# Cluster-Linking Reactions: Synthesis and Structure of the Dicluster Complex $[(Ph_3P)_2N][\{Fe_3(CO)_9(\mu_3\text{-}PMe)(\mu_3\text{-}P)\}_2Au]$ and the Definitive $^{31}P$ NMR Spectroscopic Characterization of Tricluster and Tetracluster Complexes in Oligomer Mixtures

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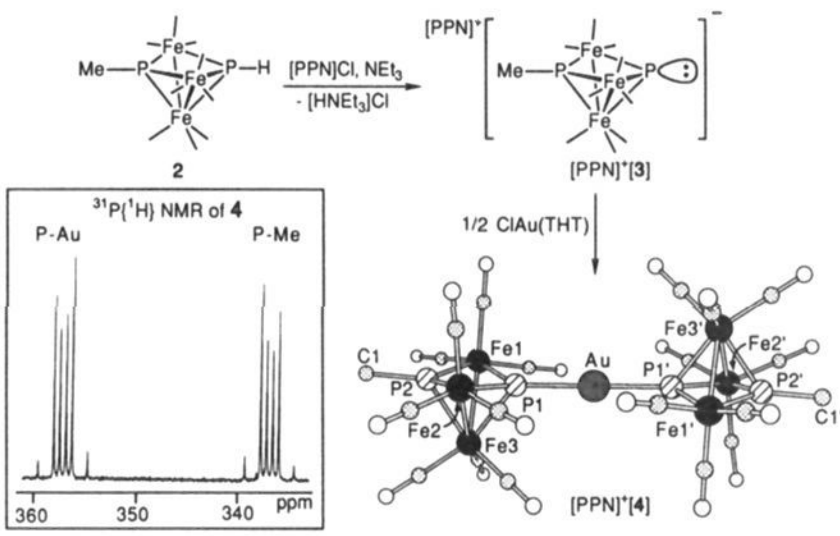
A new solid-state chemistry is emerging that utilizes tools from coordination chemistry and organometallic chemistry to develop new synthetic routes and to devise new structural types.[1] We are exploring methods for preparing extended assemblies incorporating transition-metal clusters from functionalized cluster "building blocks".[2,3] Our strategy for assembling these cluster-based materials utilizes reactions at the phosphorus heteroatoms of the bifunctional cluster building block $Fe_3(CO)_9(\mu_3\text{-}PH)_2$ (**1**),[4,5] which can potentially be linked to form a *linear* array of clusters (see **I**). The possibility of stepwise synthesis attending a building-block approach allows the synthesis of oligomeric species, intermediate between the molecular and the solid-state regimes. We report here our initial studies of cluster-linking reactions employing a Au(I) ion *linker* metal center, including the synthesis and structural characterization of the gold-bridged dicluster complex $[\{Fe_3(CO)_9(\mu_3\text{-}PMe)(\mu_3\text{-}P)\}_2Au]^-$ (**4**) and the preparation of extended cluster chains.

$$-(\text{metal cluster})-[(\text{linker})-(\text{metal cluster})]_n-(\text{linker})- \qquad \mathbf{I}$$

The monofunctional cluster $Fe_3(CO)_9(\mu_3\text{-}PMe)(\mu_3\text{-}PH)$ (**2**)[4] can be deprotonated to produce the anion $[(Ph_3P)_2N]^+[Fe_3(CO)_9(\mu_3\text{-}PMe)(\mu_3\text{-}P)]^-$ ($[PPN]^+$[**3**]), which has a phosphorus lone pair with high coordinating potential.[6] The orange-red dicluster complex **4**[7] is quantitatively prepared in $CH_2Cl_2$ solution by the reaction of 1 equiv of $[PPN]^+$[**3**] with 0.5 equiv of the Au(I) source, ClAu(THT) (THT = tetrahydrothiophene)[8] (Scheme 1). The formulation of **4** as a dicluster complex is established by $^{31}P\{^1H\}$ NMR spectroscopy, where the two sets of symmetry equivalent but magnetically inequivalent phosphorus nuclei give rise to two identical AA′XX′ patterns at δ 357.1 (P–Au) and 336.8 (P–Me) (Scheme 1).[9] The large $^2J_{PAuP}$ value of 257 Hz is in the range expected for *trans* orientation of the phosphorus nuclei,[10] and the $^2J_{PFeP}$ value of 214 Hz is similar in magnitude to those observed for metal complexes of the $[Fe_3(CO)_9(\mu_3\text{-}P)_2]^{2-}$ unit.[11] After removal of [PPN]Cl, the dicluster $[PPN]^+$[**4**] is crystallized by vapor diffusion of pentane into a $CH_2Cl_2$ solution and is isolated in 85% yield.

