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Synthesis of (η^4-2-bromo- and -iodo-5-trimethylsilylcyclopentadienone)(η^5-cyclopentadienyl)cobalt and their 3,4-tri-, tetra-, and -pentamethylene derivatives *

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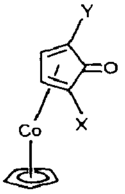
Abstract

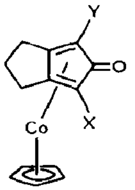
[η^4-2,5-Bis(trimethylsilyl)cyclopentadienone](η^5-cyclopentadienyl)cobalt derivatives undergo monohalogenodesilylation upon treatment with bromine and iodine at room temperature to give the novel title compounds in good yields.

Introduction

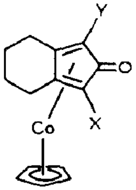
We previously reported [1] a chemo- and regio-selective one-step synthesis of the cobalt-complexed 2,5-disilyl substituted cyclopentadienones **1** to **4** by a low-temper-



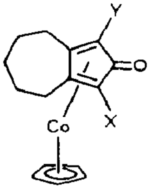
1, 5, 9



2, 6, 10, 13, 14, 16



3, 7, 11, 15



4, 8, 12

1 to **4**: $X{=}Y{=}Si(CH_3)_3$
5 to **8**: $X{=}Si(CH_3)_3$, $Y{=}Br$
9 to **12**: $X{=}Si(CH_3)_3$, $Y{=}I$
13: $X{=}Si(CH_3)_3$, $Y{=}Cl$
14 to **15**: $X{=}Y{=}Br$
16: $X{=}Br$, $Y{=}I$

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* Dedicated to Prof. W. Flitsch on the occasion of his 65th birthday.

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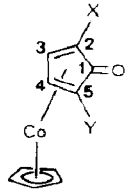
ature cobalt-mediated [2 + 2 + 2]cycloaddition of terminal trimethylsilyl-substituted alkynes and $CpCo(CO)_2$ under photolytic conditions. Compound **1** was shown [2] to be a versatile reagent for the synthesis of otherwise difficultly accessible but synthetically useful 4-substituted cyclopentenones [2]. The cyclopentadienone complexes **1** to **4** bear two readily replaceable groups (Me_3Si substituents) [3] in the two α-positions C(2) and C(5). With the objective of increasing the selectivity between the two α-positions in these complexes we studied the selective replacement of one of the Me_3Si groups by a halogen atom [4*].

Results

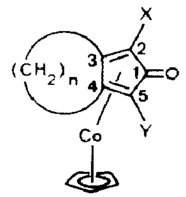
The reaction of **1** to **4** with an excess of bromine in chloroform or iodine in acetone at room temperature gave high yields of the monobromo- **6** to **8**, or the monoiodo derivatives, **9** to **12** (Table 1). The somewhat smaller yield of **5** may be partly due to oxidative demetallation. The selectivity towards monosubstitution in the reaction with bromine appeared to decrease with increasing temperature: in boiling chloroform the reaction led in part to the dibromocyclopendatienone cobalt complexes **14** and **15** (8 and 12%) in addition to the corresponding monobromo-

Table 1

Products of the halodesilylations



5, 9



6 to **8** and **10** to **16**

Complex	*n*	X	Y	Isolated yield (%) [a]	ν(CO) (cm^{-1}) (KBr)
5	–	Br	TMS	56	1580
6	3	Br	TMS	86(71) [b]	1580
7	4	Br	TMS	89(73) [b]	1600
8	5	Br	TMS	81	1600
9	–	I	TMS	95	1575
10	3	I	TMS	100	1584
11	4	I	TMS	98	1600
12	5	I	TMS	89	1592
13	3	Cl	TMS	7	1578
14	3	Br	Br	8(28) [c]	1615
15	4	Br	Br	12(43) [c]	1613
16	3	Br	I	25 [d]	1615

[a] Yields are based on non-recovered starting material after purification by column chromatography on aluminum oxide. [b] Yield given in parentheses was from reaction in boiling chloroform. [c] Yield given in parentheses was that obtained when the monobromo derivate was halodesilylated again. [d] This yield was from the reaction of **6** with iodine in acetone.

