

**Table I.** Rate Constants for Solvolysis and Elimination and Yields of  $\alpha$ -Methylstyrene for Reaction of Ring-Substituted Cumyl Derivatives, XArC(Me)<sub>2</sub>Y, in 50:50 (v/v) Trifluoroethanol/Water<sup>a</sup>

X	Y	$\sigma_x^{+b}$	$k_{\text{obsd}}^c$ , s <sup>-1</sup>	$f_{\text{elim}}^d$	$k_{\text{solv}}^e$ , s <sup>-1</sup>	$k_{\text{elim}}^f$ , s <sup>-1</sup>
3-F	Cl	0.34	0.12	0.044	0.11	$5.3 \times 10^{-3}$
	OPFB <sup>g</sup>		$2.60 \times 10^{-5h}$	0.15	$2.2 \times 10^{-5}$	$3.9 \times 10^{-6}$
	<i>d</i> <sub>5</sub> -OPFB <sup>i</sup>		$1.81 \times 10^{-5h}$	0.050	$1.7 \times 10^{-5}$	$9.1 \times 10^{-7}$
4-NO <sub>2</sub>	Cl	0.78	$2.34 \times 10^{-4}$	0.15	$2.0 \times 10^{-4}$	$3.5 \times 10^{-5}$
	OPFB			0.30		
3,5-(CF <sub>3</sub> ) <sub>2</sub>	Cl	0.95 <sup>j</sup>	$3.20 \times 10^{-5}$	0.29	$2.3 \times 10^{-5}$	$9.3 \times 10^{-6}$

<sup>a</sup> At 25 °C and ionic strength 0.50 (NaClO<sub>4</sub>). <sup>b</sup> Reference 19. <sup>c</sup> Determined spectrophotometrically for Y = Cl by following either the disappearance of the chloride (3-F at 250 or 270 nm, 3,5-(CF<sub>3</sub>)<sub>2</sub> at 265 or 280 nm) or the appearance of the  $\alpha$ -methylstyrene (4-NO<sub>2</sub> at 320 nm). <sup>d</sup> Fractional yield of  $\alpha$ -methylstyrene, determined by HPLC analysis. <sup>e</sup>  $k_{\text{obsd}}(1 - f_{\text{elim}})$ . <sup>f</sup>  $k_{\text{obsd}}f_{\text{elim}}$ . <sup>g</sup> Pentafluorobenzoate leaving group. <sup>h</sup> Determined by following the disappearance of the substrate by HPLC. <sup>i</sup> Data for 3-FArC(CD<sub>3</sub>)<sub>2</sub>OPFB. <sup>j</sup> Takeuchi, K.; Kurosaki, T.; Okamoto, K. *Tetrahedron* 1980, 36, 1557-1563.

azide ion. They are very hard to rationalize by deprotonation within an unselective carbocation-leaving group intimate or solvent-separated ion pair ( $k_{\text{p}}'$ ).

(1) There is a large kinetic  $\beta$ -deuterium isotope effect on the elimination reaction of 3-FArC(CL<sub>3</sub>)<sub>2</sub>OPFB of  $(k_{6\text{H}}/k_{6\text{D}})_{\text{elim}} = 4.3$  (Table I). For an ion pair mechanism, deprotonation competes with the rapid diffusional separation of the ion pair ( $k_{\text{d}} \approx 10^{10}$  s<sup>-1</sup>)<sup>5</sup> and/or capture of the ion pair by solvent ( $k_{\text{s}}' \approx 10^{11}$  s<sup>-1</sup> for 3-FArC(Me)<sub>2</sub><sup>+</sup>),<sup>2</sup> so that the barrier to proton transfer must also be very small. It is difficult to reconcile the large isotope effect with an extremely rapid proton transfer reaction in which little discrimination between abstraction of a proton and of a deuteron is expected.