**Scheme 1**



The proposed structure of $[PPN]^+$[**4**] was confirmed by a single crystal X-ray diffraction study;[12] a ball-and-stick diagram of the anion **4** is displayed in Scheme 1. The Au(I) ion sits on a center of inversion in the space group *C*2/*c*, with four dicluster complexes in the unit cell, rigorously restricting the P–Au–P angle to 180°. The single unique Au–P distance (2.305(2) Å) is similar in magnitude to the Au–P distances for other two-coordinate gold(I) phosphine complexes,[10b] implying that steric interactions between the two cluster ligands do not affect the Au–P bonding. Although there are no symmetry constraints for the P2···P1—Au angle (unlike for the P1—Au—P1′ angle), the observed value of 177° indicates that a nearly linear orientation is the preferred configuration, despite the asymmetric coordination environment about the phosphorus atom. Thus, longer oligomers should be essentially linear, irrespective of the relative orientations of the open edges in adjacent cluster units.

Extended cluster chains can be prepared by utilizing a mixture of bifunctional **1** and monofunctional **2** as the cluster source. The $^{31}P\{^1H\}$ NMR spectrum of the orange-red oligomer mixture obtained from reaction of a 2:1 mixture of **1** and **2** with Au(I) ion (eq 1)[13] is shown in Figure 1a. Crucial aids in the assignment of $^{31}P$ NMR spectra of the oligomers were provided by obtaining the spectra of largely pure samples of the tri- and tetracluster

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(1) See, for example: (a) Hoskins, B. F.; Robson, R. *J. Am. Chem. Soc.* **1990**, *112*, 1546. (b) Stein, A.; Keller, S. W.; Mallouk, T. E. *Science* **1993**, *259*, 1558.

(2) For examples of linked carborane clusters, see: (a) Yang, X.; Jiang, W.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1992**, *114*, 9719. (b) Müller, J.; Base, K.; Magnera, T. F.; Michl, J. *J. Am. Chem. Soc.* **1992**, *114*, 9721.

(3) For organized assemblies of tetrahedral cubane clusters, see: (a) Copp, S. B.; Subramanian, S.; Zaworotko, M. J. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 706. (b) Copp, S. B.; Subramanian, S.; Zaworotko, M. J. *J. Am. Chem. Soc.* **1992**, *114*, 8719.

(4) Bautista, M. T.; Jordan, M. R.; White, P. S.; Schauer, C. K. *Inorg. Chem.* **1993**, *32*, 5429.

(5) The bicapped phosphinidene clusters and derivatives have unique molecular cluster properties. See, for example: (a) Koide, Y.; Bautista, M. T.; White, P. S.; Schauer, C. K. *Inorg. Chem.* **1992**, *31*, 3690. (b) Huttner, G.; Knoll, K. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 743. (c) Ohst, H. H.; Kochi, J. K. *Inorg. Chem.* **1986**, *25*, 2066. (d) Halet, J.-F.; Hoffman, R.; Saillard, J.-Y. *Inorg. Chem.* **1985**, *24*, 1695.

(6) Data for $[PPN]^+$[**3**]: $^{31}P$ (δ, ppm, THF) 513.1 (d, $^2J(P,P)$ = 35 Hz, $\mu_3$-*P*) 357.1 (dq, $^2J(P,P)$ = 35 Hz, $^2J(H,P)$ = 11 Hz, $\mu_3$-*P*Me); IR ($\nu_{CO}$, cm$^{-1}$, THF) 2037 (vw), 2019 (vw), 1997 (vs), 1976 (s), 1951 (m), 1939 (sh). We have not been able to isolate $[PPN]^+$[**3**].

(7) For $[PPN]^+$[**4**]: IR ($\nu_{CO}$, cm$^{-1}$, $Et_2O$) 2062 (vw), 2050 (vw), 2029 (vs), 2006 (s), 1977 (m), 1969 (m). Anal. Calcd (found) for $C_{56}H_{36}AuFe_6NO_{18}P_6$: *C, 38.91 (38.43); H, 2.10 (2.31).*

(8) Uson, R.; Laguna, A.; Laguna, M. *Inorg. Synth.* **1989**, *26*, 85.

