A Stepwise Approach to P−P-Bonded Cluster Oligomers: Synthesis of the Dicluster Complex Me[PFe₃(CO)₉P]₂Me and the Tricluster Complex Me[PFe₃(CO)₉P]₃Me
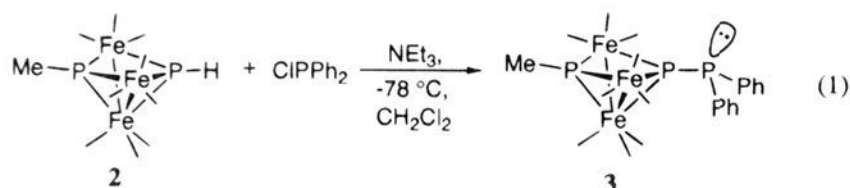
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Compounds of related structure and varying regular size have found many uses in the study of materials. Monodisperse oligomers have proven valuable in the study of the electronic properties of polymers, including the energy gap in doped poly-(*p*-phenylenes),[1] absorption maxima and conductivity in substituted polythiophenes,[2,3] and nonlinear optical properties in a conjugated porphyrin polymer.[4] Likewise, nanoclusters of semiconductors with narrow size distributions are being used to probe size-dependent properties in the region between molecules and bulk materials.[5,6] We are exploring methods to synthesize linear arrays of redox-active clusters employing derivatives of the bifunctional building block Fe₃(CO)₉(μ_3-PH)₂ (1).[7,8] The preparation of monodisperse cluster oligomers together with studies of their properties may yield a better understanding of *inter*cluster electronic interactions in this system.

A direct P−P bond between the capping phosphorus atoms of two neighboring Fe₃P₂ clusters is one possible way to assemble a linear cluster array. Many methods have been employed to form P−P bonds between organophosphine complexes,[9−11] but the one that is readily accessible for these cluster-based systems is a dehydrohalogenation reaction between a P−H group and a P−Cl group. The chlorophosphinidene-capped clusters are easily prepared by chlorination of the corresponding P−H-capped cluster employing CCl₄ as a halogenating agent.[7] A model reaction between red-orange Fe₃(CO)₉(μ_3-PMe)(μ_3-PH) (2) and Ph₂PCl in the presence of NEt₃ produces the orange diphenylphosphine-capped cluster, Fe₃(CO)₉(μ_3-PMe)[μ_3-PP(Ph)₂] (3) (eq 1).[12] This reaction

(1)

proceeds by initial deprotonation of 2 to form the reactive anion, [Fe₃(CO)₉(μ_3-PMe)(μ_3-P)]⁻.[7] The P−P-coupled product 3 has a characteristically large $^1J_{PP}$ value of 380 Hz.[13]

Figure 1. Ball and stick diagram of 5.

To develop strategies for the stepwise synthesis of P−P-coupled cluster chains, the synthesis of a dicluster complex was targeted using the monofunctional clusters Fe₃(CO)₉(μ_3-PMe)-(μ_3-PH) and Fe₃(CO)₉(μ_3-PMe)(μ_3-PCl) (4) as starting materials. A mixture of the P−H-capped cluster 2 and chlorophosphinidene 4 in CH₂Cl₂ solution shows very little reaction. Treatment of the mixture with NEt₃ at −78 °C, however, results in immediate conversion to a single deep purple product with a characteristic AA′BB′ pattern in the ³¹P{¹H} NMR spectrum (δ_A (PMe) 304.7 and δ_B 331.3) and an intense CO stretching mode at 2050 cm⁻¹. The two sets of two symmetry equivalent but magnetically inequivalent phosphorus nuclei and the largest J_{PP} value of 587 Hz[14] are indicative of a direct P−P bond between symmetry equivalent clusters. The formulation of this product as the dicluster complex Me[PFe₃(CO)₉P]₂Me (5, eq 2) is confirmed by a single crystal X-ray structure determination.[15] A ball and stick