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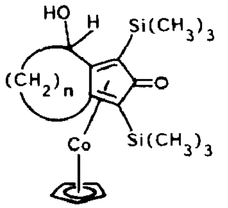
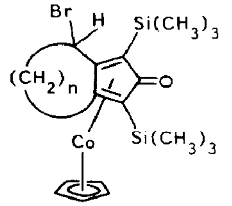
* Reference number with asterisk indicates a note in the list of references.

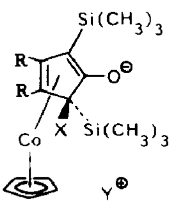
derivatives **6** (71%) and **7** (73%). Better yields of **14** and **15** (28 and 43%) were obtained by bromodesilylating the isolated **6** and **7** (Table 1) again under the same conditions. The mixed dihalo derivative **16** was isolated (25%) from the reaction of the monobromo derivatives **6** with iodine in acetone. The ν(CO) frequency found in **1** to **4** [1] at 1550–1570 cm^{-1} is shifted to 1575–1600 cm^{-1} in the monohalo derivatives **5** to **12**, and to 1600 cm^{-1} in the dihalo derivatives **14** to **16**. Irradiation with a 200 W tungsten lamp of a solution of **2** or **3** in boiling chloroform containing bromine afforded 35% of the dark-red hydroxy-substituted derivatives **17a** and **17b** [7*] (in addition to 42% of **6** and **7** and 17% of **14** and **15**). These were probably formed via the corresponding (so far unknown) allyl-type bromides **18a** and **18b** *.



17a n=2
17b n=3



18a n=2
18b n=3



19 X,Y=halogen

Reaction of **1** to **3** with chlorine did not result in monochlorodesilylation. Instead, well defined microcrystalline green compounds were obtained (40–85%) the structures of which are still unknown [5*]. They may possibly be products of oxidative addition of the chlorine to **1** to **3** [6].

Analogous products were obtained from the reactions of **1** to **3** with bromine and iodine under a variety of work-up conditions. Since the chloro derivative **13** was isolated (albeit in low yield) from the reaction of **2** and iodine chloride, we consider that the first step of the presently reported monohalodesilylation reaction might be a nucleophilic attack of a halide ion on the neutral cyclopentadienone complex to give intermediates such as **19** [7].

Experimental

General

Melting points were determined on a melting point apparatus FP-5/FP-2 (Mettler) fitted with a microscope, and are uncorrected. The ^1H NMR spectra were recorded in benzene-d_6 on the Varian Spectrometers EM-390 and XL-200. The IR spectra were recorded on the Perkin–Elmer Models 21 and 257 spectrometers using a polystyrene film for calibration. The low resolution mass spectra were obtained with CEC 21-110 and Varian MAT 711 spectrometers at 70 eV, and the high resolution mass spectra with a Varian MAT 711 spectrometer at 70 eV connected to the data-system SS-100 MS (Varian MAT): The electronic spectra were recorded with an Uvicon 810 spectrometer. Elemental analyses were provided by the Micro-

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* Use of such conditions in the case of the analogous bicyclo[5.3.0] decadienone cobalt complex **4** might afford a precursor for natural hydroazulenes with an oxygen function at the α-carbon atom of the seven-membered ring.

analytical Laboratory of the Institute for Organic Chemistry of the University of Zürich.

General procedures

A. For the selective monobromodesilylation

Bromine (8 molar equivalents) was added to a 2.5×10^{-2} *M* solution of **1**–**4** in $CHCl_3$ and the mixture was stirred in a stoppered flask at room temperature for 1–2 h. Saturated aqueous $Na_2S_2O_3$ was added to the brown-red solution until the organic layer turned red. The aqueous layer was extracted with CH_2Cl_2 (3 × 100 ml), the combined $CHCl_3$ solution and CH_2Cl_2 extracts were dried over anhydrous Na_2SO_4 and filtered, and the solvent was evaporated under reduced pressure. The residue was column chromatographed on neutral alumina (Woelm, activity 1, deactivated with 4.5% water). The remaining starting material was eluted with ether and the products with ethyl acetate.