(2) The values of  $k_{\text{solv}}$  and  $k_{\text{elim}}$  for XArC(Me)<sub>2</sub>Cl are correlated by  $\rho_{\text{solv}}^+ = -6.1$  and  $\rho_{\text{elim}}^+ = -4.6$ . Deprotonation and capture by solvent of a highly reactive and unselective ion pair should have early carbocation-like transition states of very similar polarity. Therefore, the substantial difference in these  $\rho$  values is difficult to rationalize by a mechanism that involves the partitioning of an ion pair intermediate.

(3) Similarly, there is a smaller sensitivity to solvent ionizing power ( $Y$ )<sup>10</sup> for  $k_{\text{elim}}$  ( $m_{\text{elim}} = 0.7$ ) compared with  $k_{\text{solv}}$  ( $m_{\text{solv}} = 1.0$ ) for reaction of 4-NO<sub>2</sub>ArC(Me)<sub>2</sub>Cl when the solvent is varied from 10:90 (v/v) MeOH/H<sub>2</sub>O to 90:10 (v/v) MeOH/H<sub>2</sub>O.

There is good evidence that the concerted elimination at the neutral substrate is *not* a bimolecular E2 reaction with an E1-like transition state<sup>11</sup> in which solvent assists as a general base,<sup>12</sup> because acetate (0.50 M) or trifluoroethoxide (0.10 M) ions do not catalyze elimination for cumyl derivatives with  $\sigma_x^+ \geq 0.34$ . If these strong bases do not promote elimination, then it is unlikely that the much more weakly basic solvent assists the reaction. We conclude that the elimination at 3-F-, 4-NO<sub>2</sub>-, and 3,5-(CF<sub>3</sub>)<sub>2</sub>-substituted cumyl pentafluorobenzoates and chlorides in 50:50 (v/v) TFE/H<sub>2</sub>O proceeds by a *concerted unimolecular* mechanism with a carbocation-like transition state, *without* an intermediate, in which the leaving group acts as an intramolecular general base for proton abstraction (see 1).

These reactions are an example of "pericyclic" E<sub>1</sub><sup>13</sup> (cyclo-D<sub>E</sub>D<sub>N</sub>A<sub>n</sub>)<sup>1</sup> elimination (or retro-"ene" reaction<sup>14</sup>). Such reactions (e.g., pyrolytic eliminations of acetic acid or HCl) are well documented, not only in the gas phase<sup>15</sup> but also in nonpolar aprotic solvents,<sup>15</sup> where the formation of ionic intermediates is unfavorable. A good ionizing solvent is usually *assumed* to lead to a stepwise mechanism,<sup>15a</sup> and elimination reactions at tertiary carbon are often proposed to proceed through ion pair interme-

diates.<sup>16-18</sup> Our results show that, even in polar solvents, the concerted pericyclic mechanism is followed when the intermediate of the stepwise reaction becomes very unstable. This E<sub>1</sub> mechanism and its stepwise unimolecular counterpart are distinguished by the existence of an intermediate for the latter; the former proceeds through a transition state that *resembles* the intermediate of the stepwise reaction.<sup>8</sup>

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## [2 + 2] Cyclodimerization of Ligated Benzene following Reductive Activation of [Mn( $\eta^6$ -C<sub>6</sub>H<sub>6</sub>)(CO)<sub>3</sub>]<sup>+</sup> To Give [Mn(CO)<sub>3</sub>]<sub>2</sub>μ( $\eta^4$ -C<sub>6</sub>H<sub>6</sub>- $\eta^4$ -C<sub>6</sub>H<sub>6</sub>)]<sup>2-</sup>