(2)
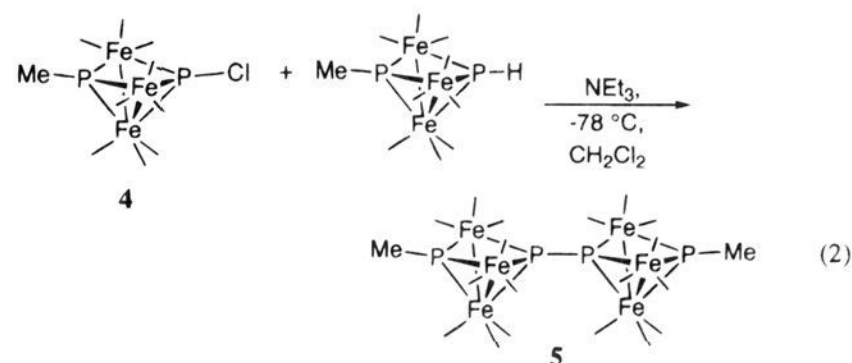
diagram of 5 is shown in Figure 1. The two cluster units are

(12) Data for 3: isolated yield, 24.5 mg (72%); ¹H NMR (CD₂Cl₂) δ 2.49 (dd, ²*J*(H,P) = 12.4 Hz, ³*J*(H,P) = 1.9 Hz, μ_3-*PMe*, 3H), 7.47 (m, 6H), 7.67 (m, 4H); ³¹P NMR (CH₂Cl₂) δ 334 (ddq, ²*J*(P,P) = 237 Hz, ³*J*(P,P) = 42 Hz, ²*J*(P,H) = 12 Hz, μ_3-*PMe*), 310 (dd, ¹*J*(P,P) = 380 Hz, ²*J*(P,P) = 237 Hz, μ_3-*PP*(Ph)₂), 24 (ddquint, ¹*J*(P,P) = 380 Hz, ³*J*(P,P) = 42 Hz, ³*J*(P,H) = 8 Hz, μ_3-*PP*(Ph)₂); IR (ν_{CO}, cm⁻¹, hexanes) 2070 (vw), 2043 (vs), 2019 (s), 2004 (m), 1989 (w), 1981 (vw), 1964 (vw). Anal. Calcd (found) for Fe₃C₂₂O₉H₁₃P₃: C, 38.76 (38.27); H, 1.92 (1.95).

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(14) Crystallization from THF/pentane yields small deep purple crystals of 5: isolated yield, 15 mg (80%); ¹H NMR (CDCl₃) δ 2.49 (d, ²*J*(P,P) = 12 Hz); ³¹P{¹H} NMR (CH₂Cl₂) δ 304.7 (δ_A, AA′BB′, μ_3-*P*), 331.3 (δ_B, AA′BB′, μ_3-*PMe*) [coupling constants obtained by simulation of the spectrum with the program LAOCN5 (Quantum Chemistry Program Exchange, No. QCMP 049): ¹J_{PP} = ±587 Hz, ²J_{PFeP} = ±252 Hz, ³J_{PP} = ∓74 Hz, and ⁵J_{PP} = ±6 Hz]; IR (ν_{CO}, cm⁻¹, CH₂Cl₂) 2063 (vw), 2050 (s), 2024 (w), 2012 (w); UV–vis (λ_{max}, nm, THF) 246 (ϵ = 4.84 × 10⁴ M⁻¹ cm⁻¹), 366 (ϵ = 3.08 × 10⁴ M⁻¹ cm⁻¹), 408 (ϵ = 1.42 × 10⁴ M⁻¹ cm⁻¹). Anal. Calcd (found) for C₂₀H₆Fe₆O₁₈P₄: C, 24.19 (24.27); H 0.61 (0.71).

