4406 Organometallics 1994, 13, 4406−4412

Transition Metal-Substituted Diphosphenes. 35.[1] On the Reactivity of Metallodiphosphenes ($(\eta^5\text{-}C_5Me_5)(CO)_2FeP{=}PR$ (R = $C(SiMe_3)_3$, 2,4,6-t-$Bu_3C_6H_2$) toward Isocyanides. Formation and Structures of Iminodiphosphiranes and 2,4-Diimino-1,3-diphosphetanes

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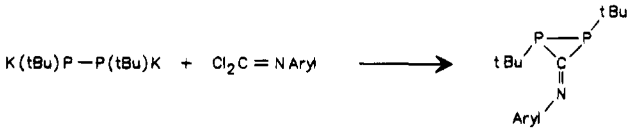
The reaction of the metallodiphosphene $(\eta^5\text{-}C_5Me_5)(CO)_2FeP{=}PC(SiMe_3)_3$ (**1**) with CF_3NC (**3a**) and PhNC (**3b**) afforded the red crystalline iminodiphosphiranes $(\eta^5\text{-}C_5Me_5)(CO)_2FePC({=}NR)PC(SiMe_3)_3$ (**4a**, R = CF_3; **4b**, R = Ph). Similarly $(\eta^5\text{-}C_5Me_5)(CO)_2FePC({=}NCF_3)P$-Mes* (**5**) was synthesized from $(\eta^5\text{-}C_5Me_5)(CO)_2Fe\text{-}P{=}P\text{-}Mes^*$ (**2**) (Mes* = 2,4,6-*t*-$Bu_3C_6H_2$) and **3a**. In contrast to this, the 2,4-diimino-1,3-diphosphetanes $(\eta^5\text{-}C_5Me_5)(CO)_2Fe\text{-}P\text{-}C({=}NR)\text{-}P(Mes^*)\text{-}C{=}NR$ (**7b**, R = Ph; **7c**, R = 2-MeC_6H_4; **7d**, R = C_6F_5) were produced by the treatment of **2** with an excess of the isocyanides. In these reactions, transient iminodiphosphiranes were detected by ^{31}P-NMR spectroscopy. The novel compounds **4**, **5**, and **7** were characterized by elemental analyses and spectroscopic data (IR, ^1H, ^{13}C, ^{19}F, and ^{31}P NMR, and MS). The molecular structures of **4a** (space group $P2_1/n$, a = 8.823(6) Å, b = 17.844(9) Å, c = 20.757(8) Å, β = 101.7(5)°) and **7c** (space group $P2_12_12_1$, a = 15.43(2) Å; b = 17.082(8) Å; c = 17.160(1) Å) were determined by complete single-crystal diffraction studies.

Introduction

Investigations on the synthesis and chemical properties of compounds with low-coordinated heavier main group elements ($n \geq 2$) have provided a major contribution to the renaissance of main group chemistry within the last three decades.[2] Our studies were concerned with the chemistry of metal-functionalized diphosphenes[3] (metallodiphosphenes, diphosphenyl complexes) and phosphaalkenes (metallophosphaalkenes, phosphaalkenyl complexes).[4] Motivated by West's synthesis of iminodisiliranes via [2 + 1] cycloaddition of isocyanides to disilenes,[5] we envisaged the synthesis of the rare class of iminodiphosphiranes by a similar cycloaddition involving diphosphenes. A few representatives of this ring system have recently been synthesized from dimetallodiphosphanes and isocyanide dichlorides[6] (Scheme 1).

The stability of the three-membered heterocycles was crucially dependent on the steric demand of the aryl substituent. Only those species with at least one *o-tert*-butyl substituent at the aryl ring proved to be stable at 20 °C, whereas the derivatives with aryl = 2,4,6-$Me_3C_6H_2$, 2-Me-C_6H_4, and 4-Cl-2-MeC_6H_3 were subject to slow decomposition with the formation 2,4-diimino-1,3-diphosphetanes.[6]

Scheme 1



The latter class of heterocycles is also accessible by the reaction of isocyanide dichlorides,[7] phenyl isocyanate, and phenyl isothiocyanate with organo(disilyl)-phosphanes. Here reactive iminomethylene phosphanes were invoked as intermediates.[8] Recently some of us gave an account on the reaction of the diphosphene $(Me_3Si)_3CP{=}PC(SiMe_3)_3$ with $CF_3N{\equiv}C$, which afforded the expected iminodiphosphirane.[9] On the other hand a 1:3 cycloadduct was obtained from the treatment of Mes*P=PMes* with the same isocyanide[9] (Scheme 2).

Here we report on the reaction of the metallodiphosphenes $(\eta^5\text{-}C_5Me_5)(CO)_2FeP{=}PC(SiMe_3)_3$ (**1**) and $(\eta^5\text{-}C_5Me_5)(CO)_2FeP{=}PMes^*$ (**2**) with the isocyanides CF_3NC (**3a**), PhNC (**3b**), 2-MeC_6H_4 (**3c**), and C_6F_5NC (**3d**).

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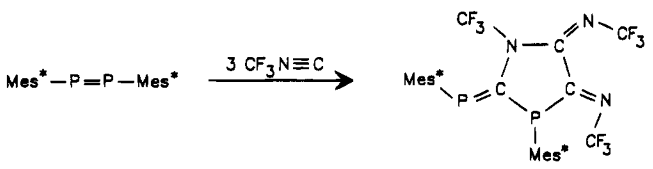
Scheme 2



Experimental Section

General Information. Standard inert-atmosphere techniques were used for the manipulation of all reagents and reaction products. Infrared spectra were recorded on a Mattson Polaris (FT-IR)/Atari 1040 STF and on a Perkin-Elmer 883 spectrometer. ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectra were taken in C$_6$D$_6$ at 22 °C on Bruker AC 100 (^{1}H, 100.131; ^{13}C, 25.180; ^{31}P, 40.539 MHz), Bruker AM 300 (^{1}H, 300.1; ^{13}C, 75.5; ^{31}P, 121.7 MHz) and JEOL FX 90 Q (^{1}H, 89.55; ^{19}F, 84.25; ^{31}P, 36.23 MHz) instruments. Spectral standards were SiMe$_4$ (^{1}H, ^{13}C), CFCl$_3$ (^{19}F), and 85% H$_3$PO$_4$ (^{31}P). Electron impact mass spectra were recorded on Varian MAT CH5-DF (70 eV, T = 250 °C) and Finnigan MAT 711 (80 eV) spectrometers. Elemental analyses were obtained from the Microanalytical Laboratory Kolbe, Mülheim/Ruhr, Germany.

Materials. The complexes (η^5-C$_5$Me$_5$)(CO)$_2$FeP=PC(SiMe$_3$)$_3$ (**1**)[10] and (η^5-C$_5$Me$_5$)(CO)$_2$FeP=PMes* (**2**)[11] and the isocyanides CF$_3$NC,[12] C$_6$F$_5$NC,[13] PhNC,[14] and 2-MeC$_6$H$_4$NC[14] were prepared as described in the literature. All solvents were rigorously dried with an appropriate drying agent and distilled before use.

