Inorg. Chem. **1993,** *32,* 5429-5430

Synthesis and Reactivity of the Phosphinidene Cluster Complex $Fe_3(CO)_9(\mu_3\text{-}PH)_2$: A Versatile Cluster Building-Block

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Received July 20, 1993

Materials based on intact molecular transition metal clusters are being actively pursued through the incorporation of molecular clusters into organic polymer matrices,[1] through utilization of functionalized clusters as ligands in mononuclear and dinuclear metal complexes,[2] and through the preparation of charge-transfer salts of transition metal clusters.[3] We are pursuing synthetic routes to functionalized transition metal clusters that will permit the synthesis of covalently-linked multicluster assemblies with the potential of cooperative interaction among the clusters. The preparation of appropriately functionalized metal clusters presents a considerable synthetic challenge given the present level of sophistication in cluster synthesis. Our approach has been to utilize the face-capping phosphorus heteroatoms in phosphinidene (PR) cluster complexes as the site of functionalization. Bicapped phosphinidene clusters comprise an attractive initial system to study because the molecular cluster units have interesting properties,[4] the cluster-bound ^{31}P nuclei provide an informative spectroscopic characterization tool, and there is a large potential array of chemistry at the phosphorus site. Furthermore, a bifunctional cluster provides two reactive sites, and such a unit can potentially be linked to form a *linear* array of clusters.[5] We report here the synthesis of a rare example[6] of an easily derivatized bicapped P–H phosphinidene cluster building-block, $Fe_3(CO)_9(\mu_3\text{-}PH)_2$ (**1**), conversion of **1** to a chlorophosphinidene cluster, $Fe_3(CO)_9(\mu_3\text{-}PCl)_2$ (**6**), and reactions of electrophiles and nucleophiles at phosphorus. These phosphorus-based transformations demonstrate that the same variety of reactions that are accessible to organophosphorus compounds are possible at a μ_3-PH moiety capping a transition metal cluster face.

The preparation of clusters with silylphosphinidene ligands enables access to chemistry at cluster-bound phosphorus atoms.[7] The parent P–H phosphinidene cluster, $Fe_3(CO)_9(\mu_3\text{-}PH)_2$ (**1**), is prepared by hydrolysis of $Fe_3(CO)_9[\mu_3\text{-}PSi(i\text{-}Pr)_3]_2$ and is isolated as a red-purple crystalline solid.[8] The structure of **1** was characterized by a single-crystal X-ray diffraction study,[9] and an ORTEP diagram for **1** is included in Scheme I. The bond distances describing **1**[9] do not differ significantly from those in the structure of the related phenylphosphinidene cluster $Fe_3(CO)_9(\mu_3\text{-}PPh)_2$.[10] Bicapped **1** is readily identified by AA′XX′ patterns that are observed in both the ^{31}P (δ 235.1 ppm) and the ^1H (δ 4.07 ppm) NMR spectra. The μ_3-PH ligands can be viewed as cluster-based phosphonium ions, where a -2 charge resides on the cluster and the μ_3-PH groups act as 3-electron donors to the 50-electron nido cluster. In accord with this view, one of the phosphorus-bound hydrogen atoms in **1** is readily removed as H^+ by reaction with NEt_3/[PPN]Cl (PPN = $(Ph_3P)_2N^+$) to produce the $[PPN]^+$ salt of red-orange $[Fe_3(CO)_9(\mu_3\text{-}PH)(\mu_3\text{-}P)]^-$ (**2**)[11] (see Scheme I). The pattern of CO stretches observed in the infrared spectrum of $[PPN]^+$[**2**] is nearly identical to that observed for **1** but is shifted by 50 cm^{-1} to lower energy. The ^{31}P resonance for the deprotonated phosphorus atom is found at δ 535.1 ppm, downfield from the resonance for the P–H phosphinidene at δ 277.5 ppm.[12] The removal of a proton from **1** has a profound effect on the coupling constants. The $^2J_{PP}$ value in $[PPN]^+$[**2**] of 35 Hz is substantially reduced from the $^2J_{PP}$ value of 338 Hz for **1**. Furthermore, there is a large change in the $^1J_{PH}$ value from 316 Hz in **1** to 211 Hz in **2**. The lone pair on phosphorus in **2** will prefer to be in an orbital with a high percentage of s character. The observed changes in coupling may result from changes in the character of the orbitals involved in cluster bonding as a result of this preference.

