Table I.[a] Yields of ^{75}Ge-Labeled Products from Reactions of ^{75}Ge Atoms

Expt	Substrate	$^{75}GeH_4$[b]	$H_3{}^{75}GeGeH_3$[b]	$H_3{}^{75}GeSiH_3$[b]	$H_3{}^{75}GeGeH_3$ / $^{75}GeH_4$	$H_3{}^{75}GeGeH_3$ / $H_3{}^{75}GeSiH_3$
A	GeH_4	3900 ± 600	17,300 ± 2,800	...	4.5 ± 1.0	...
A	1:1 GeH_4-SiH_4	1500 ± 200	7,600 ± 1,200	1900 ± 300	5.2 ± 1.2	4.0 ± 0.9
B	GeH_4	2200 ± 400	8,300 ± 1,300	...	3.8 ± 0.9	...
B	GeH_4 + 10% NO	3800 ± 600	5,400 ± 900	...	1.4 ± 0.3	...

[a] All samples at total pressure 2.2 ± 0.1 atm and, within an experiment, irradiated simultaneously at equal neutron flux. [b] Yields given as counts above background extrapolated to a common time for each experiment to correct for decay.

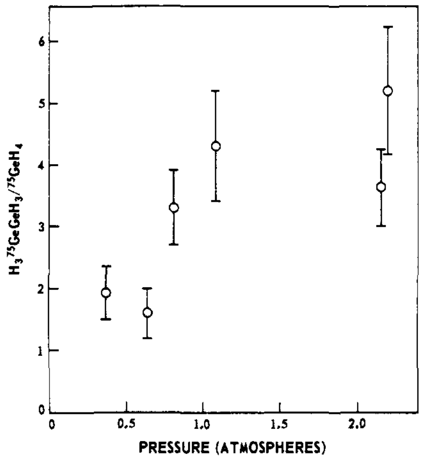

Figure 1. Variation of product ratio from pure germane with total pressure.

tained from the irradiation at equal pressure (2.2 atm) of silane-rich phosphine-silane mixtures with fast neutrons.[3] These product ratios appear to be near to the high-pressure limits for both systems. The absolute yield of volatile products from the germanium system, 20 ± 10%, is lower than that obtainable in the silicon system (>80%). The product ratio from germane shows a marked pressure dependence (Figure 1) not observed in the silicon experiments.

Fast-neutron irradiation of a 1:1 germane-silane mixture (Table I) produced $H_3{}^{75}GeSiH_3$ as well as $^{75}GeH_4$ and $H_3{}^{75}GeGeH_3$. The presence of silane in the reaction mixture seems not to change (within experimental error, *ca.* 20%) the total yield of volatile radioactive products per unit of precursor, nor the ratio of radioactive digermane to germane. This suggests that a recoiling germanium species (or set of species formed in constant ratio) can react with silane giving silylgermane as well as reacting with germane. The greater affinity for germane over silane is consistent with the relative strengths of Ge-H and Si-H bonds for a variety of possible reaction mechanisms operative in these experiments. The total dose in all experiments was less than 10^{-2} eV per molecule. Radiation damage was very slight, as indicated by the formation of less than 0.1% digermane by radiolysis of germane.[6]

The nature of the active intermediates which intervene in the reaction sequence between free germanium atoms and the stable products observed remains to be determined. In a scavenger experiment (Table I) the yield ratio of $H_3{}^{75}GeGeH_3$ to $^{75}GeH_4$ decreased upon the addition of 10% nitric oxide to germane prior to neutron irradiation. Assignment of structures to the intermediates cannot be made unambiguously at this time because of the paucity of information about the ground-state thermal chemistry of simple germanium radicals. A plausible but not unique set of product-determining steps involves the germylene radical, $:{}^{75}GeH_2$.

$$:{}^{75}GeH_2 + GeH_4 \rightarrow H_3{}^{75}GeGeH_3$$
$$:{}^{75}GeH_2 + GeH_4 \rightarrow {}^{75}GeH_4$$
$$:{}^{75}GeH_2 + SiH_4 \rightarrow H_3{}^{75}GeSiH_3$$

Germylene has been proposed as the species responsible for the formation of mixed silicon-germanium hydrides in the copyrolysis of silane and germane.[7]

Further studies of germanium atom chemistry are underway.

