$C_{38}H_{38}F_6N_2P_2Ru$: C, 57.07; H, 4.79. Found: C, 56.49; H, 4.69.

$[Cp^*Ru(bpy)CO]^+PF_6^-$ (4e). Carbon monoxide was bubbled through a methanol solution of $(\eta^5\text{-}C_5Me_5)Ru(bpy)Cl$ (0.5 g, 1.2 mmol) and NH_4PF_6 (0.95 g, 5.8 mmol). After 1 h, the solvent was removed and the residue was extracted with methylene chloride, followed by evaporation to dryness. The yellow solid obtained was washed with ether and recrystallized from CH_2Cl_2–pentane. The yield was 0.45 g (71.6%). ^1H NMR ($CDCl_3$, δ): 8.70 (H_a) (2 H, br d, $J(H_a,H_b) = 4.3$ Hz), 8.47 (H_d) (2 H, br d, $J(H_c,H_d) = 7.9$ Hz), 8.14 (H_c) (2 H, br t), 7.67 (H_b) (2 H, br t), 1.68 (Cp*) (15 H, s). ^{13}C NMR ($CDCl_3$, δ): 199.3 (CO), 155.7 (C_{bridge}), 154.1 (C_a), 139.5 (C_c), 127.3 (C_b), 124.2 (C_d), 94.1 (Cp*, cycle), 9.4 (Cp*, methyl). IR (Nujol mulls): $\nu_{CO} = 1928$ cm^{-1}. Anal. Calcd for $C_{21}H_{23}F_6N_2OPRu$: C, 44.61; H, 4.10; N, 4.95. Found: C, 44.64; H, 4.11; N, 4.95.

$[Cp^*Ru(bpy)(C_4H_6O)]^+PF_6^-$ (4f). Prepared as described above for **4a**, using 2,5-dihydrofuran as ligand L. Yield: 45%. ^1H NMR (CD_2Cl_2, δ): 8.78 (H_a) (2 H, dd, $J(H_a,H_b) = 5.8$ Hz, $J(H_a,H_c) = 1.4$ Hz), 8.19 (H_d) (2 H, dd, $J(H_c,H_d) = 7.9$ Hz, $J(H_b,H_d) = 1.4$ Hz), 8.00 (H_c) (2 H, br t), 7.64 (H_b) (2 H, br t), 3.82 (CH_1H_1') (2 H, s), 3.63 (CH_1H_1') (2 H, d, $J(H_1,H) = 10$ Hz), 2.70 (CH) (2 H, d), 1.43 (Cp*) (15 H, s). ^{13}C NMR (CD_2Cl_2, δ): 153.8 (C_a), 153.0 (C_{bridge}), 137.4 (C_c), 126.8 (C_b), 123.1 (C_d), 94.2 (Cp*, cycle), 70.7 (CH), 65.1 (CH_2), 8.0 (Cp*, methyl).

$[Cp^*Ru(bpy)(C_{10}H_8O)]^+PF_6^-$ (4g). Prepared as described above for **4a**, using 2,5-epoxy-2,5-dihydronaphthalene as ligand L. Yield: 82%. ^1H NMR (CD_2Cl_2, δ): 9.00 (H_a) (2 H, dd, $J(H_a,H_b) = 5.4$ Hz, $J(H_a,H_c) = 0.8$ Hz), 8.22 (H_d) (2 H, dd, $J(H_c,H_d) = 7.9$ Hz, $J(H_b,H_d) = 0.9$ Hz), 8.04 (H_c) (2 H, br t), 7.69 (H_b) (2 H, br t), 7.13 and 6.93 (CH_{Ar}) (2 × 2 H, m), 4.25 (CH_{ether}) (2 H, s), 3.54 ($CH_{ethylene}$) (2 H, s), 1.40 (Cp*) (15 H, s). ^{13}C NMR (CD_2Cl_2, δ): 156.0 (C_{bridge}), 153.8 (C_a), 148.6 ($C_{Ar,bridge}$), 137.7 (C_c), 126.2 (C_b), 125.8 (C_{meta}), 123.3 (C_d), 120.3 (C_{ortho}), 95.6 (Cp*, cycle), 82.6 ($CH_{ethylene}$), 68.4 (CH_{ether}), 8.0 (Cp*, methyl). Anal. Calcd for $C_{30}H_{31}F_6N_2OPRu$: C, 52.86; H, 4.58; N, 4.11. Found: C, 52.22; H, 4.53; N, 4.30.

$[CpRu(bpy)CO]^+PF_6^-$ (5). Prepared as described above for **4e**, using CpRu(bpy)Cl as reagent. Yield: 45%. ^1H NMR (CD_2Cl_2, δ): 8.96 (H_a) (2 H, br d, $J(H_a,H_b) = 5.4$ Hz), 8.33 (H_d) (2 H, br d, $J(H_c,H_d) = 8.1$ Hz), 8.14 (H_c) (2 H, br t), 7.53 (H_b) (2 H, br t), 5.22 (Cp) (5 H, s). ^{13}C NMR (CD_2Cl_2, δ): 197.6 (CO), 157.7 (Ca), 156.5 (C_{bridge}), 139.6 (C_c), 126.9 (C_b), 124.2 (C_d), 89.5 (Cp). IR (Nujol mulls): $\nu_{CO} = 1963$ cm^{-1}.