(15) Crystal data for 5: C₂₀H₆Fe₆O₁₈P₄ (fw = 993.24); space group *Cc* (No. 9), *Z* = 8, *a* = 16.299(6) Å, *b* = 8.779(4) Å, *c* = 22.619(7) Å, β = 105.55(3)°, *V* = 3118.0(20) Å³, d_{calc} = 2.116 g cm⁻³; μ(Mo Kα) = 30.0 cm⁻¹. Least-squares refinement of 242 parameters and 2273 reflections (*I* > 2.5σ(*I*)) converged at *R* (*R*_w) = 0.054 (0.071). Selected bond distances (Å): Fe1−P1, 2.153(4); Fe1−P2, 2.288(4); Fe2−P1, 2.204(5); Fe2−P2, 2.251(4); Fe3−P1, 2.250(5); Fe3−P2, 2.189(5); Fe4−P3, 2.194(5); Fe4−P4, 2.234(5); Fe5−P3, 2.226(5); Fe5−P4, 2.261(5); Fe6−P3, 2.278(5); Fe6−P4, 2.143(5); Fe1−Fe2, 2.730(3); Fe3−Fe2, 2.692(4); Fe6−Fe5, 2.725(4); Fe4−Fe5, 2.709(3); P2···P3, 2.165(6); P3···P4, 2.548(6); Fe1···Fe3, 3.600(3); Fe4···F6, 3.583(4). Angles (deg): C1−P1···P2, 178.5(5); C2−P4···P3, 175.5(5); P1···P2−P3, 177.0(2); P4···P3−P2, 177.8(2); Fe6−P3−P2−Fe3, 41.6(1).

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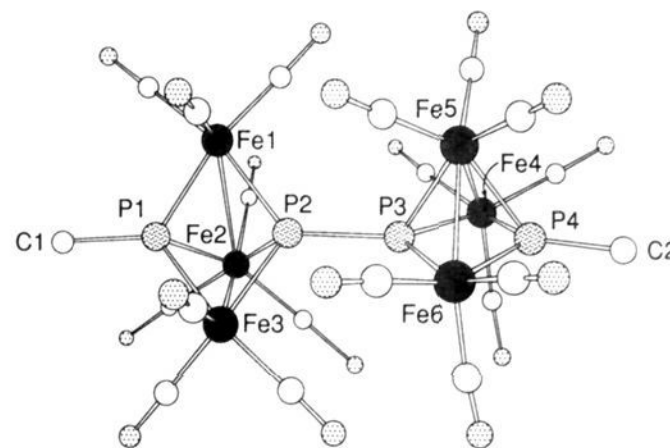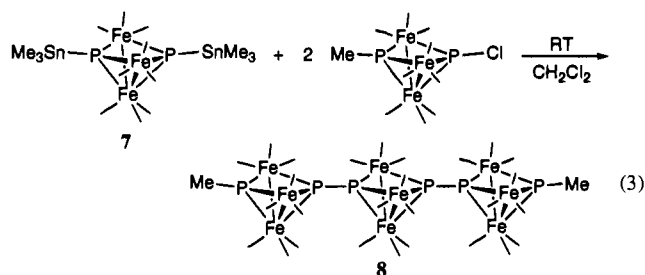(11) Grant, L. R.; Burg, A. B. *J. Am. Chem. Soc.* **1962**, *84*, 1834.

linked by a P—P bond (P2—P3 = 2.165(6) Å), which is similar in length to those observed for organodiphosphines such as P$_2$-Me$_4$ (2.192(9) Å) and P$_2$Me$_4$·2BH$_3$ (2.208(5) Å).[16,17] A noncrystallographic two-fold axis perpendicular to the P—P bond relates the two clusters. The orientation adopted by the two cluster units about the P—P bond (Fe(6)—P(3)—P(2)—Fe(3) = 41.6°) is likely dictated by the packing requirements of the CO ligands.

