p-Tolyl(trimethylsilylethynyl)sulfone as Synthon for the Synthesis of $Cp(OC)_2M-C{\equiv}CSiMe_3$ (M = Fe, Ru). Molecular Structure of $Cp(OC)_2Fe-C{\equiv}CSiMe_3$

Bernd Aechter, Kurt Polborn, Volker Weinrich, Wolfgang Beck*

Institut für Anorganische Chemie der Ludwig-Maximilians-Universität München, Butenandtstr. 5–13, D-81377 Munich, Germany

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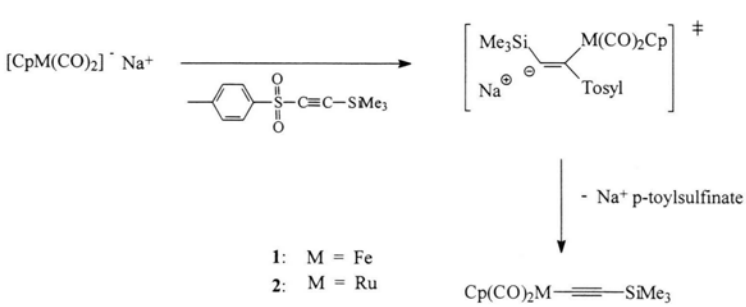
Alkynyl Complexes, X-Ray Data, *p*-Tolyl(trimethylsilylethynyl)sulfone

The alkynyl complexes $Cp(OC)_2M-C{\equiv}CSiMe_3$ (M = Fe, Ru) are formed from *p*-tolyl$SO_2C{\equiv}CSiMe_3$ and $[Cp(OC)_2M]^-Na^+$. The structure of $Cp(OC)_2Fe-C{\equiv}CSiMe_3$ was determined by X-ray diffraction.

Monometalated alkynes [1] exhibit a wide range of reactivity, *e.g.* as building blocks for metal clusters [2] or as π-ligands in metal complexes [3]. Several methods [1] are available for their synthesis, *e.g.* reactions of halo complexes with ionic acetylides [4] and 1-alkynes in the presence of a base [5] or deprotonation of vinylidene complexes [6]. Recently we used the commercially available ethynyl-*p*-tolyl sulfone and *p*-tolyl(trimethylsilylethynyl)sulfone for the reactions with $Re(CO)_5^-$ which give the alkynyl complexes $(OC)_5Re-C{\equiv}CH$ and $(OC)_5Re-C{\equiv}CSiMe_3$ [7] and *p*-tolyl sulfinate as leaving group. Various examples have been described for the reactions of ethynyl sulfones with organic nucleophiles [8].

In the following we report on the synthesis of the yellow alkynyl complexes $Cp(OC)_2M-C{\equiv}CSiMe_3$ from $Cp(OC)_2M^-$ (M = Fe, Ru) and *p*-tolyl$S(O_2)C{\equiv}CSiMe_3$.

Complex **1** [9] and $Cp^*(OC)_2Fe-C{\equiv}CSiMe_3$ [10] have been previously prepared from $Cp(OC)_2FeBr$ or $Cp^*(OC)_2FeI$ and $LiC{\equiv}CSiMe_3$, whereas **2** to our knowledge has not been reported.



Molecular Structure of $Cp(OC)_2Fe-C{\equiv}CSiMe_3$ (**1**)

Suitable crystals were obtained by slow cooling of a solution of **1** in pentane to −30 °C. Fig. 1 shows the molecular structure of **1** in the crystal.

Complex **1** exhibits the typical three-legged piano-stool structure (pseudo octahedral environment of the iron atom) as *e.g.* in $Cp^*(OC)_2Fe-C{\equiv}CH$ [10], $Cp^*(OC)_2Fe-C{\equiv}CSiMe_3$ [10] and $Cp(OC)_2Fe-C{\equiv}CPh$ [11] and the Fe-C and C≡C bond lengths in these alkynyl compounds are also essentially the same as in **1**. The Fe–C≡C–Si group in **1** is almost linear with deviations of 2.2° and 3.7° from 180° (Table I).

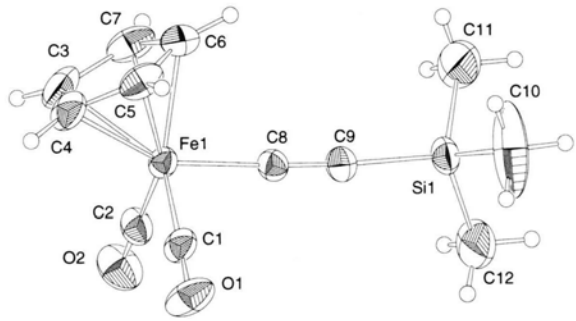


Abb. 1. Molecular structure of **1** in the crystal.

* Reprint requests to Prof. W. Beck.

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Table I. Selected bond lengths (Å) and angles (°) of **1**.