To access the doubly deprotonated cluster, $[Fe_3(CO)_9(\mu_3\text{-}P)_2]^{2-}$, it was necessary to employ *n*-BuLi as a base. Addition of 1 equiv of *n*-BuLi to a –78 °C tetrahydrofuran solution of **1** produces

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(1) For examples of polymers incorporating dinuclear compounds and clusters via functionalities on the cyclopentadienyl ligand, see: (a) Massa, M. A.; Rauchfuss, T. B. *Chem. Mater.* **1991**, *3*, 788. (b) Tenhaeff, S. C.; Tyler, D. R. *Organometallics* **1991**, *10*, 473.

(2) (a) Cen, W.; Lindenfeld, P.; Fehlner, T. P. *J. Am. Chem. Soc.* **1992**, *114*, 5451. (b) Cen, W.; Haller, K. J.; Fehlner, T. P. *Organometallics* **1992**, *11*, 3499. (c) Cen, W.; Haller, K. J.; Fehlner, T. P. *Inorg. Chem.* **1991**, *30*, 3120.

(3) See, for example: (a) Green, M. L. H.; Qin, J.; O'Hare, D.; Bunting, H. E.; Thompson, M. E.; Marder, S. R.; Chatakondu, K. *Pure Appl. Chem.* **1989**, *61*, 817. (b) Bolinger, C. M.; Darkwa, J.; Gammie, G.; Gammon, S.; Lyding, J. W.; Rauchfuss, T. B.; Wilson, S. R. *Organometallics* **1986**, *5*, 2386. (c) Pénicaud, A.; Batail, P.; Coulon, C.; Canadell, E.; Perrin, C. *Chem. Mater.* **1990**, *2*, 123.

(4) 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.

(5) The carbon heteroatom in the monofunctional $Co_3(CO)_9(\mu_3\text{-}CX)$ clusters has been a useful precursor to prepare a variety of linked dicluster molecules. The presence of only a single functional site does not permit extension of this reaction chemistry beyond a dicluster using the same strategy. (a) Worth, G. H.; Robinson, B. H.; Simpson, J. *Organometallics* **1992**, *11*, 501. (b) Worth, G. H.; Robinson, B. H.; Simpson, J. *Organometallics* **1992**, *11*, 3863. (c) Allegra, G.; Peronaci, E. M.; Ercoli, R. *J. Chem. Soc., Chem. Commun.* **1966**, 549. (d) Bor, G.; Marko, L.; Marko, B. *Chem. Ber.* **1962**, *95*, 333.

(6) For examples of monocapped μ_3-PH clusters, see: (a) Austin, R. G.; Urry, G. *Inorg. Chem.* **1977**, *16*, 3359. (b) Ebsworth, E. A. V.; McIntosh, A. P.; Schröder, M. *J. Organomet. Chem.* **1986**, *312*, C41. (c) Brauer, D.; Hasselkuss, G.; Hietkamp, S.; Sommer, H.; Stelzer, O. *Z. Naturforsch.* **1985**, *40b*, 961. (d) Honrath, U.; Liu, S. T.; Vahrenkamp, H. *Chem. Ber.* **1985**, *118*, 132.

(7) (a) Bautista, M. T.; White, P. S.; Schauer, C. K. *J. Am. Chem. Soc.* **1991**, *113*, 8963. (b) Sunick, D. L.; White, P. S.; Schauer, C. K. *Organometallics* **1993**, *12*, 245.

(8) A detailed procedure is given in the supplementary material. Following chromatography, crystallization by slow evaporation of CH_2Cl_2 yields purple crystals of **1** (335 mg, 23% based on starting $H_2PSi(i\text{-}Pr)_3$): NMR (δ, ppm, toluene-d_8) 4.07 (^1H), 235.1 (^{31}P) (AA′XX′ patterns, $^1J(H,P)$ = 316 Hz, $^3J(H,P)$ = 14 Hz, $^4J(H,H)$ = 9 Hz, $^2J(P,P)$ = 338 Hz); IR (ν_{CO}, cm^{-1}, hexanes) 2051 (vs), 2031 (vs), 2014 (s), 2006 (w), 1997 (w), 1977 (vw). Anal. Calcd (found) for $C_9H_2Fe_3O_9P_2$: C, 22.35 (22.71); H, 0.42 (0.51).