The use of this same approach to form a tricluster complex employing 1 equiv of the bifunctional cluster Fe$_3$(CO)$_9$(μ_3-PH)$_2$ (1), 2 equiv of NEt$_3$, and 2 equiv of chlorophosphinidene 4 is not successful.[18] Accordingly, an alternative strategy employing the trimethyltin-derivatized cluster Fe$_3$(CO)$_9$(μ_3-PSnMe$_3$)$_2$ (7)[19] as a source of the central cluster unit is employed. Treatment of a CH$_2$Cl$_2$ solution of 7, generated in situ, with 2 equiv of chlorophosphinidene 4 results in consumption of the starting reagents over 3 h, concomitant with appearance of a new product in the infrared spectrum with an intense CO stretching mode at 2056 cm^{-1}. The ^{31}P{^{1}H} NMR spectrum of the new product consists of a very complex pattern of resonances between δ 305 and 335. The simulation of this pattern as an AA'BB'CC' spin system by using coupling constants derived from the analysis of the dicluster complex (Figure 2) provides strong support for the formulation of the new product as the desired tricluster complex Me[PFe$_3$(CO)$_9$P]$_3$Me (8)[20] (eq 3). Additional

(3)

8

supporting evidence is provided by electrospray mass spectroscopy of the hydride derivative of 8.[21] The most intense molecular ion peak for H8$^-$ is observed at the theoretical value of *m/e* 1476.

Figure 2. Observed (top) and simulated (bottom) ^{31}P{^{1}H} NMR spectra for tricluster 8. Starred resonances are due to a small amount of dicluster 5 produced in the reaction; resonances due to 5 in the 305 ppm region overlap with resonances for 8. The following parameters were used in the simulation of Me[P$_A$Fe$_3$(CO)$_9$P$_B$]—[P$_C$Fe$_3$(CO)$_9$-P$_{C'}$]—[P$_B$Fe$_3$(CO)$_9$P$_{A'}$]Me: δ_A = 329.4, δ_B = 309.5, δ_C = 320.8, ($^1J_{BC}$ = ±590 Hz, $^2J_{AB}$ = ±250 Hz, $^2J_{CC'}$ = ±200 Hz, $^3J_{AC}$ = ∓70 Hz, $^3J_{BC'}$ = ∓70 Hz. All other coupling constants were set to 0 Hz.
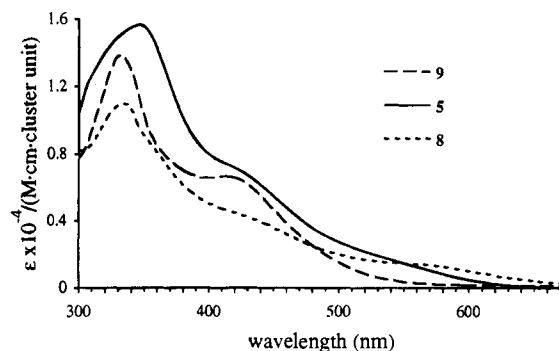
Figure 3. UV—vis spectra of Fe$_3$(CO)$_9$(μ_3-PMe)$_2$ (9), dicluster 5, and tricluster 8 in tetrahydrofuran solution. The extinction coefficients are scaled per cluster.

The electronic absorption spectra of the Me[PFe$_3$(CO)$_9$P]$_n$Me oligomers vary as a function of *n*. The UV—visible spectra of tricluster 8, dicluster 5, and the monocluster complex Fe$_3$(CO)$_9$-(PMe)$_2$ (9)[22] are shown in Figure 3. As *n* increases from 1 to 3, the absorption tail into the visible region extends to lower energy. It is this tail that is responsible for the dramatic color difference between the monocluster complexes and the higher-order oligomers. Extensions of the clean, controlled reaction chemistry reported here to prepare oligomers with *n* > 3 are underway, and the continued evolution of the electronic absorption spectra will be of interest. Also in progress are syntheses of cluster chains derivatized with redox-active end groups that will enable electronic interactions through the chain to be probed.

