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Transition-Metal-Substituted Diphosphenes. 29.[1] Cycloaddition Reactions of the Diphosphenyl Complex $(\eta^5\text{-}C_5Me_5)(CO)_2Fe\text{–}P{=}P\text{–}Mes^*$ (Mes^* = 2,4,6-$tBu_3C_6H_2$) with Hexafluoroacetone. X-ray Structure Analyses of $(\eta^5\text{-}C_5Me_5)(CO)Fe\text{–}P({=}PMes^*)OC(CF_3)_2C(O)$ and $(\eta^5\text{-}C_5Me_5)(CO)_2Fe\text{–}P\text{–}P(Mes^*)OC(CF_3)_2$

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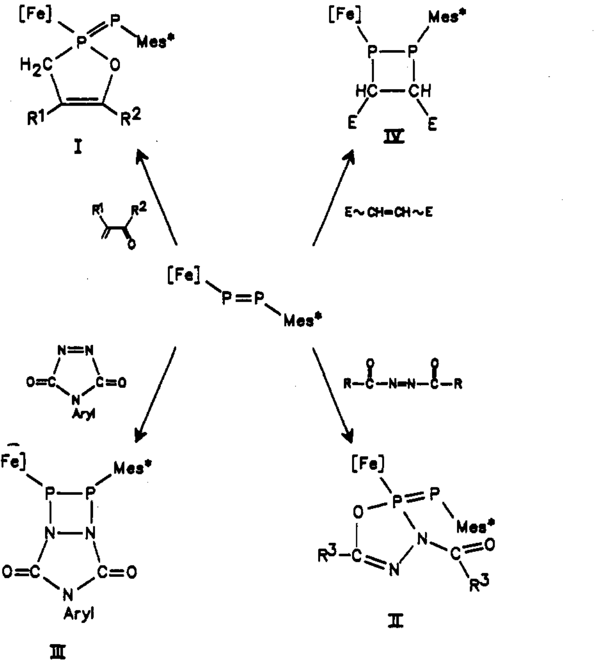
Summary: The diphosphenyl complex $(\eta^5\text{-}C_5Me_5)(CO)_2Fe\text{—}P{=}P\text{—}Mes^*$ (Mes^* = 2,4,6-$tBu_3C_6H_2$) undergoes a [3 + 2] dipolar cycloaddition with hexafluoroacetone to give the metalla heterocycle $(\eta^5\text{-}C_5Me_5)(CO)Fe\text{—}P({=}PMes^*)OC(CF_3)_2C(O)$ with a remarkably short Fe—P bond (2.084 (4) Å) and an exocyclic P=P bond. When stored in solution at −40 °C, this complex partly rearranges to the metalated 1-oxa-2,3-diphosphetane $(\eta^5\text{-}C_5Me_5)(CO)_2Fe\text{—}P\text{—}P(Mes^*)OC(CF_3)_2$. The molecular structures of both isomers were elucidated by single-crystal X-ray analyses.

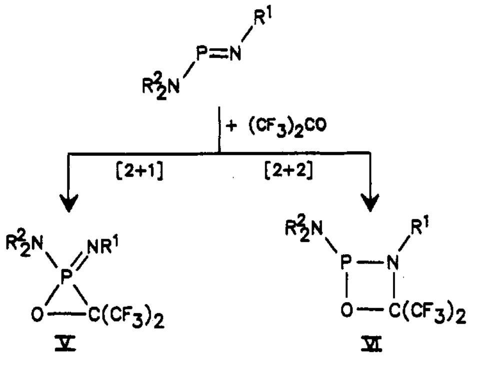
Electron-releasing organometallic complex fragments as substituents markedly enhance the nucleophilicity of a diphosphene. In molecules such as $(\eta^5\text{-}C_5Me_5)(CO)(L)M\text{—}P{=}P\text{—}R$ (M = Fe, L = CO, R = 2,4,6-$tBu_3C_6H_2$ (Mes^*), 2,4,6-$(CF_3)_3C_6H_2$, 2,6-$(CF_3)_2C_6H_3$, $C(SiMe_3)_3$; M = Ru, Os, L = CO, R = Mes^*; M = Mn, Re, L = NO, R = Mes^*) the HOMO is mainly represented by the lone pair at the metalated phosphorus atom. This is documented by a number of reactions of $(\eta^5\text{-}C_5Me_5)(CO)_2Fe\text{—}P{=}P\text{—}Mes^*$ (**1**) with organic and organometallic electrophiles. Compound **1** is converted into oxaphospholenes **I** by treatment with acrolein, methacrolein, and methyl vinyl ether.[2] Azodicarboxylates and azodiamides give rise to the formation of oxadiazaphospholenes **II**,[3] whereas the reaction of **1** with 1,2,4-triazoline-3,5-diones furnished the first 1,2-diaza-3,4-diphosphetidines **III**.[4] [2 + 2] cycloadditions to 1,2-diphosphetanes **IV** are observed with fumarodinitrile, maleodinitrile dimethyl fumarate, dimethyl maleate,[5] and maleimides.[6] In all these processes we assume that the ring formation is initiated by the attack of the lone pair of the metalated P atom at the LUMO of the electrophile.