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Orbital symmetry control of thermal and photochemical cycloaddition and dimerization of benzene has been extensively investigated both theoretically and experimentally.<sup>1</sup> One conclusion is that dimerization of benzene to *cis-anti-cis*-4a,4b,8a,8b-tetrahydrobiphenylene is photochemically allowed (from b<sub>1u</sub> and charge-transfer excited states),<sup>1,2</sup> but dimerization has never been observed under thermal or photochemical conditions. Tetrahydrobiphenylene has also, however, been of interest as an isomer of 12-annulene<sup>3</sup> and has been synthesized.<sup>4</sup> We now report (Scheme I; this includes selected <sup>13</sup>C data for some of the new compounds) that reductive activation of the benzene in [Mn( $\eta^6$ -C<sub>6</sub>H<sub>6</sub>)(CO)<sub>3</sub>]<sup>+</sup> leads to dimerization to give [Mn-

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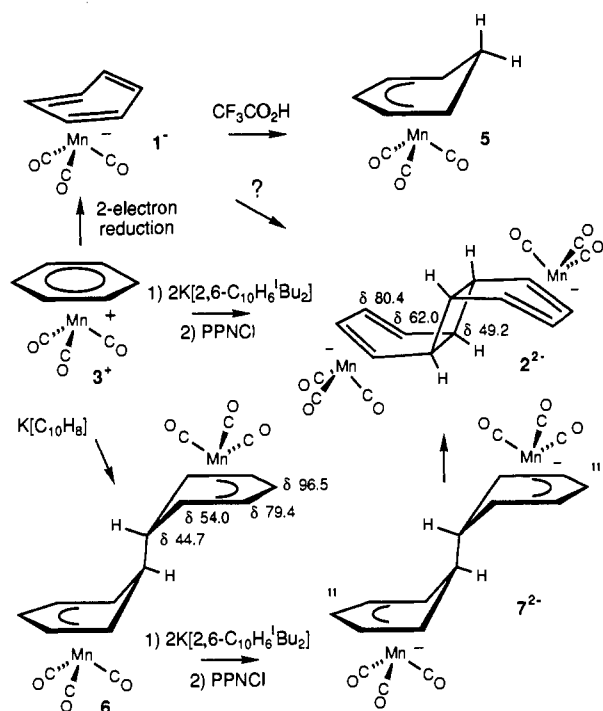
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Scheme I

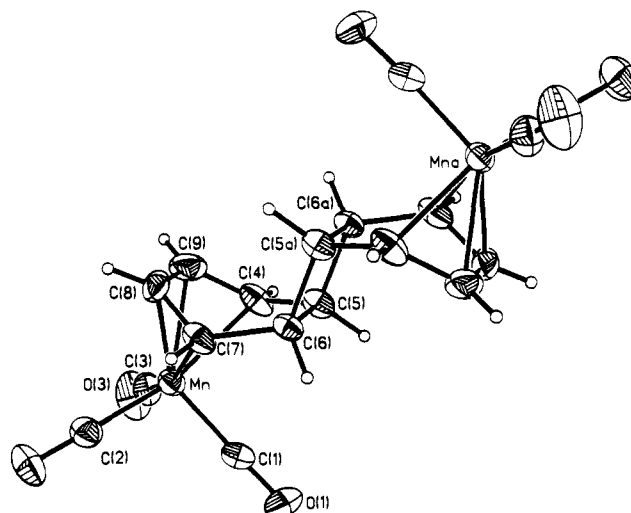


$(CO)_3\}_2\{\mu(\eta^4-C_6H_6-\eta^4-C_6H_6)\}^{2-}$  ( $2^{2-}$ ), in which the Mn centers are bridged by a tetrahydrobiphenylene ligand.

Our discovery of  $2^{2-}$  follows our observation that two-electron reduction of  $[Mn(\eta^6-C_6H_6)(CO)_3]^+$  ( $3^+$ ) gives a monoanionic species, formulated as  $[Mn(\eta^4-C_6H_6)(CO)_3]^-$  ( $1^-$ ), in which the coordinated benzene is activated toward protonation.<sup>5</sup> Attempts to isolate  $1^-$  were frustrated by facile naphthalene substitution to give  $[Mn(\eta^4-C_{10}H_8)(CO)_3]^-$  ( $4^-$ ).<sup>5</sup> In an attempt to circumvent this substitution we examined the reduction of  $3[PF_6]$  with alkylated naphthalenides, which would generate, as reduction by-products, alkylated naphthalenes, which would be less prone to substitute for the benzene in  $1^-$ .