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(6) The exact amount of digermane formed by radiolysis of germane is difficult to determine due to the presence of *ca.* 0.1% digermane as an impurity (useful as an internal carrier) in the germane subjected to neutron irradiation.

(7) P. L. Timms, C. C. Simpson, and C. S. G. Phillips, *J. Chem. Soc.*, 1467 (1964).

Structural Characterization of a New Type of Tetranuclear Metal Cluster System: $Pt_4\{P(C_6H_5)(CH_3)_2\}_4(CO)_5$[1]

Sir:

As part of a systematic study to determine the structures and nature of bonding for the different polymeric platinum phosphine carbonyl complexes recently synthesized by Booth, Chatt, and Chini[2] from the reactions of Na_2PtCl_4 with tertiary phosphines, carbon monoxide, hydrazine,

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(1) R. G. V. and L. F. D. gratefully acknowledge the financial support of the X-ray work by the National Science Foundation (GP-4919). The use of the CDC 3600 and 1604 computers at the University of Wisconsin Computing Center was made possible through the partial support of NSF and WARF through the University of Wisconsin Research Committee.

(2) G. Booth, J. Chatt, and P. Chini, *Chem. Commun.*, 639 (1965).

and potassium hydroxide in hot aqueous 90% ethanol, we wish to present here the results of an X-ray investigation of $Pt_4\{P(C_6H_5)(CH_3)_2\}_4(CO)_5$ which have established the existence of a new kind of metal atom cluster. The stoichiometry (as well as atomic arrangement) determined from the X-ray study of this brown complex, originally formulated[2] as $Pt_3\{P(C_6H_5)(CH_3)_2\}_3(CO)_4$, is in agreement with the chemical analysis[3] and infrared spectrum.[4]

Crystals of $Pt_4\{P(C_6H_5)(CH_3)_2\}_4(CO)_5$ are orthorhombic with unit cell parameters a = 19.96 Å, b = 20.29 Å, c = 10.66 Å; $\rho_{\text{obsd}} = 2.21$ g cm^{-3} (flotation method) *vs.* $\rho_{\text{calcd}} = 2.27$ g cm^{-3} based on four molecules per cell. Systematic absences of l odd for $\{0kl\}$ and $h + k$ odd for $\{hk0\}$ show the probable space groups to be either $Pc2_1n$ [nonstandard setting of $Pna2_1$ (C_{2v}^9, no. 33)] or Pcmn [nonstandard setting of Pnma (D_{2h}^{16}, no. 62)]. The choice of the centrosymmetric group, Pcmn, was made from Patterson and Fourier syntheses and subsequently was corroborated from the least-squares refinement. Three-dimensional Weissenberg data were collected with Mo Kα radiation from two extremely small crystals from which 852 independent observed reflections were obtained before both crystals decomposed. The structure was solved with difficulty by Patterson and Fourier techniques. Full-matrix least-squares refinement was carried out with the phenyl rings (including both carbon and hydrogen atoms) treated as rigid groups. The final conventional unweighted discrepancy factor is 8.9% based on anisotropic thermal parameters for the platinum and phosphorus atoms and isotropic thermal parameters for all oxygen and carbon atoms.