Preparation of Compounds: (η^5-C$_5$Me$_5$)(CO)$_2$FePP[C(SiMe$_3$)$_3$]C=NCF$_3$ (4a). Gaseous CF$_3$NC (**2a**) (143 mbar, 0.8 mmol) was condensed on a solution of 0.42 g (0.8 mmol) of (η^5-C$_5$Me$_5$)(CO)$_2$FeP=PC(SiMe$_3$)$_3$ (**1**) in 40 mL of pentane at −78 °C. The well-stirred solution was allowed to warm up to 0 °C within a period of 20 h and then filtered. The filtrate was concentrated *in vacuo* to about 20 mL and stored at −30 °C. Dark red microcrystalline **4a** (0.15 g (31%)) separated overnight. IR (KBr, cm^{-1}): 2003 vs [ν(CO)], 1974 vs [ν(CO)], 1616 m [ν(CN)], 1574 w, 1386 w, 1262 vs [δ(SiMe$_3$)], 1207 s, 1143 s, 849 vs [ϱ(SiMe$_3$)], 674 m, 579 m. ^{1}H NMR: δ 0.47 (s, 27H, SiMe$_3$), 1.34 (s, 15H, C$_5$Me$_5$). ^{13}C{^{1}H} NMR: δ 5.2 (s, Si(CH$_3$)$_3$), 9.9 (d, $^{3}J_{PC}$ = 6.7 Hz, C$_5$(CH$_3$)$_5$), 97.2 (s, C_5-(CH$_3$)$_5$), 214.3 (s, FeCO), 215.6 (d, $^{2}J_{PC}$ = 13.6 Hz. FeCO). Resonances for the CNCF$_3$ building block could not be detected. ^{19}F{^{1}H} NMR: δ −60.70 (dd, $^{4}J_{PF}$ = 13.0, 5.8 Hz). ^{31}P{^{1}H} NMR: δ −66.7 (dq, $^{1}J_{PP}$ = 56.0, $^{4}J_{PF}$ = 13.0 Hz, FeP), −157.0 (dq, $^{1}J_{PP}$ = 56.0, $^{4}J_{PF}$ = 5.8 Hz, PCSi$_3$). MS/EI: *m/z* 635 (M$^+$), 579 (M$^+$ − 2CO), 540 (M$^+$ − CF$_3$NC), 512 (M$^+$ − CF$_3$NC − CO), 484 (M$^+$ − CF$_3$NC − 2CO), 253 (Cp*FePP$^+$), 191 (Cp*Fe$^+$), 135 (Cp*$^{+}$). Anal. Calcd for C$_{24}$H$_{42}$FeF$_3$NO$_2$P$_2$Si$_3$ (635.65): C, 45.35; H, 6.66; N, 2.20. No reliable C, H, N analyses of **4a** could be obtained.

(η^5-C$_5$Me$_5$)(CO)$_2$FePP[C(SiMe$_3$)$_3$]C=NPh (4b). An excess of C$_6$H$_5$NC (**3b**) (1 mL) was added to a solution of **1** (0.30 g, 0.55 mmol) in 20 mL of *n*-pentane at 20 °C with stirring. The color of the solution changed from brown to red within the period of 1 h. Solvent and volatiles were removed *in vacuo*. The red residue was dissolved in 50 mL of *n*-pentane. The filtered solution was concentrated to about 20 mL and stored at −30 °C for 3 d to give 0.22 g (63%) of red crystalline **4b**. IR (KBr, cm^{-1}): 2002 vs [ν(CO)], 1994 vs [ν(CO)], 1958 vs [ν(CO)], 1599 m [ν(CN)], 1568 m [ν(CN)], 1484 m, 1445 m, 1384 m, 1252 s [δ(SiMe$_3$)], 1024 s, 848 vs [ϱ(SiMe$_3$)], 754 m, 692 m, 662 w, 619 w, 580 m, 543 w, 504 w. ^{1}H NMR: δ 0.53 (s, 27H, SiMe$_3$), 1.31 (s, 15H, C$_5$Me$_5$) (Ph-H are obscured by C$_6$D$_5$H). ^{13}C{^{1}H} NMR: δ 5.4 (s, Si(CH$_3$)$_3$), 10.0 (s, C$_5$(CH$_3$)$_5$), 96.6 (s, C_5(CH$_3$)$_5$), 214.8 (s, FeCO), 216.4(m, Fe(CO)). (The ring carbon atom and the quarternary carbon of the C(SiMe$_3$)$_3$-group could not be located unambigiously.) ^{31}P{^{1}H} NMR: δ −79.6 (d, $^{1}J_{PP}$ = 49.4 Hz, FeP), −158.7 (d, $^{1}J_{PP}$ = 49.4 Hz, PCSi$_3$). MS/CI: *m/z* 541 (MH$^+$ − PhNC), 525 (M$^+$ − PhNC − CH$_3$), 484 (M$^+$ − PhNC, −2CO). Anal. Calcd for C$_{29}$H$_{47}$FeNO$_2$P$_2$Si$_3$ (643.75): C, 54.11; H, 7.36; N, 2.18. Found: C, 54.12; H, 7.33; N, 2.27.

(η^5-C$_5$Me$_5$)(CO)$_2$FePP(Mes*)C=NCF$_3$ (5a). Gaseous CF$_3$-NC (**2a**) (1.75 mmol) was condensed on a solution of 1.04 g (1.75 mmol) of **2** in 50 mL of 2-methylbutane at −78 °C. The solution was stirred overnight with warming up to 0 °C and filtered thereafter. The filtrate was concentrated *in vacuo* to about 20 mL. Crystallization at −30 °C yielded 0.66 g (54%) of **5a** as red fan-shaped crystals. IR (Nujol, cm^{-1}): 1992 vs [ν(CO)], 1947 vs [ν(CO)], 1602 s [ν(CN)], 1195 vs, 1138 vs, 1022 m, 875 w, 859 s, 781 w, 745 w, 682 w, 618 m, 578 s, 562 m, 499 w, 432 w. ^{1}H NMR: δ 1.18 (s, 9H, *p*-*t*-Bu), 1.27 (s, 15H, C$_5$Me$_5$), 1.88 (s, 18H, *o*-*t*-Bu), 7.42 (d, 2H, $^{4}J_{PH}$ = 2.1 Hz, *m*-aryl-H). ^{13}C{^{1}H} NMR: facile decomposition of **5a** in solution thwarted a useful ^{13}C NMR spectrum. ^{19}F{^{1}H} NMR: δ −58.60 (dd, $^{4}J_{PF}$ = 13.0, 4.8 Hz). ^{31}P{^{1}H} NMR: δ −71.0 (dq, $^{1}J_{PP}$ = 32.0, $^{4}J_{PF}$ = 13.0 Hz, Fe-P), −168.7 (dq, $^{1}J_{PP}$ = 32.0; $^{4}J_{PF}$ = 4.8 Hz, P-Mes*). MS/EI: *m/z* 649 (M$^+$), 593 (M$^+$ − 2CO), 592 (M$^+$ − *t*-Bu), 573 (M$^+$ − *t*-Bu − F), 554 (M$^+$ − *t*-Bu − 2F), 517 (M$^+$ − *t*-Bu − 2CO − F), 247 (Cp*Fe(CO)$_2$$^+$), 135 (Cp*$^{+}$), 57 (*t*-Bu$^+$). Anal. Calcd for C$_{32}H_{44}F_3$FeNO$_2P_2$ (649.49): C, 59.18; H, 6.83; Fe, 8.60; N, 2.16. Found: C, 59.29; H, 6.76; Fe, 8.51; N, 2.21.