Naphthalenide reducing agents examined included  $K[1,6-C_{10}H_6Me_2]$ ,  $K[2,6-C_{10}H_6Me_2]$ , and  $K[C_{10}H_8]$ , prepared from the naphthalenes as reported previously,<sup>6</sup> but we obtained inconsistent results until we turned to  $K[2,6-C_{10}H_6^tBu_2]$ , with a bulky substituent on each ring. With this we have obtained reproducible yields (11–18%, eight runs) of an organometallic product after dropwise addition of 20.0 mL of a 0.13 M solution of  $K[2,6-C_{10}H_6^tBu_2]$  to a slurry of  $3[PF_6]$  (0.30 g, 0.83 mmol) at  $-78^\circ C$ . The reduction is visually similar to that observed with  $K[C_{10}H_8]$ ,<sup>5</sup> and IR spectra have confirmed that  $3^+$  is reduced to an anion with  $\nu_{C=O}$  absorptions at 1945 (s), 1860 (s), and 1830 (s)  $cm^{-1}$  similar to those previously assigned to  $1^-$ . The solution was allowed to warm to room temperature and stirred vigorously with  $[PPN]Cl$  (0.48 g, 0.84 mmol,  $[PPN]^+ = [Ph_3PNPPH_3]^+$ ; added as a slurry in 20 mL of THF). The orange plates which precipitated were recrystallized from  $CH_2Cl_2/Et_2O$  as orange-red needles ( $\nu_{C=O}$  in  $CH_2Cl_2 = 1914$  (vs), 1822 (vs), 1796 (s)  $cm^{-1}$ ) with an elemental composition corresponding to that of  $[PPN]1$ .<sup>8</sup>

The  $^{13}C$  NMR spectrum of this compound contains three methyne resonances ( $\delta$  80.4, 62.0, 49.2), as anticipated for an  $\eta^4-C_6H_6$  complex, but the  $\delta$  49.2 resonance has an unreasonably high chemical shift for assignment to  $1^-$ .<sup>9</sup> A single-crystal X-ray



**Figure 1.** Molecular structure of  $\{[Mn(CO)_3]_2\{\mu(\eta^4-C_6H_6-\eta^4-C_6H_6)\}^{2-}$  (35% probability ellipsoids). Atoms with "a" subscripts are symmetry generated through an inversion center. Selected bond lengths (Å) and angles (deg): Mn–C(1) = 1.770 (7), Mn–C(2) = 1.776 (9), Mn–C(3) = 1.769 (8), Mn–C(7) = 2.144 (7), Mn–C(8) = 2.074 (8), Mn–C(9) = 2.079 (9), Mn–C(4) = 2.153 (10), C(6)–C(7) = 1.506 (11), C(7)–C(8) = 1.394 (10), C(8)–C(9) = 1.377 (16), C(9)–C(4) = 1.413 (14), C(4)–C(5) = 1.493 (9), C(5)–C(6) = 1.532 (11), C(5)–C(6a) = 1.573 (9); C(1)–Mn–C(2) = 101.1 (4), C(1)–Mn–C(3) = 98.7 (3), C(2)–Mn–C(3) = 89.4 (4), C(8)–C(7)–C(6) = 119.6 (8), C(7)–C(6)–C(5) = 117.7 (5). Dihedral angle between C(7)–C(8)–C(9)–C(4) plane and C(7)–C(4)–C(5)–C(6) plane = 139.7°.

diffraction study established, however, that we had in fact prepared the remarkable dimer  $[PPN]_2\{[Mn(CO)_3]_2\{\mu(\eta^4-C_6H_6-\eta^4-C_6H_6)\}^{2-}$  (Figure 1;  $[PPN]_2$ , 0.11 g, 0.07 mmol  $\equiv$  18%), which contains a bridging tetrahydrobiphenylene ligand.

