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Direct Acetoacetylation of Ferrocene and a 1,1′-Diphosphaferrocene

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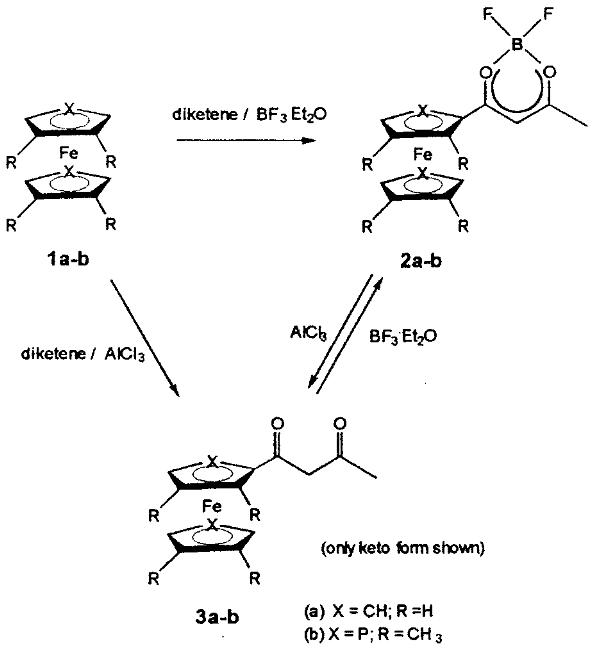
Summary: Reaction of ferrocene and 3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene with diketene in the presence of BF_3·Et_2O affords the BF_2 chelates of acetoacetylated metallocenes ***2a**,**b***. *The crystal structures of these complexes have been determined by X-ray diffraction. When the reaction is carried out in the presence of $AlCl_3$, metallocene 1,3-diketones* ***3a**,**b*** *are formed.*

Friedel−Crafts acylation has become one of the most important synthetic methods in the chemistry of ferrocene and other metallocenes,[1] as well as of the group 15 heteroferrocenes.[2] It opens access to metallocenyl ketones, which are valuable starting materials for further syntheses. Although a plethora of metallocene derivatives have been synthesized via the "Friedel−Crafts way", novel applications of these compounds in homogeneous catalysis, material science, biosensing, and photochemistry[3] have created a continuous need for efficient synthetic methods enabling introduction of lateral chains with the desired functional groups.

In this paper we describe a Friedel−Crafts-type reaction of ferrocene and 3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene[4] with diketene in the presence of a Lewis acid (boron trifluoride or aluminum trichloride), which introduces directly the acetoacetyl function (or its metal chelate) to the metallocene (Scheme 1).

Experimental Section. General Remarks. All reactions were carried out under an atmosphere of argon. Solvents were dried by using standard procedures. Chromatographic purifications were carried out on silica gel 60 (230−400 mesh ASTM), purchased from Merck, using chloroform as eluent. The NMR spectra were determined at room temperature on a Varian Gemini 200 BB instrument (200 MHz for ^{1}H). They were calibrated by using internal Me_4Si (^{1}H) and external 85% H_3PO_4 (^{31}P) references. The mass spectra (electron ionization, 70 eV) were recorded on a Finnigan MAT95 spectrometer. The combustion analyses were determined by the Analytical Services of the Center of Molecular and Macromolecular Studies of the Polish Academy of the Sciences (Łódź, Poland). 3,3′,4,4′-Tetramethyl-1,1′-diphosphaferrocene (**1b**) was prepared according to an earlier published procedure.[4] All other reagents were commercially available (Aldrich) and used without prior purification.

Scheme 1



Preparation of Compound 2a. To a solution of ferrocene (1 g, 5.36 mmol) in dichloromethane (10 mL) was added BF_3·Et_2O (6.53 g, 46 mmol), and the mixture was stirred vigorously at room temperature for 5 min. A solution of diketene (0.825 mL 10.6 mmol) in dichloromethane (4 mL) was then added dropwise, and the reaction mixture was stirred for 2 h and quenched with 20% aqueous HCl (20 mL). The organic layer was separated and the aqueous layer extracted with dichloromethane. Solvent removal and chromatography gave **2a**, identical with an authentic sample[5] in 59% yield.

