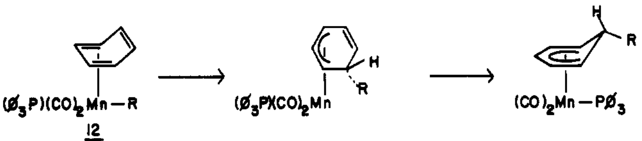
ring with 11 containing only 0.25 D all in the 6-exo position. No 6-endo D incorporation is noted.

The detailed mechanism of the alkyl reaction is not yet clear, but several points should be noted. First, alkyl migrations from the acyl complex 10 to give directly the product can be ruled out. In the presence of a 12-fold excess of PPh_3, the **5c** ⇌ **10c** equilibrium strongly favors acyl (>99:1) and the rate of isopropyl migration is greatly retarded rather than accelerated. Secondly, the surprising lack of endo migration of the hydride suggests that the mechanism is not simply irreversible migration of –R from manganese to the arene ring followed by PPh_3 trapping of the 16-electron cyclohexadienyl intermediate as was originally suggested by us.[1] Were this the case, hydrogen migration is expected to be much more rapid than alkyl migration, contrary to our observations. An attractive mechanistic alternative is the intermediacy of an (η^4-arene)$(CO)_2(PPh_3)$Mn–R complex **12**. On the basis of simple diene analogues,[11] alkyl migration is expected to be rapid in this system and the arene exchange reactions suggest accessibility of η^4-arene intermediates competitive with migration.[15] In this regard and in support of differing pathways for H vs. R migration, it is interesting to note that $C_6H_6(CO)_2$Mn–H *does not* exhibit appreciable arene ring exchange at 76 °C after 30 h (C_6D_6, presence or absence of PPh_3). This suggests that η^4-arene intermediates in the hydride system are not accessible at temperatures employed and may account for the lack of facile hydrogen migration. Further synthetic and mechanistic investigations are in progress.



Acknowledgment is made to the National Institutes of Health (Grant 1R01 GM23938) for support of this research.

Registry No. 2, 41656-02-4; 3, 100858-02-4; **5a**, 65643-62-1; **5b**, 103191-65-7; **5c**, 103191-66-8; **5d**, 103191-67-9; **5e**, 103191-69-1; **6**, 103191-68-0; **9a**, 83681-38-3; **9b**, 103191-70-4; **9c**, 103191-71-5; **10a**, 83681-39-4; **10b**, 103191-72-6; **10c**, 103191-73-7; 11, 95344-58-4.

Supplementary Material Available: Spectroscopic and analytical data for **5a–e**, **9a–c**, and **10a–c**, (2 pages). Ordering information is given on any current masthead page.

Formation and Structure of a Ferraphosphacyclopentenone

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Summary: Reaction of $Na(C_5H_5)Fe(CO)_2$ with $(C_6H_5)P(Cl)\{N[Si(CH_3)_3]_2\}$ in THF results in the formation of a metallophosphane complex $(C_5H_5)Fe(CO)_2[P(C_6H_5)\{N[Si(CH_3)_3]_2\}]$. This complex combines readily with $CF_3C{\equiv}CCF_3$, and a compound of composition $(C_5H_5)Fe(CO)_2[P(C_6H_5)\{N[Si(CH_3)_3]_2\}](CF_3C{\equiv}CCF_3)$ is isolated. The structure of the compound has been determined by single-crystal X-ray diffraction techniques and found to contain a ferraphosphacyclopentenone unit: $(C_5H_5)(CO)\overline{Fe\text{-}C(O)C(CF_3){=}C(CF_3)P}(C_6H_5)\{N[Si(CH_3)_3]_2\}$.

It has been demonstrated that the combination of the highly nucleophilic group 8 metal carbonylates $Na(C_5H_5)Fe(CO)_2$ and $Na[C_5(CH_3)_5]Fe(CO)_2$ with monohalophosphines P(X)(Y)(Cl) results in the formation of metallophosphanes $(C_5H_5)Fe(CO)_2[P(X)(Y)]$, which contain a terminal, pyramidal phosphorus atom.[1–6] The phosphorus atom in these complexes should serve as a site for nucleophilic reactivity and several reports which confirm this assumption have recently appeared.[2,4,6] We report here the synthesis of a metallophosphane $(C_5H_5)Fe(CO)_2[P(C_6H_5)\{N[Si(CH_3)_3]_2\}]$ (1) and the formation of a novel ferraphosphacyclopentenone complex, $(C_5H_5)(CO)\overline{FeC(O)C(CF_3){=}C(CF_3)P}(C_6H_5)\{N[Si(CH_3)_3]_2\}$ (2) through nucleophilic attack of the pyramidal phosphorus center on the activated acetylene $CF_3C{\equiv}CCF_3$.

