4) (a) tom Dieck, H.; Diercks, R. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 778; *Angew. Chem. Suppl.* **1983**, 1138. (b) Carbonaro, A.; Greco, A.; Dall'Asta, G. *J. Org. Chem.* **1968**, *33*, 3948. (c) Genet, J. P.; Ficini, J. *Tetrahedron Lett.* **1979**, *17*, 1499.

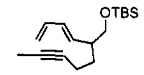
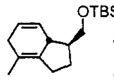
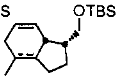
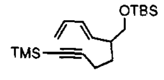
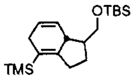
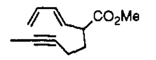
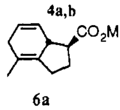
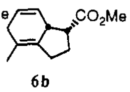
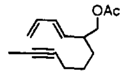
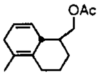
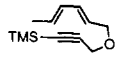
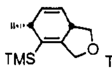
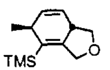
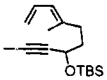
(5) Matsuda, I.; Shibata, M.; Sato, S.; Izumi, Y. *Tetrahedron Lett.* **1987**, *28*, 3361.

(6) For reviews and lead references, see: (a) Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 185. (b) Jolly, P. W. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 8, pp 613–797. (c) Jolly, P. W.; Wilke, G. *The Organic Chemistry of Nickel*; Academic: New York, 1975; Vol. 2. (d) Wender, P. A.; Ihle, N. C. *J. Am. Chem. Soc.* **1986**, *108*, 4678. (e) Wender, P. A.; Snapper, M. L. *Tetrahedron Lett.* **1987**, *28*, 2221. (f) Dienyne cyclizations are being investigated by Professor Y. Ito and co-workers and will be reported in due course (Ito, Y., personal communication, May 1989).

(7) Wender, P. A.; Ihle, N. C. *J. Am. Chem. Soc.* **1988**, *110*, 5904.

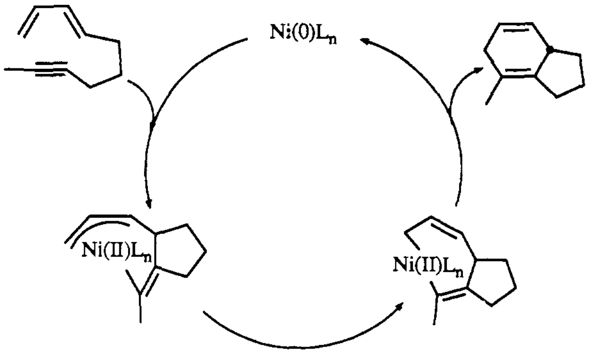
0002-7863/89/1511-6432$01.50/0

Table I. Nickel-Catalyzed and Thermal Reactions of Unactivated Dienynes[12]

		nickel(0) catalyzed[a]	thermal control[b]
dienyne	product(s)	% yield (diastereomeric ratio)/ temp	$t_{1/2}$ (h)/temp
 **1**	 **2a**  **2b**	>99% (2:1)/25 °C	16.6/160 °C
 **3**	 **4a,b**	98% (1.2:1)/25 °C	11/140 °C
 **5**	 **6a**  **6b**	88% (2.2:1)/25 °C	15/150 °C
 **7**	 **8a,b**	85% (1.8:1)/55 °C	76/200 °C
 **9**	 **10a**  **10b**	98% (>99:1)/25 °C	22.5/80 °C
 **11**		N. R.	

[a] Dienyne 0.01 M in THF; 10 mol % Ni(COD)$_2$; 30 mol % tri-o-biphenyl phosphite.[9] [b] Thermal control reactions were run in a resealable tube with either toluene or benzene as solvent. The reactions were monitored by gas chromatography and/or NMR. Half-life values and the reported temperatures are for conversion of starting dienyne at the temperature where Diels–Alder products were initially observed.