Preparation of Compound 2b. The above procedure applied to 3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene[4] afforded **2b** as a purple solid in 39% yield. ^{1}H NMR ($CDCl_3$): δ 6.03 (s, 1H, =CH); 4.39 (d, $^2J_{P-H}$ = 37.6 Hz, 1H, phospholyl); 3.84 (d, $^2J_{P-H}$ = 38.0 Hz, 1H,

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phospholyl); 3.64 (d, $^{2}J_{P-H} = 38.7$ Hz, 1H, phospholyl); 2.45 (s, 3H, CH_3CO); 2.18 (s, 6H, 2 × CH_3); 2.03 (s, 6H, 2 × CH_3). ^{31}P NMR ($CDCl_3$): δ −48.27 (d, $^{2}J_{P-P} = 14.2$ Hz); −65.28 (d, $^{2}J_{P-P} = 14.2$ Hz). MS (70 eV): *m/z* (%) 410 (100) [M^+]. Anal. Calcd for $C_{16}H_{19}BF_2FeO_2P_2$: C, 46.86; H, 4.67. Found: C, 47.14; H, 4.87.

Preparation of Diketones 3a,b. When in the procedure described for **2a**,**b** $BF_3{\cdot}Et_2O$ was replaced by $AlCl_3$ (22.5 mmol), **3a**,**b** were obtained in 41% and 39% yields, respectively. **3a** obtained in this way was identical with an authentic sample.[8d] **3b** was obtained as a red solid. ^{1}H NMR (benzene-d_6): enol form, δ 16.66 (s, OH), 5.89 (s, =CH), 3.91 (d, $^{2}J_{P-H} = 37.4$ Hz, phospholyl), 3.72 (d, $^{2}J_{P-H} = 36.8$ Hz, phospholyl), 3.44 (d, $^{2}J_{P-H} = 36.6$ Hz, phospholyl), 2.41, 1.80, 1.78, and 1.65 (all s, Me); keto form, 3.61 (s, CH_2), 2,36, 1.97, 1.69, 1.67, 1.41 (all s, Me), other signals overlapped with those of the keto form. ^{31}P NMR (benzene-d_6): enol form, δ −55.5 (d, $^{2}J_{P-P} = 10.6$ Hz); −66.8 (d, $^{2}J_{P-P} = 10.6$ Hz); keto form, δ −52.1 (d, $^{2}J_{P-P} = 13.2$ Hz); −69.0 (d, $^{2}J_{P-P} = 10.6$ Hz). MS: *m/z* (%) 362 (100) [M^+], 251 (23) [M − (less substituted phospholyl ligand)$^+$], 167 (18) [M − (more substituted phospholyl ligand)$^+$]. Anal. Calcd for $C_{16}H_{20}FeO_2P_2$: C, 53,07; H, 5.57. Found: C, 53.28; H, 5.82.

Transformation of 2a,b into 3a,b. Solutions of **2a**,**b** (0.4 mmol) in chloroform (10 mL) were treated, with vigorous stirring, with $AlCl_3$ (400 mg, 3 mmol). After 30 min of stirring at room temperature the blue reaction mixtures were quenched with 20% aqueous HCl (25 mL), extracted with chloroform, and chromatographed to afford **3a**,**b** in 94−96% yield.

Transformation of 3a,b into 2a,b. Solutions of **3a**,**b** (0.4 mmol) in chloroform (5 mL) were treated, with vigorous stirring, with $BF_3{\cdot}Et_2O$ (2 mL). After 1 h of stirring at room temperature. reaction mixtures were quenched with 20% aqueous HCl (25 mL), extracted with chloroform, and chromatographed to afford **2a**,**b** in 95% yield.

