Syntheses and Structures of (η^4-2-Phosphabutadiene)tricarbonyliron Complexes

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Summary: The complexation behavior of the stable 2-phosphabutadienes ***3a,b****, [M(CO)$_5${(SiMe$_3$)$_2$C═P−C-(OEt)═C(H)Ph}] (***3a*** M = Cr;* ***3b*** *M = W), is investigated in their reaction with [Fe$_2$(CO)$_9$] (***4***), which yields the corresponding (η^4-2-phosphabutadiene)tricarbonyliron complexes* ***5a,b****, [Fe(CO)$_3${η^4-(SiMe$_3$)$_2$C═P−C(OEt)═C-(H)Ph[M(CO)$_5$]}] (***5a*** M = Cr;* ***5b*** *M = W). Single-crystal X-ray structural analyses of complexes* ***3b*** *and* ***5b*** *establish a s-trans 2-phosphabutadiene unit for the former complex and a s-cis configuration for the latter.*

Introduction

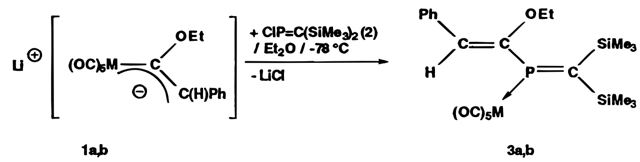
During the past two decades, extensive studies have been focused on the synthesis and bonding potential of phosphabutadienes. The replacement of one carbon atom in butadiene by a two-coordinate phosphorus atom affords either a 1- or 2-phosphabutadiene.[1] In spite of numerous studies, there are so far only a few established routes to 1-phosphabutadienes[2a−c] or 2-phosphabutadienes.[2a,3a,b] The tendency of free 1-phosphabutadienes to cyclize,[4,5] coupled with the low reactivity of kinetically-stabilized phosphabutadienes,[2a,6] has made it difficult to develop an extensive chemistry of these butadiene analogues. In 1991, Mathey *et al.*[3b] described the synthesis of a stable coordinated 2-phosphabutadiene utilizing a phospha−Wittig reaction.

We have been interested in developing a quite different approach to 2-phosphabutadiene complexes and have recently reported a novel synthetic route to the η^1-2-phosphabutadiene complexes **3a,b** (**3a** M = Cr; **3b** M = W)[7] by treatment of metal−carbene complex anions **1a,b** with the chlorophosphaalkene **2**, as shown in Scheme 1.

Results and Discussion

Here, we report on (i) the single-crystal X-ray structure analysis of complex **3b**, (ii) the synthesis of the new (η^4-2-phosphabutadiene)tricarbonyliron complexes **5a** and **5b** derived from **3a** and **3b**, and (iii) the crystal and molecular structure of the latter.

Scheme 1. Synthesis of η^1-2-Phosphabutadiene Complexes 3a,b[a]



[a] 1a,b: M = Cr; 3a, 3b: M = W

The single-crystal X-ray structure analysis of **3b** establishes the *s-trans* configuration of the 2-phosphabutadiene unit according to the central P−C(2) bond (1.839(10) Å; Figure 1 and Table 1) and the η^1-coordination mode of the [W(CO)$_5$] fragment.

The P═C and C═C bond lengths in **3b** (P−C(1) 1.65(10) Å and C(2)−C(3) 1.316(14) Å) are comparable with η^1-ligated phosphaalkenes[8] and free alkenes, respectively,[9] indicating no significant delocalization within the C═P−C═C moiety, and are similar to data recently obtained for the corresponding 2-phosphabutadienes **3a**,[7] as well as for both [W(CO)$_5${Me$_2$HC(H)C═P−C-(H)═C(H)Ph}][3b] and [Mo(CO)$_5${(Me$_3$Si)$_2$NP═C−(H)-SiMe$_3$−C(H)═C(H)SiMe$_3$}],[6] which also show the η^1-coordination mode of the metal fragment and the basic structure of a 2-phosphabutadiene ligand.

We have also studied the further coordinating potential of the 2-phosphabutadienes **3a,b**. Our initial investigation involved [Fe$_2$(CO)$_9$] (**4**) as a reactant, in view of the wide variety of different complexation modes typified by η^1-,[6,8] η^2-,[2c] or η^4-coordination[2c,3b,8,10] of phosphabutadienes which have been previously reported. Treatment of **3a,b** (**3a** M = Cr; **3b** M = W) with an excess of [Fe$_2$(CO)$_9$] (**4**) at room temperature, with exclusion of light, affords the (η^4-2-phosphabutadiene)tricarbonyliron complexes **5a,b** (Scheme 2).