The simplest interpretation of the formation of  $2^{2-}$  was that it involved a thermal  $[2 + 2]$  cyclodimerization<sup>10</sup> of  $1^-$ , and this is consistent with much of the available data. The formation of  $1^-$  following reduction of  $3^+$  has been confirmed by protonation at  $-78^\circ C$  of a solution freshly prepared by reduction of  $3^+$  with  $K[2,6-C_{10}H_6^tBu_2]$ ; as in the case of the  $K[C_{10}H_8]$  reduction,<sup>5</sup> this gives the cyclohexadienyl complex  $[Mn(\eta^5-C_6H_7)(CO)_3]$  ( $5$ ) ( $IR^{11}$ ). We have also unambiguously established that the reaction does not require photopromotion (which might result in an orbitally allowed concerted dimerization of  $1^-$ );<sup>10</sup> initial control experiments with methylnaphthalenide were ambiguous, but with  $K[2,6-C_{10}H_6^tBu_2]$ , yields of  $[PPN]_2$  are unaffected if  $3[PF_6]$  is reduced and metathesized in the dark.

Thermal  $[2 + 2]$  cycloadditions of olefins, which provide the closest model for formation of  $2^{2-}$ , typically involve diradical intermediates,<sup>10</sup> and formation of  $2^{2-}$  may similarly involve diradicals and hence not be subject to orbital symmetry restrictions (Scheme I). This is supported by the result of one-electron reduction of  $3^+$  with 1 equiv of  $K[C_{10}H_8]$ : this gives the dimer  $\{[Mn(CO)_3]_2\{\mu(\eta^5-C_6H_6-\eta^5-C_6H_6)\}^{2-}$  ( $6$ ,  $\nu_{C=O} = 2024$  (vs), 1942 (vs, br)  $cm^{-1}$  in toluene), closely related to a structurally characterized analogue containing linked mesitylene ligands.<sup>13</sup> Further

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(12) The dimer is readily purified by washing a toluene solution with water and precipitating the product from the filtered, dried, concentrated toluene solution at  $-80^\circ C$ . The product was recrystallized in 33% yield from toluene/pentane.

reduction of purified **6** in the dark at  $-78\text{ }^\circ\text{C}$  with 1 equiv of  $\text{K}[\text{2,6-C}_{10}\text{H}_6\text{tBu}_2]$  and subsequent  $[\text{PPN}]\text{Cl}$  metathesis gives  $[\text{PPN}]_2\mathbf{2}$  in 22% yield, suggesting that  $\mathbf{2}^{2-}$  may be formed via a diradical intermediate such as  $\mathbf{7}^{2-}$ , in which a single C-C bond links the monomer units.

The formation of  $\mathbf{2}^{2-}$  from  $\mathbf{3}^+$  is of interest within the context of benzene dimerization and of the ability of a transition-metal center to promote this reaction. The reaction also, however, has wider implications for the potential existence of a broad range of other cycloaddition reactions<sup>10</sup> of coordinated arenes in both the chromium and manganese systems, and experiments exploring these possibilities are underway in our laboratories together with detailed mechanistic studies.

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**Registry No.** **1**, 136115-43-0;  $[\text{PPN}]\mathbf{2}$ , 136115-45-2;  $\mathbf{3}^+$ , 41656-02-4; **5**, 12108-14-4; **6**, 136115-46-3;  $[\text{Mn}(\eta^4\text{-C}_{10}\text{H}_8)(\text{CO})_3]^+$ , 131130-38-6.