Fe(1)–C(1)	1.765(5)	Fe(1)–C(5)	2.083(5)	O(1)–C(1)	1.133(5)
Fe(1)–C(2)	1.753(5)	Fe(1)–C(6)	2.086(5)	O(2)–C(2)	1.138(5)
Fe(1)–C(3)	2.095(5)	Fe(1)–C(7)	2.090(4)	Si(1)–C(10)	1.814(6)
Fe(1)–C(4)	2.082(5)	Fe(1)–C(8)	1.920(4)	Si(1)–C(9)	1.820(4)
C(8)–C(9)	1.201(5)				

C(2)–Fe(1)–C(1)	94.2(2)	C(10)–Si(1)–C(11)	109.6(4)
C(2)–Fe(1)–C(8)	88.8(2)	C(9)–Si(1)–C(11)	110.0(2)
C(1)–Fe(1)–C(8)	91.6(2)	O(1)–C(1)–Fe(1)	177.9(4)
C(2)–Fe(1)–C(5)	156.0(2)	O(2)–C(2)–Fe(1)	179.4(4)
C(1)–Fe(1)–C(5)	92.2(2)	C(9)–C(8)–Fe(1)	177.8(4)
C(8)–Fe(1)–C(5)	114.2(2)	C(8)–C(9)–Si(1)	176.3(4)
C(10)–Si(1)–C(9)	110.5(3)		

Experimental

The reactions were carried out in Schlenk tubes under Ar atmosphere. *p*-Tolyl(trimethylsilyl-ethynyl)sulfone is avaible from Fluka.

$Cp(OC)_2Fe-C{\equiv}CSiMe_3$ (**1**)

A solution of $[Cp(OC)_2Fe]_2$ (350 mg, 0.99 mmol) in 20 ml of THF was treated with 1.5 ml of sodium amalgam (0.8%) for 2 h. The solution of $Na[Fe(CO)_2Cp]$ was added to a solution of *p*-tolyl-(trimethylsilylethynyl)sulfone (480 mg, 1.9 mmol) at −78 °C. After 30 min the solution was allowed to warm to room temperature and the solvent was removed *in vacuo*. The brown residue was extracted with pentane.

Yellow needles were obtained from the pentane solution at −30 °C. Yield 275 mg (56%). – IR (CH_2Cl_2, cm^{-1}): ν = 2054s, 2024m, 1994vs (C≡C, CO). – ^1H NMR (400 MHz, $CDCl_3$): δ = 4.98 (s, 5H, C_5H_5), 0.08 (s, 9H, $SiMe_3$).

$C_{12}H_{14}FeO_2Si$ (274,17)
Calcd C 52.57 H 5.15%,
Found C 51.51 H 5.04%.

$Cp(OC)_2Ru-C{\equiv}CSiMe_3$ (**2**)

A solution of $[Cp(OC)_2Ru]_2$ (180 mg, 0.40 mmol) in 15 ml of THF was treated with 1.0 ml of sodium amalgam (0.8%) at 0 °C for 1.5 h. This solution was added to a solution of *p*-tolyl (trimethylsilyl-ethynyl)sulfone (125 mg, 0.5 mmol) at −78 °C. After 15 min the solution was warmed to room temperature, and after 2.5 h a yellow-brown suspension formed from which the solid was removed. The solvent was removed *in vacuo* and the brown residue was extracted with pentane. Cooling to −30 °C gave a yellow powder. Yield 115 mg (36%). – IR (nujol, cm^{-1}): 2060s, 2031s, 1979vs (C≡C, CO). – IR (CH_2Cl_2; cm^{-1}): ν = 2064s, 2032s, 1996vs (C≡C, CO). – ^1H NMR (270 MHz, CD_2Cl_2): δ = 5.46 (s, 5H, C_5H_5), 0.10 (s, 9H, $SiMe_3$). – ^{13}C NMR (68 MHz, CD_2Cl_2): δ = 197.4 (CO), 116.9, 89.3 (C≡C), 88.4 (C_5H_5), 1.28 (Me).

$C_{12}H_{14}RuO_2Si$ (1319.40)
Calcd C 45.12 H 4.42%,
Found C 43.93 H 3.89%.

X-ray crystal structure determination of **1** [12]

Yellow needles from pentane. $C_{12}H_{14}FeO_2Si$, 274.17 g/mol, monoclinic, $P2_{1/C}$, a = 5.999(2), b = 18.028(5), 12.997(8) Å, V = 1375.9(10) $Å^3$, ϱ(calcd.) = 1.324 g/cm^3, Z = 4, crystal size 0.07x0.27x0.47 mm^3. F(000) = 568.

ENRAF NONIUS CAD 4, θ range 2.26–23.99, 294(2) K, index ranges $-6 \leq h \leq 0$, $-20 \leq k \leq 0$, $-14 \leq l \leq 14$, collected reflections 2377, independent reflections 2151, observed reflections ($I > 2\sigma I$) 1617, corrections linear decay correction −0.1%, empirical absorption correction (0.8162, 0.9985).

SHELXS-86, SHELXL-93, GOOF 1.124, refined parameter 148, $R1$ [2σ(I)] = 0.0420, $wR2$ [2σ(I)] = 0.0687, $R1$ (all data) = 0.0687, $wR2$ (all data) = 0.1032, largest diff. peak/hole 0.284/−0.253 $e/Å^3$.

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[12] Further details of crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. 113862 Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033;
e-mail: deposit@ccdc.cam.ac.uk).

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