B. For the selective monoiododesilylation

The procedure was analogous to that described under A, but reaction was carried out in acetone for 25 h.

(η^4-2-Bromo-5-trimethylsilylcyclopentadienone)(η^5-cyclopentadienyl)cobalt (5)

By procedure A: 2.00 g (5.74 mmol) **1** and 7.30 g (45.67 mmol) Br_2 in 200 ml $CHCl_3$ gave, after purification, unchanged **1** (0.15 g, 0.42 mmol), 11%) and **5** (1.06 g, 2.98 mmol, 56%*) *; m.p. 193° C (red needles from acetone); mass spectrum *m/e* (rel. intensity): 356/354 (8/8, M^+), 341/339 (6/6, $M^+ - CH_3$), 275 (100, $M^+ - Br$), 124 (15, C_5H_5Co), and 73 (67, $Si(CH_3)_3$); ^1H NMR. (benzene-d_6) $\delta = 4.82$ (1H, d, $^3J = 3.0$ Hz, CH), 4.37 (5H, s, C_5H_5), 4.27 (1H, d, $^3J = 3.0$ Hz, CH), and 0.27 (9H, s, 3 Si-CH_3); UV (cyclohexane): λ_{max} $(\epsilon) = 292$ (22200), 361 (2350), 428 nm (1110). Anal. Found: C, 44.24; H, 4.62. $C_{13}H_{16}BrOSiCo$ calc: C, 43.96; H, 4.54%.

(η^4-2-Bromo-5-trimethylsilyl-3,4-cyclopentacyclopentadienone)(η^5-cyclopentadienyl) cobalt (6)

By procedure A: 500 mg (1.29 mmol) **2** and 1.65 g (10.29 mmol) Br_2 in 50 ml $CHCl_3$ gave, after purification, unchanged **2** (270 mg, 0.70 mmol, 54%) and **6** (202 mg, 0.51 mmol, 86%*); m.p. 203° C (red needles from acetone); mass spectrum *m/e* (rel. intensity): 396/394 (27/26, M^+), 381/379 (6/6, $M^+ - CH_3$), 368/366 (19/20, $M^+ - CO$), 315 (100, $M^+ - Br$), 124 (11, C_5H_5Co), and 73 (41, $Si(CH_3)_3$); ^1H NMR (benzene-d_6) $\delta = 4.28$ (5H, s, C_5H_5), 2.1–1.5 (6H, m, 3 CH_2), and 0.35 (9H, s, 3 Si-CH_3); UV (cyclohexane): λ_{max} $(\epsilon) = 292$ (21790), 361 (1690), 427 nm (1100). Anal. Found: C, 48.73; H, 5.20. $C_{16}H_{20}BrOSiCo$ calc: C, 48.62; H, 5.10%.

(η^4-2-Bromo-5-trimethylsilyl-3,4-cyclohexacyclopentadienone)(η^5-cyclopentadienyl) cobalt (7)

By procedure A: 2.00 g (4.97 mmol) **3** and 6.40 g (40.04 mmol) Br_2 in 200 ml $CHCl_3$ gave, after purification, unchanged **3** (1.03 g, 2.56 mmol, 52%) and **7** (0.88 g,

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* Yields marked * are based on non-recovered starting material.