(9) Analysis of the AA′XX′ pattern yields $|^2J_{PAuP}|$ = 257 Hz, $|^2J_{PFeP}|$ = 214 Hz, and $|^4J_{PP}|$ = 3 Hz.

(10) (a) Sunick, D. L.; White, P. S.; Schauer, C. K. *Organometallics* **1993**, *12*, 245. (b) Sunick, D. L.; White, P. S.; Schauer, C. K. *Inorg. Chem.* **1993**, *32*, 5665.

(11) Bautista, M. T.; White, P. S.; Schauer, C. K. *J. Am. Chem. Soc.* **1991**, *113*, 8963.

(12) Crystal data for $[PPN]^+$[**4**]: $C_{56}H_{36}AuFe_6NO_{18}P_6$ (fw = 1728.79); space group *C*2/*c* (No. 15), *Z* = 4, *a* = 21.272(2) Å, *b* = 20.153(1) Å, *c* = 17.020(1) Å, *β* = 107.535(6)°, *V* = 6957.4(8) Å$^3$; $d_{calc}$ = 1.685 g cm$^{-3}$; *μ* (Mo Kα) = 35.1 cm$^{-1}$. Least-squares refinement of 426 parameters and 4538 reflections ($I > 2.5\,\sigma(I)$) converged at $R$ ($R_w$) = 0.036 (0.048). Selected bond distances (Å): Au1–P1 = 2.305(2), Fe1–P1 = 2.264(2), Fe1–P2 = 2.186(2), Fe2–P1 = 2.257(2), Fe2–P2 = 2.192(2), Fe3–P1 = 2.268(2), Fe3–P2 = 2.223(2), P1···P2 = 2.648(3), Fe1–Fe3 = 2.695(2), Fe2–Fe3 = 2.692(2), Fe1···Fe3 = 3.549(2). Angles (deg): P2···P1—Au = 177.2(1), P1···P2—C1 = 177.4(3).

(13) Impurities of Au–Cl-terminated clusters are observed if chloride salts are used, so the reagents $[Au(THT)_2][PF_6]$ and $[PPN][PF_6]$ are employed. The THF solution of the clusters with the appropriate amount of $NEt_3$ is added to the THF solution of Au(I) and counterion. The resulting oligomer mixture is stable, and removal of solvent produces an orange powder, which can be quantitatively redissolved to yield a $^{31}P\{^1H\}$ NMR spectrum identical to one taken before solvent removal. The particular ratio of **1** and **2** employed was chosen to provide the most informative NMR spectrum of the oligomer *mixture. A soluble mixture of oligomers is also obtained when a 1:1 ratio of* **1** and **2** is employed.

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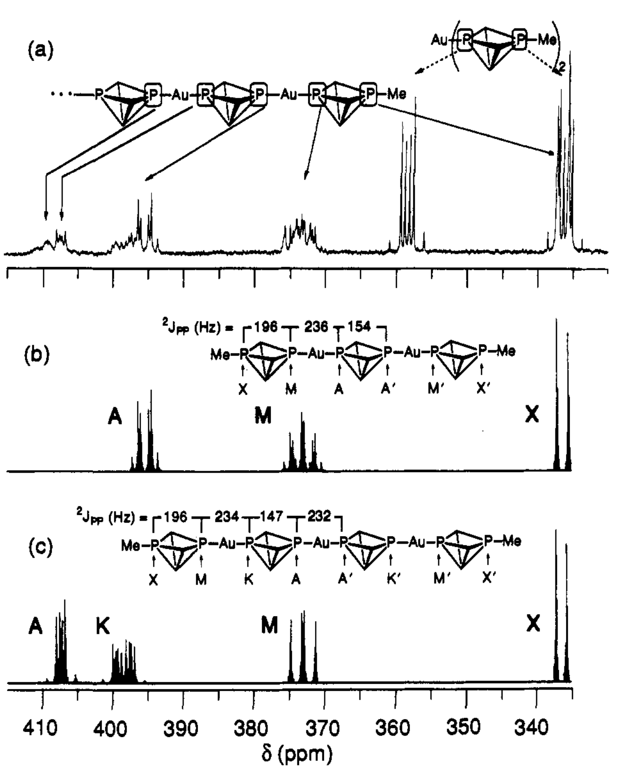
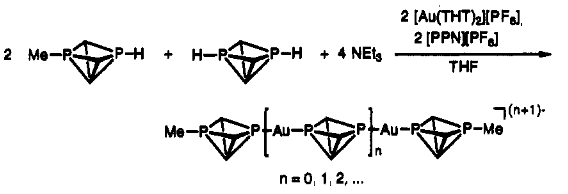