R^1, R^2 = H, Me; R^3 = OEt, OtBu, OCH_2Ph, NC_5H_{10}; E = CN, CO_2Me

Aryl = Ph, 4-$EtOC_6H_4$; [Fe] = $(\eta^5\text{-}C_5Me_5)(CO)_2Fe$

The step from electron-poor alkenes and azo compounds to other electrophiles with heteroatomic double bonds is obvious. Here we report on the chemical behavior of **1** toward anhydrous hexafluoroacetone, which is known to undergo oxidative additions to trivalent phosphorus compounds.[7] Low-coordinated phosphorus systems such as iminophosphanes are converted by hexafluoroacetone to λ^5-oxaphosphiranes **V** (for R = Me_3Si)[8] or to λ^3-1-oxa-3-aza-2-phosphetanes **VI** (for R = alkyl).[9] A different mode of reaction, however, is encountered with **1** and the ketone.



R^1 = Me_3Si or tBu
R^2 = Me_3Si

R^1 = tBu, R^2 = iPr

Condensing an excess of gaseous hexafluoroacetone into

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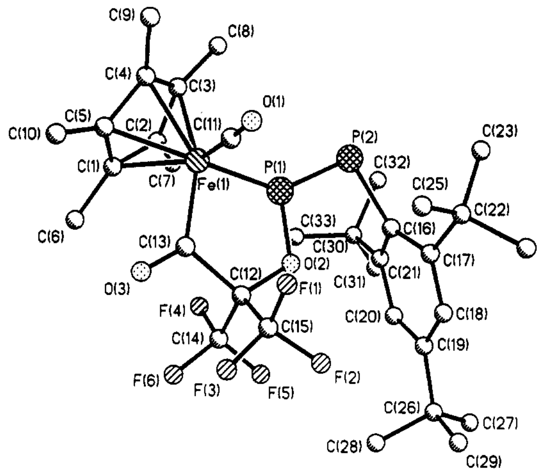
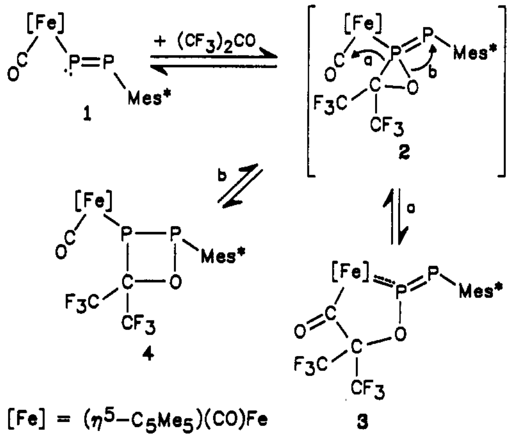


Figure 1. Molecular structure of 3.