2.15 mmol, 89%*); m.p. 177 °C (red needles from acetone); mass spectrum *m/e* (rel. intensity): 410/408 (55/52, M^+), 395/393 (7/8, $M^+ - CH_3$), 337/335 (10/11, $M^+ - Si(CH_3)_3$), 329 (100, $M^+ - Br$), 124 (19, C_5H_5Co), and 73 (72, $Si(CH_3)_3$); ^1H NMR (benzene-d_6) = 4.27 (5H, s, C_5H_5), 2.4–1.6 (4H, m, 2 CH_2), 1.6–0.9 (4H, m, 2 CH_2), and 0.38 (9H, s, 3 Si-CH_3); UV (cyclohexane): λ_{max} (ϵ) = 203 (21430), 294 (22630), 370 nm (1920). Anal. Found: C, 49.67; H, 5.34. $C_{17}H_{22}BrOSiCo$ calc: C, 49.89; H, 5.24%.

(η^4-2-Bromo-5-trimethylsilyl-3,4-cycloheptacyclopentadienone)(η^5-cyclopentadienyl) cobalt (8)

By procedure A: 200 mg (0.48 mmol) **4** and 614 mg (3.84 mmol) Br_2 in 25 ml $CHCl_3$ gave, after purification, **4** (140 mg, 0.34 mmol, 71%) and **8** (48 mg, 0.11 mmol, 81%*); m.p. 158 °C (red needles from acetone); mass spectrum *m/e* (rel. intensity): 424/422 (53/51, M^+), 409/407 (9/12), $M^+ - CH_3$), 396/394 (6/6, $M^+ - CO$), 351/349 (13/12, $M^+ - Si\ (CH_3)_3$), 343 (100, $M^+ - Br$), 124 (30, C_5H_5Co), and 73 (69, $Si(CH_3)_3$); ^1H NMR (benzene-d_6) $\delta = 4.37$ (5H, s, C_5H_5), 2.4–1.7 (4H, m, 2 CH_2), 1.7–1.1 (6H, m, 3 CH_2), and 0.36 (9H, s, 3 Si-CH_3); UV (cyclohexane): λ_{max} (ϵ) = 204 (20880), 293 (23060), 365 nm (1860). Found: *m/e* 422.0101. Exact mass calc for $C_{18}H_{24}OSiCoBr$: *m/e* 422.0106.

(η^4-2-Iodo-5-trimethylsilylcyclopentadienone)(η^5-cyclopentadienyl)cobalt (9)

By procedure B: 1.75 g (5.02 mmol) **1** and 10.22 g (40.27 mmol) I_2 in 200 ml acetone gave, after purification, unchanged **1** (1.33 g, 382 mmol, 76%) and **9** (0.46 g, 1.14 mmol, 95%*); m.p. 190 °C (red needles from acetone); mass spectrum *m/e* (rel. intensity): 402 (14, M^+), 387 (7, $M^+ - CH_3$) 275 (100, $M^+ - I$), 124 (20, C_5H_5Co), and 73 (56, $Si(CH_3)_3$); ^1H NMR (benzene-d_6) $\delta = 4.82$ (1H, d, $^3J = 3.0$ Hz, CH), 4.37 (1H, d, $^3J = 3.0$ Hz, CH), 4.30 (5H, s, C_5H_5), and 0.23 (9H, s, 3 Si-CH); UV (cyclohexane): λ_{max} (ϵ) = 306 (15500), 363 (2120), 430 nm (1160). Found: *m/e* 401.9356. Exact mass calc for $C_{13}H_{16}IOSiCo$: *m/e* 401.9351.

(η^4-2-Iodo-5-trimethylsilyl-3,4-cyclopentacyclopentadienone)(η^5-cyclopentadienyl)cobalt (10)

By procedure B: 500 mg (1.29 mmol) **2** and 2.61 g (10.29 mmol) I_2 in 50 ml acetone gave, after purification, unchanged **2** (310 mg, 0.80 mmol, 62%) and **10** (215 mg, 0.49 mmol, 99%*); m.p. 211 °C (red needles from acetone); mass spectrum *m/e* (rel. intensity): 442 (100, M^+), 427 (15, $M^+ - CH_3$) 414 (35, $M^+ - CO$), 315 (74, $M^+ - I$), 124 (15, C_5H_5Co), and 73 (60, $Si(CH_3)_3$); ^1H NMR (benzene-d_6) $\delta = 4.27$ (5H, s, C_5H_5), 2.2–1.4 (6H, m, 3 CH_2), and 0.35 (9H, s, 3 Si-CH_3); UV (cyclohexane): λ_{max} (ϵ) = 202 (25710), 305 (17300), 363 (1640), 428 nm (1240). Anal. Found: C, 43.70; H, 4.55. $C_{16}H_{20}IOSiCo$ calc: C, 43.45; H, 4.56%.