Acknowledgment. We thank Rhône-Poulenc Ltd. for the financial support of this work.

Registry No. **3**, 119886-13-4; **4a**, 137365-61-8; **4b**, 137365-63-0; **4c**, 137365-65-2; **4d**, 137365-67-4; **4e**, 137365-69-6; **4f**, 137365-71-0; **4g**, 137365-73-2; **5**, 137365-75-4; CpRu(bpy)Cl, 93966-27-9; $[Cp^*RuCl_2]_n$, 92390-47-1.

Supplementary Material Available: Tables of atomic coordinates and anisotropic thermal parameters, all bond lengths and angles, and root mean square amplitudes (23 pages); a listing of observed and calculated structure factors (33 pages). Ordering information is given on any current masthead page.

New Access to 1,3-Diphospholyl Anions. Application to the Synthesis of the First Phosphorus Analogue of a Ferrocenophane

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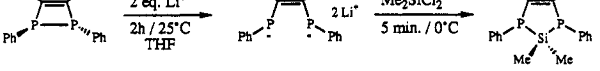
Summary: The reaction of acyl chlorides RC(O)Cl with a 2-sila-1,3-diphosphacyclopent-4-ene gives the corresponding 2-R-2-siloxy-1,3-diphosphacyclopent-4-enes via the formal replacement of the silicon by the acyl carbon in the five-membered ring. The substituents at P1, P3, and C2 in the resulting heterocycles are all cleaved by an excess of lithium in THF to afford the 1,3-diphospholyl anions. The dianion obtained from glutaryl dichloride, $ClC(O)C(CH_2)_3C(O)Cl$, reacts with a bis(η^6-*p*-xylene)iron(II) salt, $([(p\text{-xylene})_2Fe][PF_6]_2$, to give the corresponding 2,2′-trimethylene-1,1′,3,3′-tetraphosphaferrocene, $\{[(PhC)_2P_2CCH_2]_2CH_2\}Fe$ (**9**), whose structure has been established by X-ray crystallography. **9** crystallizes in the monoclinic space group $P2_1/c$ with unit cell parameters $a = 18.913$ (1) Å, $b = 11.362$ (1) Å, $c = 29.621$ (3) Å, $\beta = 106.49$ (1)°, and $d_{calcd} = 1.396$ g cm^{-3} for $Z = 8$. Least-squares refinement based on 2441 observed reflections with intensities $F_o \geq 3\sigma(F)$ in the range of $2° \leq 2\theta \leq 50°$ converged at $R = 4.5\%$ ($R_w = 5.6\%$).

In a recent paper,[1] we have described the first general synthesis of 1,3-diphospholyl anions. Compared to earlier syntheses of the 2,4,5-tris-*tert*-butyl-1,3-diphospholyl anion,[2] the new method produces these species free from other phosphorus-containing products and allows for various substitution schemes on carbons C_4 and C_5. It has one major drawback, however; the substitution on carbon C_2 is not possible. Thus, we have looked for access to those anions that would circumvent this limitation.

Results and Discussion

We chose the readily available 1,2,3,4-tetraphenyl-1,2-dihydro-1,2-diphosphete[3] as our starting product. Lithium cleavage of the P–P bond followed by reaction with dimethyldichlorosilane afforded the corresponding 1-sila-2,5-diphosphacyclopent-3-ene (1) as a single isomer according to the ^{31}P NMR spectrum of the reaction mixture (eq 1).



(1)

1

The crude product was used as such without further purification due to its very high sensitivity toward oxygen

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[1] Maigrot, N.; Ricard, L.; Charrier, C.; Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 534.

[2] Cowley, A. H.; Hall, S. W. *Polyhedron* **1989**, *8*, 849. Bartsch, R.; Nixon, J. F. *Polyhedron* **1989**, *8*, 2407.

[3] Ricard, L.; Maigrot, N.; Charrier, C.; Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 548.