**Supplementary Material Available:** Spectroscopic and analytical data for  $[\text{PPN}]\mathbf{2}$  and **6**, crystal data for  $[\text{PPN}]\mathbf{2}$ , and tables of atomic coordinates, bond lengths and angles, anisotropic displacement coefficients, and H atom positional and displacement parameters for  $[\text{PPN}]\mathbf{2}$  (6 pages); tables of structure factors for  $[\text{PPN}]\mathbf{2}$  (21 pages). Ordering information is given on any current masthead page.

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## Metal Complexes of the Bridging Bidentate Metallophosphine Ligand, $[\text{Fe}_3(\text{CO})_9(\mu_3\text{-P})_2]^{2-}$

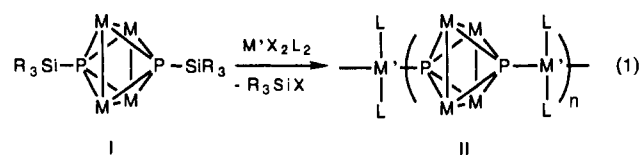
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Bicapped phosphinidene clusters form an extensively studied class of compounds that have drawn both chemical and theoretical attention due to their interesting structures, their facile redox chemistry, and their coordinative unsaturation.<sup>1</sup> We are exploring chemistry that will enable incorporation of the versatile bicapped  $\text{M}_x(\text{CO})_y(\mu_x\text{-P})_2$  unit ( $x = 3, 4$ ) into an extended array with the potential of cooperative interaction among the clusters by exploiting the coordinating ability of the cluster-bound phosphorus atoms (see II).<sup>2</sup> The strategy being employed to synthesize the chains involves preparation of bicapped silylphosphinidene clusters (for example, I), followed by removal of the silyl group in condensation reactions between the bicapped clusters and metal dihalide complexes (eq 1).<sup>3</sup> We report here preliminary inves-

tigations toward this goal involving reactions of the bifunctional



cluster,  $(\mu_2\text{-H})\text{Fe}_3(\text{CO})_9[\mu_2\text{-P}(\text{H})\text{SiMe}_3][\mu_3\text{-PSiMe}_3]$  (**1**), with metal monohalides belonging to the family  $(\text{C}_5\text{R}_5)\text{Fe}(\text{CO})_2\text{X}$  ( $\text{R} = \text{Me}$ ,  $\text{X} = \text{Cl}$ ;  $\text{R} = \text{H}$ ,  $\text{X} = \text{Cl}$ , I) to selectively produce discrete metal complexes of the bridging bidentate metallophosphine ligand,  $[\text{Fe}_3(\text{CO})_9(\mu_3\text{-P})_2]^{2-}$ . This study lays the foundation for the chemistry to *rationally* prepare extended cluster chains.

The cluster,  $(\mu_2\text{-H})\text{Fe}_3(\text{CO})_9[\mu_2\text{-P}(\text{H})\text{SiMe}_3][\mu_3\text{-PSiMe}_3]$  (**1**), is prepared as the primary product upon warming a hexanes/*cis*-cyclooctene reaction mixture containing 2 equiv of  $\text{PH}_2\text{SiMe}_3$  and 3 equiv of  $\text{Fe}(\text{CO})_3(\text{cis-cyclooctene})_2$ <sup>4</sup> from  $-40\text{ }^\circ\text{C}$  to room temperature.<sup>5</sup> Due to the difficulties encountered in chromatographic purification of complexes containing readily hydrolyzed P-SiMe<sub>3</sub> linkages, reactions of spectroscopically determined molar quantities of **1** with metal halides are performed *in situ*.

