

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 stereoselection, 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.

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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.

(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) Dienes **1-7** were derived from a sorbic acid dianion alkylation (see ref 8), followed by either esterification with diazomethane or LAH reduction and protection. Diene **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**.

²⁵²Cf Plasma Desorption Mass Spectrometry as a Tool for Studying Very Large Clusters. Evidence for Vertex-Sharing Icosahedra as Components of Au₆₇(PPh₃)₁₄Cl₈

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The potential of mass spectrometry in characterizing large clusters is illustrated by a ²⁵²Cf-PDMS¹ 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 Schmid² and formulated as Au₅₅(PPh₃)₁₂Cl₆ (based on elemental analysis and molecular weight measurements), with a proposed two-layer cuboctahedron structure³ involving an Au₁₃ cuboctahedron 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

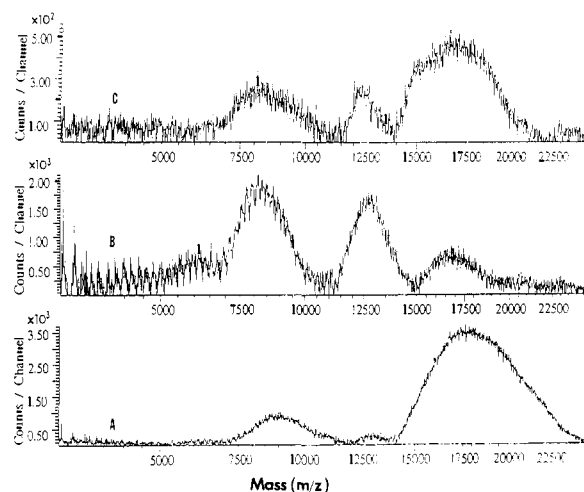


Figure 1. ²⁵²Cf plasma desorption positive ion mass spectra of samples (A), (B), and (C) showing the three high mass zones of high intensity. The low mass region indicates that the apparent width of the peaks is the result of a broad distribution of peaks containing varying numbers of Au atoms, PPh₃ and PPh₂ ligands, and Cl⁻ anions.

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).

²⁵²Cf-PDMS of smaller Au clusters⁵ 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 Au₅₅(PPh₃)₁₂Cl₆ (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 Teo⁸ has suggested that a series of highly symmetric supraclusters of this type should exist for I₅ (M₅₆, trigonal bipyramidal), I₇ (M₇₆, pentagonal bipyramidal), and I₁₂ (M₁₂₇, icosahedral) in addition to known compounds for I₂,⁹ I₃,⁸

(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 CH₂Cl₂ solutions onto an aluminumized 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 Au₁₃Ag₁₂ 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 Au₆Ag₇(PPh₃)₈⁺, Au₁₂Ag₁₃(PPh₃)₁₀⁺, and Au₁₈Ag₁₉(PPh₃)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 M₁₃ units without sharing vertices, while explaining the highest and lowest mass zones (as due to 5 × M₁₃ and 2 × M₁₃, 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.

(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.

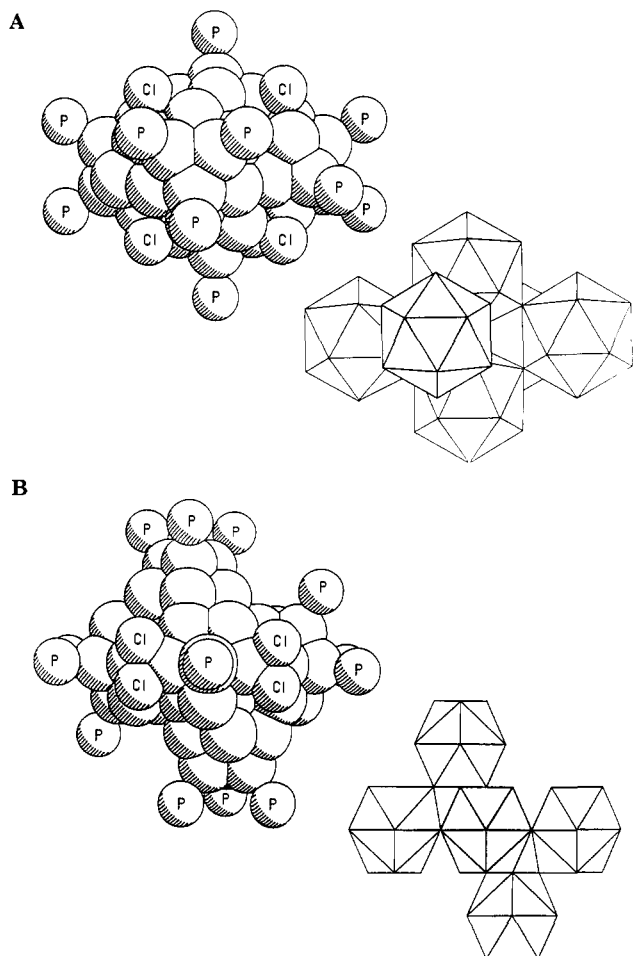


Figure 2. Space-filling representation of the proposed structure for $\text{Au}_{67}(\text{PPh}_3)_{14}\text{Cl}_8$ viewed (A) plan and (B) elevation. The phosphine positions are labeled P (with phenyl rings omitted for clarity), all unlabeled atoms are Au. The icosahedral framework is indicated in the accompanying line drawings.

and I_4 .¹⁰ Similar, but less symmetric, clusters can also be proposed. In particular an I_6 , M_{67} cluster sharing eleven vertices can be postulated (Figure 2). This can be visualized as two tetrahedral I_4 units sharing two icosahedra in a centrosymmetric manner.