Scheme I



*30 mol % tri-o-biphenyl phosphite in THF at room temperature affords cyclohexadienes **2a** and **2b** (2:1, respectively) in >99% yield.*[9] In contrast, the uncatalyzed reaction of **1** can be effected only at temperatures >160 °C. The preparative potential of this process is considerable as suggested by the conversion of dienyne **9** to cyclohexadiene **10a** on a multigram (8.0 g) scale. The catalytic cycle proposed for these cycloadditions is given in Scheme I.

As generally observed for transition-metal-catalyzed reactions, product-type selectivity and yield are sensitive to variations in the nickel catalyst and reaction conditions. For example, when the catalyst (Ni(COD)$_2$/Ph$_3$P) and solvent (toluene) which efficiently effect [4 + 4] cycloadditions of tethered dienes[6c,d] are employed with dienyne **1**, a sluggish reaction ensues, attended by substrate decomposition and product aromatization. Modification of the nickel(0) catalyst with tricyclohexylphosphine results in an efficient reaction, but only conjugated cyclohexadiene products are obtained. Of the several ligand/solvent combinations tested, tri-*o*-biphenyl phosphite and THF proved superior. For this system, a ligand:nickel(0) ratio of 3:1 provides optimal efficiency and product type selectivity. When a 1:1 ratio is used, β-hydride elimination products are observed, and the catalyst lifetime is reduced. Conversely, a 5:1 ratio inhibits the desired catalytic activity.

The generality of the above catalytic system was tested with several substrates (Table I) which were selected to address the principal issues associated with the use of this cycloaddition in synthesis. Comparison of the catalyzed and control (uncatalyzed) reactions reveals that the former proceed at temperatures 55–145 °C lower than those minimally needed to effect the latter. In one case (dienyne **7**), representing a substrate type commonly encountered in synthesis, the mildest conditions (ca. 200 °C) required for the uncatalyzed process are sufficiently harsh to cause decomposition. Importantly, the catalyzed reactions work comparably well with 3- and 4-atom connectors between the diene and alkyne functionalities and with an oxygen heteroatom in the tether. Substrates with 2- or 5-atom tethers do not cyclize under these conditions. Various functionalities are tolerated in this reaction,[6c,10] but it is sensitive to substituents on the diene and alkyne groups. For example, while substitution at the external terminus of the diene (substrate **9**) has no effect, substitution at the internal terminus renders substrate **11** unreactive. Interestingly, this effect is not found in analogous nickel(0)-catalyzed [4 + 4] cycloadditions.[6d] The reaction works well for internal alkynes, whereas terminal alkynes undergo competitive coupling. This problem is mitigated, however, by the efficient cyclizations of silyl-substituted alkynes, as desilylation of the products offers an attractive route to the same cyclohexadienes that would otherwise arise from terminal alkynes. Finally, while it is premature to generalize about the stereochemistry attending these reactions,

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(8) Ballester, P.; Costa, A.; Garcia-Raso, A.; Gomez-Solivellas, A.; Mestres, R. *Tetrahedron Lett.* **1985**, *26*, 3625.

(9) Commercially available Ni(COD)$_2$ is conveniently stored at -20 °C (freezer) as a stock solution approximately 0.08 M in THF. In a typical experiment, **3** (1.48 mmol) and tri-*o*-biphenyl phosphite (0.44 mmol) are placed in a base-washed, oven-dried, N$_2$-purged Schlenk flask and dissolved in dry, oxygen-free THF (150 mL). The Ni(COD)$_2$ stock solution (0.148 mmol) is added dropwise under N$_2$ with a gas-tight syringe; the resulting light yellow solution is stirred at room temperature for 11 h (when a shorter reaction time is desired the reaction can be heated to 45 °C). The reaction is then permitted to air oxidize for 30 min during which time insoluble nickel colloids are obtained. The reaction mixture is eluted through a small pad of silica gel with hexanes, and the eluant is concentrated. Flash chromatography on silica gel using hexanes gives **4a,b** (97%).