As seen from Figure 1, the molecular geometry of $Pt_4\{P(C_6H_5)(CH_3)_2\}_4(CO)_5$ may be considered as the first example of a basic $M_4Y_4X_5$ structure which can possess C_{2v}-2 mm symmetry. The four metal atoms (M) in this idealized structure are arranged at the apices of a distorted tetrahedron with one nonbonding and five bonding metal–metal distances. The four terminal Y ligands are each bonded to a different metal atom, while the five doubly bridging X ligands span the five *bonding* edges of the markedly deformed tetrametal tetrahedron. The resulting molecular architecture thereby contains two different kinds of metal atoms: two equivalent seven-coordinated metal atoms, which each form bonds with the other three metal atoms and with one Y and three X ligands, and two equivalent five-coordinated metal atoms, which each are linked with the two seven-coordinated metal atoms and with one Y and two X ligands.

In the case of $Pt_4\{P(C_6H_5)(CH_3)_2\}_4(CO)_5$ the four terminal Y ligands all correspond to phenyldimethylphosphine donors, while the five doubly bridging X ligands are all carbonyl groups. The approximate C_{2v} symmetry for the $Pt_4(P)_4(CO)_5$ fragment (*i.e.*, without the phenyl and methyl groups) gives rise to three stereochemically different platinum–platinum distances: one nonbonding and two bonding ones. The symmetry-unique bonding Pt(2)–Pt(3) distance of 2.790 Å (esd, 0.007 Å) is 0.038 Å longer than the average bonding distance of 2.752 Å for the other four equivalent Pt–Pt bonds; this latter value is the mean of the two crystallographically independent Pt(1)–Pt(2) and Pt(1)–Pt(3) bond lengths of 2.750 and 2.754 Å (individual esd, 0.006 Å), respectively. These values, considered to be "normal" for Pt–Pt single bonds, are approximately 0.2 Å longer than the three Pt–Pt distances of average value 2.58 ± 0.01 Å found in the platinum–tin cluster complex $Pt_3(SnCl_3)_2(C_8H_{12})_3$.[5-10] The nonbonding Pt(1) · · · Pt(1′) distance of 3.543 (8) Å is not unlike the nonbonding Pt · · · Pt distances in the tetrameric trimethylplatinum derivatives, $[Pt(CH_3)_3Cl]_4$

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[3] *Anal.* Calcd for $Pt_4\{P(C_6H_5)(CH_3)_2\}_4(CO)_5$: C, 30.17; H, 3.01; CO (ml/g at STP), 76.0. Found: C, 30.29; H, 2.99; CO (ml/g at STP), 81.8. No molecular weight measurements were made in solution.

[4] The possibility that this compound contains hydrogen atoms coordinated to the platinum atoms was excluded not only from stereochemical and bonding considerations but also from chemical and physical evidence. The solid-state infrared spectra of both $Pt_4\{P(C_6H_5)(CH_3)_2\}_4(CO)_5$ and the triphenylphosphine analog, $Pt_4\{P(C_6H_5)_3\}_4(CO)_5$ (also initially formulated[2] as the trinuclear platinum complex of type F but later shown from preliminary X-ray data to have the tetranuclear platinum structure), revealed no absorption bands characteristic of Pt–H vibrational modes. Furthermore, no hydrogen gas was detected by mass spectrometry when the triphenylphosphine analog was decomposed by the reaction $Pt_4\{P(C_6H_5)_3\}_4(CO)_5 + 8DPPE \rightarrow 4Pt(DPPE)_2 + 5CO + 4P(C_6H_5)_3$ (where DPPE = 1,2-bisdiphenylphosphinoethane); instead, the mass spectrometric analysis showed the evolved gas to be pure carbon monoxide.

[5] L. J. Guggenberger, *Chem. Commun.*, 512 (1968).