(η^5-C$_5$Me$_5$)(CO)$_2$FePC(=NPh)P(Mes*)C=NPh (7b). One milliliter of PhNC (**2b**) (excess) was added to a solution of 0.35 g (0.63 mmol) of **2** in 30 mL of benzene at 20 °C. Within 1 h of stirring the color of the solution turned red. Solvent and volatiles were removed *in vacuo*. The residue was stirred with pentane (50 mL), and the resulting slurry was filtered. The red filtercake was washed with 5 mL of ether and dried *in vacuo*. This material is a 2:1 mixture of isomers A and B of **7b** (0.30 g, 63%). IR (KBr, cm^{-1}): 2000 vs [ν(CO)], 1958 vs [ν(CO)], 1589 w [ν(CN)], 1557 s [ν(CN)], 1483 w, 1261 m, 1098 m, 1025 m, 903 w, 869 w, 802 m, 755 w, 693 w, 534 w. ^{1}H NMR: δ 0.95 (s, C$_5$Me$_{5,B}$), 1.19 (s, *p*-*t*-Bu$_A$), 1.22 (s, *p*-*t*-Bu$_B$), 1.33 (s, C$_5$Me$_{5,A}$), 1.80 (s, *o*-*t*-Bu$_A$), 1.92 (s, *o*-*t*-Bu$_B$), 7.34 (d, 8 Hz) and 7.54 (d, 8 Hz, *m*-H aryl$_{A+B}$), 6.30−7.73 (*m*, H phenyl$_{A+B}$). ^{13}C{^{1}H} NMR: δ 8.8 (d, $^{3}J_{PC}$ = 3.5 Hz, C$_5$(CH$_3$)$_{5,B}$) 9.4 (d, $^{3}J_{PC}$ = 5.8 Hz, C$_5$(CH$_3$)$_{5,A}$), 31.2 (s, *p*-C(CH$_3$)$_{3,A}$), 31.3 (s, *p*-C(CH$_3$)$_{3,B}$), 34.1 (s, *o*-C(CH$_3$)$_{3,A+B}$), 35.0 (s, *p*-C(CH$_3$)$_{3,A+B}$), 39.2 (s, *o*-C(CH$_3$)$_{3,A+B}$), 96.5 (s, C_5(CH$_3$)$_{5,B}$), 96.8 (s, C_5(CH$_3$)$_{5,A}$), 120.6 s, 120.9 s, 121.4 s, 123.1 s, 123.5 s, 128.4 s, 129.0 s, 129.2, 152.5 (s, C-phenyl and C-aryl), 158.1 (d, J_{PC} = 12.4 Hz, C=N$_A$), 158.7 (d, J_{PC} = 12 Hz, C=N$_B$), 215.1 (s, Fe(CO)$_A$), 215.6 (s, Fe(CO)$_B$). ^{31}P{^{1}H} NMR: δ 66.4 (d, $^{2}J_{PP}$ = 40.0 Hz, FeP$_A$), 34.7 (d, $^{2}J_{PP}$ = 24.4 Hz, FeP$_B$), 17.9 (d, $^{2}J_{PP}$ = 24.4 Hz, PMes*$_B$), 7.4 (d, $^{2}J_{PP}$ = 40.0 Hz, PMes*$_A$). MS: *m/z* 760 (M$^+$), 704 (M$^+$ − 2CO), 657 (M$^+$ − PhNC), 629 (M$^+$ − PhNC − CO), 601 (M$^+$ − PhNC − 2CO), 554 (M$^+$ − 2PhNC), 441 (M$^+$ − 2PhNC − 2CO − *t*-Bu), 381 (Cp*(CO)$_2$FePCNPh$^+$), 379 (Mes*PCNPh$^+$), 325 (Cp*FePCNPh$^+$), 278 (Cp*(CO)$_2$FeP$^+$), 276 (Mes*P$^+$), 219 (Cp*FeCO$^+$), 191 (Cp*Fe$^+$), 135 (Cp*$^{+}$), 103 (PhNC$^+$), 57 (*t*-Bu$^+$). Anal. Calcd for C$_{44}$H$_{54}$FeN$_2$O$_2$P$_2$ (760.72): C, 69.47; H, 7.16; N, 3.68. Found: C, 68.61; H, 7.16; N, 3.89.

(η^5-C$_5$Me$_5$)(CO)$_2$FePC(=N-*o*-Tol)P(Mes*)C(=N-*o*-Tol) (7c). An excess of 2-MeC$_6$H$_4$NC (**2c**) (1 mL) was added to a solution of 0.49 g (0.88 mmol) of **2** in 30 mL of benzene at 20 °C and stirred for 2 h. The color of the mixture changed to red. The solution was freed from volatiles, and the residue was dissolved in 50 mL of *n*-pentane. After filtration and concentration to

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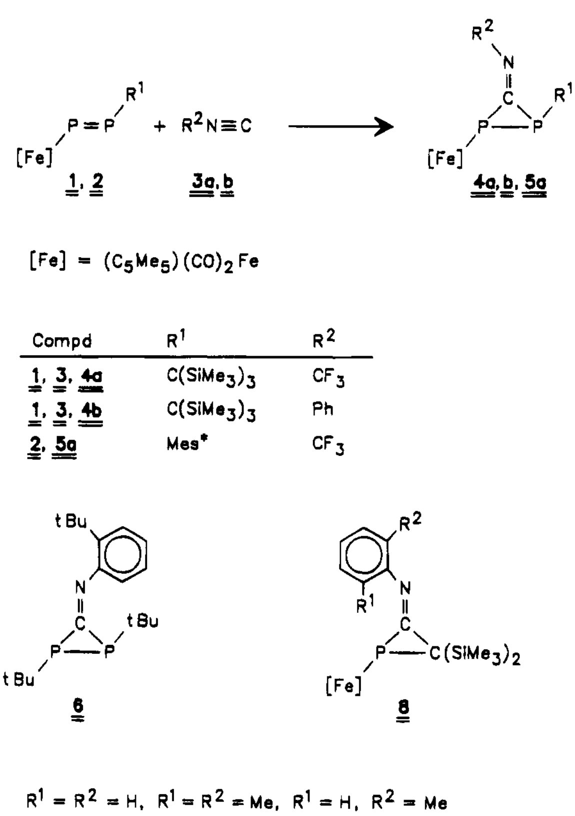
Table 1. $^{31}P\{^1H\}$ NMR Data of 4a,b, 5a−d, and 7b−d in C_6D_6, δ in ppm (85% H_3PO_4 Standard)

compd	δ(P−Fe)	J_{PP}	J_{PF}	δ(P−C)	J_{PP}	J_{PF}
4a	−66.7 dq	56.0	13.0	−157.0 dq	56.0	5.0
4b	−79.6 d	49.4		−158.6 d	49.4	
5a	−71.0 dq	32.0	13.0	−168.7 dq	32.0	4.0
5b	−91.2 d	24.3		−178.7 d	24.3	
5c	−94.0 d	22.5		175.9 d	22.5	
5d	−79.3 m			−149.85 m		
anti-**7b**	66.4 d	40.0		7.4 d	40.0	
syn-**7b**	34.7 d	24.5		17.9 d	24.5	
anti-**7c**	65.2 d	43.5		5.3 d	43.5	
syn-**7c**	33.5 d	26.8		21.8 d	26.8	
anti-**7d**	79.9 dt	73	44	1.0 dtt	73	31; 5
syn-**7d**	96.5 d	56		13.4 dquint	56	10

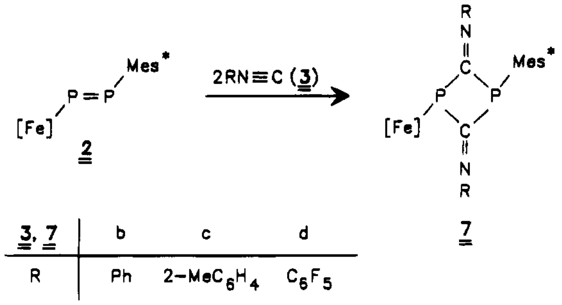
Table 2. Experimental Data for the X-ray Diffraction Study of 4a and 7c

	4a	**7c**
formula	$C_{24}H_{42}F_3FeNO_2P_2Si_3$	$C_{46}H_{58}FeN_2O_2P_2$
mol wt	635.65	788.7
diffractometer	Stoe four-circle diffractometer	
cryst dim, mm	1.0 × 0.3 × 0.15	0.8 × 0.3 × 0.23
data collecn T, °C	−65	20
cryst syst	monoclinic	orthorhombic
space group	$P2_1/n$	$P2_12_12_1$
a (Å)	8.823(6)	15.43(2)
b (Å)	17.844(9)	17.082(8)
c (Å)	20.757(8)	17.16(1)
β (deg)	101.7(5)	
V (Å^3)	3211.3	4521
Z	4	4
d(calcd) (g cm^{-3})	1.32	1.16
μ (cm^{-1})	6.9	4.4
radiation	Mo Kα, λ = 0.710 69 Å	
measured reflcns	5926	4453
θ range (deg)	$2 \le \theta \le 25$	$2 < \theta < 25$
scantype	ω scan	
no. of indep data coll	5539 (R = 0.026)	4427
no. of obsd reflens (n_o)	3092 ($F_o > 4\sigma(F_o)$)	2863 ($F_o > 3\sigma(F_o)$)
absorption correct.	DIFABS	
transm coeff	0.475 min; 0.966 max	0.7 min; 1.19 max
no. of params refined	369	478
R	0.055	0.059
R_w	0.054	0.060
	$w = [\sigma(F_o)^2 + 0.0005(F_o)^2]^{-1}$	$w = 1.65[\sigma(F_o)^2 + 0.0005(F_o)^2]^{-1}$
temperature factors	anisotropic H atoms isotropic on calculation position U_H = 0.14 Cp*, U_H = 0.10 SiMe$_3$ C−H 0.95 Å	no hydrogen positions
residual electron density min/max	0.40/−0.44 e Å^{-3}	0.45/−0.30 e Å^{-3}