(10) Ihle, N. C. Ph.D. Dissertation, Stanford University, 1988.

the cyclization of substrate **9** proceeds with complete stereocontrol, involving a formal syn facial addition of the alkyne to the diene. While the cyclization of substrates **1–7** currently exhibits modest stereoinduction, more recent studies have revealed that stereoselectivity is enhanced at higher concentrations.[11]

In summary, this study establishes a mild (25–55 °C), efficient (85 → 99%), and practical method for effecting the direct [4 + 2] cycloaddition of unactivated alkynes, allowing for the broader use of this otherwise thermally limited process in the synthesis of 1,4-cyclohexadienes. This process can also be applied to heterocyclic synthesis as heteroatom substitution in the tether is well tolerated. Furthermore, the 1,4-cyclohexadienes obtained in these reactions are readily aromatized with DDQ, thus providing an efficient route to functionalized arenes. Finally, in contrast to the Birch reduction of arenes as a route to 1,4-cyclohexadienes, this approach is regiocontrolled for all substitution patterns. Further studies are in progress.

Acknowledgment. Support was provided by NSF (CHE 87-06051). NMR spectra were obtained with instruments provided by NSF (CHE 81-09064 and CHE 84-14329) and NIH (1 S10 RR04205). We thank Dr. John M. Nuss for his efforts concerning this work.

Supplementary Material Available: NMR, IR, and analytical data for compounds **1–10**, along with the chemical methods used to assign stereochemistry for **2a,b** and **6a,b** (4 pages). Ordering information is given on any current masthead page.

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[11] When the reaction concentration was increased from 0.01–0.1 M in dienyne **3**, the diastereoselectivity increased from 1.2:1 to 4.5:1, without a change in overall yield. Similar behavior was also observed with dienyne **1**.

[12] Dienynes **1–7** were derived from a sorbic acid dianion alkylation (see ref 8), followed by either esterification with diazomethane or LAH reduction and protection. Dienyne **9** was derived from sorbol alcohol and propargyl bromide. Stereochemistry was not determined for products resulting from cycloadditions proceeding with <2:1 stereoselectivity but is expected to follow that observed for **2a,b**.

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^{252}Cf Plasma Desorption Mass Spectrometry as a Tool for Studying Very Large Clusters. Evidence for Vertex-Sharing Icosahedra as Components of $Au_{67}(PPh_3)_{14}Cl_8$

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College Station, Texas 77843

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Minneapolis, Minnesota 55455

Received March 6, 1989

The potential of mass spectrometry in characterizing large clusters is illustrated by a ^{252}Cf-PDMS[1] study of a gold cluster of molecular weight ca. 17 000 amu. The results of this study indicate that the structure of this compound consists of vertex-sharing icosahedra.

The title Au cluster (**1**), synthesized by Schmid[2] and formulated as $Au_{55}(PPh_3)_{12}Cl_6$ (based on elemental analysis and molecular weight measurements), with a proposed two-layer cuboctahedron structure[3] involving an Au_{13} cuboctahedra surrounded by 42 further Au atoms in a cubic close packed array, gave mass spectra as shown (Figure 1). Although both (A) and (B) were similarly prepared,[4] the spectra are different. Both samples give a wide distribution of well-resolved assignable peaks, with three high mass zones of high intensity. These zones are centered at 8570, 12 800, and 16 600 *m/z* with the zone at 16 600 *m/z* of greatest intensity in (A) while the reverse is true in (B).

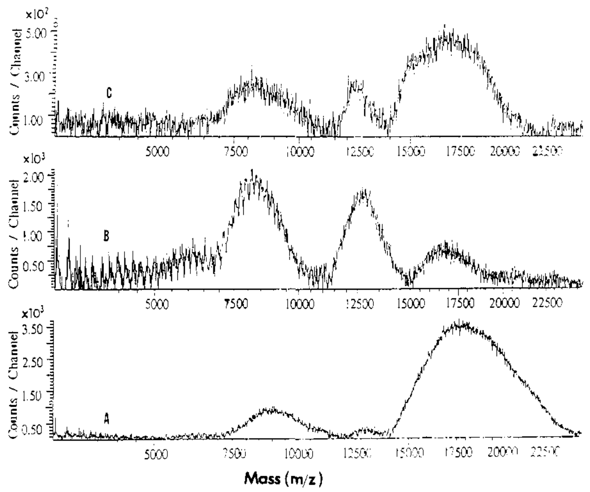

Figure 1. ^{252}Cf plasma desorption positive ion mass spectra of samples (A), (B), and (C) showing the three high mass zones of high intensity. The low mass region indicates that the apparent width of the peaks is the result of a broad distribution of peaks containing varying numbers of Au atoms, PPh_3 and PPh_2 ligands, and Cl^- anions.