[6] Although the $Pt_3(SnCl_3)_2(C_8H_{12})_3$ structure (which consists of an equilateral triangle of platinum atoms each coordinated to the two double bonds of a cyclooctadiene ring and capped above and below by $SnCl_3$ groups) was described[5] in terms of Pt–Pt single bonds, an LCAO–MO formulation similar to those utilized in the description of the $[Re_3Cl_{12}]^{3-}$ anion[7] and other stereochemically related triangular metal carbonyl cluster systems[8-10] instead indicates that the valence-bond Pt–Pt bond order is intermediate between 1 and 2. For convenience the idealized geometry of this molecular complex may be approximated as D_{3h}-62m. The qualitative MO model assumes that four of the nine basis functions of each platinum atom are primarily involved in localized electron-pair bonding with the two double bonds of the cyclooctadiene ring and the two $SnCl_3$ groups, and hence are separable from the Pt–Pt interactions by the perfect-pairing approximation. Local orthogonal coordinate systems were chosen at each platinum atom with the z axis centripetally directed toward the centroid of each platinum triangle and with the x and y axes parallel and perpendicular, respectively, with the triplatinum plane. The s, p_y, $(p_x + p_z)/\sqrt{2}$, and $(p_x - p_z)/\sqrt{2}$ orbitals on each platinum atom have both the proper symmetry properties and favorable directional character to interact strongly in forming electron-pair bonds with the two olefinic double bonds and the two tin atoms; these orbitals are presumed to be completely utilized in the platinum–ligand bonding and hence not available for the Pt–Pt interactions. The remaining *five* d valence orbitals per platinum atom are then transformed under D_{3h} symmetry to give *seven* bonding platinum symmetry orbital combinations (*viz.*, $d_{z^2}(a_1')$, $d_{xz}(e')$, $d_{yz}(a_2'')$, $d_{x^2-y^2}(a_1')$, and $d_{xy}(e'')$) and *eight* antibonding combinations (*viz.*, $d_{xy}(a_1'')$, $d_{x^2-y^2}(e'^*)$, $d_{yz}(e''^*)$, $d_{xz}(a_2'^*)$, and $d_{z^2}(e'^*)$). Of the 30 valence electrons possessed by the triplatinum system, 10 electrons are used to complete the σ bonding with the two one-electron-donating $SnCl_3$ groups. If it is assumed that the splittings due to the Pt–Pt interactions predominate over the splittings due to the nonspherical environment about each platinum atom, then orbital overlap considerations predict (with the neglect of mixing of atomic orbitals belonging to the same irreducible representation) a relative orbital energy level pattern in which the 20 valence electrons available for the triplatinum system occupy all the energy levels except the highest unfilled $d_{yz}(e''^*)$, $d_{xz}(a_2'^*)$, and $d_{z^2}(e'^*)$ antibonding ones. Since the corresponding occupied bonding and antibonding levels are presumed effectively to cancel one another's bonding, the resulting Pt–Pt interactions in the platinum triangle are due to eight bonding valence electrons corresponding from a valence bond formalism to a Pt–Pt bond order of greater than 1.0 but less than 2.0. These symmetry arguments ignore metal–ligand π-bonding effects which obviously provide a mechanism for delocalization of negative charge from the filled platinum symmetry orbitals onto the appropriate empty ligand orbitals. It is noteworthy that $Pt_3(SnCl_3)_2C_8H_{12}$ is an exception to the "noble gas" rule in that with the assumption of Pt–Pt electron-pair bonds the entire molecule contains four less electrons than that required for a closed-shell electronic configuration for each platinum atom corresponding to the antibonding $d_{yz}(e''^*)$ platinum symmetry orbital being empty rather than filled. Hence, it is expected that the Pt–Pt interactions are stronger in $Pt_3(SnCl_3)_2(C_8H_{12})$ than those in $Pt_4\{P(C_6H_5)(CH_3)_2\}(CO)_5$ in agreement with the shorter Pt–Pt distances observed for the former molecule.

[7] F. A. Cotton and T. E. Haas, *Inorg. Chem.*, **3**, 10 (1964); F. A. Cotton, *ibid.*, **4**, 334 (1965).

[8] C. H. Wei and L. F. Dahl, *J. Am. Chem. Soc.*, **90**, 3960 (1968).

