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 $CF_3C{=}CCF_3$ 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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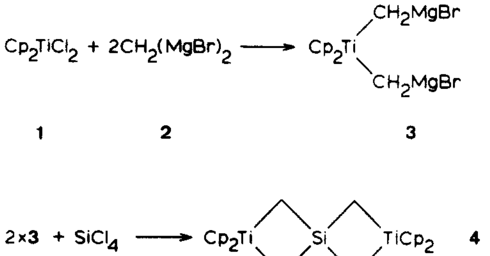
Table I. Spectroscopic Data of 4 and 5

	^{1}H NMR[a]			^{13}C NMR[b]				
compd	Cp	CH_2	CH_3	Cp	CH_2	CH_3	^{29}Si NMR[c]	UV
4	5.71	2.55	...	109.9 (d, 173)	70.9 (t, 131)	...	−145.3 (n, 5.6)	528
5	5.57	2.51	0.13	110.1 (d, 173)	70.6 (t, 130)	0.97 (q, 119)	−76[e]	478

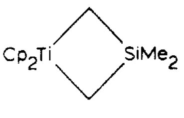
[a] δ in ppm; 90 MHz; C_6D_6 (C_6HD_5 at 7.17 ppm as internal standard); integrals in agreement with number of protons. [b] δ in ppm (multiplicity, ^{1}J(CH) in Hz); 62.89 MHz; C_6D_6 (at 128.0 ppm as internal standard). [c] δ in ppm (multiplicity (n = nonet), ^{2}J(SiH) in Hz); 79.48 MHz; C_6D_6 (Me_4Si as external standard). [d] λ_{max} in nm. [e] ^{2}J(Si–CH_2) = 4.9 Hz and ^{2}J(Si–CH_3) = 6.7 Hz determined from ^{29}Si satellites in the ^{1}H NMR spectrum.

Scheme I

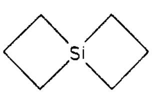


chloride (0.35 mmol) was added. The reaction mixture was then warmed to room temperature whereupon the red precipitate dissolved. After 4 h, the solvent was evaporated to dryness and the residue extracted with benzene followed by filtration. The filtrate was evaporated to dryness and gave purple-red crystals of 4 (48% yield), which are only slightly sensitive to oxygen and moisture and can be sublimed (150 °C; 10^{-6} mbar). Compound 4 was identified by elemental analysis[3] and by its spectral properties (Table I).

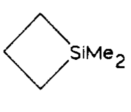
To our surprise and initial discomfort, the ^{1}H and ^{13}C NMR data were very close to those of the monocyclic model 5;[2a,4] the structure of 5 had been confirmed by X-ray crystallography.[4] Reassuring differences, however, were found in the ^{29}Si NMR and UV spectra. The latter reveal a bathochromic shift for 4 relative to 5, indicating a smaller HOMO–LUMO gap in 4. On the one hand, it is tempting to ascribe this to ground-state destabilization due to rehybridization at silicon;[5] the well-known strain effect of spiro-annelation could be invoked.[6] On the other hand, ring strain is usually associated with downfield shifts of ^{29}Si.[7,8] This is well-illustrated by the "carbon analogues" of 4 and 5, i.e., 6 (δ(^{29}Si) 37.2) and 7 (δ(^{29}Si) 18.4),[7] respectively; relative to tetramethylsilane, 6 and 7 show a downfield shift which is nearly additive per four-membered ring.



5



6



7

An analogous additivity is observed for 4 and 5, but its direction is opposite and the increments are much larger (Table I). The cause for this dramatic upfield shift is not yet clear. Transannular bonding has been suggested to explain the downfield shift in 6 and 7. In view of the short Ti–Si distance in 5 (d = 2.786 Å;[9] cf. the sum of radii r(Ti) + r(Si) = 2.5 Å[10]) a direct interaction in 4 and 5 seems not impossible; anisotropic shielding by the Cp_2Ti unit[11] is another possibility. In this context and in view of the thermal stability of 4 and 5, it is also relevant to point out that the endocyclic angle strain at silicon in 5 (CH_2SiCH_2 = 101.3°)[4] is much smaller than in 7 (CH_2SiCH_2 = 80.6°).[12]

Compound 4 has been characterized chemically by reaction with iodine to give tetrakis(iodomethyl)silane (32% yield) and with trimethyltin chloride to give tetrakis[(trimethylstannyl)methyl]silane; both are new compounds and were characterized by their spectral properties.[13]

$$Si(CH_2I)_4 \xleftarrow{I_2} 4 \xrightarrow{Me_3SnCl} Si(CH_2SnMe_3)_4$$

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Registry No. 1, 1271-19-8; 2, 27329-47-1; 3, 96242-28-3; 4, 103259-05-8; $SiCl_4$, 10026-04-7; $Si(CH_2I)_4$, 103259-03-6; Me_3SnCl, 1066-45-1; $Si(CH_2SnMe_3)_4$, 103259-04-7.

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(13) $Si(CH_2I)_4$: ^{1}H NMR ($CDCl_3$; 90 MHz) δ 2.44 (s, 8 H); MS, m/e (relative intensity) 465 (100, $[M - I]^+$), 451 (5.9), 437 (3.6), 423 (15.2), 409 (18, SiI_3^+), 339 (3.3). $Si(CH_2SnMe_3)_4$: ^{1}H NMR (C_6D_6; 90 MHz) δ 0.30 (s, 36 H), 0.10 (s, 8 H).

Preparation of a Mixed-Metal Ketenylidene Complex from $Mn(CO)_5(CX_3)$ (X = Cl, Br)

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Summary: The reaction of $Mn(CO)_5(CBr_3)$ and [PPN]-[$Co(CO)_4$] yields the mixed-metal ketenylidene complex [PPN][$MnCo_2(CO)_9(\mu_3\text{-}CCO)$]. The structure of the ketenylidene complex was determined by X-ray crystallography.

Numerous transition-metal cluster carbide complexes have been prepared by reactions between CCl_4 or $CHCl_3$