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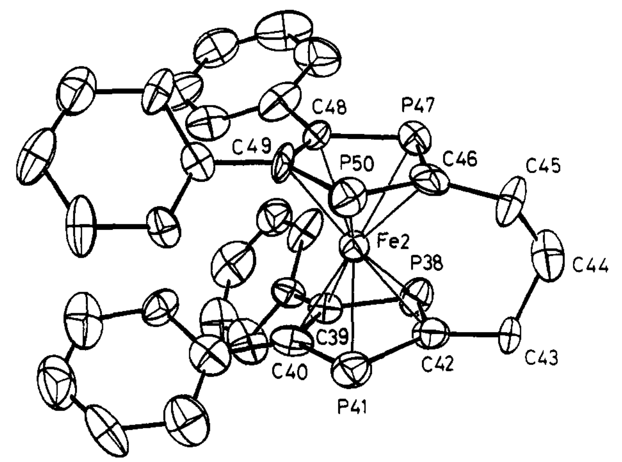
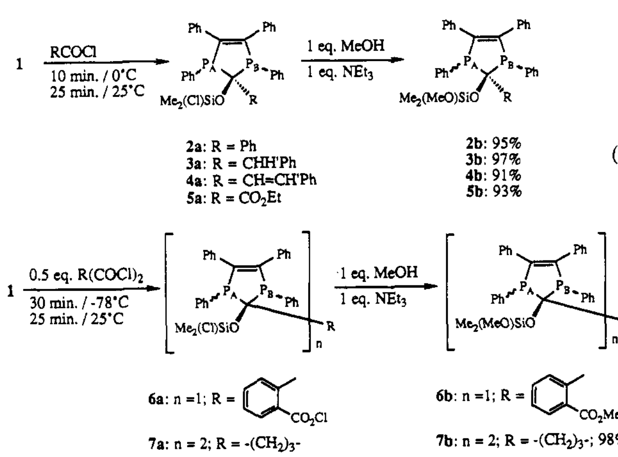


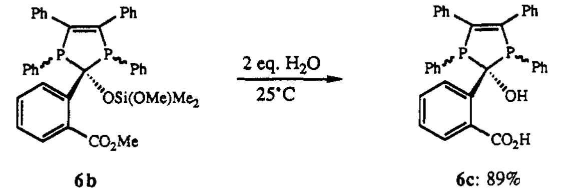
Figure 1. ORTEP drawing of molecule 2 in the asymmetric unit of **9** with the atomic numbering scheme, which includes Fe2 and atoms P38–C74. The hydrogen atoms are omitted for clarity. The ellipsoids are scaled to enclose 50% of the electronic density.

and moisture. Its stereochemistry (i.e., cis or trans disposition of the phosphorus substituents) is unknown. The reaction of **1** with acyl chlorides led to the displacement of silicon by carbon within the five-membered ring (eq 2).



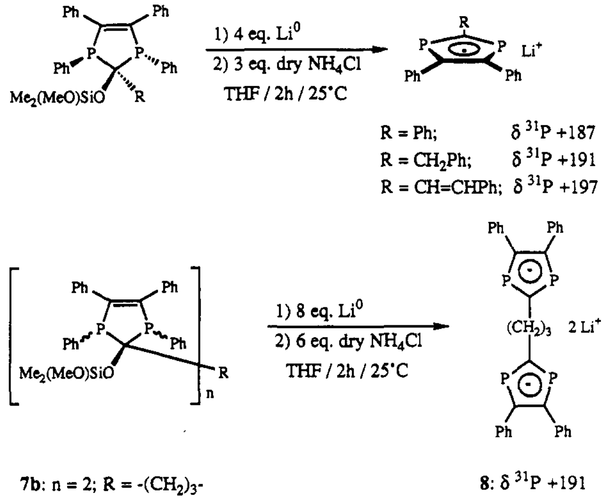
(2)

The mechanism most probably involves an initial ring opening leading to a *P*-silyl, *P*-acyl species followed by ring closure via the intramolecular attack of the *P*-silyl moiety onto the *P*-acyl carbonyl. This second step is more or less reminiscent of the reaction of silylphosphines with trifluoromethyl ketones.[4] However, as far as we know, the reaction of acylphosphines with silylphosphines as a route to substituted methylenebis(phosphines) has not been described in the literature.[5] The formation of a five-membered heterocycle perhaps serves as a driving force for this condensation. The reaction proceeds in almost quantitative yield with a wide variety of acyl chlorides. In the final products, the two substituents at the phosphorus centers can be either trans (major isomer) or cis (minor isomer) with respect to the five-membered ring with a ratio of trans to cis greater than 4:1 as determined from the ^{31}P NMR spectrum. The trans isomer gives rise to an AB pattern in the ^{31}P NMR spectrum, while the cis isomer gives rise to a singlet. Interestingly, only the trans isomers are obtained after purification, suggesting an equilibrium between the trans and cis forms with the trans isomer thermodynamically favored. Product **6b** proved to be sensitive to hydrolysis: the methoxy and siloxy groups were cleaved during the workup to afford **6c** (eq 3), otherwise, **2b**–**7b** were fully characterized.



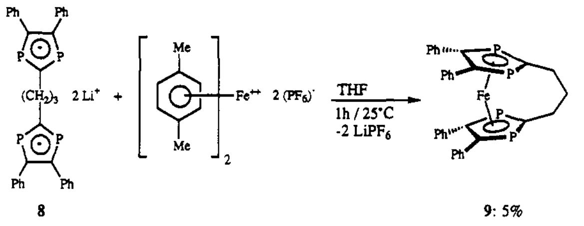
(3)

The reaction of compounds **2b**–**4b** and **7b** with lithium in THF produced the corresponding 1,3-diphospholyl anions via the cleavage of the C–OSi and the two P–Ph bonds (eq 4).