Combination of $Na(C_5H_5)Fe(CO)_2$ with $(C_6H_5)P(Cl)\{N[Si(CH_3)_3]_2\}$[7] in equimolar amounts in tetrahydrofuran at 25 °C (12 h) resulted in a blood red solution containing $(C_5H_5)Fe(CO)_2[P(C_6H_5)\{N[Si(CH_3)_3]_2\}]$ (1). The solution was filtered to remove NaCl, the THF[8] solution evaporated to dryness, extracted with benzene, and filtered to remove remaining traces of NaCl, and the filtrate evaporated to dryness. 1 was recovered in 90% yield as a dark red microcrystalline solid which was characterized by analytical and spectroscopic techniques.[9] Elemental analysis and mass spectrometric data confirm the composition of 1. An infrared spectrum shows the expected two-band pattern, 2007 and 1960 cm^{-1}, in the terminal carbonyl stretching

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region. These frequencies compare favorably with the spectra obtained for $(C_5H_5)Fe(CO)_2P(CF_3)_2$,[4a] 2046 and 2000 cm^{-1}, $(C_5H_5)Fe(CO)_2P(C_6F_5)_2$,[1] 2034 and 1989 cm^{-1}, $(C_5H_5)Fe(CO)_2PPh_2$, 2015 and 1966 cm^{-1}, and $[C_5(CH_3)_5]Fe(CO)_2PPh_2$,[2] 1997 and 1957 cm^{-1}. These observations contrast with the four-band ν_{CO} pattern found in $[C_5(CH_3)_5]Fe(CO)_2\overline{PN(CH_3)CH_2CH_2N}CH_3$ (**3**),[3] 2002, 1969, 1954, and 1914 cm^{-1}, and in some other $FeCp(CO)_2X$ complexes.[10] The more complex four-band spectra have been interpreted to result from the presence of two isomers derived from hindered rotation about the Fe–P bond. The simple spectrum for **1** suggests that such a process is not operating in the new complex. The $^{31}P\{^1H\}$ spectrum for **1** consists of a singlet at δ 110, which is *upfield* of the resonance for $PhP(Cl)\{N[Si(CH_3)_3]_2\}$, δ 143, and downfield of the ^{31}P resonance in the organophosphine $(CH_3)(Ph)P\{N[Si(CH_3)_3]_2\}$, δ 37.6.[11] This contrasts with the large downfield shift for the ^{31}P resonance, δ 286, upon formation of **3** relative to δ 169 in $Cl\overline{PN(CH_3)CH_2CH_2N}CH_3$.[12] Although there are some interesting differences in spectroscopic properties between **1** and **3**, it appears that both complexes are metallophosphanes, and they possess pyramidal phosphorus environments.[13]

Organophosphanes are known to undergo complex addition reactions with activated acetylenes;[14] therefore, it was of interest to determine the nature of the reactivity of metallophosphanes with acetylene fragments. A methylcyclohexane solution of **1** mixed with excess $F_3CC{\equiv}CCF_3$ (1:2) at 25 °C for 12 h produces a red-orange solid[15] and a blood red solution[16] which are separated by filtration. The solid **2**, rinsed with methylcyclohexane, is recovered in 33% yield. Elemental analyses and mass spectra of the solid are consistent with the formulation $Fe(C_5H_5)(CO)_2(CF_3C{\equiv}CCF_3)[P(Ph)\{N[Si(CH_3)_3]_2\}$. Infrared spectra display absorptions at 1942, 1604, and 1580 cm^{-1} which are assigned to a terminal metal carbonyl stretch, a bridging carbonyl or acyl stretch, and an olefinic C=C stretch, respectively. The $^{31}P\{^1H\}$ NMR spectrum shows a strong singlet at δ 164 which is attributed to **2** and a minor resonance (<10%) at δ 157 which is presently unassigned. The ^{19}F NMR spectrum shows two quartets of doublets centered at δ –47.4 ($^3J_{FP}$ = 3.6 Hz, $^5J_{FF}$ = 11.2 Hz) and δ –49.6 ($^4J_{FP}$ = 2.6 Hz, $^5J_{FF}$ = 11.2 Hz) which require the presence of two inequivalent CF_3 groups.

