

taphenylnickelocenium dication compared to that of  $[\text{Ni}(\text{C}_5\text{H}_5)_2]^{2+}$  is probably due to the sterically very bulky pentaphenylcyclopentadienyl ring. By way of contrast electronic effects are responsible for the stability of the corresponding permethylated dication.<sup>[11]</sup>

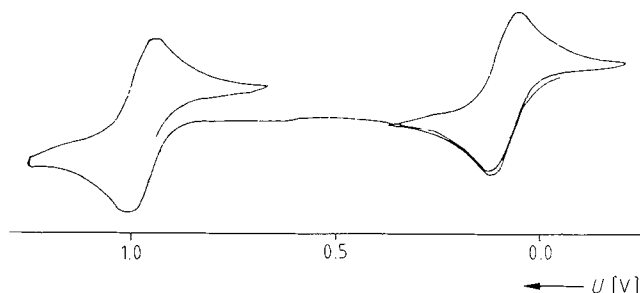


Fig. 1. Cyclic voltammogram of **5** in  $\text{CH}_2\text{Cl}_2/[\text{Bu}_4\text{N}]\text{PF}_6$ ; Pt electrodes,  $100 \text{ mV s}^{-1}$ .

Reaction of  $\text{C}_5\text{Ph}_5\text{Br}$  with octacarbonyldicobalt in THF led to a product mixture from which we were unable to isolate any pentaphenylcyclopentadienyl complexes. However, we were able to synthesize dicarbonylpentaphenylcyclopentadienyl cobalt **6** in good yields by reaction of  $\text{C}_5\text{Ph}_5\text{Br}$  with  $\text{K}[\text{Co}(\text{CO})_4]$ .<sup>[12]</sup> This compound too is distinguished by its exceptional thermal stability compared to that of the corresponding  $\text{C}_5\text{H}_5$ - and  $\text{C}_5\text{Me}_5$ -compounds. It is, e.g., sublimable in vacuo at  $180^\circ\text{C}$ . However, in the solid state it is rather sensitive to oxidation. Preliminary investigations have shown that **6** is suitable as starting compound for the photochemical synthesis of cyclooctadiene(pentaphenylcyclopentadienyl)cobalt and probably also for a series of analogous bis(olefin) complexes.

Five phenyl groups appear to stabilize cyclopentadienyl complexes even more strongly than do five methyl groups. We have now found that the oxidative addition of halogenopentaphenylcyclopentadienes also constitutes a simple strategy for the synthesis of  $\text{C}_5\text{Ph}_5$  complexes of 4d and 5d metals.

Received: September 6, 1985 [Z 1454 IE]  
German version: *Angew. Chem.* 98 (1986) 107

- [1] See, e.g., P. T. Wolczanski, J. E. Bercaw, *Acc. Chem. Res.* 13 (1980) 121; P. M. Maitlis, *ibid.* 11 (1978) 301; R. B. King, *Coord. Chem. Rev.* 20 (1976) 155.  
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[5] S. McVey, P. L. Pauson, *J. Chem. Soc.* 1965, 4312.  
[6] We have prepared  $\text{C}_5\text{Ph}_5\text{Br}$  and  $\text{C}_5\text{Ph}_5\text{Cl}$  from tetracyclone on a 50 g scale (see, e.g., A. K. Youssef, M. A. Ogliaruso, *J. Org. Chem.* 37 (1972) 2601; W. Broser, P. Siegle, H. Kurreck, *Chem. Ber.* 101 (1968) 69; K. Ziegler, B. Schnell, *Justus Liebigs Ann. Chem.* 445 (1925) 266).  
[7] U. Kölle, B. Fuss, F. Khouzami, J. Gersdorf, *J. Organomet. Chem.* 290 (1985) 77.  
[8] **Procedure. 1:** A solution of  $\text{C}_5\text{Ph}_5\text{Br}$  (5.0 g, 9.5 mmol) in anhydrous THF (30 mL) was treated with 1.25 mL (9.6 mmol) of  $\text{Ni}(\text{CO})_4$ , and the mixture stirred for 24 h. The resulting reddish brown precipitate was filtered off, washed with a small amount of THF, and then dried in a high vacuum. Yield 5.2 g (90%). The product contained a small amount of **2** and was suitable in this form for further reactions.—**2:** Upon passage of CO through a suspension of **1** in THF at  $25^\circ\text{C}$  a dark-red, clear solution was obtained. The solvent was removed by bubbling with CO, and the reddish brown product that separated was briefly dried in vacuo. IR (KBr):  $2047 \text{ cm}^{-1}$  ( $\nu(\text{CO})$ ).—**1**, Cl instead of Br:  $\text{C}_5\text{Ph}_5\text{Cl}$  (1.0 g, 2.1 mmol) and  $\text{Ni}(\text{CO})_4$  (0.27 mL, 2.1 mmol) in THF (10 mL),  $50^\circ\text{C}$ , analogously to the preparation of **1**. Yield 0.99 g (88%), correct C,H analysis.—**3:** By gassing a suspension of **1**, Cl instead of Br, with CO as de-