X-ray Structure Determinations. A summary of crystallographic data collection parameters and refinement parameters is collected in Table 1. In the final step of the refinement procedure, all non-hydrogen atoms for both structures were refined with anisotropic thermal displacement parameters. First, the hydrogen atoms were introduced in calculated positions as riding atoms with idealized geometry. In the last step of refinement only the methyl hydrogen atoms and H11, H12, H13, H14, and H15 in **2a** were constrained to their parent C atom using the riding body model (U_{iso}(H37A,H37B,H37C) = 1.5[U_{eq}(C37)]; U_{iso}(H14,H15) = 1.2[U_{eq}(C14,C15)]), while the other H atoms had all their parameters refined.

Results and Discussion. We have found that treatment of ferrocene **1a** with diketene in the presence of $BF_3{\cdot}Et_2O$ in dichloromethane at room temperature leads to purple **2a** (Scheme 1), which was isolated in 59% yield by column chromatography. This compound was earlier prepared from ferrocenoylacetone and BF_3.[5] Similarly, **2b** was obtained in 39% yield from 3,3′4,4′-tetramethyl-1,1′-diphosphaferrocene (**1b**).

Table 1. Summary of Crystallographic Data and Structure Refinement Details

	2a	**2b**
	Crystal Data	
formula	$C_{14}H_{13}BF_2FeO_2$	$C_{16}H_{19}BF_2FeO_2P_2$
fw	317.90	409.91
cryst descripn	dark red plate	dark red plate
cryst size, mm	0.2 × 0.2 × 0.05	0.1 × 0.2 × 0.4
space group	$P2_1/c$	$P2_1/n$
a, Å	10.5020(5)	12.2294(9)
b, Å	10.1884(5)	11.2742(9)
c, Å	12.8778(6)	13.5370(7)
β, °	105.341(4)	110.445(5)
V, Å^3	1328.8(1)	1748.5(2)
Z	4	4
d_{exptl}, g/cm^3	1.589	1.557
	Data Collection	
diffractometer	Rigaku AFC5S	
radiation type (λ), Å	Cu Kα (1.541 78)	
μ, mm^{-1}	9.305	8.887
temp, K	293(2)	293(2)
data collected (*h*,*k*,*l*)	$0 \le h \le 12$ $0 \le k \le 12$ $-15 \le l \le 15$	$-1 \le h \le 15$ $0 \le k \le 13$ $-16 \le l \le 15$
no. of rflns measd	2691	3425
no. of indep rflns	2546	3264
R_{int}	0.030	0.066
no of rflns with $I > 2\sigma(I)$	1374	1883
	Solution and Refinement	
soln	direct methods	
refinement method	full-matrix least squares on F^2	
H atom treatment	mixed	refined
no. of params	206	294
$R(F)^a$	0.114	0.096
$R_w(F^2)^b$	0.121^d	0.118^c
$R(F)^a$	0.047 for 1374 rflns	0.045 for 1883 rflns
$R_w(F^2)^b$	0.107 for 1374 rflns^d	0.107 for 1883 rflns^c
$(\Delta/\sigma)_{max}$	0.003	0.001
diff peak/hole, e/Å^3	0.515/−0.411	0.448/−0.511

[a] $R(F) = \sum(|F_o - F_c|)/\sum|F_o|$. [b] $R_w(F^2) = [\sum w(|F_o - F_c|)^2/\sum|F_o|^2]^{1/2}$. [c] $w = 1/[\sigma^2(F_o^2) + (0.062P)^2]$. [d] $w = 1/[\sigma^2(F_o^2) + (0.058P)^2]$, where $P = [(F_o^2) + 2(F_c^2)]/3$.

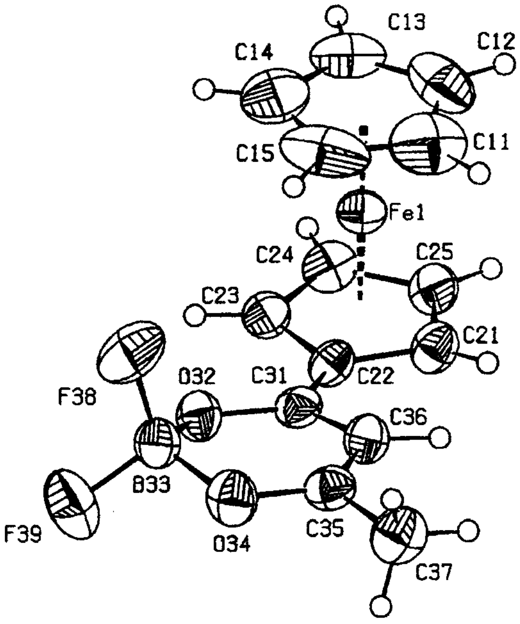

Figure 1. ORTEP drawing of the molecular structure of compound **2a** with the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level.