(4)

The resulting anions were the sole phosphorus-containing products of the reaction. They were characterized by their low-field ^{31}P NMR resonances (+ for downfield shifts from external 85% H_3PO_4) in the range of those recorded for the previously described 1,3-diphospholyl anions.[1,2] Furthermore, we took advantage of the unique structure of **8** to prepare the first phosphorus analogue of a [3]ferrocenophane (eq 5).



(5)

The structure of **9** was unambiguously established by X-ray crystallography (Figure 1). The iron atom 1 is 1.67 Å midway of the two 1,3-diphospholyl mean planes. This distance is longer than in the 1,3-diphosphaferrocene that has been structurally characterized previously (1.62 Å).[1] This fact is most probably an indication of some strain present due to the $-(CH_2)_3-$ bridge. The angle between the two 1,3-diphospholyl planes is 11°. This value is very similar to those already reported for classical [3]-ferrocenophanes.[6] The bond angles and bond distances of the two diphospholyl rings are similar in all respects to

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[4] Franke, R.; Heine, J.; Roschenthaler, G. V. *Chem.-Ztg.* **1988**, *112*, 146.

[5] Stelzer, O.; Langhans, K.-P. In *The Chemistry of Organophosphorus Compounds*; Hartley, F. R., Ed.; John Wiley and Sons: Chichester, England, 1990; Vol. I, pp 191–254.

[6] See for example: Batail, P.; Grandjean, D.; Astruc, D.; Dabard, R. *J. Organomet. Chem.* **1975**, *102*, 79.

those of the [(η^5-(^{t}BuC)$_3$P$_2$)Fe(η^5-(^{t}BuC)$_2$P$_3$)] complex reported by Nixon et al.[7]

Experimental Section

General Data. All reactions were performed under an argon atmosphere due to the sensitivity of these compounds to oxygen and water. Solvents were purified and dried by standard techniques. All glassware used in the synthetic work was oven dried. [(p-xylene)$_2$Fe][PF$_6$]$_2$ was prepared as reported by Helling et al.[8] ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 200 SY instrument operating at 200.13 and 50.32 MHz, respectively, while ^{31}P spectra were recorded on a Bruker WP 80 SY instrument operating at 32.44 MHz. All chemical shifts are reported in ppm downfield from internal TMS (^{1}H and ^{13}C) and external 85% H$_3$PO$_4$ (^{31}P). Mass spectra (EI) were obtained at 70 eV with a Shimadzu GC-MS QP 1000 instrument by the direct-inlet method. Elemental analyses were performed by the Service de Microanalyse, Gif-sur-Yvette, France.

Synthesis of 1. A solution of 1,2,3,4-tetraphenyl-1,2-dihydro-1,2-diphosphete (5 g, 12.7 mmol) in ca. 50 mL of THF was stirred with lithium metal (176 mg, 25.4 mmol) for 2 h at room temperature. The reaction was then cooled at 0 °C, and 1.54 mL (12.7 mmol) of Me$_2$SiCl$_2$ was added by syringe. The formation of **1** was complete within 5 min and was then used directly without further purification. ^{31}P NMR (THF): $\delta = -12.2$.

General Procedure for Compounds 2–5. To a solution of **1** (5.75 g, 12.7 mmol) in ca. 50 mL of THF at 0 °C was added by syringe 1 equiv (12.7 mmol) of the corresponding acid chloride. After being stirred for 10 min at 0 °C, the reaction was allowed to warm to room temperature and stirred an additional 25 min. Then the Si–Cl bond was hydrolyzed with 1 equiv (513 μL, 12.7 mmol) of MeOH (or EtOH) in the presence of 1 equiv (1.77 mL, 12.7 mmol) of NEt$_3$. After evaporation of THF, the mixture was dissolved in toluene and the solution filtered. The product was then washed with 3 × 25 mL portions of very cold hexane (−78 °C).

Compound 2a. ^{31}P NMR (THF): trans isomer (major), δ = 73.3 (P$_A$) and 64.7 (P$_B$) ($^2J(P_AP_B)$ = 10 Hz); cis isomer (minor), δ = 70.9.

Compound 2b. Yield: 95%. Mp: 160–162 °C. Data for the trans isomer are as follows. Mass spectrum: m/e 588 (M$^+$, 100%), 511 (M − Ph, 25%). Anal. Calcd for C$_{36}$H$_{34}$O$_2$P$_2$Si: C, 74.06 (73.53); H, 6.24 (5.83). ^{31}P NMR (CDCl$_3$): δ = 72.5 (P$_A$) and 63.9 (P$_B$) ($^2J(P_AP_B)$ = 12 Hz. ^{1}H NMR (CDCl$_3$): δ 7.50–7.00 (m, 25 H, phenyl), 3.52 (s, 3 H, OMe), 0.32 (s, 3 H, SiMe), 0.05 (s, 3 H, SiMe). ^{13}C NMR (CDCl$_3$): δ 149.2 (s, C:), 140.9–126.0 (phenyl), 83.5 (dd, $^1J(CP_{A,B})$ = 30 Hz, $^1J(CP_{B,A})$ = 10 Hz, P$_2$CO), 50.3 (s, OMe), −0.3 (s, SiMe).