(η^4-2-Iodo-5-trimethylsilyl-3,4-cyclohexacyclopentadienone)(η^5-cyclopentadienyl)cobalt (11)

By procedure B: 2.00 g (4.97 mmol) **3** and 10.15 g (40.04 mmol) I_2 in 200 ml acetone gave, after purification, unreacted **3** (1.33 g, 3.30 mmol, 66%) and **11** (1.48 g, 3.24 mmol, 98%*); m.p. 205 °C (red needles from acetone); mass spectrum *m/e* (rel. intensity): 456 (100, M^+), 441 (11, $M^+ - CH_3$), 383 (11, $M^+ - Si(CH_3)_3$), 329 (48, $M^+ - I$), 124 (13, C_5H_5Co), and 73 (43, $Si(CH_3)_3$); ^1H NMR (benzene-d_6)

$\delta = 4.25$ (5H, s, C_5H_5), 2.3–1.7 (4H, m, 2 CH_2), 1.7–1.0 (4H, m, 2 CH_2), and 0.38 (9H, s, 3Si-CH_3); UV (cyclohexane): λ_{max} (ϵ) = 203 (24050), 306 (17770), 370 (1780), 431 nm (1120). Anal. Found: C, 44.64; H, 4.98. $C_{17}H_{22}IOSiCo$ calc: C, 44.75; H, 4.86%.

(η^4-2-Iodo-5-trimethylsilyl-3,4-cycloheptacyclopentadienone)(η^5-cyclopentadienyl)cobalt (12)

By procedure B: 300 mg (0.72 mmol) **4** and 1.46 g (5.76 mmol) I_2 in 40 ml acetone gave, after purification, unchanged **4** (230 mg, 0.55 mmol, 76%) and **12** (70 mg, 0.15 mmole, 89%*); m.p. 165 °C (red needles from acetone); mass spectrum *m/e* (rel. intensity): 470 (100, M^+), 455 (12, $M^+ - CH_3$), 442 (10, $M^+ - CO$), 397 (10, $M^+ - Si(CH_3)_3$), 343 (28, $M^+ - I$), 124 (11, C_5H_5Co), and 73 (47, $Si(CH_3)_3$); ^1H NMR (benzene-d_6) $\delta = 4.37$ (5H, s, C_5H_5), 2.5–1.7 (4H, m, 2 CH_2), 1.7–1.0 (6H, m, 3 CH_2), and 0.39 (9H, s, 3 Si-CH_3); UV (cyclohexane): λ_{max} (ϵ) = 203 (21060), 306 (16460), 370 (1580), 425 nm (900). Anal. Found: C, 46.22; H, 5.26. $C_{18}H_{24}IOSiCo$ calc: C, 45.97; H, 5.26%.

Reaction of 2 with Br_2 in boiling $CHCl_3$ under irradiation

A solution of 200 mg (0.50 mmol) **2** and 3.00 g (18.77 mmol) Br_2 in 30 ml $CHCl_3$ was heated under reflux for 4 h with irradiation from a 200 W tungsten lamp. Work-up was analogous to that in procedure A.

Fraction 1 contained unchanged **2** (70 mg, 0.18 mmol, 35%).