Stirring a solution of **1** and excess  $\text{CpFe}(\text{CO})_2\text{Cl}$  ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ) in benzene over a period of 1 day results in desilylation of the cluster<sup>6</sup> concomitant with rearrangement to the  $\text{Fe}_3(\mu_3\text{-P})_2$  core to produce the disubstituted cluster,  $\text{Fe}_3(\text{CO})_9[\mu_3\text{-PFe}(\text{CO})_2\text{Cp}]_2$  (Scheme I).<sup>7</sup> The structure of **2**, as established by a single-crystal X-ray diffraction study (Figure 1a),<sup>8</sup> consists of an open  $\text{Fe}_3$  triangle, with only two Fe-Fe bonds (like **1**), which is capped on each face by a triply bridging  $\text{PFe}(\text{CO})_2\text{Cp}$  unit. The phosphorus atoms are bound nearly equidistantly to the  $\text{Fe}_3$ -cluster iron atoms ( $\text{Fe}(\text{cluster})\text{-P} = 2.25$  (1) Å) and the capping iron atoms ( $\text{Fe}(\text{cap})\text{-P} = 2.262$  (6) Å). The isostructural phenylphosphinidene cluster,  $\text{Fe}_3(\text{CO})_9(\mu_3\text{-PPh})_2$ ,<sup>9</sup> has shorter Fe-P bonds ( $\text{Fe-P}(\text{av}) = 2.218$  (5) Å), which result in a much shorter P...P nonbonding distance for the phenyl-capped cluster (2.587 (5) Å) than for **2** (2.725 (6) Å).

The reactivity of the silyl cluster **1** toward the halides,  $\text{CpFe}(\text{CO})_2\text{X}$ , depends on the identity of X, as well as the substituents on the Cp ring. Excesses of  $\text{CpFe}(\text{CO})_2\text{I}$  and  $(\text{C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{Cl}$  do not react with **1** in benzene solution over a period of several days; however, reaction can be initiated by adding a stoichiometric amount of water into the reaction mixture to generate a mixture of the hydrolyzed clusters,  $\text{Fe}_3(\text{CO})_9(\mu_3\text{-PH})_2$  and  $(\mu_2\text{-H})\text{Fe}_3(\text{CO})_9(\mu_2\text{-PH}_2)(\mu_3\text{-PH})$ .<sup>10</sup> Reaction between the halides and the hydrolyzed clusters occurs over 1 day, to produce the monosubstituted clusters,  $\text{Fe}_3(\text{CO})_9[\mu_3\text{-PFe}(\text{CO})_2\text{Cp}'](\mu_3\text{-PH})$  (**3a**,  $\text{Cp}' = \text{C}_5\text{H}_5$ ; **3b**,  $\text{Cp}' = \text{C}_5\text{Me}_5$ ),<sup>11</sup> as the principle products. The above

(4) Fleckner, H.; Grevels, F. W.; Hess, D. *J. Am. Chem. Soc.* **1984**, *106*, 2027.

(5) Bautista, M.; White, P.; Schauer, C. K., manuscript in preparation. See supplementary material.

(6) Observation of this reaction by <sup>1</sup>H NMR spectroscopy in benzene-*d*<sub>6</sub> solution shows  $\text{Me}_3\text{SiCl}$  to be the primary silicon product.

(7) Following chromatography, crystallization from  $\text{CH}_2\text{Cl}_2/\text{pentane}$  yielded orange-red crystals of **2** (60 mg, 70%). <sup>31</sup>P NMR ( $\delta$ , ppm,  $\text{C}_6\text{H}_6$ ): 476 (s). <sup>1</sup>H NMR ( $\delta$ , ppm,  $\text{C}_6\text{D}_6$ ): 4.32 (d, <sup>3</sup>J(H,P) = 4 Hz,  $\text{C}_5\text{H}_5$ ). IR ( $\nu_{\text{CO}}$ ,  $\text{cm}^{-1}$ ,  $\text{Et}_2\text{O}$ ): 2061 (w), 2037 (m), 2019 (s), 1993 (m), 1967 (m), 1948 (w). Satisfactory C and H analyses were obtained.