Table I. Selected Bond Lengths (Å) and Angles (deg) for 3

Fe–P(1)	2.084 (4)	P(2)–C(16)	1.860 (13)
Fe–C(11)	1.795 (16)	O(1)–C(11)	1.128 (19)
Fe–C(13)	1.937 (14)	O(2)–C(12)	1.427 (15)
P(1)–P(2)	2.014 (5)	O(3)–C(13)	1.191 (16)
P(1)–O(2)	1.647 (9)	C(12)–C(13)	1.640 (19)
Fe–P(1)–P(2)	140.3 (2)	P(1)–O(2)–C(12)	115.6 (7)
Fe–P(1)–O(2)	109.5 (3)	O(2)–C(12)–C(13)	111.8 (10)
P(2)–P(1)–O(2)	109.9 (3)	Fe–C(13)–C(12)	116.3 (9)
P(1)–P(2)–C(16)	99.0 (4)	P(1)–Fe–C(13)	86.4 (4)

a pentane solution of 1 at −196 °C and warming to 20 °C afforded the cycloadduct 3 as an orange crystalline solid. No other product could be observed in the reaction mixture by means of ^{31}P NMR spectroscopy, and no intermediate was detected during the course of the reaction.



[Fe] = (η^5-C_5Me_5)(CO)Fe

The structure of 3 was assigned on the basis of spectral evidence[10] and confirmed by the single-crystal X-ray diffraction study.[11] The ^{31}P NMR spectrum exhibits two doublets at δ 483.49 and 180.68 with the large coupling constant $^1J_{PP}$ = 633 Hz, suggesting the presence of a P═P double bond in 3. In the ^{19}F NMR spectrum two quartets at δ −70.55 and −71.35 ($^4J_{FF}$ = 7.3 Hz) agree with two magnetically nonequivalent CF_3 groups with no PF coupling and infer the absence of any direct $PC(CF_3)_2$ linkage. The appearance of two discrete singlets for the *o*-*tert*-butyl substituents of the Mes* ring in the ^1H NMR spectrum at δ 1.65 and 1.68 is due to the chiral Fe center in 3. The IR spectrum (Nujol mull) displays only one intense band at ν = 1960 cm^{-1} for the stretching mode of one terminal CO ligand. The acylic carbonyl group gives rise to a band at 1650 cm^{-1} of medium intensity.

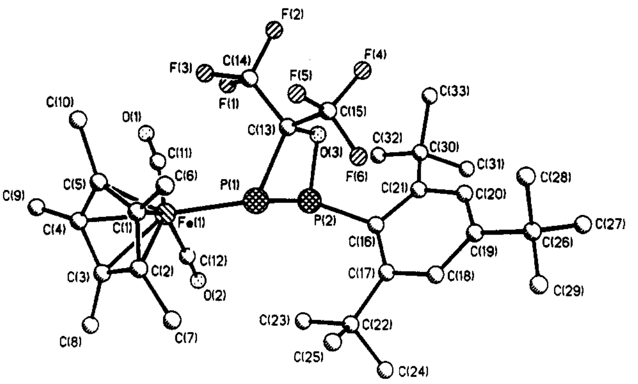
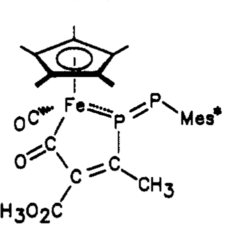


Figure 2. Molecular structure of 4.

Table II. Selected Bond Lengths (Å) and Angles (deg) for 4

Fe–P(1)	2.327 (4)	P(1)–C(13)	1.927 (13)
Fe–C(11)	1.779 (15)	P(2)–O(3)	1.722 (8)
Fe–C(12)	1.744 (15)	O(3)–C(13)	1.409 (13)
P(1)–P(2)	2.249 (5)	O(1)–C(11)	1.139 (18)
P(2)–C(16)	1.865 (11)	O(2)–C(12)	1.144 (18)
Fe–P(1)–P(2)	110.7 (2)	O(3)–P(2)–C(16)	96.6 (5)
Fe–P(1)–C(13)	118.5 (4)	P(1)–Fe–C(11)	103.0 (4)
P(1)–P(2)–C(16)	105.9 (4)	P(1)–Fe–C(12)	92.0 (5)
P(1)–C(13)–O(3)	102.2 (8)	C(11)–Fe–C(12)	90.4 (7)
P(2)–O(3)–C(13)	104.2 (7)		