Fraction 2 contained 48 mg (0.12 mmol, 37%*) of [η^4-6-hydroxy-2,5-bis(trimethylsilyl)-3,4-cyclopentacyclopentadienone](η^5-cyclopentadienyl)cobalt (**17a**); m.p. 235 °C (red needles from acetone); IR ($CHCl_3$) ν_{max} = 3580w (O–H), 1570s and 1555s (C=O), 1245s (SiC–H), 845s and 815s cm^{-1} (-$Si(CH_3)_3$); mass spectrum *m/e* (rel. intensity): 404 (81, M^+), 389 (22, $M^+ - CH_3$), 331 (100, $M^- Si(CH_3)_3$), 124 (40, C_5H_5Co), and 73 (97, $Si(CH_3)_3$); ^1H NMR (benzene-d_6) $\delta = 4.70$ (1H, d, $^3J = 4.8$ Hz, OH), 4.36 (5H, s, C_5H_5), 2.5–1.9 (5H, m, 2CH_2 and HCOH), 0.45 (9H, s, 3 Si-CH_3), and 0.38 (9H, s, 3 Si-CH_3). Anal. Found: C, 56.38; H, 7.22. $C_{19}H_{29}O_2Si_2Co$ calc: C, 56.41; H, 7.23%.

Fraction 3 contained **6** (53 mg, 0.13 mmol, 42%*).

Fraction 4 contained (η^4-2,5-dibromo-3,4-cyclopentacyclopentadienone)(η^5-cyclopentadienyl)cobalt (**14**) (22 mg, 0.05 mmol, 17%*); m.p. 235 °C (red needles from acetone); mass spectrum, *m/e* (rel. intensity): 404/402/400 (35/74/35, M^+), 389/387/385 (4/9/4, $M^+ - CH_3$) 376/374/372 (13/24/11, $M^+ - CO$), 322/320 (26/26, $M^+ - Br$), 124 (70, C_5H_5Co), and 59 (100, Co); ^1H NMR (benzene-d_6) $\delta = 4.20$ (5H, s, C_5H_5) and 2.2–1.0 (6H, m, 3CH_2). Anal. Found: C, 38.69; H, 2.76. $C_{13}H_{11}Br_2OCo$ calc: C, 38.84; H, 2.75%.

Reaction of 3 with Br_2 in boiling $CHCl_3$ under irradiation

A solution of 220 mg (0.55 mmol) **3** and 3.00 g (18.77 mmol) Br_2 in 30 ml $CHCl_3$ was heated under reflux for 4 h with irradiation from a 200 W tungsten lamp. The work-up was as in procedure A.

Fraction 1 contained unchanged **3** (90 mg, 0.22 mmol, 40%).

Fraction 2 contained 42 mg (0.10 mmol, 31%*) of [η^4-6-hydroxy-2,5-bis(trimethylsilyl)-3,4-cyclohexaclopentadienone](η^5-cyclopentadienyl)cobalt (**17b**); m.p. 225 °C (red needles from acetone); IR($CHCl_3$) ν_{max} = 3600w (O–H), 1570s and 1550s

(C=O), 1243s (SiC–H), 845s and 820s cm^{-1} (-Si(CH$_3$)$_3$); mass spectrum m/e (rel. intensity): 418 (63, M^+), 403 (33, $M^+-\mathrm{CH_3}$), 345 (75, $M^+-\mathrm{Si(CH_3)_3}$), 124 (23, C_5H_5Co), and 73 (100, Si(CH$_3$)$_3$); ^{1}H NMR (benzene-d_6) $\delta = 4.38$ (5H, s, C_5H_5), 2.2–1.8 (2H, m), 1.8–1.6 (6H, m), 0.52 (9H, s, 3 Si-CH_3), and 0.40 (9H, s, 3 Si-CH_3). Anal. Found: C, 57.17; H, 7.24. $C_{20}H_{31}O_2Si_2Co$ calc: C, 57.39; H, 7.47%.

Fraction 3 contained **7** (60 mg, 0.15 mmol, 45%*).