Complexes **2a** and **2b** were characterized by X-ray diffraction (Figures 1 and 2, Table 2). The conformation of the metallocene moiety is nearly eclipsed in **2a** and staggered in **2b**. Like other 1,1′-diphosphaferrocene derivatives bearing a carbonyl function in the 2-position,[6] **2b** adopts in the solid state a conformation with a relatively low value of the dihedral angle θ (defined as the angle between the planes normal to each phospholyl ring that contain both Fe and P atoms), which is 38.1(1)°, and a short intramolecular P−P distance,

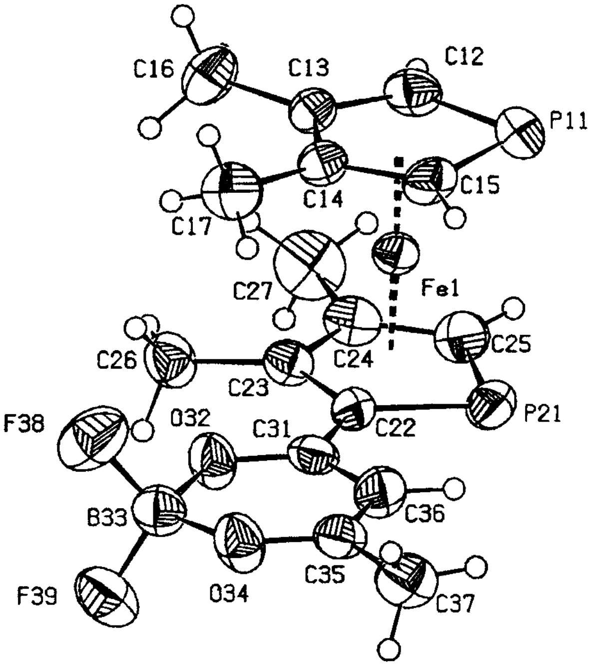

Figure 2. ORTEP drawing of the molecular structure of compound **2b** with the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level.

3.539(2) Å. The chelate ring is almost planar in **2b** and is moderately puckered in **2a** (the deviations of the boron atoms from the best planes of the chelate rings are 0.046(6) and 0.220(6) Å, respectively). The chelate rings are almost coplanar with the adjacent η^5-ligands, the dihedral angles between their planes being 2.8(1)° (**2a**) and 6.9(2)° (**2b**). This suggests extensive conjugation between both rings, confirmed by the relatively short lengths of the C−C bonds linking them—1.436(6) Å in **2a** and 1.453(5) Å in **2b**—and the deep purple color of these complexes. The BF_2 moiety in **2b** is oriented trans to the P21 atom with respect to the C22−C31 bond (Figure 2).

The boron chelates **2a**,**b** are remarkably stable (e.g., they are recovered after brief dissolution in concentrated sulfuric acid and pouring onto water). However, treatment with $AlCl_3$ in dichloromethane leads to fast decomplexation of the BF_2 moiety and formation of the corresponding 1,3-diketones **3a**,**b**. These diketones are formed directly from **1a**,**b** upon treatment with diketene/$AlCl_3$ (Scheme 1). According to the ^1H and ^{31}P NMR spectra **3b** exists in solution in benzene-d_6 at room temperature as a mixture of the enol (88%) and keto (12%) forms. Treatment of **3a**,**b** with $BF_3{\cdot}Et_2O$ transforms them back into **2a**,**b** in almost quantitative yield.

