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Preliminary communication

Isolation of $[Cp(CO)(Ph_3P)FeN\equiv CCH_3]^+$ BF_4^- from a vinylidene precursor; an organometallic Beckmann rearrangement

**Anthony G.M. Barrett, Nancy E. Carpenter and Michal Sabat**

Department of Chemistry, Northwestern University, Evanston, Illinois 60208 (U.S.A.)

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Abstract

The reaction of $[Cp(CO)(Ph_3P)Fe=C=CH_2]^+$ BF_4^- (3) with several hydrazine derivatives yielded the acetonitrile complex $[Cp(CO)(Ph_3P)Fe-N\equiv CCH_3]^+$ BF_4^- (4) (62–71%). The formation of this product is apparently the result of a facile Beckmann-type rearrangement.
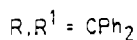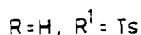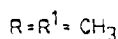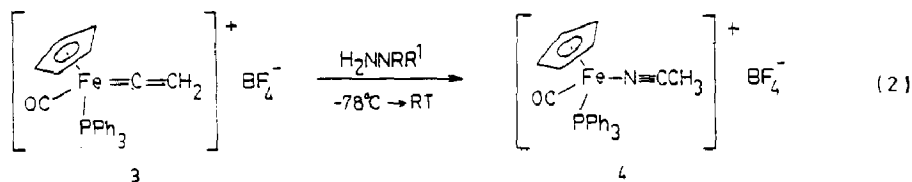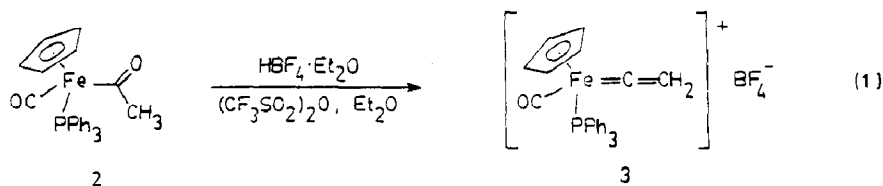
Terminal metal vinylidene complexes **1** are species which contain the formal metal–carbon–carbon cumulene bond system [1*]. Their reactivity is dominated by nucleophilic addition to the central α-carbon atom. In addition, several reports of


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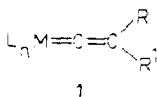
what are formally [2 + 2] cycloadditions across the vinylidene α–β bond have been published [2] and work in this laboratory has demonstrated the utility of iron(II) vinylidene complexes in the synthesis of β-lactams and in the Claisen rearrangement [3]. In our efforts to expand the utility of these species, we have examined the reactions of $[Cp(CO)(Ph_3P)Fe=C=CH_2]^+$ BF_4^- (3) with several hydrazine derivatives. We wish to report herein that the condensation of **3** with RR^1NNH_2 gave the unexpected acetonitrile complex $[Cp(CO)(Ph_3P)FeN\equiv CCH_3]^+$ BF_4^- (4) (eq. 2), the apparent result of a novel organometallic Beckman rearrangement.

The vinylidene **3** was readily prepared from the corresponding acyl precursor **2** via dehydration with tetrafluoroboric acid and trifluoromethanesulfonic anhydride, following the procedure of Boland–Lussier and Hughes [4] (eq. 1). Complex **3**, dispersed in diethyl ether at $-78°C$, was condensed with a solution of 1,1-dimethylhydrazine in diethyl ether and allowed to warm to room temperature, whereupon

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* Reference number with asterisk indicates a note in the list of references.

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$$\underset{2}{\text{Fe(Cp)(OC)(PPh}_3\text{)(COCH}_3)} \xrightarrow[\text{(CF}_3\text{SO}_2)_2\text{O, Et}_2\text{O}]{\text{HBF}_4\cdot\text{Et}_2\text{O}} \underset{3}{\left[\text{Fe(Cp)(OC)(PPh}_3)=\text{C=CH}_2\right]^+ \text{BF}_4^-} \qquad (1)$$

$$\underset{3}{\left[\text{Fe(Cp)(OC)(PPh}_3)=\text{C=CH}_2\right]^+ \text{BF}_4^-} \xrightarrow[-78^\circ\text{C} \rightarrow \text{RT}]{\text{H}_2\text{NNRR}^1} \underset{4}{\left[\text{Fe(Cp)(OC)(PPh}_3)-\text{N}\equiv\text{CCH}_3\right]^+ \text{BF}_4^-} \qquad (2)$$