Supplementary Material Available: Detailed experimental procedures; details of procedures for electrospray mass spectral analysis of 5 and 8, including fits of parent ion to theoretical mass; and crystallographic results for 5, including a complete numbering scheme, crystal data, fractional atomic coordinates, thermal parameters, and complete bond lengths and angles (14 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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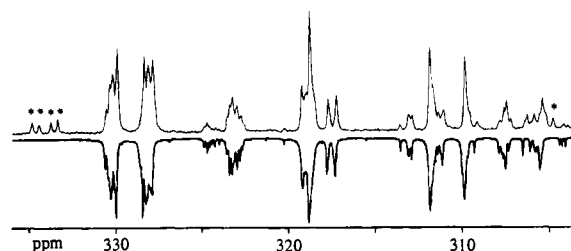
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(18) The primary products observed in the reaction mixture are the unsymmetrical dicluster complex Me[PFe$_3$(CO)$_9$P]$_2$H (6) and unreacted Fe$_3$-(CO)$_9$(μ_3-PMe)(μ_3-PCl). The fact that the reaction stops at the dicluster stage implies that the P—H moiety in 6 is considerably less acidic than in the starting material 1. Reactions employing a stronger base resulted in undesired reactions.

(19) The tin derivative 7 is prepared by treatment of 1 with 2 equiv of Me$_3$SnCl and excess NEt$_3$ in CH$_2$Cl$_2$ solution. The reaction proceeds quantitatively as monitored by ^{31}P NMR spectroscopy. An oil of 7 used in subsequent reactions is obtained by precipitation of [NEt$_3$H]$^+$Cl$^-$ by addition of hexanes, filtration, and removal of the solvent. Data for 7: ^{1}H NMR (CDCl$_3$) δ 0.653 (virtual triplet with ^{117}Sn and ^{119}Sn satellites, ^2J(H,^{119}Sn) = 55.0 Hz, ^2J(H, ^{117}Sn) = 52.8 Hz, ^3J(H,P) = 4.6 Hz); ^{31}P{^{1}H} NMR (toluene) δ 283 (s, plus Sn satellites); IR (ν_{CO}, cm^{-1}, hexanes) 2031 (vs), 2011 (s), 1987 (m).

(20) The reaction to prepare tricluster 8 proceeds essentially quantitatively. 8 is only slightly soluble in THF solution and can be isolated as a brown powder by removal of solvent and washing the residue with Et$_2$O: isolated yield, 11.0 mg (47%); IR (ν_{CO}, cm^{-1}, THF) 2072 (vw), 2056 (s), 2021 (w), 2005 (w), 1991 (w). A crystalline sample was utilized for electronic absorption spectroscopy: UV—vis (λ_{max}, nm, THF) 220 (ϵ = 7.0 × 10^4 M^{-1} cm^{-1}), 328 (ϵ = 3.3 × 10^4 M^{-1} cm^{-1}), 410 (ϵ = 1.4 × 10^4 M^{-1} cm^{-1}), 560 (ϵ = 4.1 × 10^3 M^{-1} cm^{-1}).

(21) Fast atom bombardment mass spectral analysis of 5 in a *m*-nitrobenzyl alcohol matrix (negative ion detection) yields the expected parent ion at *m/e* 993, but analysis of 8 under analogous conditions was unsuccessful. Anionic samples of dicluster 5 and tricluster 8 for electrospray mass spectral analysis are prepared by hydride addition to the terminal μ_3-PMe ligands to produce μ_2-P(H)R groups. Treatment of a THF solution of the cluster oligomer with 1 equiv of NaBH$_4$ produces the monohydride addition product as judged by ^{31}P NMR spectroscopy and infrared spectroscopy (see supplementary material). Metathesis with [NEt$_4$]Cl yields the NEt$_4^+$ salts on which analyses were performed. The hydride addition products are stable in solution. The most intense peak for the parent ion of H5$^-$ is observed at *m/e* 994. Fragments of the molecular ion derived from P—P bond cleavage are also observed in the spectra for H5$^-$ and H8$^-$.

(22) For synthesis and spectral characterization (except UV—vis), see: Lang, H.; Zsolnai, L.; Huttner, G. *J. Organomet. Chem.* **1985**, *282*, 23. UV—vis of 9: (λ_{max}, nm, THF) 222 (ϵ = 4.34 × 10^4 M^{-1} cm^{-1}), 322 (ϵ = 1.39 × 10^4 M^{-1} cm^{-1}), 416 (ϵ = 6.38 × 10^3 M^{-1} cm^{-1}).