Compound 3a. ^{31}P NMR (THF): trans isomer (major), δ = 67.6 (P$_A$) and 65.3 (P$_B$) ($^2J(P_AP_B)$ = 17 Hz); cis isomer (minor), δ = 63.6.

Compound 3b. Yield: 97%. Mp: 62–64 °C. Data for the trans isomer are as follows. Mass spectrum: m/e 602 (M$^+$, 50%), 511 (M − CH$_2$Ph, 100%). Anal. Calcd for C$_{37}$H$_{36}$O$_2$P$_2$Si: C, 74.35 (73.82); H, 6.11 (6.03). ^{31}P NMR (CDCl$_3$): δ = 66.8 (P$_A$) and 65.5 (P$_B$) ($^2J(P_AP_B)$ = 15 Hz). ^{1}H NMR (CDCl$_3$): δ 8.30–7.00 (m, 25 H, phenyl), 3.89 (s, 3H, OMe), 3.50 (ddd, $^2J_{H'H}$ = 13.5 Hz, ^3J(H′P$_{A,B}$) = 32 Hz, ^3J(H′P$_{B,A}$) = 5 Hz, 1 H, P$_2$CHH'), 3.08 (dd, $^2J_{H'H}$ = 13.5 Hz, $^3J(HP_{A,B})$ = 4 Hz, 1 H, P$_2$CHH′), 0.79 (d, ^5J(HP$_{A,B}$) = 1 Hz, 3 H, SiMe), 0.76 (d, ^5J(HP$_{A,B}$) = 0.6 Hz, 3 H, SiMe). ^{13}C NMR (CDCl$_3$): δ 151.7 (pt (=pseudo triplet) (ABX), C:), 141.5–126.6 (phenyl), 80.3 (pt (ABX), P$_2$CO), 50.6 (s, OMe), 45.0 (pt (ABX), CH$_2$Ph), 0.3 (d, $^4J(CP_{A,B})$ = 4 Hz, SiMe), 0.1 (d, ^4J(CP$_{A,B}$) = 4 Hz, SiMe).

Compound 4a. ^{31}P NMR (THF): trans isomer (major), δ = 68.4 (P$_A$) and 63.2 (P$_B$) ($^2J(P_AP_B)$ = 10 Hz); cis isomer (minor), δ = 69.4.

Compound 4b. Yield: 91%. Mp: decomposes at 78 °C. Data for the trans isomer are as follows. Mass spectrum: m/e 614 (M$^+$, 100%), 436 (M − Ph$_2$C$_2$, 80%). Anal. Calcd for C$_{38}$H$_{36}$O$_2$P$_2$Si: C, 74.84 (74.32); H, 5.93 (5.86). ^{31}P NMR (CDCl$_3$): δ = 67.8 (P$_A$) and 62.3 (P$_B$) ($^2J(P_AP_B)$ = 10 Hz). ^{1}H NMR (CDCl$_3$): δ 7.90–7.00 (m, 25 H, phenyl), 6.37 and 6.27 (AB system, $^2J_{HH'}$ = 16 Hz, 2H, HC═CH′), 3.48 (s, 3 H, OMe), 0.24 (s, 6 H, SiMe). ^{13}C NMR (CDCl$_3$): δ 150.8 (pt (ABX), PhC:), 138.5–126.5 (m, phenyl and CH═CH), 81.4 (dd, $^1J(CP_{A,B})$ = 30 Hz, $^1J(CP_{B,A})$ = 10 Hz, P$_2$CO), 50.6 (s, OMe), 0.0 (d, $^4J(CP_{A,B})$ = 5.5 Hz, SiMe), −0.7 (d, $^4J(CP_{A,B})$ = 5.0 Hz, SiMe).

Compound 5a. ^{31}P NMR (THF): trans isomer (major), δ = 74.1 (P$_A$) and 67.8 (P$_B$) ($^2J(P_AP_B)$ = 7.3 Hz); cis isomer (minor), δ = 72.8.