[9] *Cf.*, H. Vahrenkamp, V. A. Uchtman, and L. F. Dahl, *ibid.*, **90**, 3272 (1968).

[10] C. E. Strouse and L. F. Dahl, *Disc. Faraday Soc.*, in press, and references cited therein.

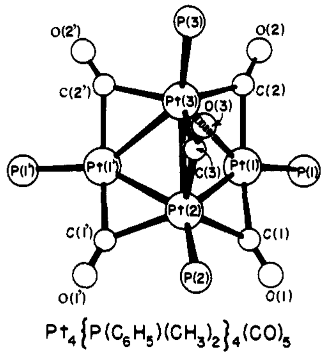

Figure 1. Geometry of the $Pt_4(P)_4(CO)_5$ fragment of the $Pt_4\{P(C_6H_5)(CH_3)_2\}_4(CO)_5$ molecule (*i.e.*, for clarity the phenyl and methyl groups have been omitted from the drawing). The entire molecule crystallographically conforms to the C_s-m point group with the mirror plane passing through Pt(2), Pt(3), P(2), P(3), C(3), O(3), and the two phenyl groups, $C_6H_5(2)$ and $C_6H_5(3)$, attached to P(2) and P(3), respectively. The $Pt_4(P)_4(CO)_5$ fragment ideally has C_{2v}-2mm symmetry with the perpendicular noncrystallographic mirror plane encompassing Pt(1), Pt(1'), P(1), P(1'), C(3), and O(3); the twofold principal axis located along the line of intersection of these two vertical mirror planes passes through C(3) and O(3).

(3.73 Å)[11] and $[Pt(CH_3)_3OH]_4$ (3.430 Å).[11-14] The stereochemically equivalent lengths of 2.26 Å for the Pt(2)–P(2) bond and 2.29 Å for the Pt(3)–P(3) bond are close to the Pt(1)–P(1) bond length of 2.27 Å (individual esd, 0.03 Å). The relatively large standard deviations for the molecular parameters involving the light atoms (due to the limited number of intensity data per parameter as well as the scattering power differences between the platinum and light atoms) preclude any further detailed analysis.

The nature of the metal–metal interactions in this particular complex can be qualitatively described in terms of a valence-bond formalism involving the use of localized electron-pair σ bonds.[15] In accord with the closed-shell electronic configuration for simple tetrahedral-like derivatives of zerovalent platinum such as $Pt\{P(C_6H_5)_3\}_3(CO)$ and $Pt\{P(C_6H_5)_3\}_2(CO)_2$, the two seven-coordinated zerovalent platinum atoms, Pt(2) and Pt(3), each possess a closed-shell electronic configuration. On the other hand, each of the two crystallographically related five-coordinated platinum atoms, Pt(1) and Pt(1'), has only a 16-electron count (a total of two electrons less than that required for a closed-shell "magic number") as also occurs in $Pt\{P(C_6H_5)_3\}_3$.[16]

This structure is stereochemically related to the basic $M_4Y_4X_6$ structure of cubic T_d-$\bar{4}3m$ symmetry in which the X ligands symmetrically bridge all six edges of a regular bonding tetrahedron of metal atoms. Although as yet unknown for any complexes of platinum, this configuration recently was found by Bennett, Cotton, and Winquist[17] from an X-ray analysis of a metal phosphine carbonyl complex of the congener element nickel, *viz.*, $Ni_4(PR_3)_4(CO)_6$ where $R = C_2H_4CN$. In this nickel cluster system the reasonable assumption of nickel–nickel single bonds (which conform with the mean Ni–Ni distance of 2.508 ± 0.004 Å) leads to a closed-shell electronic configuration for each nickel atom.