Ferrocenyl 1,3-diketones were up to now accessible only via Claisen condensation of acetyloferrocene with esters in the presence of strong bases.[7] Because 1,1′-diphosphaferrocene is sensitive to bases,[8] there is some doubt that 1,3-diketo derivatives of this metallocene can be prepared by this way.

In conclusion, we have discovered a direct method of introduction of the acetoacetyl group (or its BF_2 chelate) into ferrocene and 1,1′-diphosphaferrocene systems. The reported yields are moderate, but these were not optimized and the experimental procedure is simple. Because ferrocenyl 1,3-diketones are expected to display rich and varied chemistry (including formation of metal chelate complexes),[7] we believe that an easy way to prepare such compounds will stimulate further study of their properties and applications.

Table 2. Selected Bond Lengths (Å) and Angles (deg) and Their Average Values

param	**2a**	av in **2a**	**2b**	av in **2b**
		Fe Coordination		
Fe1−P11 or −C11	2.008(6)	2.024(3)	2.280(2)	2.081(2)
Fe1−C12	2.019(6)		2.084(5)	
Fe1−C13	2.035(6)		2.107(4)	
Fe1−C14	2.025(7)		2.078(4)	
Fe1−C15	2.028(6)		2.054(5)	
Fe1−P21 or −C21	2.036(5)	2.039(2)	2.278(1)	2.081(2)
Fe1−C22	2.010(4)		2.066(4)	
Fe1−C23	2.041(5)		2.090(4)	
Fe1−C24	2.043(5)		2.092(4)	
Fe1−C25	2.066(5)		2.076(5)	
		Phospholyl or Cyclopentadienyl Rings		
P11− or C11−C12	1.388(9)	1.376(4)	1.758(5)	1.756(2)
P11− or C11−C15	1.368(9)		1.754(5)	
C12−C13	1.366(9)		1.413(6)	1.418(3)
C13−C14	1.349(9)		1.425(5)	
C14−C15	1.409(9)		1.415(6)	
C15−P11−C12			87.8(2)	
P21− or C21−C22	1.427(6)	1.420(2)	1.792(4)	1.768(2)
P21− or C21−C25	1.402(6)		1.744(4)	
C22−C23	1.431(6)		1.446(6)	1.432(3)
C23−C24	1.408(6)		1.428(6)	
C24−C25	1.431(7)		1.423(6)	
C25−P21−C22			88.5(2)	
		BF_2 Chelate		
O32−C31	1.308(4)	1.302(2)	1.286(5)	1.290(2)
O34−C35	1.297(5)		1.295(6)	
C31−C36	1.395(6)		1.398(7)	
B33−O32	1.475(6)	1.470(2)	1.493(8)	1.487(3)
B33−O34	1.465(6)		1.482(6)	
B33−F38	1.371(6)	1.371(1)	1.354(6)	1.352(2)
B33−F39	1.371(6)		1.351(7)	
C35−C36	1.373(6)		1.364(8)	
C35−C37	1.497(6)		1.479(8)	
C36−H36	0.96(4)			
C22−C31−C36	123.0(4)		122.2(4)	
C22−C31−O32	116.7(4)		118.0(4)	
O32−C31−C36	120.2(4)		119.7(4)	
C31−O32−B33	120.4(4)	120.2(2)	124.1(4)	123.8(2)
C35−O34−B33	129.9(4)		123.4(4)	
O32−B33−O34	112.8(4)		110.4(4)	
F38−B33−F39	110.5(4)		111.7(5)	
O32−B33−F38	106.7(4)	108.4(3)	108.0(5)	108.7(3)
O34−B33−F39	108.8(5)		109.2(5)	
O32−B33−F39	108.7(4)		108.3(4)	
O34−B33−F38	109.4(4)		109.2(5)	
O34−C35−C37	115.4(4)		115.2(5)	
O34−C35−C36	122.6(5)		121.1(5)	
C36−C35−C37	122.0(4)		123.8(5)	
C31−C36−C35	119.9(4)		120.9(5)	

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Supporting Information Available: Text and tables giving crystallographic data, including files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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