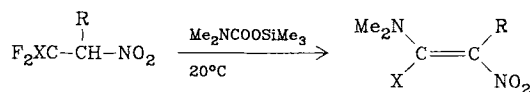
scribed for **2**. IR (KBr):  $2052 \text{ cm}^{-1}$  ( $\nu(\text{CO})$ ).—**4:** A suspension of **2** (200 mg, 0.33 mmol) in acetone was treated with excess NaI. After 5 h the solvent was removed by distillation and the residue was taken up in dichloromethane; undissolved NaI and NaBr were removed by filtration, and the filtrate evaporated to dryness. Yield: 180 mg (83%). IR (KBr):  $2039 \text{ cm}^{-1}$  ( $\nu(\text{CO})$ ). The mass spectrometrically controlled bromide/iodide exchange went to completion.

- [9] Complexes of type **B** are formed upon reaction of **1** with stoichiometric amounts of L, e.g. tertiary phosphites, at room temperature in dichloromethane. Purification by column chromatography on silica gel; yield ca. 70%. Cationic complexes **C** are formed upon reaction of **1** with an excess of L in the presence of  $\text{TlBF}_4$  in dichloromethane. Purification on a silica gel column with acetone. Yield ca. 80%.  
[10] **Procedure. 5:** A suspension of **1** (300 mg, 0.26 mmol) in freshly distilled THF (10 mL) was treated with 140 mg (0.52 mmol) of thallium cyclopentadienide. After 2 h the green solution was filtered and evaporated to dryness. Subsequent purification by chromatography on silica gel with THF ( $2 \times$ ) under nitrogen followed by removal of the eluent by distillation afforded 260 mg (88%) of **5** as an olive-green microcrystalline powder. Correct C,H analysis. MS (EI,  $70 \text{ eV}$ ,  $160^\circ\text{C}$ )  $m/z$  568 ( $M^+$ ,  $^{58}\text{Ni}$ ).  
[11] U. Kölle, F. Khouzami, *Angew. Chem.* 92 (1980) 658; *Angew. Chem. Int. Ed. Engl.* 19 (1980) 640.  
[12] **Procedure. 60:** A solution of  $\text{K}[\text{Co}(\text{CO})_4]$  (0.69 g, 3.3 mmol) in THF (50 mL) was treated with 1.72 g (3.3 mmol) of  $\text{C}_5\text{Ph}_5\text{Br}$  and the mixture stirred for 3 d at room temperature. The solvent was then removed by distillation and the reddish-brown residue chromatographed at  $+10^\circ\text{C}$  on a silica gel column (eluent: first hexane, then ether/dichloromethane 1:1). The dicarbonyl complex **6** was eluted as a purple solution, which, after evaporation to dryness, furnished 1.50 g (81%) of **6** as a reddish brown, microcrystalline powder. The product is air-sensitive and can be purified by sublimation at  $180^\circ\text{C}$  in vacuo. Correct C,H analysis. IR ( $\text{CH}_2\text{Cl}_2$ ):  $2010, 1952 \text{ cm}^{-1}$  ( $\nu(\text{CO})$ ). MS (EI,  $70 \text{ eV}$ ,  $25^\circ\text{C}$ )  $m/z$  560 ( $M^+$ ).