(9) Crystal data for **1**: $C_9H_2Fe_3O_9P_2$ (fw = 483.60); space group $P\bar{1}$ (No. 2), $Z = 2$; at –150 °C, $a = 9.159(6)$ Å, $b = 12.792(4)$ Å, $c = 6.975(2)$ Å, $\alpha = 94.29(3)°$, $\beta = 112.03(3)°$, $\gamma = 93.77(5)°$, $V = 751.5(6)$ Å^3; $d_{calc} = 2.137$ g cm^{-3}; μ(Mo Kα) = 31.1 cm^{-1}. Least-squares refinement of 209 least-squares parameters and 2160 reflections converged at R (R_w) = 0.036 (0.048). Selected bond distances (Å) in **1**: Fe1–Fe3 = 2.727(2), Fe2–Fe3 = 2.713(1), Fe1⋯Fe2 = 3.561(2), Fe1–P1 = 2.206(2), Fe1–P2 = 2.218(2), Fe2–P1 = 2.207(2), Fe2–P2 = 2.219(2), Fe3–P1 = 2.221(2), Fe3–P2 = 2.227(2), P1⋯P2 = 2.582(2), P–H = 1.36.

(10) Cook, S. L.; Evans, J.; Gray, L. R.; Webster, M. *J. Organomet. Chem.* **1982**, *236*, 367.

(11) Data for $[PPN]^+$[**2**]: ^1H (δ, ppm, THF-d_8) 6.28 (dd, $^1J(H,P)$ = 211 Hz, $^3J(H,P)$ = 11 Hz, μ_3-P*H*); ^{31}P (δ, ppm, THF) 535.1 (dd, $^2J(P,P)$ = 35 Hz, $^3J(H,P)$ = 11 Hz, μ_3-*P*), 277.5 (dd, $^2J(P,P)$ = 35 Hz, $^1J(H,P)$ = 211 Hz, μ_3-*P*H); IR (ν_{CO}, cm^{-1}, THF) 2040 (vw), 2024 (vw), 2002 (vs), 1980 (s), 1956 (m), 1944 (sh). We have not yet succeeded in isolating the highly reactive anions.

(12) A downfield shift of the ^{31}P resonance is also observed in the replacement of a phosphorus-bound hydrogen atom in primary or secondary phosphines by lithium, and sequestering of the lithium ion by a complexation agent results in a further shift downfield: (a) Zschunke, A.; Bauer, E.; Schmidt, H.; Issleib, K. *Z. Anorg. Allg. Chem.* **1982**, *495*, 115. (b) Bartlett, R. A.; Olmstead, M. M.; Power, P. P.; Siegel, G. A. *Inorg. Chem.* **1987**, *26*, 1941.

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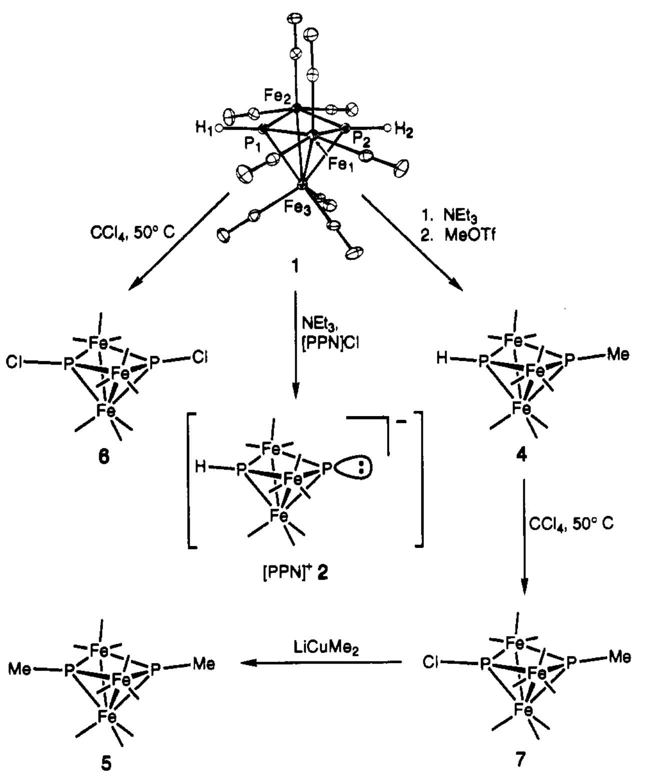
Scheme I



Li^+[**2**].[13] The energies of the CO stretches for the Li^+ salt of **2** are nearly identical to those for $[PPN]^+$[**2**], indicating that Li^+ is not coordinated to phosphorus as it is observed to be in many lithium phosphides.[12b,14] After addition of a second equivalent of *n*-BuLi to Li^+[**2**] at −78 °C, a color change is observed to a deep orange-brown, and a new species is observed in the ^{31}P NMR spectrum with a broad singlet at δ 616.2 ppm (−60 °C). The corresponding changes in the infrared spectrum are much more subtle. The energies of the CO stretches[15] are nearly identical to those for Li^+[**2**], but the pattern of intensities is quite distinct. On the basis of the IR data, it is suggested that the charge on the cluster is compensated by association of more than one lithium cation in the doubly deprotonated species, $Li_2Fe_3(CO)_9P_2$ (**3**).[16] Addition of 10 equiv of CD_3OD to the NMR tube containing **3** generates $[Fe_3(CO)_9(\mu_3\text{-PD})(\mu_3\text{-P})]^-$,[17] and the infrared spectrum in the CO stretching region and the color of **2** are restored. This differentiation in the reactivity of the first and second cluster sites permits reaction chemistry to be sequentially performed at each of the two phosphorus atoms.