(8) For  $2\text{-C}_6\text{H}_6$  ( $\text{C}_{29}\text{H}_{16}\text{Fe}_3\text{O}_{13}\text{P}_2$ ):  $a = 12.839$  (9) Å,  $b = 14.663$  (8) Å,  $c = 18.001$  (12) Å,  $\beta = 107.00$  (6) $^\circ$ , at  $-100\text{ }^\circ\text{C}$ . Space group  $\text{P2}_1/c$  ( $Z = 4$ ). Data collection on an Enraf-Nonius CAD4 diffractometer yielded 2647 unique observed ( $I \geq 2.5\sigma(I)$ ) reflections. Least-squares refinement of 443 parameters converged at  $R$  ( $R_w$ ) = 0.063 (0.088), GOF = 2.31.

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

(10) A <sup>31</sup>P NMR spectrum taken immediately after addition of  $\text{H}_2\text{O}$  shows conversion of **1** to  $\text{Fe}_3(\text{CO})_9(\mu_3\text{-PH})_2$  and  $(\mu_2\text{-H})\text{Fe}_3(\text{CO})_9(\mu_2\text{-PH}_2)(\mu_3\text{-PH})$  (combined spectroscopic yield by <sup>31</sup>P NMR spectroscopy, 60%). We have not yet been able to successfully chromatograph and isolate the hydrolyzed clusters.  $\text{Fe}_3(\text{CO})_9(\mu_3\text{-PH})_2$ : <sup>31</sup>P NMR ( $\delta$ ,  $\text{C}_6\text{H}_6$ , ppm) 234 (AA'XX', <sup>1</sup>J(H,P) = 315 Hz, <sup>3</sup>J(H,P) = 15 Hz, <sup>2</sup>J(P,P) = 346 Hz). Coupling constants obtained by simulation of the spectrum with LAOCN5 (Quantum Chemistry Program Exchange, No. QCMP 049).  $(\mu_2\text{-H})\text{Fe}_3(\text{CO})_9(\mu_2\text{-PH}_2)(\mu_3\text{-PH})$ : <sup>31</sup>P NMR ( $\delta$ ,  $\text{C}_6\text{H}_6$ , ppm) 215 (ddm, <sup>1</sup>J(H,P) = 337 Hz, <sup>2</sup>J(P,P) = 248 Hz, <sup>3</sup>J(P,H), -184 (dtm, <sup>1</sup>J(H,P) = 325 Hz, <sup>2</sup>J(P,P) = 248 Hz,  $\mu_2\text{-PH}_2$ ).

(1) See, for example: (a) Huttner, G.; Knoll, K. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 743. (b) Halet, J.-F.; Hoffmann, R.; Saillard, J.-Y. *Inorg. Chem.* **1985**, *24*, 1695. (c) Ohst, H. H.; Kochi, J. K. *Inorg. Chem.* **1986**, *25*, 2066. (d) Jaeger, J. T.; Vahrenkamp, H. *Organometallics* **1988**, *7*, 1746. (e) Jaeger, J. T.; Field, J. S.; Collison, D.; Speck, G. P.; Peake, B. M.; Hähnle, J.; Vahrenkamp, H. *Organometallics* **1988**, *7*, 1753.

(2) Direct intercluster coordination by cluster-bound phosphorus, arsenic, and sulfur to yield cyclic cluster trimers has been observed. Vizi-Orosz, A.; Galamb, V.; Palyi, G.; Marko, L. *J. Organomet. Chem.* **1976**, *111*, 61. Adams, R. D.; Maennig, D.; Segmueller, B. E. *Organometallics* **1983**, *2*, 149.

(3) Reactions of silylphosphines  $(\text{SiMe}_3)_2\text{PR}$  and  $(\text{SiMe}_3)\text{PR}_2$  with metal halides have been utilized to prepare phosphido bridged complexes and phosphinidene capped clusters. See, for example: (a) Fenske, D. M.; Ohmer, J.; Hachgenei, J.; Merzweiler, K. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1277. (b) Schäfer, H.; Zipfel, J.; Gutekunst, B.; Lemmert, U. *Z. Anorg. Allg. Chem.* **1985**, *529*, 157.