In known supraclusters, $[\text{Au}_{12}\text{Ag}_{13}(\text{PPh}_3)_{12}\text{Cl}_6]^{m+}$ ($\mathbf{2}$)⁹ (I_2 , linear), $[\text{Au}_{18}\text{Ag}_{19}[\text{P}(\text{Tol})_3]_{12}\text{Br}_9]^{2+}$ ($\mathbf{3}$)⁸ (I_3 , trigonal + one capping Ag), and $\text{Au}_{22}\text{Ag}_{24}(\text{PPh}_3)_{12}\text{Cl}_{10}$ (I_4 , tetrahedral), the phosphine ligands are bound only to those metal atoms which are *not* involved in binding to the other icosahedra. If this is a general condition, then 14 phosphines would be attached to I_6 (Figure 2). With triphenylphosphine as the ligand the metallic core is well encapsulated allowing for conventional cone angles.¹¹ The number of anions is more problematic. Electron-counting rules¹² predict 12 or 13 Cl^- ions, but elemental analysis² indicates eight. As physical data must be preferred to theory eight anions are included in our model (Figure 2).

The zones in the mass spectra observed for "Au₅₅" are therefore due to the fragmentation of I_6 , $\text{Au}_{67}(\text{PPh}_3)_{14}\text{Cl}_8$ (at ca. 16 600 m/z); I_4 , $\text{Au}_{46}(\text{PPh}_3)_{12}\text{Cl}_6$ (at ca. 12 800 m/z); and I_2 , $\text{Au}_{25}(\text{PPh}_3)_{12}\text{Cl}_6$ (at ca. 8590 m/z).¹³ The two samples contain differing amounts of these three supraclusters. (A) can be re-

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(10) Teo, B. K.; Shi, X.; Zhang, H. *Chem. Eng. News.* **1989**, *67*(2), p 6.

(11) Tollman, C. A. *Chem. Rev.* **1977**, *77*, 313. In $\text{Au}_{67}(\text{PPh}_3)_{14}\text{Cl}_8$ the distance between the centers of the bases of the triphenylphosphine "cones" is 6.0 Å cf. sterically required 6.3 Å.

(12) Teo, B. K.; Zhang, H. *Inorg. Chem.* **1988**, *27*, 414.

(13) Additional peaks may be caused by the presence of supraclusters "capped" by individual Au atoms and associated anions as seen in the M_{37} and M_{38} clusters reported previously (ref 8). The number of anions attached to the smaller supraclusters is uncertain.

precipitated by dissolving in CH_2Cl_2 and adding pentane, giving (C) (Figure 1). The ratio of $\text{I}_4:\text{I}_6$ increases markedly, suggesting that an equilibrium exists in solution between these various supraclusters¹⁴ and that the mole ratios in the solid sample depend on the rate of precipitation.

The cluster produced by Schmid² (A) is therefore formulated to be $\text{Au}_{67}(\text{PPh}_3)_{14}\text{Cl}_8$ with smaller clusters as impurities. This formulation fits the analytical data and observed molecular weight better than $\text{Au}_{55}(\text{PPh}_3)_{12}\text{Cl}_6$. The slight, but necessary modification of Teo's supracluster model⁸ allows us to predict the existence of many more supraclusters of low rotational symmetry. ²⁵²Cf-PDMS can provide essential information about these large clusters in spite of considerable fragmentation.

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(14) Reprecipitation of sample (B) gave a sample with an identical spectrum to that of (B); this indicates that the solution equilibrium is close to that in the solid sample (B). Very slow reprecipitation, by vapor diffusion of pentane at low temperatures, gave a gold mirror.

Zirconium-Mediated Ring Construction from Dienes: Remarkable Effect of Ligands on Stereochemistry[†]

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Recently there has been growing interest in transition-metal-mediated cyclization of enynes and diynes as a tool for organic synthesis.² It is therefore surprising that the synthetic potential of the corresponding intramolecular cyclometalation of nonconjugated dienes has remained unexplored.³ We have recently discovered conditions that allow such cyclometalations to be carried out efficiently. Our preliminary studies suggest that these transformations will prove quite useful in organic synthesis.

Our approach allows the selective cyclization of 1,6-dienes to either *cis*- or *trans*-1,2-disubstituted cyclopentanes. Treatment of 1,6-heptadiene with zirconocene dichloride (1 equiv) and butyllithium (2 equiv)⁴ followed by bromination at -78°C as shown in eq 1a afforded *trans*-1,2-bis(bromomethyl)cyclopentane in 88% isolated yield (crude product 97% *trans* by GLC).⁵ In contrast

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[‡] Contribution No. 5062.

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(2) For a review, see: Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047-1058.

(3) The literature contains several reports of cyclization of 1,7-octadiene by early transition metals to give isomeric mixtures of metallaindanes: McDermott, J. X.; Wilson, M. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6529-6536. Grubbs, R. H.; Miyashita, A. *J. Chem. Soc., Chem. Commun.* **1977**, 864-865. McLain, S. J.; Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 4558-4570. Gell, K. I.; Schwartz, J. *J. Chem. Soc., Chem. Commun.* **1979**, 244-246.

(4) This superb "zirconocene equivalent" was developed and first applied to organic synthesis by Negishi and co-workers: Negishi, E.-i.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1986**, *27*, 2829-2832.