The lone pair on phosphorus resulting from removal of a phosphorus-bound hydrogen in **1** is highly reactive toward organic electrophiles. Although **1** is unreactive to $MeOSO_2CF_3$, reaction of a −78 °C CH_2Cl_2 solution of **1** with 0.9 equiv of NEt_3 followed by 0.9 equiv of $MeOSO_2CF_3$ produces $Fe_3(CO)_9(\mu_3\text{-PMe})(\mu_3\text{-PH})$ (**4**)[18] as the primary product. Reaction conditions are optimized to minimize production of the dimethyl cluster, $Fe_3(CO)_9(\mu_3\text{-PMe})_2$ (**5**).[19] The monomethylated cluster, **4**, has only one reactive P–H moiety and can be used as the end group for a chain of clusters or in the production of discrete dicluster complexes.[5]

Access to nucleophilic reactions at the cluster-bound phosphorus atom is achieved by replacement of the P–H moieties in **1** and **4** by the P–Cl functional group using CCl_4 as a chlorinating reagent.[20] Warming CCl_4 solutions of **1** or **4** to 50 °C results in production of the chlorophosphinidene clusters $Fe_3(CO)_9(\mu_3\text{-PCl})_2$ (**6**)[21] and $Fe_3(CO)_9(\mu_3\text{-PMe})(\mu_3\text{-PCl})$ (**7**),[22] respectively, together with $CHCl_3$ as a byproduct. To the best of our knowledge, no other examples of carbonyl clusters with face-capping P–Cl ligands have been reported.[23] The exchange of H for Cl is accompanied by a downfield shift in the ^{31}P resonance (δ 439.1 ppm for **6** and 444.0 ppm for **7**) and a shift in the infrared CO stretching frequencies to slightly higher energy in comparison to **1** (10 cm^{-1} for **6** and 5 cm^{-1} for **7**). The reactivity of the cluster-bound P–Cl moiety with nucleophiles is demonstrated through reaction of **7** with $LiCuMe_2$, which affords the dimethyl cluster, **5**, as the major product.[24] Thus, reaction chemistry not accessible through electrophilic routes (such as reactions with acetylides) should be possible for chlorophosphinidene clusters.

Reactions are in progress that take advantage of this versatile cluster building-block in the synthesis of cluster chains linked by coordination to a bridging metal complex,[25] by P–P bonds,[26] and by unsaturated organic bridges.

Acknowledgment. Partial financial support provided by the National Science Foundation (PYI award CHEM-8958027 and CHE-9222617) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. M.R.J. was supported, in part, by a fellowship from the Department of Education. Partial funds for equipping the single-crystal X-ray diffraction facility at UNC-CH were provided by the National Science Foundation (Grant CHE-8919288).

Supplementary Material Available: Text giving detailed experimental procedures and tables listing crystallographic results for **1** (8 pages). Ordering information is given on any current masthead page.

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(13) Data for Li^+[**2**]: ^{31}P (δ, ppm, THF-d_8, −60 °C) 530.6 (dd, $^2J(P,P) = 34$ Hz, $^3J(H,P) = 10$ Hz, μ_3-*P*), 277.5 (dd, $^2J(P,P) = 34$ Hz, $^1J(H,P) = 216$ Hz, μ_3-*P*H); IR (ν_{CO}, cm^{-1}, THF) 2043 (vw), 2003 (vs), 1980 (s), 1956 (m), 1944 (sh).

(14) See, for example: (a) Jones, R. A.; Stuart, A. L.; Wright, T. C. *J. Am. Chem. Soc.* **1983**, *105*, 7459. (b) Hitchcock, P. B.; Lappert, M. F.; Power, P. P.; Smith, S. J. *J. Chem. Soc., Chem. Commun.* **1984**, 1669. (c) Hey, E.; Hitchcock, P. B.; Lappert, M. F.; Rai, A. K. *J. Organomet. Chem.* **1987**, *325*, 1. (d) Bartlett, R. A.; Olmstead, M. M.; Power, P. P. *Inorg. Chem.* **1986**, *25*, 1243.