$$R = R^1 = CH_3$$
$$R = H, \quad R^1 = Ts$$
$$R, R^1 = CPh_2$$

the mustard-gold solid slowly became deep red-orange. Removal of the solvent and chromatography (silica, MeOH/CH_2Cl_2 0–1/49) or recrystallization of the crude residue (CH_2Cl_2/Et_2O) gave the acetonitrile complex **4** (62%). Condensation of **3** with benzophenone hydrazone or toluene-4-sulfonylhydrazine similarly gave **4** in 63% (unrecrystallized) and 71% (recrystallized) yields, respectively. The spectroscopic data obtained for **4** differs somewhat from that reported previously for the C_5Me_5 analog and the PF_6^- salt (¹H NMR: δ 1.98 (s, 3H), 4.85 (s, 5H), 7.19–7.52 (m, 15H). ¹³C NMR: δ 4.3, 84.6, 129.2 (d, J(P–C) 10 Hz), 131.3, 132.0, (d, J(P–C) 46 Hz), 132.7 (d, J(P–C) 10 Hz), 133.1 (d, J(P–C) 10 Hz), 216.7 (d, J(P–C) 28.2 Hz)] [5*].

$$\underset{5}{\left[\text{Fe(Cp)(OC)(PPh}_3)=\text{C(CH}_3)-\overset{H}{\text{N}}-\text{N(CH}_3)_2\right]^+ \text{BF}_4^-}$$
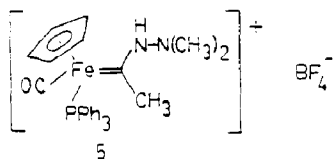
The condensation of the vinylidene **3** with 1,1-dimethylhydrazine was expected to give the hydrazino-carbene **5** by analogy with early studies using dimethylamine [4]. However, the spectral data clearly indicated the absence of the $N(CH_3)_2$ group. An X-ray crystallographic study was employed to confirm the identity of the product. A summary of crystal and intensity data is presented in Table 1, and of selected bond lengths and angles in Table 2. All X-ray measurements were carried out on an Enraf–Nonius CAD4 diffractometer at $-100\,^\circ$C using Mo-K_α radiation. Systematic absences of the type: $0kl\ l = 2n$ and $h0l\ h = 2n$ indicated the orthorhombic space groups $Pca2_1$ (No. 29) and $Pcam$ (non-standard No. 57). The former has

Table 1

Crystal data

Formula	$C_{26}H_{23}BF_4FeNP$
FW	539.10
Crystal system	orthorhombic
Space group	$Pca2_1$
a, Å	14.767(2)
b, Å	9.914(2)
c, Å	16.883(3)
V, Å^3	2472(1)
d_{calcd}, g cm^{-3}	1.45
Z	4
μ(Mo-K_α) cm^{-1}	7.45
Radiation used	graphite-monochromated Mo-K_α (λ 0.71069 Å)
Scan type	$\theta/2\theta$
2θ range, deg.	4-50
Total no. of data	2486
No. of unique data, $I > 3\sigma(I)$	1546
No. of parameters	221
R	0.036
R_w	0.048

been proven to be correct on the basis of the successful structure solution and refinement. The intensities of three standard reflections were measured every 3 h of X-ray exposure and showed no significant variation. The data were corrected for Lorentz and polarization effects. All calculations were performed on a VAX11/730 computer using the TEXSAN crystallographic software package [6]. The structure was solved by heavy atom methods (Patterson and Fourier techniques) and refined by full-matrix least-squares procedures. Anisotropic thermal parameters were employed for all non-hydrogen atoms of the complex cation but the phenyl ring carbon atoms. The BF_4^- anion atoms were refined isotropically. Contributions from the H atom in calculated positions were included in the final cycles of refinement. The

Table 2

Selected Bond Lengths (Å) and Angles (deg)

Atom–atom	Distance	Atom–atom	Distance
Fe–P	2.227(2)	Fe–C(8)	2.123(8)
Fe–N	1.915(5)	P–C(21)	1.817(6)
Fe–C(1)	1.763(7)	P–C(11)	1.817(6)
Fe–C(4)	2.110(7)	P–C(31)	1.845(6)
Fe–C(5)	2.117(8)	O(1)–C(1)	1.149(8)
Fe–C(6)	2.062(7)	N–C(2)	1.136(8)
Fe–C(7)	2.064(6)	C(2)–C(3)	1.46(1)