## Di- and Trifluoro-Substituted Dilithium Compounds for Organic Syntheses\*\*

By Dieter Seebach,\* Albert K. Beck, and Philippe Renaud

Fluoroorganic compounds are of increasing interest, mainly for the synthesis of biologically active products.<sup>[1]</sup> Fluoro substitution can cause problems in synthetic transformations, since fluoride can act as a leaving group.<sup>[2]</sup> Thus, the  $\beta$ -fluoro-substituted nitroalkanes **1**<sup>[3]</sup> do not undergo base-catalyzed nitroaldol additions to carbonyl compounds.<sup>[4]</sup>  $\beta$ -elimination is so strongly favored that reaction of **1** with *N,N*-dimethyl(trimethylsilyl)carbamate affords fluorine-free nitroenamines **2**. To our great surprise, the dilithio derivatives **3** and **4** of the fluoronitroalkanes **1a**,



**1a:** R = H, X = F

**1b:** R = X = H

**1c:** R = Me, X = F

**2a:** R = H, X = NMe<sub>2</sub> (75%)

**2b:** R = X = H (62%)

**2c:** R = Me, X = NMe<sub>2</sub> (67%)

**1b** could be generated with butyllithium, were of comparable stability (up to  $-70^\circ\text{C}$ ) to the nonfluorinated analogues,<sup>[5]</sup> and reacted with aldehydes and ketones to give the adducts **6–9** (Table 1; for experimental procedure see ref. [5]). The adducts were formed in 50–60% yield but

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[\*\*] Partially from the projected Ph. D. thesis of P. R.—The fluoronitroethanes were supplied by Bayer AG, Leverkusen.

readily decomposed during purification (chromatography or distillation), so that they were often hydrogenated directly to the corresponding amino alcohols.

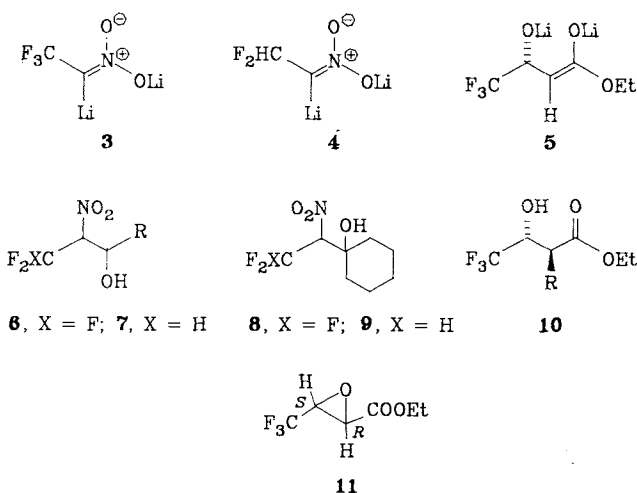


Table 1. Products **6-9** from the dilithio derivatives **3** and **4** of fluorinated nitroethanes [3] and carbonyl compounds (yields of pure products from distillation; ratios of diastereomers from  $^{13}\text{C}$ -NMR spectra; NMR data of major isomers; enrichment of diastereomers is possible as described for the nonfluorinated analogues [6]).

Product	Yield [%] crude (pure) [ratio of diast.]	$^{13}\text{C}$ -NMR, $\delta$ $J$ (C,F) [Hz]
<b>6a</b> , R = <i>t</i> Bu	90 (60) [1 : 1]	$\delta(\text{CNO}_2)^{2/2}J$ 84.6/29.8
<b>6b</b> , R = $\text{C}_6\text{H}_5$	60 (40) [2 : 1]	91.1/29.1
<b>6c</b> , R = 4- $\text{NO}_2$ - $\text{C}_6\text{H}_4$	55 (35) [3 : 1]	90.5/29.1
<b>6d</b> , R = 3,4-( $\text{OCH}_2\text{O}$ ) $\text{C}_6\text{H}_3$	50 (25) [2.5 : 1]	91.0/28.4
<b>8</b>	60 (30)	92.9/28.4
<b>7a</b> , R = <i>t</i> Bu	40 (15) [a]	$\delta(\text{CHF}_2)^{1/2}J$ 112.9/246.6
<b>7b</b> , R = $\text{C}_6\text{H}_5$	30 (12) [2 : 1]	111.5/247.8
<b>9</b>	60 (4)	112.8/245.6

[a] Determination of the ratio of diastereomers not possible by  $^{13}\text{C}$ -NMR.