**Figure 1.** (a) $^{31}P\{^1H\}$ NMR spectrum of the oligomer mixture with assignments. (b) Simulated spectrum of tricluster **5** with assignments and $|^2J_{PP}|$ values. (c) Simulated spectrum of tetracluster **6** with assignments and $|^2J_{PP}|$ values. In spectra b and c, inclusion of small four-bond couplings ($|^4J_{PP}|$ = 0–6 Hz) is required to fit the experimental spectra.



(1)

complexes under different reaction conditions (see supplementary material). Simulated $^{31}P\{^1H\}$ NMR spectra of the tricluster complex (**5**, an AA′MM′XX′ spin system) and the tetracluster complex (**6**, an AA′KK′MM′XX′ spin system) are shown in Figures 1b and 1c, respectively.[14] The chemical shifts for the Au-bound phosphorus nuclei are quite sensitive to the identity of both cluster ligands bound to the gold(I) ion. For example, in tetracluster **6**, the resonance for the Au-bound phosphorus nucleus shifts progressively downfield as one proceeds to the center of the chain (δ 373 for M, δ 398 for K, and δ 407 for A). The difference in the chemical shifts for each successive movement toward the center of the chain becomes smaller.

Additional information is provided by the splitting patterns observed in the spectrum. In analyzing the spectrum of a particular cluster oligomer, the splitting pattern will appear first order until the center of the chain, where the two sets of two symmetry equivalent phosphorus nuclei are coupled.[15] For tetracluster **6**, first-order patterns are observed for the X and M resonances with splitting due to the adjacent phosphorus nuclei in the chain. The central [P···P—Au—P···P] portion of the chain is an AA′KK′ spin system (like the dicluster **4**). For the K resonance, however, an additional first-order splitting is observed as a result of coupling to the adjacent M nuclei in the chain. The same rationale applies for the interpretation of the NMR spectrum of tricluster **5** as for **6**.[16]

In Figure 1a (the $^{31}P\{^1H\}$ NMR spectrum for a reaction with appropriate stoichiometry to prepare a tricluster complex) overlapping resonances are observed for dicluster, tricluster, and tetracluster complexes, as well as for higher order oligomers. Obvious features in the oligomer spectrum are observed for the A resonance of tetracluster **6** as well as for the A resonance of tricluster **5**. Oligomers of higher order than tetracluster are evident by the broad downfield resonance at δ 409, 2 ppm further downfield than the central tetracluster resonance. The central cluster resonances of all higher order oligomers beyond tetracluster would be expected to fall near δ 410 on the basis of the observed chemical shift trends. The efficiency of the oligomerization reaction is evidenced by the fact that no resonances are observed in the spectrum for P–H-capped clusters (δ 230–270) or clusters with substituent-free P atoms (δ 500–530).

Coordination of Au(I) ions to bifunctional clusters with face-capping phosphorus ligands is an effective way to prepare cluster chains. Our current efforts are focused on understanding the fundamental issues in these coordination polymerization reactions taking advantage of the $^{31}P$ NMR characterization tool, including an assessment of the factors influencing the M–P bond lability together with attempts to control these factors to prepare monodisperse oligomers. The electrochemical properties of these cluster chains are also receiving attention, where the individual cluster units in model systems undergo a single two-electron oxidation reaction.[5a]

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**Supplementary Material Available:** Detailed experimental procedures, details of spectral simulations, and crystallographic results for [PPN]$^+$[**4**], including fractional atomic coordinates, thermal parameters, and complete bond lengths and angles (15 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(14) Coupling constants were obtained by simulation of the spectra with the program LAOCN5 (Quantum Chemistry Program Exchange, No. QCMP 049).

(15) The observed patterns are simplified because all $^{31}P$ nuclei are not coupled to each other, and the $^4J_{PP}$ values are small in comparison to the $^2J_{PP}$ values.

(16) The qualitative difference in the appearance of the non-first-order patterns for the central portion of the tricluster chain results from the fact that connectivity is [P—Au—P···P—Au—P].