Angle	Degrees	Angle	Degrees
P–Fe–N	91.8(2)	P–Fe–C(1)	97.1(3)
N–Fe–C(1)	97.1(3)	Fe–N–C(2)	179.7(6)
Fe–C(1)–O(1)	175.0(7)	N–C(2)–C(3)	178.6(7)
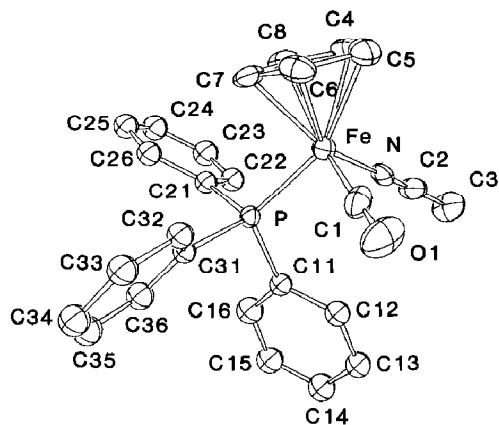
Fig. 1. ORTEP drawing of [(Cp)Fe(CO)(Ph₃P)(CH₃CN)]⁺ complex cation.

goodness of fit was 1.30. The largest peak on the final difference map was 0.32 e/$\mathring{A}^3$ high.

The molecular structure of the complex consists of the [(Cp)Fe(CO)(Ph₃P)(CH₃-CN)]⁺ complex cation and tetrafluoroborate anion. An ORTEP drawing of the complex cation is shown in Fig. 1. The geometry of the (Cp)Fe(CO)(PPh₃) moiety is unexceptional and similar to those found in other structures [7*]. The acetonitrile molecule is bonded to the Fe atom through its nitrogen atom. The Fe–N distance of 1.915(5) $\mathring{A}$ can be compared to that observed in the macrocyclic complex of iron(II) [Fe(C₁₈H₁₈N₆)(CN₃CN)₂](ClO₄)₂ containing *trans* disposed acetonitrile molecules (1.938(4) $\mathring{A}$) [8]. The distances within the acetonitrile moiety found in our complex are: N–C(2), 1.136(8) and C(2)–C(3), 1.46(1) $\mathring{A}$. The CH₃CN ligand is almost exactly linear with the N–C(2)–C(3) angle of 178.6(7)°.

The unexpected isolation of the acetonitrile complex from the reaction of **3** with several different hydrazines suggests that this reaction models the familiar Beckmann rearrangement of oximes [9*]. Indeed, isolation of toluene-4-sulfonamide (**6**, 84%, eq. 3) from the reaction of toluene-4-sulfonylhydrazine with **3** further supports this conclusion. Although it was initially believed that the rearrangement was not occurring until chromatographic work up, ¹H NMR spectra showed that the rearrangement took place readily without an acid catalyst [10*]. The ease with which this rearrangement takes place is noteworthy, and this rearrangement of

(3)
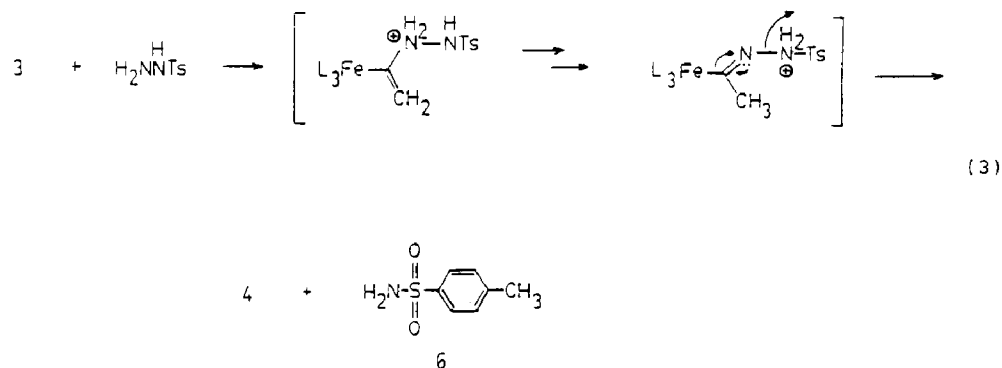
hydrazinocarbene adducts to give the acetonitrile complex is an interesting and novel addition to the wide variety of Beckmann rearrangements already known.

Supplementary material available. Details of the structure determination, atomic positional and thermal parameters, complete tables of bonds and angles and structure factor tables are available on request from M.S.

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