Fraction 4 contained (η^4-2,2-dibromo-3,4-cyclohexacyclopentadienone)(η^5-cyclopentadienyl)cobalt (**15**) (20 mg, 0.05 mmol, 15%*); m.p. 231°C (red needles from acetone); mass spectrum m/e (rel. intensity): 418/416/414 (40/82/43, M^+), 390/388/386 (16/32/17, $M^+-\mathrm{CO}$), 336/334 (87/91, $M^+-\mathrm{Br}$), 254 931, M^+- 2Br), 224 (100), and 124 (45, C_5H_5Co); ^{1}H NMR (benzene-d_6) $\delta = 4.17$ (5H, s, C_5H_5), 2.3–1.6 (4H, m, 2 CH_2), and 1.5–0.8 (4H, m, 2 CH_2). Anal. Found: c, 40.22; H, 3.45. $C_{14}H_{13}Br_2OCo$ calc: C, 40.42; H, 3.15%.

*Reaction of **6** with Br_2*

by procedure A: 300 mg (0.76 mmol) **6** and 980 mg (6.13 mmol) Br_2 in 35 ml $CHCl_3$ gave, after purification, unchanged **6** (115 mg, 0.29 mmol, 38%) and **14** (53 mg, 0.13 mmol, 28%*).

Reaction of 7 with Br_2

By procedure A: 300 mg (0.73 mmol) **7** and 940 mg (5.87 mmol) Br_2 in 35 ml $CHCl_3$ gave, after purification, unchanged **7** (90 mg, 0.22 mmol, 30%) and **15** (91 mg, 0.22 mmol, 43%*).

*Reaction of **6** with I_2*

By procedure B: 300 mg (0.76 mmol) **6** and 1530 mg (6.08 mmol) I_2 in 35 ml acetone gave, after purification, unchanged **6** (65 mg, 0.16 mmol, 21%) and (η^4-2-bromo-5-iodo-3,4-cyclopentacyclopentadienone)(η^5-cyclopentadienyl)cobalt (**16**) (67 mg, 0.15 mmol, 25%*); m.p. 219°C (red needles from acetone); mass spectrum m/e (rel. intensity): 450/448 (13/13, M^+), 368 (11, $M^+-\mathrm{Br}$) and 124 (61, C_5H_5Co). Anal. Found: C, 34.82; H, 2.50. $C_{13}H_{11}BrIOCo$ calc: C, 34.78; H, 2.47%.

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References

1 (a) E.R.F. Gesing, J.P. Tane and K.P.C. Vollhardt, Angew. Chem., 92 (1980) 1057; Angew. Chem. Int. Ed. Engl., 19 (1980) 1023; (b) E.R.F. Gesing and K.P.C. Vollhardt, J. Organomet. Chem., 217 (1981) 105; (c) P.C. Auderset and E.R.F. Gesing, unpublished results.

2 (a) J.P. Tane and K.P.C. Vollhardt, Angew. Chem., 94 (1982) 642; Angew. Chem. Int. Ed. Engl., 21 (1982) 617; Angew. Chem. Suppl., (1982) 1360; (b) E.R.F. Gesing, H. Kaulen, J.P. Tane and K.P.C. Vollhardt, in preparation.

3 For a review see: T.H. Chan and J. Fleming, Synthesis, (1979) 761.

4 For the synthesis of stable monomeric halo-substituted cyclopentadienones, see: (a) M.A. Ogliaruso, M.G. Romanelli and E.J. Becker, Chem. Rev., 65 (1965) 261; (b) G. Maier, S. Pfriem, U. Schäfer and R. Matusch, Angew. Chem., 90 (1978) 552; Angew. Chem. Int. Ed. Engl., 17 (1978) 520; (c) G. Maier, H.W. Lage and H.P. Reisenauer, Angew. Chem., 93 (1981) 1010; Angew. Chem. Int. Ed. Engl., 20 (1981) 976.

5 Attempts to obtain crystals suitable for X-ray studies have so far been unsuccessful.

6 E.R.F. Gesing, unpublished results.

7 Application of the title compounds in the synthesis of novel transition metal complexes is under current investigation.