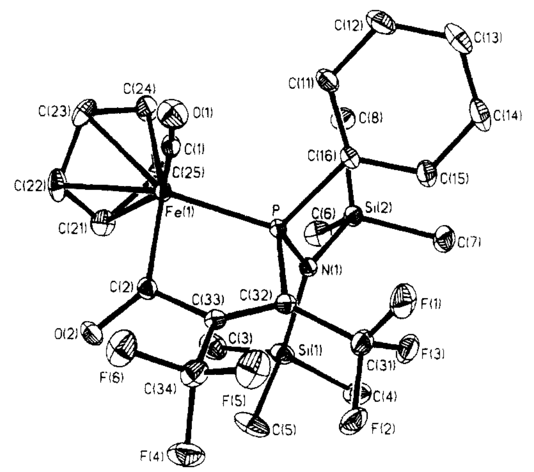

Figure 1. Molecular geometry and atom-labeling scheme for $Cp(CO)\overline{FeC(O)C(CF_3){=}C(CF_3)P}(C_6H_5)\{N[Si(CH_3)_3]_2\}$. Selected bond distances (Å) and angles (deg) include the following: Fe–C(Cp)$_{av}$ = 2.103 (3), Fe–C(1) = 1.739 (3), Fe–C(2) = 1.907 (2), Fe–P = 2.179 (1), C(1)–O(1) = 1.156 (3), C(2)–O(2) = 1.223 (3), C(2)–C(33) = 1.542 (3), C(32)–C(33) = 1.330 (3), P–C(32) = 1.873 (2), P–N = 1.689 (2), and P–C(16) = 1.837 (2); C(1)–Fe–C(2) = 86.9 (1), C(1)–Fe–P = 94.3 (1), C(2)–Fe–P = 83.8 (1), Fe–C(2)–C(33) = 115.6 (2), Fe–C(2)–O(2) = 129.2 (2), O (2)–C(2)–C(33) = 115.2 (2), Fe–P–C(16) = 115.9 (1), Fe–P–C(32) = 101.2 (1), Fe–P–N = 121.6 (1), N–P–C(16) = 105.6 (1), and N–P–C(32) = 108.5 (1).

Single crystals of **2** are obtained from a concentrated THF solution. X-ray diffraction analysis confirms the proposed elemental composition;[17] however, the molecular structure is more complex than suggested by the simple stoichiometric formula given above. A view of the structure is shown in Figure 1. The iron atom is bonded to a η^5-C_5H_5 ring, Fe—C(ring)$_{av}$ = 2.103 Å and C—C(ring)$_{av}$ = 1.394 Å, and a single terminal CO group with Fe—CO = 1.739 (3) Å and C≡O = 1.156 (3) Å. The latter pair of distances are comparable with related average distances in **3**, 1.766 (7) and 1.145 (14) Å. The iron atom is also incorporated into an envelope-shaped five-membered $\overline{FeC(O)C(CF_3){=}C(CF_3)P}$ ferraphosphacyclopentenone ring: the four atoms P, C(2), C(32), and C(33) define a least-squares plane with deviations from the plane of –0.03, 0.04, 0.08, and –0.09 Å, respectively. The iron atom resides 0.68 Å above the plane with a fold angle between the C(2)–Fe–P and C(2)–C(33)–C(32)–P planes of 152.8°. The acyl oxygen atom and CF_3 groups are distorted above and below the latter plane: O(2), 0.62 Å; C(31), 0.28 Å, C(34), –0.28 Å. The sum of the angles about C(2) is 360°. The Fe–P distance 2.179 (1) Å is considerably shorter than the Fe–P distances in **3**, 2.340 (2) Å,[3] and in **1**, 2.338 (1) Å.[13] The iron–acyl carbon atom bond distance Fe–C(2), 1.907 (2) Å, is shorter than related iron–acyl carbon atom distances in $[C_5H_4C_6H_6CO]Fe_2(CO)_5$,[18] 1.960 (3) Å, in $(C_5H_5)Fe(COCF_2C_5H_5)$,[19c] 1.99 (1) Å, and in a ferr-

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(13) A single-crystal X-ray diffraction structure determination confirms the proposed structure of **1**. McNamara, W. F.; Duesler, E. N.; Paine, R. T., to be submitted for publication.