Scheme 3



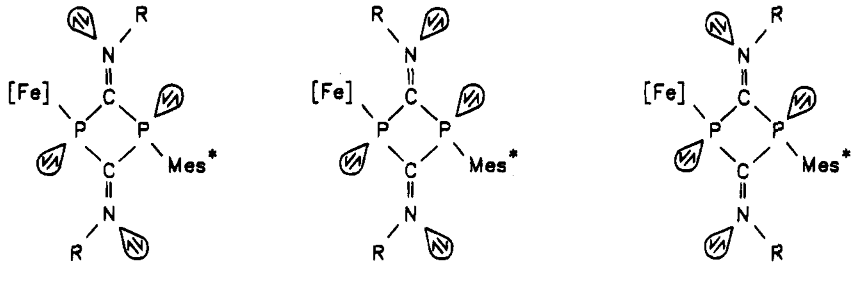
Scheme 4



about 20 mL, the solution was stored at −30 °C to yield 0.33 g (48%) of **7c** as a 2:1 mixture of two isomers A and B. IR (KBr, cm^{-1}): 2090 m, 2006 vs [ν(CO)], 1959 vs [ν(CO)], 1589 w [ν(CN)], 1537 s [ν(CN)], 1480 w, 1459 sh, 1210 w, 1111 w, 1028 w, 887 w, 757 m, 718 w, 585 m, 563 w. ^{1}H NMR: δ 1.00 (s, $C_5Me_{5,B}$), 1.21 (s, *p*-*t*-Bu_{A+B}), 1.38 (s, $C_5Me_{5,A}$), 1.78 (s, br, *o*-*t*-Bu_A), 1.93 (s, br, *o*-*t*-Bu_B), 2.55 (s, *o*-$CH_{3,A+B}$), 2.59 (s, *o*-$CH_{3,A}$), 6.6−7.3 (m, H-*o*-$tolyl_{A+B}$), 7.61 (m, *m*-H-$aryl_{A+B}$). ^{13}C{^{1}H} NMR: δ 9.4 (d, J_{PC} = 5.7 Hz, $C_5(CH_3)_{5,A}$), 10.1 (d, J_{PC} = 8.5 Hz, $C_5(CH_3)_{5,B}$), 17.3 (s, *o*-$CH_{3,B}$), 18.5 (s, *o*-$CH_{3,A}$), 31.3 (s, *p*-C(CH_3)$_3$), 33.9 s and 34.0 (s, *o*-C(CH_3)$_{3,A+B}$), 35.0 (s, *p*-*C*(CH_3)$_{3,A+B}$), 39.0 s and 39.1 (s, *o*-*C*(CH_3)$_{3,A+B}$), 96.8 (s, C_5(CH_3)$_{5,A+B}$), 116.25 (m), 122.8 (s), 123.1 (s), 123.9 (s), 126.1 (s), 128.9 (s), 130.6 (s), 130.7 (s), 133.25 (s), 152.5 (d, J_{PC} = 2.8 Hz, C-tolyl and C-aryl), 157.9 (d, J_{PC} = 12 Hz, C=N_A), 158.7 (dm, J_{PC} = 12 Hz, C=N_B), 192.5 m and 194.6 (m, N-C-$aryl_{A+B}$), 214.8 (s, Fe(CO)$_{A+B}$). ^{31}P{^{1}H} NMR: δ 65.2 (d, $^2J_{PP}$ = 43.5 Hz, FeP_A), 33.5 (d, $^2J_{PP}$ = 27.2 Hz, FeP_B), 21.8 (d, $^2J_{PP}$ = 26.8 Hz, PMes*$_B$), 5.3 (d, $^2J_{PP}$ = 43.3 Hz, PMes*$_A$). MS: *m/z* 788 (M^+), 671 (M^+ − TolNC), 643 (M^+ − TolNC − CO), 615 (M^+ − TolNC − 2CO), 554 (M^+ − 2TolNC), 441 (M^+ − 2TolNC − 2CO − *t*-Bu), 395 (Cp*(CO)$_2$FePCNTol$^+$), 393 (Mes*PCNTol$^+$), 339 (Cp*FePCNTol$^+$), 278 (Cp*(CO)$_2$FeP$^+$), 276 (PMes*$^+$), 219 (Cp*(CO)Fe$^+$), 191 (Cp*Fe$^+$), 135 (Cp*$^+$), 117 (TolNC$^+$), 57 (*t*-Bu$^+$). Anal. Calcd for $C_{46}H_{58}FeN_2O_2P_2$ (788.77): C, 70.04; H, 7.41; N, 3.55. Found: C, 69.01; H, 7.48; N, 3.75.

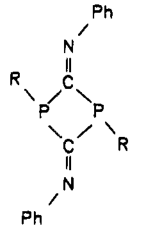
(η^5-C_5Me_5)(CO)$_2$FePC(=NC_6F_5)P(Mes*)C=NC_6F_5 (7d). To a solution of 0.60 g (1.08 mmol) of **2** in 40 mL of toluene at −78 °C was added 2 mL of a 1 M solution of C_6F_5NC **2d** in *n*-pentane. The mixture was warmed up to 20 °C with stirring. After evaporation to dryness the residue was dissolved in 50 mL of *n*-pentane and filtered. Concentration to ca. 20 mL and crystallization at −40 °C afforded 0.47 g (46%) of red microcrystalline **7d**. IR (Nujol, cm^{-1}): 2020 vs [ν(CO)], 1965 vs [ν(CO)], 1550 m [ν(CO)], 1378 s, 1365 s, 1130 s, 996 m, 975 w, 585 w, 555 w, 505 w. ^{1}H NMR: δ 1.17 (s, 9H, *p*-*t*-Bu), 1.29 (s, 15H, C_5Me_5), 1.70 (s, 18H, *o*-*t*-Bu), 7.27 (d, $^4J_{PH}$ = 2.0 Hz, *m*-aryl-H). ^{13}C{^{1}H} NMR (C_6D_6, 22 °C): δ 9.1 (d, $^3J_{PC}$ = 5.3 Hz, C_5(CH_3)$_5$), 30.9 (s, *p*-C(CH_3)$_3$), 33.9 (d, $^4J_{PC}$ = 2.0 Hz, *o*-C(CH_3)$_3$), 34.6 (d, $^4J_{PC}$ = 1.7 Hz, *o*-C(CH_3)$_3$), 35.0 (s, *p*-*C*(CH_3)$_3$), 39.1 (s, *o*-*C*(CH_3)$_3$), 39.3 (s, *o*-*C*(CH_3)$_3$), 97.5 (s, C_5(CH_3)$_5$), 122.7 s, 123.0 s, 129.0 s, 133.1 s br, 133.5 s br, 143 s br, 153.6 s, 153.8 (s, aryl-C), 159.7 (dd, $^1J_{PC}$ = 13, 0.5 Hz, C=N), 213.5 (m, CO), 213.7 (m, CO). ^{19}F{^{1}H} NMR: δ = −147.3 m, −162.5 m, −163.6 m (C_6F_5). ^{31}P{^{1}H} NMR (−50 °C, toluene-

Scheme 5



anti (A) syn (B-1) syn (B-2)

Scheme 6



9: R = CH$_2$Ph

10: R = Et

d_8): δ 96.5 (d, $^2J_{PP}$ = 56 Hz, P-Fe$_B$), 79.9 (dt, $^2J_{PP}$ = 73, $^5J_{PF}$ = 44 Hz, P-Fe$_A$), 13.4 (dquint, $^2J_{PP}$ = 56, $^5J_{PF}$ = 10 Hz, P-Mes*$_B$), 1.0 (dtt, $^2J_{PP}$ = 73, $^5J_{PF}$ = 31 and 5 Hz, P-Mes*$_A$); A:B ≈ 6:1. MS/EI: *m/z* 940 (M$^+$), 498 (M$^+$ − 2C$_6$F$_6$NC − 2CO), 471 (Cp*(CO)$_2$FePCNC$_6$F$_5$$^+$), 415 (Cp*FePCNC$_6F_5$$^+$), 276 (PMes*$^+$), 193 (C$_6F_5NC^+$), 135 (C$_5Me_5$$^+$), 57 (*t*-Bu$^+$). Anal. Calcd for C$_{44}H_{44}F_{10}FeN_2O_2P_2$ (940.62): C, 56.15; H, 4.72; N, 2.98; Fe, 5.95. Found: C, 56.36; H, 4.89; N, 2.89; Fe, 5.96.