(15) Data for **3**: IR (ν_{CO}, cm^{-1}, THF) 2003 (vs), 1980 (m), 1974 (sh), 1954 (m), 1942 (sh), 1924 (sh).

(16) The electronegativity of lithium (1.0) is considerably less than that of hydrogen (2.2). A simple replacement of one hydrogen by one lithium in **2** would be expected to result in a shift of the CO stretching frequencies to lower energy.

(17) ^{31}P NMR of $[Fe_3(CO)_9(\mu_3\text{-PD})(\mu_3\text{-P})]^-$: ^{31}P (δ, ppm, THF, −60 °C) 531.8 (dd, $^2J(P,P) = 34$ Hz, μ_3-*P*), 278.4 (dt, $^2J(P,P) = 34$ Hz, $^1J(D,P) = 34$ Hz, μ_3-*P*D).

(18) Following chromatography, crystallization from hexanes produces red needles of **4** (50 mg, 54%): ^1H (δ, ppm, C_6D_6) 4.07 (dd, 1H, $^1J(H,P) = 315$ Hz, $^3J(H,P) = 14$ Hz, μ_3-P*H*), 1.62 (dd, 3H, $^2J(H,P) = 13$ Hz, $^4J(H,P) = 3$ Hz, μ_3-PC*H*$_3$); ^{31}P (δ, ppm, THF) 327 (dquart, $^2J(P,P) = 323.1$ Hz, $^2J(H,P) = 13$ Hz, μ_3-*P*CH$_3$), 231.0 (dd, $^2J(P,P) = 323$ Hz, $^1J(H,P) = 315$ Hz, μ_3-*P*H), IR (ν_{CO}, cm^{-1}, hexanes) 2047 (vs), 2026 (vs), 2008 (s), 1999 (w), 1990 (w), 1971 (vw). Anal. Calcd (found) for $C_{10}H_4Fe_3O_9P_2$: C, 24.14 (24.37); H, 0.81 (0.83).

(19) Lang, H.; Zsolnai, L.; Huttner, G. *J. Organomet. Chem.* **1985**, *282*, 23.

(20) Carbon tetrachloride has been previously employed as a halogenating agent for the preparation of the PCl_2-bridged complex from the PH_2-bridged complex $[Mn(CO)_4(PH_2)]_2$: Schäfer, H.; Zipfel, J.; Gutekunst, B.; Lemmert, U. *Z. Anorg. Allg. Chem.* **1985**, *529*, 157.

(21) The yield of **6** is reduced by the formation of P–P-coupled oligomers. Following chromatography, recrystallization from hexanes produces a crystalline orange solid (4.4 mg, 11%). Data for **6**: ^{31}P NMR (δ, ppm, CCl_4) 439.1 (s); IR (ν_{CO}, cm^{-1}, hexanes) 2062 (vs), 2039 (s), 2032 (m), 2017 (w), 2008 (vw), 1984 (vw). MS (EI): M^+ at *m/e* 552 and ions due to sequential loss of nine CO ligands. Anal. Calcd (found) for $C_9Cl_2Fe_3O_9P_2$: C, 19.57 (19.69); H, 0.0 (0.06).

(22) Recrystallization from hexanes produces an orange crystalline solid (14 mg, 74%). Data for **7**: ^{31}P NMR (δ, ppm, CCl_4) 287.8 (dquart, $^2J(P,P) = 228$ Hz, $^2J(P,H) = 13$ Hz, μ_3-*P*Me), 444.0 (d, $^2J(P,P) = 228$ Hz, μ_3-*P*Cl); IR (ν_{CO}, cm^{-1}, hexanes) 2052 (vs), 2031 (s), 2018 (m), 2005 (w), 1996 (vw), 1975 (vw). MS (EI): M^+ at *m/e* 532 and ions due to sequential loss of nine CO ligands. Anal. Calcd (found) for $C_{10}H_3ClFe_3O_9P_2$: C, 22.57 (22.71); H, 0.57 (0.76).

(23) Planar μ_2-PX complexes have been reported. For a review see: Huttner, G.; Evertz, K. *Acc. Chem. Res.* **1986**, *19*, 406.

(24) The major byproduct observed in the $LiCuMe_2$ reactions is the cluster $[Fe_3(CO)_9(\mu_3\text{-PMe})(\mu_2\text{-PMe}_2)]^-$. We are attempting to optimize reaction conditions for the production of the desired dimethyl product. Reactions between **7** and MeMgBr or MeLi do not proceed cleanly.

(25) Bautista, M. T.; White, P. S.; Schauer, C. K. Manuscript in preparation.

(26) Jordan, M. R.; White, P. S.; Schauer, C. K. Manuscript in preparation.