^{252}Cf-PDMS of smaller Au clusters[5] suggests that such profiles are caused by fragmentation of compounds with molecular weights near, but above, that at the center of the zones. The influence of sample preparation has been investigated. In addition to the electrosprayed samples reported herein, samples of **1** have been prepared by direct evaporation and by adsorption on nitrocellulose. In all cases the spectra were qualitatively very similar, with the exception that additional high mass cluster ions (in excess of *m/z* 50 000) were observed when nitrocellulose was used. Negative ions were also observed for each sample, although the zones were broader. The most intense negative ion zone was observed at ca. 16 500 in (A) but at ca. 13 000 *m/z* in (B). The negative ion data and the independence of the spectra from the preparation technique support the idea that the spectra observed are independent of sample morphology and therefore are due to the chemistry of the system and not the result of ion formation processes.[6] None of the observed zones coincide with the calculated weight of $Au_{55}(PPh_3)_{12}Cl_6$ (14 165 amu) nor is the presence of zones explicable by the Schmid double-layer structure.

The spectra are explicable if the clusters are built of vertex-sharing icosahedra, I.[7] Teo[8] has suggested that a series of highly symmetric supraclusters of this type should exist for I_5 (M_{56}, trigonal bipyramidal), I_7 (M_{76}, pentagonal bipyramidal), and I_{12} (M_{127}, icosahedral) in addition to known compounds for I_2,[9] I_3,[8]

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[1] Sundqvist, B.; Macfarlane, R. D. *Mass. Spec. Rev.* **1985**, *4*, 421.

[2] Schmid, G.; Pfeil, R.; Boese, R.; Bandermann, F.; Meyer, S.; Calis, G. H. M.; van der Velden, J. W. A. *Chem. Ber.* **1981**, *114*, 3634.

[3] Schmid, G. *Struct. Bonding* **1985**, *62*, 51.

[4] Sample (A) was prepared by Schmid et al. (ref 2); sample (B) by Pignolet and co-workers, following the same procedure. Mass spectral analysis was performed on samples which had been electrosprayed as 10^{-3} M CH_2Cl_2 solutions onto an aluminized Mylar film. Both spectra were highly reproducible both in terms of relative intensities and masses. For a description of instrumentation, see: Macfarlane, R. D. *Anal. Chem.* **1983**, *55*, 1247A.

[5] Cox, S.; Fackler, Jr., J. P.; McNeal, C. J.; Shi, X.; Teo, B. K.; Winpenny, R. E. P.; Zhang, H. Unpublished results. The compounds studied include a sample containing the $Au_{13}Ag_{12}$ cluster structurally characterized by Teo and co-workers.[9] This sample, a mixture, gave three zones at ca. 3800, 6100, and 8000 *m/z*, which correspond to $Au_6Ag_7(PPh_3)_8{}^+$, $Au_{12}Ag_{13}(PPh_3)_{10}{}^+$, and $Au_{18}Ag_{19}(PPh_3)_{10}{}^+$, respectively. In a collaboration with Professor B. Teo, we plan to study the mass spectra of single crystals of materials which have been structurally characterized.

[6] Very recent results on more highly purified samples show that the zones can be significantly narrowed with a direct correspondence between the positive and negative ion spectra.

[7] The alternative concept of packing M_{13} units without sharing vertices, while explaining the highest and lowest mass zones (as due to 5 × M_{13} and 2 × M_{13}, respectively), cannot account for the middle zone. For a discussion of this proposal, see: Schmid, G. *Polyhedron* **1988**, *7*, 2321.

[8] Teo, B. K.; Hong, M. C.; Zhang, H.; Huang, D. B. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 897.

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