X-ray Crystal Structure Determinations. Suitable crystals of **4a** and **7c** were obtained by crystallization from *n*-pentane at −40 °C. The crystals were mounted ot the end of a glas fiber. Details on data collection and structure solution are summerized in Table 2. Data were reduced to structure factors by correction for Lorentz and polarization effects. The space groups $P2_1/n$ (No. 14) for **4a** and $P2_12_12_1$ (No. 19) for **7c** were uniquely defined by systematic absences. Empirical absorption corrections, DIFABS,[15] were applied. The structures were solved by direct methods, SHELXS 86.[16] Successive, difference Fourier maps, and least-squares refinement cycles, SHELX 76, revealed the position of all non-hydrogen atoms. Inversion of the atomic coordinates of **7c** on a least-squares refinement with isotopic thermal parameters results in an increase if the *R* factor. SCHAKAL 88 was used for molecular drawings.[17]

Results and Discussion

The metallodiphosphenes (η^5-C$_5$Me$_5$)(CO)$_2$FeP=PR (**1**; R = C(SiMe$_3$)$_3$, **2**, R = 2,4,6-*t*-Bu$_3$C$_6$H$_2$=Mes*) smoothly react with equimolar amounts of the isocyanides CF$_3$NC (**3a**) and PhNC (**3b**) in *n*-pentane (20 °C) to afford the red crystalline iminodiphosphiranes **4a**,**b** and **5a**. The treatment of **1** with *o*-tolyl isocyanide (**3c**) under similar conditions led to decomposition (Scheme 3).

The air- and moisture-sensitive compounds **4a**,**b** and **5a** were isolated by crystallization from *n*-pentane. They were stored under an inert atmosphere at ambient temperature without significant decomposition. The course of the reaction was monitored by ^{31}P NMR spectroscopy. The low-field doublets of the educts **1** and **2** were replaced by two signals in the characteristic high-field region for three-membered rings. In **4b** two doublets were observed at δ −79.6 (P-Fe) and −158.7 (P-CSi) ($^1J_{PP}$ = 49.4 Hz). For **6**, resonances at δ −137.1 and −176.4 (J_{AB} = −38.3 Hz) were reported.[6] In the spectra of **4a** and **5a** the metalated phosphorus atoms show stronger couplings to fluorine ($^4J_{PF}$ = 13 Hz) than the organically substituted ones (**4a**, 5; **5a**, 4 Hz), suggesting that the CF$_3$ group is oriented toward the complex fragment.

The thermolability of **5a** thwarted the registration of a useful ^{13}C NMR spectrum. In the ^{13}C NMR spectrum of **4a**,**b** resonances of the CNCF$_3$-building block were not observed. From the IR spectra of **4a** (ν(CO) = 2003, 1974 cm^{-1}) and **4b** (ν(CO) = 2002, 1958 cm^{-1}) it is evident that the iminodiphosphiranyl ligand in **4** is a less powerful donor than the iminophosphiranyl unit in **8** (ν(CO) = 1985−1995 and 1933−1948 cm^{-1}).[4] Bands of medium-strong intensity at 1599−1602 cm^{-1} are assigned to the ν(CN) stretch of the exocyclic iminofunction of **4a**,**b** and **5**.

In contrast to the situation in metallophosphaalkene chemistry,[4] the metallodiphosphene **2** reacts with two molecules of the isocyanides **3b**−**d** in benzene or toluene solution to give the red crystalline 2,4-diimino-1,3-diphosphetanes **7b**−**d**. It was not possible to analogously convert diphosphene **1** into the 2,4-diiminodiphosphetanes. When subjected even to large excesses of **3a** or **3b** compound **1** only adds one equivalent of isocyanide to afford **4a** or **4b**, respectively (Scheme 4).

At the beginning of the reaction between **2** and the isocyanides **3b**−**d** the iminodiphosphiranes **5b** (δ = −91.2 d; −178.7 d, $^1J_{PP}$ = 24.3 Hz), **5c** (δ = −94.0 d; −175.9 d, $^1J_{PP}$ = 22.5 Hz), and **5e** (δ = −79.3 m; −149.9 m) were detected by ^{31}P NMR spectroscopy. The isolation of these compounds, however, failed.

From ^{31}P NMR evidence (Table 1) it is clear that the four-membered rings **7b**,**c** were formed as a 2:1 mixture of isomers. For **7d** a 6:1 ratio of isomers was determined. The isomers differ in the orientation of the substituents at the nitrogen atoms. In the major isomers A they possess an anti configuration. For the minor products B two possible syn configurations (B-1; B-2) are conceivable (Scheme 5).

From NMR evidence anti configurations are assigned to the major isomers of **7b**, **7c**, and **7d**. Thus in the ^{1}H NMR spectrum of **7c** two singlets at δ 2.55 and 2.59 in

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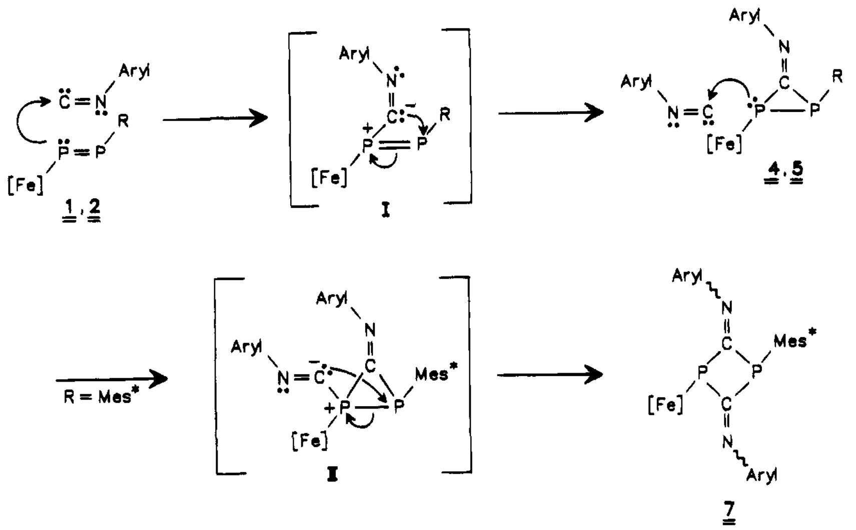
[15] Walker, N.; Stuart, D. *Acta Crystallogr. Sect. A* **1983**, *39*, 158.

[16] Sheldrick, G. M. SHELXS 86, A Program for Crystal Structure Solution, Göttingen, 1986.

[17] Keller, E. SCHAKAL 88, FORTRAN Program for the Graphic Representation of Molecular and Crystallographic Models, Freiburg, 1988.

Scheme 7



the ratio of 2:1 were observed for the methyl protons of the *o*-tolyl rings. Both resonances are caused by the major isomer A. The double intensity of the high-field singlet is due to the fortituous superposition with the singlet of the minor isomer B-1 or B-2. The anti orientation of the major isomer of **7c** is underlined by an X-ray analysis.