Compound 5b. Yield: 93%. Mp: decomposes at 80 °C. Data for a mixture of two trans diastereoisomers are as follows. Mass spectrum: m/e 584 (M$^+$, 70%), 511 (M − CO$_2$Et, 100%). Anal. Calcd for C$_{33}$H$_{34}$O$_4$P$_2$Si: C, 67.81 (67.80); H, 5.90 (5.86). ^{31}P NMR (CDCl$_3$): major, δ = 73.1 (P$_A$) and 63.8 (P$_B$) ($^2J(P_AP_B)$ = 7.3 Hz); minor, δ = 74.1 (P$_A$) and 67.8 (P$_B$) ($^2J(P_AP_B)$ = 10 Hz). ^{1}H NMR (acetone-d_6): δ 7.80–7.08 (m, 20 H, phenyl), 3.75 (m, 2 H, OCH$_2$), 3.35 (s, 3 H, OMe), 1.05 (pt, 3 H, OCH$_2$CH_3), 0.19 (s, 3 H, SiMe), −0.05 (s, 3 H, SiMe). ^{13}C NMR (acetone-d_6): δ 172.5 (d, $^2J(CP_{A,B})$ = 20 Hz, CO$_2$ minor), 171.5 (dd, $^2J(CP_{A,B})$ = 21 Hz, ^2J(CP$_{B,A}$) = 3.5 Hz, CO$_2$ major), 148.1 (pt, C: major), 145.0 (pt, C: minor), 138.8–127.6 (m, phenyl of two isomers), 82.0 (pt, P$_2$CO major), 79.0 (pt, P$_2$CO minor), 61.8 and 61.7 (s, OCH$_2$ of two isomers), 50.1 (s, OMe of two isomers), 14.0 (s, OCH$_2$$CH_3$ of two isomers), −0.7 (s, SiMe of two isomers).

General Procedure for Compounds 6 and 7. To a solution of **1** (5.75 g, 12.7 mmol) of ca. 50 mL of THF at −78 °C was added by syringe 0.5 equiv (6.34 mmol) of the corresponding acid chloride. After being stirred for 30 min at −78 °C, the reaction was allowed to warm to room temperature and stirred an additional 25 min. Then the Si–Cl bond was hydrolyzed with 1 equiv (513 μL, 12.7 mmol) of MeOH in the presence of 1 equiv (1.77 mL, 12.7 mmol) of NEt$_3$. After evaporation of THF, the mixture was dissolved in toluene and the solution filtered. The product was then washed with 3 × 25 mL portions of very cold hexane (−78 °C). Note: Compound **6b** was unstable, and only the hydrolysis product **6c** could be isolated cleanly.

Compound 6b. ^{31}P NMR (THF): trans isomer (major), δ = 61.3 (P$_A$) and 54.5 (P$_B$) ($^2J(P_AP_B)$ = 7.3 Hz); cis isomer (minor), δ = 38.6.

Compound 6c. Yield: 89%. Mp: decomposes at 76 °C. Mass spectrum: m/e 543 (M − H, 7%), 542 (M − 2H, 17%), 526 (M − H$_2$O, 100%). Anal. Calcd for C$_{34}$H$_{26}$O$_3$P$_2$: C, 75.13 (74.99); H, 4.62 (4.82). ^{31}P NMR (CDCl$_3$): trans isomer (major), δ = 62.0 (P$_A$) and 54.7 (P$_B$) ($^2J(P_AP_B)$ = 7 Hz); cis isomer (minor), δ = 35.9. ^{1}H NMR (CDCl$_3$): δ 7.70–7.00 (m, 24 H, phenyl). ^{13}C NMR (CDCl$_3$): δ 169.2 (s, CO$_2$), 149.2 (pt, PhC:), 147.2–122.7 (m, phenyl, 87.4 (dd, $^1J(CP_{A,B})$ = 41 Hz, $^1J(CP_{B,A})$ = 10 Hz, P$_2$COH).

Compound 7b. Yield: 98%. Mp: decomposes at 72 °C. Data for a mixture of diastereoisomers are as follows. Mass spectrum: m/e 774 (M − 2Ph; −OSi(OMe)Me$_2$; −OMe, 15%). Anal. Calcd for C$_{63}$H$_{64}$O$_4$P$_4$Si$_2$: C, 70.71 (71.03); H, 6.07 (6.06). ^{31}P NMR (CDCl$_3$): δ = 65.3 (P$_A$) and 60.3 (P$_B$) ($^2J(P_AP_B)$ = 15 Hz) and 65.9 (P$_A$) and 62.9 (P$_B$) ($^2J(P_AP_B)$ = 14.7 Hz). ^{1}H NMR (CDCl$_3$): δ 8.00–7.00 (m, 40 H, phenyl), 3.53 and 3.48 (s, 6 H, OMe), 1.85–1.50 (m, 6 H, CH$_2$CH$_2$CH$_2$), 0.29, 0.27, 0.23, and 0.21 (s, 12 H, SiMe). ^{13}C NMR (CDCl$_3$): δ 151.5 and 150.5 (pt, PhC:), 143.0–126.8 (phenyl), 80.7 and 80.2 (dd, P$_2$CO), 50.3 and 50.2 (s, OMe), 40.4–39.7 (m, CH$_2$CO), 22.5 (m, CH$_2$$CH_2CH_2$), 0.5 to −0.7 (m, SiMe).

Synthesis of 8. A solution of **7b** (2 g, 1.88 mmol) in ca. 20 mL of THF was stirred with Li metal (104 mg, 15.0 mmol) for 2 h at room temperature. The reaction was then cooled to 0 °C, and 603 mg (11.3 mmol) of NH$_4$Cl was added slowly. Compound **8** was then used directly without further purification. ^{31}P NMR (THF): δ = 191.