The most interesting feature of the molecular structure of 3 (Figure 1 and Table I) is the geometry of the nearly planar five-membered metalla heterocycle (mean deviation from the plane 0.024 Å). The Fe–P bond of 2.084 (4) Å is remarkably short and strongly suggests multiple-bond contributions. Similarily short Fe–P bond distances were reported for complexes 5 (2.117 (2) Å)[12] and 6 (2.112 (1) and 2.202 (1) Å).[13] In 1 the Fe–P contact was determined to be 2.260 (1) Å.[14] The exocyclic P–P bond length (2.014 (5) Å) is comparable to the P–P bond in 1 (2.027 (3) Å). The bond length P(1)–O(2) (1.647 (9) Å) is shorter than the sum of the covalent single-bond radii for P (1.10 Å) and O (0.66 Å).[15] The atoms Fe, P(1), P(2), and O(2) are



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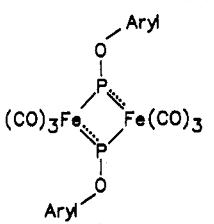

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(Aryl = 2,6-tBu_2-4-MeC_6H_2)

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[10] 3: ^1H NMR (100 MHz, C_6D_6) δ 1.33 (s, *p*-*t*Bu), 1.49 [s, $C_5(CH_3)_5$], 1.65 (s, *o*-*t*Bu), 1.68 (s, *o*-*t*Bu), 7.56 (m, *m* aryl H); $^{19}F\{^1H\}$ NMR (84.2 MHz, *n*-C_5H_{12}, $CFCl_3$ standard) δ −70.55 (q, $^4J_{FF}$ = 7.3 Hz, CF_3), −71.35 (q, $^4J_{FF}$ = 7.3 Hz, CF_3); $^{31}P\{^1H\}$ NMR (40 MHz, *n*-C_5H_{12}, 85% H_3PO_4 standard) δ 483.49 (d, $^1J_{PP}$ = 633 Hz, Fe–P), 180.68 (d, $^1J_{PP}$ = 633 Hz, P-Mes*).

[11] Crystal data for complex 3: space group $P2_1/c$, a = 21.809 (4) Å, b = 10.066 (2) Å, c = 16.250 (3) Å, β = 95.87 (1)°, V = 3560 (2) Å^3, Z = 4, ρ_{calcd} = 1.344 g cm^{-3}, Mo Kα (graphite monochromator, λ = 0.71073 Å), ω-scan data collection at 183 K ($3.0 \leq 2\theta \leq 50.0°$), 6228 unique reflections, 2383 unique observed reflections ($F > 4.0\sigma(F)$), Siemens $P2_1$ four-circle diffractometer, structure solved by direct methods and refinement by full-matrix least squares, with use of the Siemens SHELTXL PLUS software on a Micro VAXII computer. All non-hydrogen atoms were refined anisotropically with 232 parameters (hydrogen atoms in calculated positions riding on the corresponding C atoms), U(H) = 0.08 Å^2, R = 0.106, R_w = 0.072, $w^{-1} = \sigma^2(F)$, and maximum rest electron density 0.88 e/Å^3.

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located in the same plane (mean deviation from plane 0.023 Å).

Crystals of **3** were grown from pentane solutions at −40 °C in several experiments. In one sample after 4 weeks of crystallization compound **3** decomposed to some extent. The ^{31}P NMR spectrum displayed a doublet at δ 194.68 ($^1J_{PP}$ = 94 Hz) and a doublet of quartets at δ 136.00 ($^1J_{PP}$ = 94, $^3J_{PF}$ = 26 Hz) in addition to the resonances of **3**. Both compounds were present in the ratio **3**:**4** = 3:1. The PP coupling constant is consistent with a PP single bond, whereas the size of the PF coupling suggests the presence of a $PC(CF_3)_2$ group. Both complexes could not be separated on a preparative scale.