In the ^{31}P NMR spectrum the major product of **7d** displays a doublet of triplets at δ 79.9 ($^2J_{PP}$ = 73.0; $^5J_{PF}$ = 44 Hz) for the metalated phosphorus which reflects a PF coupling to the ortho fluorines of the one C_6F_5 ring which is oriented toward this phosphorus atom in the anti configuration. The arylated phosphorus center gives rise to a doublet of triplet of triplets at δ 1.0 ($^2J_{PP}$ = 73, $^5J_{PF}$ = 31; 5 Hz), which reflects $^5J_{PF}$ couplings to one *Z*-oriented and one *E*-oriented C_6F_5 group, respectively.

In the minor isomer the metalated phosphorus is observed as a doublet at δ 96.5 ($^2J_{PP}$ = 56 Hz), whereas a doublet of quintets is attributed to the arylated phosphorus (δ 13.4, $^2J_{PP}$ = 56, $^5J_{PF}$ = 10 Hz). A coupling to four equivalent fluorines is only possible in the syn-B 2 geometry. By analogy it is conceivable that the major isomer of **7b** also possesses the anti geometry A. The assignment of the signals of the ring carbons in the ^{13}C NMR spectra of **7b**–**7d** is not straightforward. This is not only due to the unsatisfactory solubility of the products in C_6D_6 but also to absorptions of aryl carbons in the respective region. In line with Becker's findings on the 2,4-diimino-1,3-diphosphetanes **9** and **10**,[8b] ^{13}C signals at δ 157.9–159.7 were tentatively assigned to the ring carbons atoms (Scheme 6).

The presence of the Cp*(CO)$_2$Fe fragment in **7b**–**7d** is documented by two intense CO stretches at ν = 2000–2020 cm^{-1} and ν = 1958–1965 cm^{-1}. Two bands of medium to weak intensity in the range of 1550–1589 cm^{-1} are attributed to the symmetric and antisymmetric C=N stretches of the 2,4–diimino-1,3-diphosphetanes.

It is reasonable that the formation of the iminodiphosphiranes is initiated by the electrophilic attack of the metalated phosphorus at the carbene-like carbon atom of the isocyanide. The attack of the negatively polarized carbon atom of the isocyanide fragment at the positively polarized arylphosphorus center in the intermediate **I** leads to compounds **4** and **5**. The ring expansion from iminodiphosphiranes to 2,4-diimino-1,3-diphosphetanes resulted from the electrophilic attack of the carbon atom of the isocyanide at the metalated phosphorus in **4** or **5**. Carbon attack at the arylated phosphorus and cleavage of the P–P bond of intermediate **II** afforded compounds **7** (Scheme 7).

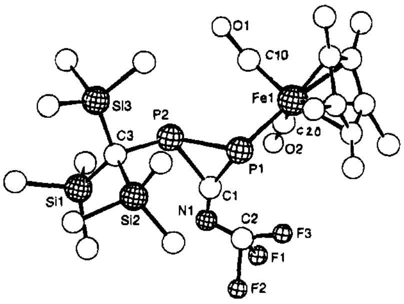


Figure 1. SCHAKAL plot of the molecular structure of **4a** in the crystal.

The reaction of **2** with an excess of CF_3NC in *n*-pentane gave rise to the precipitation of transparent orange platelets. Spectroscopic evidence agreed with an 1:2 adduct. MS: *m/e* 744 (M$^+$). ^{31}P NMR: δ 110.0 (dq, $^1J_{PP}$ = 142, $^4J_{PF}$ = 20 Hz, PFe), 136.5 (d, $^1J_{PP}$ = 142 Hz, P-aryl). ^{19}F-NMR: δ −52.6 (d, $^4J_{PF}$ = 22 Hz, CF$_3$), −56.6 (s, CF$_3$). IR (Nujol): 2012 vs, 1970 vs [ν(CO)], 1630 s [ν(CN)], cm^{-1}. Purification and a full characterization of this product, however, was not possible as yet.

X-ray Structure Analysis of 4a. An X-ray structure analysis was necessary to unambigiously determine the stereochemistry of the iminodiphosphiranes. Single crystals of **4a** were grown from *n*-pentane at −40 °C. The results of the structural determinations are shown in Figure 1. Positional parameters for the complex are given in Table 3, and selected distances and angles are presented in Table 4. The analysis confirms the presence of an iminodiphosphirane system linked to the metal by an Fe–P single bond (2.303(1) Å), which is lengthened as compared to the corresponding bond length in **1** (2.261(3) Å), but compares will with the Fe–P distance in **11** [2.310(1) Å].[18] Usually Fe–P bond distances in low-valent carbonyl iron complexes fall in the range 2.11–2.37 Å.[19] The organophosphorus ligand could be regarded as one leg in a distorted three-legged

Table 3. Final Positional Parameters and Equivalent Temperature Factors (Å²) for 4a

atom	*x*	*y*	*z*	B_{eq}
Fe(1)	0.1089(1)	0.1365(0)	0.9563(0)	2.97
C(10)	0.1682(11)	0.0463(4)	0.9438(3)	5.01
O(1)	0.2117(9)	−0.0129(3)	0.9371(2)	8.23
C(20)	−0.0869(11)	0.1154(5)	0.9465(3)	6.03
O(2)	−0.2150(8)	0.1007(4)	0.9414(3)	9.33
P(1)	0.0751(2)	0.1622(1)	0.8458(1)	2.25
P(2)	0.0036(2)	0.0572(1)	0.7899(1)	2.34
Si(1)	−0.1466(2)	0.0183(1)	0.6529(1)	3.30
C(11)	−0.1147(9)	−0.0341(5)	0.5791(3)	6.36
C(12)	−0.2442(8)	−0.0458(4)	0.7012(3)	4.35
C(13)	−0.2917(8)	0.0920(4)	0.6226(3)	5.04
Si(2)	0.0926(2)	0.1512(1)	0.6703(1)	3.46
C(21)	−0.0300(9)	0.2325(4)	0.6818(3)	4.58
C(22)	0.0797(10)	0.1440(5)	0.5789(3)	6.18
C(23)	0.2934(8)	0.1803(4)	0.7070(3)	4.66
Si(3)	0.2063(2)	−0.0112(1)	0.7129(1)	3.73
C(31)	0.3631(8)	0.0119(5)	0.7854(4)	5.38
C(32)	0.1442(10)	−0.1075(4)	0.7281(4)	6.14
C(33)	0.2953(10)	−0.0139(5)	0.6390(4)	6.69
C(1)	−0.1133(7)	0.1354(3)	0.8027(3)	2.68
N(1)	−0.2532(7)	0.1539(3)	0.7834(3)	4.80
C(2)	−0.3021(12)	0.2225(7)	0.8065(6)	8.12
F(1)	−0.4207(8)	0.2101(4)	0.8344(3)	12.39
F(2)	−0.3595(7)	0.2659(3)	0.7536(4)	9.68
F(3)	−0.2049(7)	0.2596(4)	0.8477(4)	15.34
C(3)	0.0391(6)	0.0583(3)	0.7043(2)	2.29
C(1R)	0.2711(15)	0.2249(6)	0.9741(4)	7.23
C(2R)	0.1381(14)	0.2482(4)	0.9877(3)	5.83
C(3R)	0.0994(8)	0.2046(4)	1.0371(3)	3.78
C(4R)	0.2129(8)	0.1499(3)	1.0549(3)	3.02
C(5R)	0.3224(8)	0.1637(5)	1.0144(4)	4.91
C(1M)	0.3592(18)	0.2599(8)	0.9277(5)	18.78
C(2M)	0.0539(20)	0.3162(4)	0.9556(6)	16.56
C(3M)	−0.0371(11)	0.2155(8)	1.0696(6)	11.74
C(4M)	0.2234(14)	0.0951(4)	1.1098(3)	7.67
C(5M)	0.4729(11)	0.1236(7)	1.0210(8)	14.95