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(15) **2** was isolated under inert-atmosphere conditions. Characterization: mp 170–173 °C dec; mass spectrum (70 eV), *m/e* 607 (M$^+$), 579 (M – CO$^+$), 268 ($PhP[N(SiMe_3)]_2^+$); IR (KBr) 1942, 1604, 1580, 1260 cm^{-1}; ^1H NMR (25 °C, CH_2Cl_2/CD_2Cl_2) δ 7.62-7.55 (m, phenyl), 4.84 (Cp), 0.36 ($SiMe_3$); $^{31}P\{^1H\}$ NMR (CH_2Cl_2) δ 164, 157 (impurity); ^{19}F NMR (CH_2Cl_2/CD_2Cl_2, $CFCl_3$ reference) δ – 47.40 (q of d, $^3J_{FP}$ = 3.6 Hz, $^5J_{FF}$ = 11.2 Hz), –49.56 (q of d, $^4J_{FP}$ = 2.6 Hz, $^5J_{FF}$ = 11.2 Hz); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 136–128 (m, phenyl), 87.6 (s, Cp), 5.9 (d, J_{CP} = 10 Hz, $SiMe_3$). Anal. Calcd for $FePSi_2F_6O_2NC_{23}H_{28}$: N, 2.3; C, 45.5; H, 4.6. Found: N, 2.2; C, 45.6; H, 4.8.

(16) The red methylcyclohexane solution from the reaction mixture contains several products indicated by ^{31}P NMR spectra: $^{31}P\{^1H\}$ NMR δ 136, 56, 50, 29.

(17) Crystal data: $FePSi_2F_6O_2NC_{23}H_{28}$, M_r 607.5, monoclinic space group $P2_1/n$, a = 10.285 (2) Å, b = 14.595 (3) Å, c = 18.025 (4) Å, α = 90.0°, β = 96.68 (2)°, V = 2687.6 (9) Å^3, Z = 4, and D_{calcd} = 1.50 g cm^{-3}. Data were collected at 20 °C on a Syntex P3/F diffractometer with a graphite-monochromated Mo Kα (λ = 0.71069 Å) radiation using the ω scan technique. The structure was solved by heavy-atom methods. Solution and refinement were performed by using the SHELXTL system (Sheldrick, G. M. Crystallographic Computing System, Revision 1982). Of a total of 6146 unique, space group allowed reflections, 4468 reflections were considered observed at the $4\sigma(F)$ level, and anisotropic refinements converged at R_F = 4.30% and R_{wF} = 3.38%.

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athiacyclopentenone,[20,21] $(C_5H_5)(CO)FeC(O)C(CF_3)=C(H)SCH_3$ (4), 1.954 (2) Å, while the acyl C=O distance in **2**, 1.223 (3) Å, compares with acyl C=O distances of 1.206 (4), 1.21 (1), and 1.215 (3) Å found in the preceding three complexes. The $CF_3C{\equiv}CCF_3$ bond distance, C(32)–C(33) = 1.330 (3) Å, is comparable with the related distance in **4**, 1.323 (4) Å, and intermediate between distances found for metal hexafluoro-2-butyne π complexes, 1.27–1.29 Å,[19] and for group 6 metal thia enone compounds: $(C_5H_5)(CO)MoC(O)C(CF_3)C(CF_3)C(O)SMe$,[20] 1.461 (5) Å, and $(C_5H_5)(CO)_2WC(CO_2CH_3)C(CO_2CH_3)C(O)SCH_3$,[22] 1.46 (1) Å. The phosphorus atom possesses a distorted tetrahedral geometry with bond angles ranging between 101.2° and 121.6°. The P–N bond distance 1.689 (2) Å is slightly shorter than the average P–N distance in **3**, 1.701 (6) Å, and significantly shorter than the P–N distance in the parent compound **1**, 1.734 (4) Å.[13] The P–N bond shortening in **2** is consistent with electron release from the phosphorus lone pair onto the C(32) atom. The P–C(16) distance 1.837 (2) Å in **2** is comparable with the related distance in **1**, 1.834 (5) Å.