^{31}P{^{1}H} NMR spectroscopic data, summarized in the Experimental Section, readily confirm the molecular structure of compounds **5a,b**. Noteworthy are the upfield ^{31}P chemical shifts of **5a,b** (**5a** δ = 91.6; **5b** δ = 36.2) compared to the ^{31}P resonances of the uncomplexed phosphabutadienes **3a,b** (**3a** δ = 341.6; **5b** δ = 283.5).

The molecular structure of **5b** (Figure 2 and Table 2) shows a *s-cis* configuration of the C(2)−C(3) and P−C(1)

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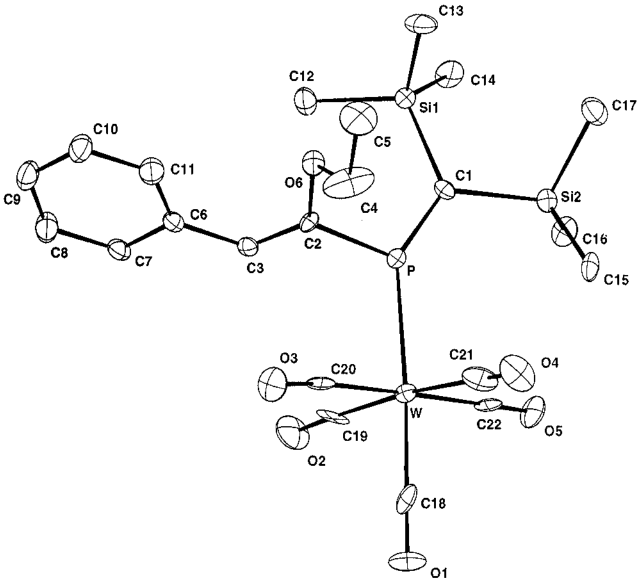
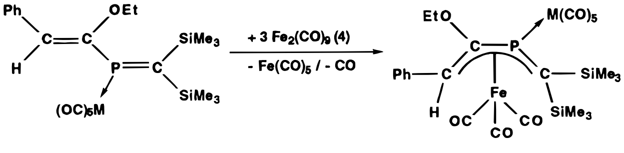


Figure 1. Molecular structure of **3b** (ellipsoids represent 50% probability levels; hydrogen atoms are omitted for clarity).

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 3b

P–C(1)	1.650(10)	P–C(2)	1.839(10)
C(2)–C(3)	1.316(14)	P–W	2.486(3)
W–C(18)	1.978(13)	W–C(20)	2.040(12)
W–P–C(1)	139.5(4)	W–P–C(2)	112.3(3)
P–C(2)–C(3)	120.0(8)	P–C(2)–O(6)	116.0(7)
P–C(1)–Si(1)	124.0(6)	P–C(1)–Si(2)	120.2(6)

Scheme 2. Synthesis of η^1,η^4-2-Phosphabutadiene Complexes 5a,b[a]



3a,b **5a,b**

[a] 3a, 5a: M = Cr; 3b, 5b: M = W

subunits. The bond lengths of the C=P–C=C moiety indicate partial delocalization (C(1)–P 1.754(8) Å, P–C(2) 1.814(8) Å, C(2)–C(3) 1.401(12) Å). In contrast, full delocalization occurs in the η^4-2-phosphabutadiene [Fe(CO)$_3${η^4-Ph(H)C=C(H)–P=C(H)CHMe$_2$[W(CO)$_5$]}][3b] (C(1)–P 1.753(4) Å, P–C(2) 1.743(4) Å, C(2)–C(3) 1.397(6) Å).

The P–W bond lengths in **3b** and **5b** (**3b** P–W 2.486(3) Å; **5b** P–W 2.476(3) Å) are approximately the same. This suggests an electronic independency within the 2-phosphabutadiene of the η^1-ligating behavior of the phosphorus lone pair and the η^4-complexation mode of the CPCC unit. This is further verified by the observation of only a slight chance of the ^1J(P,W) coupling constants on conversion of **3b** to **5b** (**3b** ^1J(P,W) = 264.5 Hz; **5b** ^1J(P,W) = 270.1 Hz). Further investigations on the complexation behavior of the 2-phosphabutadienes are currently in progress.