Table 4. Selected Interatomic Distances (Å) and Angles (deg) for 4a

	Bond Distances		
Fe(1)−C(10)	1.728(7)	C(10)−O(1)	1.141(8)
Fe(1)−C(1R)	2.115(8)	C(11)−Si(1)	1.860(6)
Fe(1)−C(20)	1.743(9)	C(12)−Si(1)	1.837(6)
Fe(1)−C(2R)	2.097(7)	C(13)−Si(1)	1.862(7)
Fe(1)−C(3R)	2.084(5)	C(20)−O(2)	1.146(9)
Fe(1)−C(4R)	2.095(5)	C(21)−Si(2)	1.851(7)
Fe(1)−C(5R)	2.096(7)	C(22)−Si(2)	1.884(6)
Fe(1)−P(1)	2.303(1)	C(23)−Si(2)	1.867(7)
C(1)−N(1)	1.270(8)	C(3R)−C(4R)	1.399(9)
C(1)−P(1)	1.801(6)	C(31)−Si(3)	1.892(7)
C(1)−P(2)	1.783(6)	C(32)−Si(3)	1.848(8)
C(2)−F(1)	1.31(1)	C(33)−Si(3)	1.849(7)
C(2)−F(2)	1.36(1)	P(1)−P(2)	2.232(2)
C(2)−F(3)	1.278(9)		
C(2)−N(1)	1.41(1)		
C(3)−P(2)	1.860(5)		
C(3)−Si(1)	1.919(6)		
C(3)−Si(2)	1.896(6)		
C(3)−Si(3)	1.910(6)		
	Bond Angles		
C(10)−Fe(1)−C(20)	95.8(4)	P(1)−C(1)−P(2)	77.1(3)
C(10)−Fe(1)−P(1)	91.3(2)	P(1)−C(1)−N(1)	147.4(5)
C(20)−Fe(1)−P(1)	89.1(2)	P(2)−C(1)−N(1)	135.4(5)
Fe(1)−C(10)−O(1)	177.6(7)	C(1)−N(1)−C(2)	117.3(6)
Fe(1)−C(20)−O(2)	178.4(8)	P(2)−C(3)−Si(1)	104.5(3)
Fe(1)−P(1)−P(2)	108.8(1)	P(2)−C(3)−Si(2)	117.5(3)
Fe(1)−P(1)−C(1)	112.3(2)	P(2)−C(3)−Si(3)	99.7(2)
P(2)−P(1)−C(1)	51.1(2)	Si(1)−C(3)−Si(2)	111.3(3)
P(1)−P(2)−C(1)	51.8(2)	Si(1)−C(3)−Si(3)	112.1(3)
P(1)−P(2)−C(3)	114.0(2)	Si(2)−C(3)−Si(3)	111.1(3)
C(1)−P(2)−C(3)	109.8(2)		

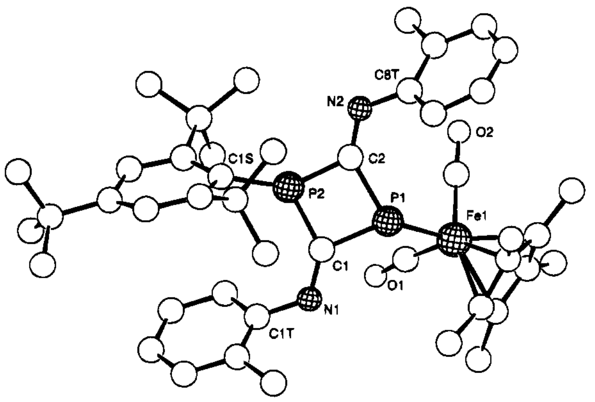
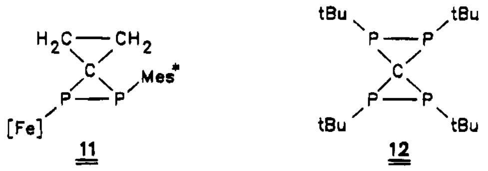


Figure 2. SCHAKAL plot of the molecular structure of **7c** in the crystal.

piano stool arrangement. The three angles the ligands form with the metal center are C(10)−Fe−C(20) = 95.8(4)°, C(10)−Fe−P(1) = 91.3(2)°, and C(20)−Fe−P(1) = 89.1(2)°. Two legs of the piano stool are represented by terminal, nearly linear carbonyl groups.

The most interesting feature of **4a** is the geometry of the iminodiphosphirane unit. In the P_2C triangle the P(1)−P(2) distance (2.232(2) Å) is expectedly longer than the P−C distances [P(1)−C(1) = 1.801(6) Å; P(2)−C(1) = 1.783(6) Å]. This causes a widening of the angle P(1)−C(1)−P(2) to 77.1(3)°, whereas the endocyclic angles at the phosphorus atoms are compressed to 51.1(2)° and 51.8(2)°. A similar situation was encountered in **11**[18] and in the tetraphospha[2.2]spiropentane (*t*-BuP)$_2$C(*t*-BuP)$_2$ (**12**).[20] There, however, the P−P single bond is considerably shortened (**11**, 2.206(2) Å; **12**, 2.175(2) Å) as compared to **4a**. A value of 2.225 Å represents an average phosphorus−phosphorus single bond distance of numerous structures.[21] The endocyclic P−C bonds (P(1)−C(1) = 1.801(6) Å; P(2)−P(1) = 1.783(6) Å) are markedly shorter than the exocyclic distance P(2)−C(3) [1.860(5) Å]. The exocyclic angles at P(1) [Fe−P(1)−C(1) = 112.3(2)°; Fe−P(1)−P(2) = 108.8(1)°] and at P(2) [P(1)−P(2)−C(3) = 114.0(2)°; C(1)−P(2)−C(3) = 109.8(2)°] indicate a slight *ψ*-tetrahedral distortion. In the starting material **1** the atoms Fe, P(1), P(2), and C(3) are located in the same plane. This is no longer true for **4a**, where C(3) deviates from the plane of the remaining atoms by −0.61(1) Å (torsion angle Fe−P(1)−P(2)−C(3) = −159.2(2)°).

Scheme 8



The planar ring carbon atom (sum of angles 359.9°) is linked to the exocyclic nitrogen atom by a C=N double bond of 1.270(8) Å. The corresponding value in **8**

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Table 5. Final Positional Parameters and Equivalent Temperature Factors (Å^2) for 7c