The $M_4Y_4X_5$ structure can be formally derived for the platinum complex $Pt_4(PR_3)_4(CO)_5$ from the $M_4Y_4X_6$ structure by the removal of one carbonyl X ligand from the tetrahedral metal framework. Such a carbonyl extraction from two platinum atoms would formally decrease the electron count by one for each of these platinum atoms, which apparently results in the fragmentation of the platinum–platinum bond for these two platinum atoms to give the observed $M_4Y_4X_5$ structure in order that the electron count on each of these platinum atoms be reduced to two electrons below the closed-shell configuration. The drastic symmetrical deformation of the tetrametal framework from the regular tetrahedral geometry in the $M_4Y_4X_6$ structure to the "butterfly" form in the $M_4Y_4X_5$ structure through the effective loss of two valence electrons from each of two metal atoms is evidenced by the large change in the dihedral angle[18] from 109.3 to 83.2°.

These structural interrelationships enable the geometry of the reported[19] diamagnetic tetranuclear nickel carbonyl anion, $Ni_4(CO)_9{}^{2-}$, to be predicted with a confident degree of certainty as an $M_4Y_4X_5{}^{2-}$ structure which with two electrons formally substituted in place of a bridging carbonyl must still maintain a completely bonding tetrahedron of nickel atoms in order for the metal atoms to be electronically equivalent with those in the cubic-T_d $M_4Y_4X_6$ structure possessed by the $Ni_4\{P(C_2H_4CN)_3\}_4(CO)_6$ complex.[20,21]

Other X-ray work in progress on the two types of trinuclear platinum complexes, $Pt_3\{P(C_6H_5)_3\}_4(CO)_3$ and $Pt_3\{P(C_6H_5)_2(CH_2C_6H_5)\}_3(CO)_3$, has substantiated for the former compound the Booth–Chatt–Chini structural proposal[2] of a metal cluster system of type E. Details of these investigations will be reported elsewhere.

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(11) R. E. Rundle and J. H. Sturdivant, *J. Am. Chem. Soc.*, **69**, 1561 (1947).

(12) M. N. Hoechstetter, Ph.D. Thesis, Michigan State University, 1960; M. N. Hoechstetter and C. H. Brubaker, Jr., *Inorg. Chem.*, **8**, 400 (1969), and references cited therein.

(13) D. O. Cowan, N. G. Krieghoff, and G. Donnay, *Acta Cryst.*, **B24**, 287 (1968).

(14) T. G. Spiro, D. H. Templeton, and A. Zalkin, *Inorg. Chem.*, **7**, 2165 (1968).

(15) Although qualitative representations of the electronic structure for this complex in terms of both valence-bond and molecular orbital models lead in this instance to the same stereochemical predictions, such is not the case in other metal–atom cluster systems.[9]

(16) *Cf.* V. Albano, P. L. Bellon, and V. Scatturin, *Chem. Commun.*, 507 (1966), and references cited therein.

(17) M. J. Bennett, F. A. Cotton, and B. H. C. Winquist, *J. Am. Chem. Soc.*, **89**, 5366 (1967).

(18) Defined here as the angle between the normals of the two planes in the tetrametal system each formed by three metal atoms.

(19) W. Hieber, W. Kroder, and E. Zahn, *Z. Naturforsch.*, **15b**, 325 (1960); E. Zahn, Dissertation, Technische Hochschule Munchen, 1959.

(20) Although the corresponding $Pt_4(CO)_9{}^{2-}$ anion is unknown, alkali carbonylplatinates have been obtained by reduction of $Pt(CO)_2Cl_2$ either with alkali metals in THF or less cleanly with KOH in methanol. Several highly colored reduced anions containing 12 to 3 platinum atoms per alkali cation have been characterized from their infrared spectra which show the presence of both terminal carbonyl frequencies (from 2060 to 2000 cm^{-1}) and presumably bridging carbonyl frequencies (from 1870 to 1800 cm^{-1}). Due to extreme sensitivity of these complexes to air oxidation, pure compounds as yet have not been isolated.[21]

(21) P. Chini, G. Longoni, and J. Chatt, to be submitted for publication.

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