Experimental Section

General Procedures. All reactions were carried out under dry dinitrogen in freshly degassed dry solvents using standard Schlenk techniques. NMR spectra were recorded on an Bruker DPX 300 spectrometer operating at 300.1 MHz for ^{1}H, 75.5 MHz for ^{13}C, and 121.5 MHz for ^{31}P. Chemical shifts are expressed in parts per million (ppm) downfield from internal TMS (^{1}H and ^{13}C) and external 85% H_3PO_4 (^{31}P). Infrared spectra were recorded with a Perkin Elmer 1710 spectrometer. Mass spectra were obtained at 70 eV with a Kratos MS 80 RF by electron ionization. Elemental analysis were performed by Beller, Göttingen, Germany (**5a**) and Medac, Ltd., U.K. (**5b**).

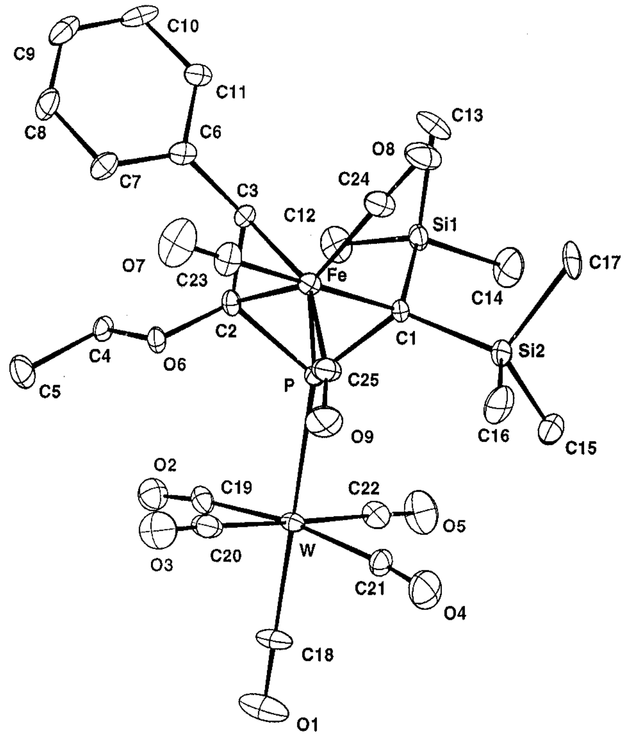


Figure 2. Molecular structure of **5b** (ellipsoids represent 50% probability levels; hydrogen atoms are omitted for clarity).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 5b

P–C(1)	1.754(8)	P–C(2)	1.814(8)
C(2)–C(3)	1.401(12)	P–W	2.476(2)
W–C(18)	1.978(9)	W–C(20)	2.054(11)
Fe–C(3)	2.185(8)	Fe–C(2)	2.102(8)
Fe–P	2.289(2)	Fe–C(1)	2.261(8)
W–P–C(1)	134.8(3)	W–P–C(2)	122.9(3)
P–C(2)–C(3)	122.0(6)	Fe–P–W	138.64(10)

Syntheses of Compounds 5a,b. A suspension of [Fe$_2$(CO)$_9$] (0.52 g, 1.43 mmol) in toluene (4 mL) and petroleum ether (60–80 °C, 6 mL) was cooled to 0 °C, with exclusion of light. A solution of **3a,b** (**3a** 0.25 g, 0.48 mmol; **3b** 0.31 g, 0.48 mmol) in toluene (4 mL), petroleum ether (60–80 °C, 6 mL) and diethyl ether (6 mL) was then added. The reaction mixture continued to stir after warming up to room temperature (1 h) for 20 h, with exclusion of light. After solvent removal, the residue was dissolved in petroleum ether (60–80 °C, 30 mL) and the excess [Fe$_2$(CO)$_9$] was separated by filtration. Concentration of the filtrate to a volume of 8 mL followed by crystallization at –20 °C gave the complexes **5a,b**.