A double deprotonation is also possible with the (*R*)-tri-fluorohydroxybutanoate **10a**. This compound is readily available in >90% enantiomeric excess (*ee*) through yeast reduction of the corresponding  $\beta$ -ketoester.<sup>[7]</sup> At low temperatures ( $\leq -25^\circ\text{C}$ ), the enolate-alkoxide **5** does not undergo  $\gamma$ -elimination (to an epoxide or a cyclopropane), and, like the nonfluorinated analogue,<sup>[8]</sup> can be alkylated ( $\rightarrow$  **10b-10d**) or cyclized ( $\rightarrow$  **11**) diastereoselectively (Table 2; for experimental procedure see ref. [8]).

Table 2. Products **10** and **11** from the dilithio derivative **5** of ethyl (*R*)-4,4,4-trifluoro-3-hydroxybutanoate **10a** (92% *ee*) [7] and  $\text{CH}_3$ ,  $\text{CH}_2=\text{CH}-\text{CH}_2\text{Br}$ ,  $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$ ,  $\text{I}_2$  (yields of >95% configurationally pure samples from flash chromatography; % *ds* =  $[(A/A+B) \times 100]$  from  $^{13}\text{C}$ -NMR spectra of crude products; NMR signal of C(3) of major isomer;  $[\alpha]_D^{25}$  at  $c=1.2$  in  $\text{CHCl}_3$ ).

Product	Yield [%] (% <i>ds</i> )	$[\alpha]_D^{25}$	$^{13}\text{C}$ -NMR, $\delta$ values $^2J$ (C,F) [Hz]
<b>10a</b> , R = H		+20.1	67.4/32
<b>10b</b> , R = Me		+10.0	72.7/31
<b>10c</b> , R = $\text{CH}_2=\text{CH}-\text{CH}_2$	45 (86)	-0.8	70.8/31
<b>10d</b> , R = $\text{CH}_2-\text{C}_6\text{H}_5$	52 (93)	-31.6	70.5/31
<b>11</b>	47 (80)	-18.6	52.6/42

Although monolithiated fluoro compounds capable of undergoing  $\alpha$ -,  $\beta$ -, and/or  $\gamma$ -elimination have been known for a long time,<sup>[2,9]</sup> the reagents **3-5** are the first polyli-thiated derivatives of this type.<sup>[10]</sup> They offer accessibility to a variety of new fluorinated organic compounds with additional functional groups.

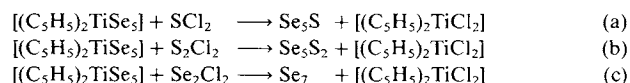
Received: September 16, 1985 [Z 1463 1E]  
German version: *Angew. Chem.* 98 (1986) 96

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## Selenium-rich Chalcogen Rings $\text{Se}_5\text{S}$ , $\text{Se}_5\text{S}_2$ , and $\text{Se}_7$ from Titanocene Pentaselenide\*\*

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While the synthesis of sulfur-containing homocycles and heterocycles by reaction of titanocene pentasulfide with non-metal chlorides has been studied in detail, nothing has hitherto been reported about analogous reactions of titanocene pentaselenide.<sup>[1]</sup> We report here on the synthesis and properties of the six- and seven-membered ring molecules  $\text{Se}_5\text{S}$  and  $\text{Se}_5\text{S}_2$  and  $\text{Se}_7$ , respectively, which can be prepared according to Equations (a) to (c).



$\text{Se}_5\text{S}$  was obtained from  $\text{CS}_2$  in the form of deep-red, shiny, hexagonal needles,<sup>[2]</sup> whose composition,<sup>[3]</sup> Raman spectrum,<sup>[4a]</sup> and crystal structure<sup>[5]</sup> proved the presence of thiapentaselecyclohexane. The HPLC retention time<sup>[6]</sup> lies, as expected, between that of  $\text{Se}_5\text{S}_2$  and  $\text{Se}_6$  ( $\text{Se}_4\text{S}_2$  2.94,  $\text{Se}_5\text{S}$  3.07,  $\text{Se}_6$  3.40 min; dead time 1.40 min; eluent: methanol).

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[\*\*] Sulfur compounds, Part 95. This work was supported by the Deutsche Forschungsgemeinschaft, the Alexander-von-Humboldt Stiftung, the Fonds der Chemischen Industrie, and the TU Berlin (MIT-Sondermittel). — Part 94: [10a].