Synthesis of 9. A solution of **8** (1.05 g, 1.88 mmol) in ca. 20 mL of THF was stirred with [(p-xylene)$_2$Fe][PF$_6$]$_2$ (1.05 g, 1.88 mmol) at room temperature. The reaction was exothermic, and formation of **9** was complete within 1 h. After evaporation of THF, the mixture was chromatographed over silica gel (60 mesh) with hexane/toluene (70:30). Compound **9** was then recrystallized from a mixture of benzene/methanol (5:95) as a violet solid. Yield: 5%. Mp: decomposes at 266 °C. Mass spectrum: m/e 602 (M$^+$, 100%). Anal. Calcd for C$_{33}$H$_{26}$FeP$_4$: C, 65.23 (65.79); H, 4.83 (4.35). ^{31}P NMR (CD$_2$Cl$_2$): δ = 10.6. ^{1}H NMR (CD$_2$Cl$_2$): δ

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[7] Bartsch, R.; Hitchcock, P. B.; Nixon, J. F. *J. Chem. Soc., Chem. Commun.* **1987**, 1146.

[8] Helling, J. F.; Braitsch, D. M. *J. Am. Chem. Soc.* **1970**, *92*, 7207.

7.01–6.75 (m, 20 H, phenyl), 1.60–1.45 (m, 6 H, $CH_2CH_2CH_2$). ^{13}C NMR (CD_2Cl_2): δ 136.1 (C_{ipso}), 130.7 (C_{ortho}), 127.8 (C_{meta}), 127.0 (C_{para}), 114.5 (m, PhC:), 103.8 (m, P_2C), 35.9 (m, $CH_2\mathit{C}H_2CH_2$), 25.7 (m, $\mathit{C}H_2CH_2\mathit{C}H_2$).

X-ray Structure Determination for 9. Crystals of **9**, $C_{33}H_{26}FeP_4\cdot{}^1/_2C_6H_6$, were grown at room temperature from a benzene/methanol solution of the compound. Data were collected at 20 ± 1 °C on an Enraf-Nonius CAD4 diffractometer. The crystal structure was solved and refined using the Enraf-Nonius supplied SDP package. The compound crystallizes in space group $P2_1/c$, with $a = 18.913$ (1) Å, $b = 11.362$ (1) Å, $c = 29.621$ (3) Å, $\beta = 106.49$ (1)°, $V = 6103.55$ (1.8) Å^3, $Z = 8$, $d_{calc} = 1.396$ g/cm^3, $\lambda = 0.71073$ Å (Mo Kα radiation with a graphite monochromator), $\mu = 7.2$ cm^{-1}, and $F(000)$ 2648. A total of 10728 unique reflections were recorded in the range $2° \le 2\theta \le 50.0°$ of which 8287 were considered as unobserved ($F^2 < 3.0\sigma(F^2)$), leaving 2441 for the solution and refinement (due to the small size of the crystal, a large number of reflections were unobservable; hence, there is a poor ratio of observed reflections to refined parameters). The structure was solved by direct methods, yielding a solution for the iron and phosphorus atoms. The hydrogen atoms were included as a fixed contribution in the final stages of least-squares refinement while anisotropic temperature factors were used for all other atoms except C7, corresponding to C44 in the second molecule. This atom is librating between the two possible conformations of the aliphatic chain and can only be refined at the average position listed in the tables of supplementary material. A non-Poisson weighting scheme was applied with a *p* factor equal to 0.08. The final agreement factors were $R = 0.045$, $R_w = 0.056$, and GOF = 1.13.

Registry No. **1**, 136911-21-2; **2a**, 136911-22-3; *trans*-**2a**, 136983-85-2; *trans*-**2b**, 136911-23-4; **3a**, 136911-24-5; *trans*-**3a**, 136983-86-3; *trans*-**3b**, 136911-25-6; **4a**, 136911-26-7; *trans*-**4a**, 136983-87-4; *trans*-**4b**, 136911-27-8; **5a**, 136911-28-9; *trans*-**5a**, 136983-88-5; *trans*-**5b**, 136911-29-0; **6b**, 136911-30-3; *trans*-**6b**, 136983-89-6; **6c**, 136911-31-4; *trans*-**6c**, 136983-90-9; **7b**, 136911-32-5; **8**, 136911-36-9; **9**, 136946-97-9; **9**$\cdot{}^1/_2C_6H_6$, 136946-98-0; Me_2SiCl_2, 75-78-5; PhCOCl, 98-88-4; $PhCH_2COCl$, 103-80-0; PhCH=CHCOCl, 102-92-1; $ClCOCO_2Et$, 4755-77-5; $ClCOC_6H_4$-*o*-COCl, 88-95-9; $ClCO(CH_2)_3COCl$, 2873-74-7; $[(p\text{-xylene})_2Fe][PF_6]_2$, 103123-09-7; *trans*-1,2,3,4-tetraphenyl-1,2-dihydro-1,2-diphosphete, 96693-28-6; lithium 2,4,5-triphenyl-1*H*-1,3-diphosphole, 136911-33-6; lithium 2-benzyl-4,5-diphenyl-1*H*-1,3-diphosphole, 136911-34-7; lithium 2-styryl-4,5-diphenyl-1*H*-1,3-diphosphole, 136911-35-8.