5a: brown solid, mp 156 °C dec.; yield 0.12 g (38%). ^{1}H NMR (C_6D_6): δ 0.32 (s, 9 H, Si(CH_3)$_3$), 0.36 (s, 9 H, Si(CH_3)$_3$), 1.06 (t, ^3J(H,H) = 7.0 Hz, 3 H, OCH$_2$CH_3), 3.64 (m$_c$, 2 H, OCH_2CH$_3$), 4.18 (d, ^3J(H,P) = 3.0 Hz, 1 H, CHPh), 7.06 (m$_c$, 3 H, *o*-, *p*-Ph), 7.55 (m$_c$, 2 H, *m*-Ph). ^{13}C{^{1}H} NMR (C_6D_6): δ 5.4 (d, ^3J(C,P) = 3.1 Hz, Si(CH$_3$)$_3$), 5.8 (d, ^3J(C,P) = 2.7 Hz, Si(CH$_3$)$_3$), 13.4 (s, OCH$_2$$CH_3$), 34.4 (d, ^1J(C,P) = 56.1 Hz, C[Si(CH$_3$)$_3$]$_2$), 65.2 (d, ^2J(C,P) = 6.5 Hz, HPhC), 68.9 (s, OCH$_2$CH$_3$), 126.5 (s, *o*-Ph), 127.0 (s, *p*-Ph), 128.0 (s, *m*-Ph), 136.2 (d, ^3J(C,P) = 4.0 Hz, *i*-Ph), 139.9 (d, ^1J(C,P) = 9.1 Hz, C=C–P), 210.8 (s, Fe-

Table 3. Crystal Data and Structure Refinement

	3b	**5b**
empirical formula	$C_{22}H_{29}O_6PSi_2W$	$C_{25}H_{29}FeO_9PSi_2W$
fw	660.5	800.33
temp	293(2) K	173(2) K
wavelength	0.710 73 Å	0.710 73 Å
cryst syst	monoclinic	triclinic
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
unit cell dimens	$a = 7.791(3)$ Å	$a = 9.359(4)$ Å
	$b = 21.378(7)$ Å	$b = 11.009(3)$ Å
	$c = 16.699(6)$ Å	$c = 16.491(4)$ Å
	$\alpha = 90°$	$\alpha = 92.61(2)°$
	$\beta = 101.35(3)°$	$\beta = 93.75(3)°$
	$\gamma = 90°$	$\gamma = 114.56(3)°$
volume	2727(2) Å^3	1537.1(9) Å^3
Z	4	2
density (calcd)	1.61 Mg/m^3	1.73 Mg/m^3
abs coeff	4.42 mm^{-1}	4.39 mm^{-1}
F(000)	1304	788
cryst size	0.40 × 0.30 × 0.30 mm	0.20 × 0.20 × 0.10 mm
θ range for data collection	2−25°	2−25°
index ranges	$0 \leq h \leq 9$, $0 \leq k \leq 25$, $-19 \leq l \leq 19$	$0 \leq h \leq 11$, $-13 \leq k \leq 11$, $-19 \leq l \leq 19$
no. of reflns collected	5155	5387
no. of independent reflns	4790 (R(int) = 0.0428)	5387
no. of reflns with $I > 2\sigma(I)$	3844	4570
structure solution	heavy atom methods	direct methods and difference map
refinement method	full-matrix least-squares on all F^2	full-matrix least-squares on all F^2
data/restraints/parameters	4790/0/289	5387/0/352
goodness-of-fit on F^2	1.056	1.081
final R indices ($I > 2\sigma(I)$)	$R_1 = 0.056$, w$R_2 = 0.179$	$R_1 = 0.045$, w$R_2 = 0.125$
R indices (all data)	$R_1 = 0.072$, w$R_2 = 0.200$	$R_1 = 0.058$, w$R_2 = 0.133$
largest diff peak and hole	2.32 and −3.57 e·Å^{-3} (near W)	1.07 and −1.72 e·Å^{-3}
abs corr from Ψ scans	$T_{max} = 1.00$, $T_{min} = 0.83$	$T_{max} = 1.00$, $T_{min} = 0.83$
maximum shift/esd	0.001	0.001

(CO)$_3$), 214.7 (d, ^2J(C,P) = 15.2 Hz, *cis*-CO), 218.4 (d, ^2J(C,P) = 3.3 Hz, *trans*-CO). ^{31}P{^{1}H} NMR (C_6D_6): δ 91.6 (s). MS: m/z 688 ((M)$^+$, 7), 612 ((M − 2CO)$^+$, 9), 584 ((M − 3CO)$^+$, 15), 556 ((M − 4CO)$^+$, 10), 528 ((M − 5CO)$^+$, 46), 392 (($Fe_2(CO)_{10}$)$^+$, 83), 103 ((C_8H_7)$^+$, 33), 73 ((C_3H_9Si)$^+$, 91), 45 ((C_2H_5O)$^+$, 24). IR (CH_2Cl_2): ν(CO) 1947.0 (vs, br), 2006.0 (s), 2050.0 (vs), 2073.0 (m) cm^{-1}. Anal. Calcd for $C_{25}H_{29}CrFeO_9PSi_2$ (668.49): C, 44.92; H, 4.37. Found: C, 45.31; H, 4.58.