The formation of a ferraphosphacyclopentenone structural unit from the combination of **1** with $CF_3C{\equiv}CCF_3$ is interestingly reminiscent of the results of reactions of metal thiolates $(C_5H_5)Fe(CO)_2(SR)$[20,23] and $(C_5H_5)W(CO)_3(SR)$[22,24] with $CF_3C{\equiv}CCF_3$. It has been proposed[24] that the nucleophilic thiolate sulfur atom attacks one carbon of the activated acetylene forming dipolar intermediates, of the general type $(CO)M{-}S^+(R')C(R){=}C^-(R)$. This intermediate may then produce a metal vinyl thiolate, $(CO)M{-}C(R){=}C(R)(SR')$, or a metallathiacyclopentenone, $M{-}S(R')C(R){=}C(R)C(O)$, identical in nature with **2**. The thiolate eneones have also been found to undergo ring expansion and ring rearrangement reactions,[24] and it is likely that the additional, cyclohexane-soluble products of the reaction of **1** with $CF_3C{\equiv}CCF_3$ are phosphorus analogues of one or more of the metal thiolate products. At this time, these products as well as the products formed by combination of **1** and other alkynes are under study.

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Registry No. 1, 103192-37-6; 2, 103192-38-7; $Na(C_5H_5)Fe(CO)_2$, 12152-20-4; $(C_6H_5)P(Cl)\{N[Si(CH_3)_3]_2\}$, 84174-75-4; $F_3CC{\equiv}CCF_3$, 692-50-2.

Supplementary Material Available: Experimental data and listings of observed and calculated structure factors, positional parameters, and anisotropic thermal parameters and full listings of bond distances and angles (25 pages). Ordering information is given on any current masthead page.

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(21) Molecular parameters have been obtained, and selected bond distances are listed here by using a parallel numbering system related to the structure of **2**: Fe–S = 2.185 (1) Å, Fe–C(2) = 1.954 (2), C(2)–C(33) = 1.522 (3), C(32)–C(33) = 1.323 (4), C(32)–S = 1.752 (3), C(2)–O(2) = 1.215 (3), and C(33)–C(34) = 1.495 (4). Muir, K. W., personal communication.

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A New Type of Organometallic Spiro Compounds: 2,2,6,6-Tetracyclopentadienyl-4-sila-2,6-dititanaspiro[3.3]heptane

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Summary: The reaction of Cp_2TiCl_2 with $CH_2(MgBr)_2$ gave the di-Grignard reagent $Cp_2Ti(CH_2MgBr)_2$ which on treatment with 0.5 molar equiv of $SiCl_4$ furnished the title compound $Cp_2TiCH_2Si(CH_2)Ti(Cp_2)CH_2$ (**4**) in 48% yield. Compound **4** was characterized by NMR and UV spectra. The ^{29}Si chemical shift (δ −145.3) is unusually shielded; this is briefly discussed in the context of other silicon spiro compounds. Reaction of **4** with iodine or Me_3SnCl gave $Si(CH_2I)_4$ or $Si(CH_2SnMe_3)_4$, respectively.

We have recently developed a number of routes to prepare 1,1- and 1,3-di-Grignard reagents and explored their potential for the synthesis of metal-containing four-membered rings.[1,2] Here we report the application of this approach to the preparation of 2,2,6,6-tetracyclopentadienyl-4-sila-2,6-dititanaspiro[3.3]heptane (**4**) which belongs to a new type of compounds combining the structural features of a silicon-centered spiro compound with those of 1,3-dimetallacyclobutanes. Compound **4** is remarkably stable and has interesting spectroscopic properties.

The concept for the synthesis of **4** is rather simple. It consists of the reaction of the 1,3-di-Grignard reagent **3**, which can be obtained from dichlorodicyclopentadienyltitanium (**1**) and methylenedimagnesium dibromide (**2**) in situ with silicon tetrachloride (Scheme I).

In a typical experiment, **1** (0.7 mmol) was added at −20 °C to the solution of **2** (1.4 mmol) in diethyl ether/benzene (1:1; 50 mL). After the solution was stirred for 1 h, **3** was formed as a red, viscous precipitate,[2a] and silicon tetra-

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