Supplementary Material Available: Tables of crystallographic details, least-squares planes and dihedral angles, positional and thermal parameters, anisotropic thermal parameters, bond distances, and bond angles (19 pages); a table of structure factors (13 pages). Ordering information is given on any current masthead page.

Transition-Metal-Containing Inorganic Ring Systems: Synthesis and X-ray Crystal Structure of the First Cyclozincadisilatriazane

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Summary: Reaction of $ZnCl_2$ with $MeN(Me_2SiNEtLi)_2$ results in the formation of the first stable six-membered Si_2N_3Zn metallacycle. Spectral and X-ray crystal structure studies of this compound, crystallized from toluene–pyridine mixtures, indicate the molecule to be dimeric in nature with the formula $[MeN(Me_2SiNEt)_2Zn\cdot py]_2$ (py = pyridine). The Zn atom is tetrahedrally coordinated, and pyridine and three of the nitrogens bonded to ethyl groups are involved in the coordination.

Recent developments in inorganic heterocyclic chemistry include syntheses of novel Zn–O and Zn–S heterocycles.[1] In contrast, studies on cyclic metal amides of Zn have been quite limited.[2] In their contributions to the silazane chemistry, Bürger and co-workers have also reported on the synthesis of a few group 4 and 5 transition-metal-containing cyclic silylamides. These include six-membered Si–N rings of Ti,[3] Zr,[4] and V,[5] which have been characterized by various spectral techniques. X-ray crystal structure studies on four-membered Ti, Zr,[6] Hf, V, and Nb[7] cyclic silylamides and for the five-membered $TiSi_2N_2$[8] ring system have also been reported, many of them being spirocyclic in nature. In continuation of our contributions in syntheses of novel transition-metal-containing inorganic ring systems,[9] we report herein the synthesis and X-ray structure of the first example of a six-membered Si_2N_3Zn ring system.

Experimental Section

All manipulations were performed under an atmosphere of dry oxygen-free nitrogen by using standard Schlenk techniques. Solvents were appropriately dried and distilled in an inert atmosphere prior to use.

Infrared spectra were obtained with Bio-Rad FTS 7 spectrophotometer as Nujol mulls. Proton, carbon-13, and silicon-29 NMR spectra were recorded on Bruker WP80SY and 250M spectrometers. Chemical shifts are reported in δ units downfield from tetramethylsilane with the solvent as the reference signal. C_6D_6 was used for room-temperature measurements, while toluene-d_8 was used at low temperatures. Mass spectra were recorded on Finnigan MAT system 8230, and microanalysis was carried out at the Analytical Laboratories of the Institute of Inorganic Chemistry of the University of Göttingen.

Preparation of 4. A 0.88-g (3.8 mmol) sample of $MeN(Me_2SiNEtH)_2$ prepared by the literature method,[10] taken in 10 mL of hexane was treated with 3.2 mL of of an *n*-butyllithium solution (2.36 M in hexane). After warming for a short period,

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[1] Power, P. P. *J. Organomet. Chem.* **1990**, *400*, 49.

[2] Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. *Metal and Metalloid amides*; Ellis Horwood Limited: Chichester, U.K., 1980; p 545.

[3] (a) Bürger, H.; Wiegel, K. *J. Organomet. Chem.* **1977**, *124*, 279. (b) Brauer, D. J.; Bürger, H.; Wiegel, K. *J. Organomet. Chem.* **1978**, *150*, 215.

[4] Bürger, H.; Wiegel, K. *Z. Anorg. Allg. Chem.* **1976**, *426*, 301.

[5] Wiegel, K.; Bürger, H. *J. Organomet. Chem.* **1977**, *129*, 309.

[6] (a) Brauer, D. J.; Bürger, H.; Essig, E.; Geschwandtner, W. *J. Organomet. Chem.* **1980**, *190*, 343. (b) Beiersdorf, W. D.; Brauer, D. J.; Bürger, H. *Z. Anorg. Allg. Chem.* **1981**, *475*, 56.

[7] Brauer, D. J.; Bürger, H.; Liewald, G. R.; Wilke, J. *J. Organomet. Chem.* **1986**, *310*, 317.

[8] Bürger, H.; Wiegel, K.; Thewalt, U.; Schomburg, D. *J. Organomet. Chem.* **1975**, *87*, 301.

[9] (a) Roesky, H. W. *Synlett* **1990**, *11*, 651. (b) Roesky, H. W. In *Rings, Clusters and Polymers of Main Group and Transition Elements*; Roesky, H. W., Ed.; Elsevier: Amsterdam, 1989; p 369.

[10] Wannagat, U.; Braun, R. *Monatsh. Chem.* **1969**, *100*, 1910.

0276-7333/92/2311-0462$03.00/0