5b: brown solid, mp 157 °C dec.; yield 0.13 g (33%). ^{1}H NMR (C_6D_6): δ 0.27 (s, 9 H, Si(CH_3)$_3$), 0.32 (s, 9 H, Si(CH_3)$_3$), 1.03 (t, ^3J(H,H) = 6.9 Hz, 3 H, OCH$_2$CH_3), 3.57 (m$_c$, 2 H, OCH_2CH$_3$), 4.12 (d, ^3J(H,P) = 3.8 Hz, 1 H, CHPh), 7.03 (m$_c$, 3 H, *o*-, *p*-Ph), 7.54 (m$_c$, 2 H, *m*-Ph). ^{13}C{^{1}H} NMR (C_6D_6): δ 6.8 (d, ^3J(C,P) = 3.2 Hz, Si(CH$_3$)$_3$), 7.2 (d, ^3J(C,P) = 2.7 Hz, Si(CH$_3$)$_3$), 14.9 (s, OCH$_2$$CH_3$), 32.4 (d, ^1J(C,P) = 51.6 Hz, C[Si(CH$_3$)$_3$]$_2$), 66.5 (d, ^2J(C,P) = 8.0 Hz, HPhC), 69.3 (s, OCH$_2$CH$_3$), 128.2 (s, *o*-Ph), 128.5 (s, *p*-Ph), 129.4 (s, *m*-Ph), 137.6 (d, ^1J(C,P) = 4.6 Hz, C═C—P), 138.8 (s, *i*-Ph), 194.7 (d, ^1J(C,W) = 126.1 Hz, ^2J(C,P) = 8.1 Hz, *cis*-CO), 195.5 (d, ^2J(C,P) = 33.6 Hz, *trans*-CO), 207.5 (br, Fe(CO)$_3$). ^{31}P{^{1}H} NMR (C_6D_6): δ 36.2 (s, ^1J(P,W) = 270.1 Hz). MS: m/z 800 ((M)$^+$, 5), 744 ((M − 2CO)$^+$, 9), 716 ((M − 3CO)$^+$, 35), 688 ((M − 4CO)$^+$, 6), 660 ((M − 5CO)$^+$, 38), 632 ((M − Fe(CO)$_3$ − CO)$^+$, 62), 576 ((M − Fe(CO)$_3$ − 3CO)$^+$, 66), 392 (($Fe_2(CO)_{10}$)$^+$, 81), 336 ((M − Fe(CO)$_3$ − W(CO)$_5$)$^+$, 14), 159 (($C_7H_{19}Si_2$)$^+$, 25), 103 ((C_8H_7)$^+$, 47), 73 ((C_3H_9Si)$^+$, 100), 45 ((C_2H_5O)$^+$, 35). IR (CH_2Cl_2): ν(CO) 1948.0 (vs, br), 1994.0 (s), 2008.0 (s), 2053.0 (s) cm^{-1}. Anal. Calcd for $C_{25}H_{29}FeO_9PSi_2W$ (800.33): C, 37.52; H, 3.65. Found: C, 37.54; H, 3.73.

Crystallographic Data Collection and Structure Determination for Complexes 3b and 5b. Relevant crystal and data statistics are summarized in Table 3. Suitable air-stable crystals were mounted on an Enraf-Nonius CAD4. Structure solution was by direct methods in each case using SHELXS-86 and 93 and refined by full-matrix least-squares on all F^2. All non-H atoms were anisotropic. Hydrogen atoms were included in the riding mode with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(C)$ for methyl groups.

Acknowledgment. This work was supported by the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft.

Supporting Information Available: Complete tables of atomic coordinates, bond lengths, bond angles, anisotropic parameters, and H-atom coordinates for **3b** and **5b** (17 pages). Ordering information is given on any current masthead page.

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