atom	x	y	z	B_{eq}
Fe(1)	0.0461(1)	0.7932(1)	0.5547(1)	3.35
P(1)	0.0910(2)	0.6673(1)	0.5659(1)	3.46
P(2)	−0.0093(1)	0.5438(1)	0.5197(1)	2.98
C(1C)	0.1059(9)	0.8851(7)	0.4940(7)	5.66
C(2C)	0.1715(7)	0.8344(6)	0.5226(8)	5.13
C(3C)	0.1609(8)	0.8359(6)	0.6072(7)	5.29
C(4C)	0.0938(8)	0.8844(6)	0.6282(8)	5.40
C(5C)	0.0581(7)	0.9154(5)	0.5565(10)	6.22
C(1CM)	0.0942(14)	0.9076(13)	0.4079(10)	14.20
C(2CM)	0.2405(8)	0.7923(8)	0.4778(9)	8.48
C(3CM)	0.2204(11)	0.7980(9)	0.6647(9)	10.68
C(4CM)	0.0676(12)	0.9060(10)	0.7065(9)	10.44
C(5CM)	−0.0159(11)	0.9762(7)	0.5469(16)	13.24
C(1)	0.0736(6)	0.6069(5)	0.4787(5)	3.46
N(1)	0.1107(6)	0.6173(4)	0.4124(5)	4.59
C(1T)	0.0980(8)	0.5641(5)	0.3504(5)	4.44
C(2T)	0.0161(7)	0.5354(6)	0.3319(5)	4.46
C(3T)	0.0079(8)	0.4795(7)	0.2726(6)	5.62
C(4T)	0.0757(9)	0.4552(7)	0.2329(7)	6.31
C(5T)	0.1641(9)	0.4826(6)	0.2498(6)	6.22
C(6T)	0.1738(8)	0.5409(6)	0.3100(6)	5.38
C(7T)	0.2617(8)	0.5757(9)	0.3273(7)	8.42
C(2)	0.0180(6)	0.5929(5)	0.6106(5)	3.40
N(2)	−0.0125(5)	0.5779(4)	0.6779(4)	4.15
C(8T)	0.0143(9)	0.6234(5)	0.7439(6)	4.97
C(9T)	−0.0503(10)	0.6467(6)	0.7972(6)	6.06
C(10T)	−0.0259(16)	0.6888(8)	0.8627(7)	9.86
C(11T)	0.0673(14)	0.7025(9)	0.8801(9)	8.68
C(12T)	0.1230(11)	0.6772(9)	0.8297(8)	8.08
C(13T)	0.1012(9)	0.6366(7)	0.7599(7)	6.07
C(14T)	−0.1462(9)	0.6301(9)	0.7794(8)	8.04
C(1S)	−0.0010(6)	0.4378(4)	0.5039(5)	3.13
C(2S)	0.0775(5)	0.3949(5)	0.4968(5)	3.19
C(3S)	0.0778(6)	0.3290(5)	0.4461(6)	3.74
C(4S)	0.0037(6)	0.3034(5)	0.4074(5)	3.75
C(5S)	−0.0752(6)	0.3364(5)	0.4305(5)	3.55
C(6S)	−0.0783(5)	0.4029(5)	0.4783(5)	3.02
C(1B)	0.1630(6)	0.4091(5)	0.5443(7)	4.70
C(2B)	0.2125(9)	0.3338(7)	0.5521(11)	10.32
C(3B)	0.2214(9)	0.4713(9)	0.5081(12)	10.83
C(4B)	0.1375(12)	0.4331(14)	0.6283(9)	14.43
C(5B)	0.0068(7)	0.2337(5)	0.3503(5)	4.40
C(6B)	−0.0080(10)	0.1590(6)	0.3945(8)	7.43
C(7B)	0.0959(9)	0.2263(8)	0.3118(8)	7.91
C(8B)	−0.0619(9)	0.2443(8)	0.2892(7)	7.71
C(9B)	−0.1717(5)	0.4332(5)	0.5006(6)	3.72
C(10B)	−0.2051(7)	0.4941(6)	0.4434(8)	6.07
C(11B)	−0.1731(7)	0.4659(7)	0.5845(7)	6.07
C(12B)	−0.2365(7)	0.3628(7)	0.4985(8)	6.44
C(10)	−0.0117(8)	0.7679(6)	0.4715(7)	5.33
C(20)	−0.0422(8)	0.7790(5)	0.6191(7)	5.26
O(1)	−0.0511(7)	0.7552(5)	0.4136(6)	8.19
O(2)	−0.1011(6)	0.7711(5)	0.6594(6)	7.85

Table 6. Selected Interatomic Distances (Å) and Angles (deg) for 7c

Bond Distances			
Fe(1)−C(1C)	2.10(1)	C(1C)−C(2C)	1.42(2)
Fe(1)−C(10)	1.74(1)	C(1C)−C(5C)	1.40(2)
Fe(1)−C(2C)	2.13(1)	C(1T)−N(1)	1.41(1)
Fe(1)−C(20)	1.77(1)	C(10)−O(1)	1.18(1)
Fe(1)−C(3C)	2.12(1)	C(1S)−P(2)	1.835(7)
Fe(1)−C(4C)	2.14(1)	C(2C)−C(3C)	1.46(1)
Fe(1)−C(5C)	2.095(9)	C(20)−O(2)	1.15(1)
Fe(1)−P(1)	2.269(2)	C(3C)−C(4C)	1.37(2)
C(1)−N(1)	1.29(1)	C(4C)−C(5C)	1.45(2)
C(1)−P(1)	1.837(9)	C(8T)−N(2)	1.44(1)
C(1)−P(2)	1.814(9)		
C(2)−N(2)	1.27(1)		
C(2)−P(1)	1.863(9)		
C(2)−P(2)	1.821(9)		
Bond Angles			
P(1)−Fe(1)−C(10)	89.4(4)	C(10)−Fe(1)−C(20)	94.8(5)
P(1)−Fe(1)−C(20)	93.0(3)	Fe(1)−P(1)−C(1)	114.8(3)
P(1)−C(2)−P(2)	95.8(4)	Fe(1)−P(1)−C(2)	119.8(3)
P(1)−C(2)−N(2)	137.3(7)	C(1)−P(1)−C(2)	82.2(4)
P(2)−C(2)−N(2)	126.8(7)	C(1)−P(2)−C(2)	84.0(4)
C(2)−N(2)−C(8T)	120.0(8)	C(1)−P(2)−C(1S)	118.7(4)
P(1)−C(1)−P(2)	97.0(4)	C(2)−P(2)−C(1S)	124.4(4)
P(1)−C(1)−N(1)	125.3(7)	Fe(1)−C(10)−O(1)	176(1)
P(2)−C(1)−N(1)	137.6(7)	Fe(1)−C(20)−O(2)	178(1)
C(1)−N(1)−C(1T)	121.0(8)		

amounts to 1.273(7) Å.[4] The N atom is arranged in the same plane as the ring atoms, which is also given for the carbon atom C(2) of the CF_3 substituent. The latter is directed to the metal complex fragment. Similarly in **8** the *N*-phenyl group points to the Cp*$(CO)_2$Fe moiety. In both ring systems the angles at the nitrogens compare well [**4a**, 117.3(6)°; **8**, 117.9(6)°].

X-ray Structure Analysis of 7c. An X-ray structure determination of **7c** was carried out in order to get some insight into the nature of the two spectroscopically observed isomers. Single crystals suitable for the analysis were grown from *n*-pentane at −40 °C. The analysis features a planar 1,3-diphosphetane ring with the (η^5-C_5Me_5)$(CO)_2$Fe fragment at P(1) and the supermesityl substituent at P(2) in the trans position. The nitrogen atoms N(1) and N(2) as well as the ipso carbon atoms C1T and C8T are also located in the plane defined by the atoms P(1), C(1), and C(2). The exocyclic C═N double bonds (1.29(1) and 1.27(1) Å) are well matching the sum of the covalent radii of sp^2-hybridized C (0.66 Å) and N (0.60 Å). The *o*-tolyl substituents are *E*-oriented with angles C(1)−N(1)−C1T and C(2)−N(2)−C8T of 121.0(8)° and 120.0(8)°, respectively. The endocyclic PC bond distances of (1.814(9)−1.863(9) Å) closely resemble those found in **9** (1.838−1.862 Å) and **10** (1.828(2)−1.852(2) Å).[8b] The average P−C single bond determined from a number of structures is 1.85 Å.[21]

The endocyclic angles at the phosphorus atoms are markedly more acute (82.2(4)−84.0(4)°) in respect to the angles at the C(1) (97.0(4)°) and C(2) (95.8(4)°). In **9** and **10** the corresponding angles are 82° and 98° and 81° and 99°, respectively.[8b] The exocyclic angles at P(2) [C(1S)−P(2)−C(1) = 118.7(4)°; C(1S)−P(2)−C(2) = 124.4(4)° are more obtuse than the corresponding exocyclic angles at P(1) [Fe−P(1)−C(1) = 114.8° and Fe−P(1)−C(2) = 119.8(3)°], which reflects the increased steric demand of the supermesityl group as compared to the Cp*$(CO)_2$Fe fragment. The exocyclic angles P(2)−C(1)−N(1) [137.6(7)°] and P(1)−C(2)−N(2) [137.3(7)°] are considerably widened as compared to the exocyclic angles P(1)−C(1)−N(1) [125.3(7)°] and P(2)−C(2)−N(2) [126.8(7)°], which is presumably due to steric interactions between the phosphorus atoms and the *o*-tolyl rings.

Supplementary Material Available: Crystallographic data and ORTEP diagrams for **7c** and **4a** (20 pages). Ordering information is given on any current masthead page.

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