A red crystal of **4** was picked out of the crop and submitted to an X-ray diffraction study (Figure 2 and Table II). The analysis shows the presence of an essentially planar 1-oxa-2,3-diphosphetane (mean deviation from plane 0.01 Å) which is linked to the $(\eta^5\text{-}C_5Me_5)(CO)_2Fe$ fragment via an Fe–P single bond (2.327 (4) Å). Compound **4** is obviously the result of a formal [2 + 2] cycloaddition between **1** and hexafluoroacetone. The P–P bond of 2.249 (5) Å reveals a bond order of unity. In the four-membered ring the oxygen atom of the ketone is added to the arylated P atom (P(2)–O(3) = 1.722 (8) Å). In keeping with this, the $(CF_3)_2C$ fragment in **4** is connected to the metalated phosphorus via a long P–C single bond (P(1)–C(13) = 1.927 (13) Å), which is quite common for diphosphetane derivatives.[5,6]

Due to the longer distance P(1)–P(2) the bond angles at the phosphorus atoms are markedly more acute (C(13)–P(1)–P(2) = 72.3 (4)°, P(1)–P(2)–O(3) = 81.3 (3)°) as compared to the angles at carbon and oxygen (102.2 (9) and 104.2 (7)°, respectively). The *E* configuration of **1** has been maintained throughout the cycloaddition.

At room temperature solutions of **3** and **4** in benzene decompose within 1 week to give **1** and unidentified species. We suggest that the formation of **3** and **4** is initiated by a [2 + 1] cycloaddition to the transient adduct **2**. Subsequent scission of the P–C linkage in **2** and attack of the carbanion at a positively polarized carbon atom of a terminal carbonyl ligand affords metallaheterocycle **3** (path a), whereas P–O bond rupture in **2** and attack of the oxygen at the arylated P atom yields **4**. The dissociation of **3** into **1** and free $(CF_3)_2CO$ and a subsequent [2 + 2] cycloaddition to compound **4** cannot be excluded at the moment. The nature of the transformation of **3** into **4** is presently under investigation.

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Supplementary Material Available: Listings giving details of the crystal data, data collection, and structure solution and refinement and tables of atomic coordinates, bond lengths and angles, and thermal parameters for **3** and **4** (17 pages). Ordering information is given on any current masthead page.

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(16) Crystal data for complex **4**: space group $C2/c$, a = 46.97 (3) Å, b = 9.316 (5) Å, c = 16.611 (5) Å, β = 101.52 (3)°, V = 7121 (6) Å^3, Z = 8, ρ_{calcd} = 1.344 g cm^{-3}, Mo Kα (graphite monochromator, λ = 0.71073 Å), ω-scan data collection at 179 K ($3.0 \le 2\theta \le 45.0°$), 4661 unique reflections, 2143 unique observed reflections ($F > 4.0\sigma(F)$), Siemens $P2_1$ four-circle diffractometer, structure solved by direct methods and refinement by full-matrix least squares, with use of the Siemens SHELXTL PLUS software on a Micro VAXII computer. All non-hydrogen atoms were refined anisotropically with 254 parameters (hydrogen atoms in calculated positions, riding on the corresponding C atoms), U(H) = 0.08 Å^2, R = 0.080, R_w = 0.058, $w^{-1} = \sigma^2(F)$, maximum rest electron density 0.50 e/Å^3.

Platinum-Complex-Catalyzed 1,4-Disilylation of 1,3-Dienes Using Organodisilanes: Remarkable Effect of a Phenyl Functionality on a Silicon Atom

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Summary: **Organodisilanes having a phenyl functionality on the silicon atom smoothly react with 1,3-dienes at 130 °C to afford the corresponding 1,4-disilylation adducts in high yields in the presence of platinum catalyst. However, other substituents such as Me, *n*-Bu, *t*-Bu, $CH_2C_6H_5$, $CH_2CH{=}CH_2$, and $CH{=}CH_2$ on the silicon atom are totally ineffective.**

Activation of a silicon–silicon bond by a transition-metal catalyst[1] and subsequent insertions of 1,3-dienes,[2] acetylenes,[3] and olefins[4a,b] into silicon–silicon linkages are of current interest. 1,4-Disilylation of 1,3-dienes is especially important, since it affords adducts[5] having two versatile allylic silane[6] moieties. Transition-metal-catalyzed 1,4-

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