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An Unexpected S_N' Reaction on Cobaltocenium Triflates: Substitution on One Ring and Elimination on the Other

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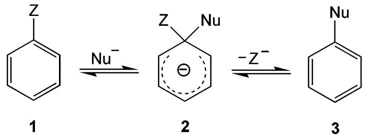
Scheme 1



Summary: CpCo-capped tetra-n-propylcyclopentadienone complexes were O-alkylated and O-acylated. Reactions of the O-triflated product with organolithium compounds afford a substitution of the Cp ring in 40−80% yield; as products the RCpCo-capped tetra-n-propyl-cyclopentadienone complexes were isolated.

The aromatic nucleophilic substitution reaction is a well-studied process which proceeds with second-order kinetics (Scheme 1). Most of these reactions require some activation by electron-withdrawing groups to stabilize the anionic intermediate **2**, also sometimes called the Meisenheimer intermediate.[1]

In organometallic π-systems the role of the electron-withdrawing groups can be taken over by a metal in a higher oxidation state. The nucleophilic substitution is accompanied by a change of hapticity of the metal and reduction of the metal at the same time. The role of the leaving groups can be taken by a ligand at the metal or by hydride abstraction at the π-system if we are dealing with metallocenes. Although this view seems to be a logical extension of the aromatic S_N2 process shown in Scheme 1, to the best of our knowledge only a few processes are known which fit into this concept. According to Scheme 2, the nucleophile adds to a $CpFeL_3$ (eq 1)[2] and a $CpOsL_4$ system (eq 2),[3] respectively, or to a cobaltocenium salt (eq 3).[4] All reactions can be rationalized by assuming that the negative charge introduced by the nucleophile is taken over by the metal (intramolecular redox process). In the final step the original formal charge on the metal is reestablished by protonating a ligand (e.g. eq 1), by splitting off a leaving group and protonating the metal[3] (e.g. eq 2), or by hydride abstraction[4] (eq 3).

Scheme 2

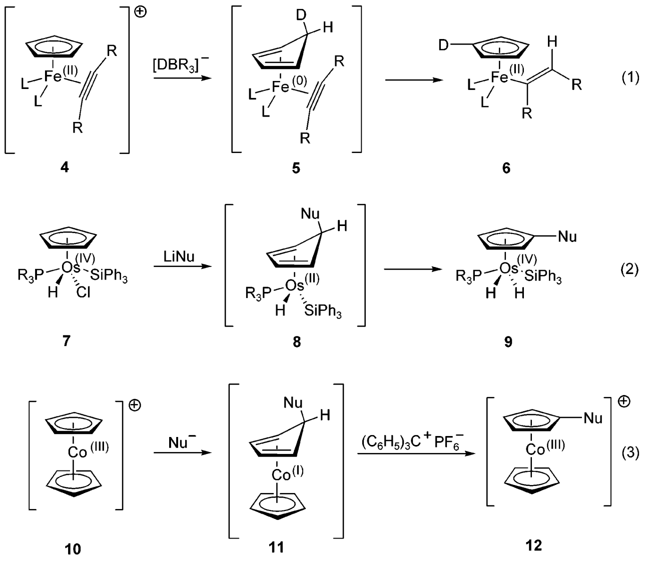
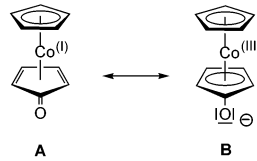


Chart 1



In this paper we present an example where the nucleophile attacks at one ring of a cobaltocenium ion whereas the leaving group is at the other ring. This probably goes along with a change of hapticity of the ligand. We furthermore demonstrate the usefulness of this process in synthesis.

During our endeavor to synthesize superphanes with two CpCo-capped cyclopentadienone rings,[5] we explored the electronic properties of CpCo-stabilized cyclopentadienones.[6] The electronic structure of the cyclopentadienone complexes can be described by the resonance structures **A** and **B** (Chart 1). The complexation by the metal fragment goes along with a higher electron density at the cyclopentadienone ring, as expressed by valence structure **B**. Consequently, a high-field shift of the ^{13}C signal at the CO group by about 40−50 ppm has been encountered, in contrast to the uncomplexed cyclopentadienone. A further consequence is the higher electron density at the oxygen atom. As anticipated, we were able to protonate, to alkylate, and to acylate the oxygen center and to create the corresponding cobaltocenium salts in good yields (Scheme 3). The protonation,

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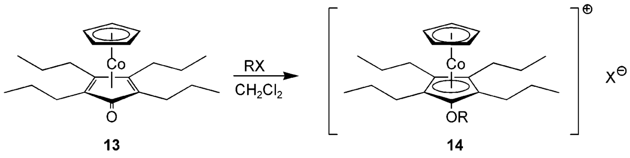
Scheme 3



R		Yield [%]
H	**14a**	>95
Et	**14b**	82
Ms	**14c**	76
Ts	**14d**	72
Tf	**14e**	85

the alkylation, and the acylation of the cyclopentadienone complex **13**[7] have been carried out with CF_3COOH,[8] $(Et_3O)BF_4$,[8] CH_3SO_2Cl,[8] $CH_3C_6H_4SO_2Cl$,[8] and $(CF_3SO_2)O$,[9] respectively, in methylene chloride.

By reacting **14e** with various C-nucleophiles such as MeLi, *n*-BuLi, and PhLi we observed a substitution in the unsubstituted Cp ring in yields between 40 and 80%.[10] Even the lithium salt of (trimethylsilyl)acetylene gave the corresponding alkyne derivative (Scheme 4). The yield of the ethynyl-substituted complex could be increased to 41% by using (triethylsilyl)acetylene,[11] followed by removal of the triethylsilyl group. The latter process is the simplest way of introducing an alkyne unit into the Cp ring. In the case of **15c** we were able to introduce a second *n*-butyl group in the β-position of the first one in 80% yield in two further steps: triflation and reaction with *n*-BuLi (Scheme 5).[11]

The nucleophile attacks the cyclopentadienyl ligand at the exo position. Elimination of the HSO_2CF_3 leads to the substituted cyclopentadienone complex **15**. The elimination of $SO_2CF_3^-$ was detected by mass spectrometry during the synthesis of **15c**.

This kind of nucleophilic attack at cyclopentadienyl ligands of alkoxy-substituted cobaltocenium salts, which were synthesized by alkylation of CpCo-cyclopentadienone complexes, was known, but the formation of the cyclopentadienone complex could not be observed.[12]

To check the net charges at the cyclopentadienyl ligands, we carried out density functional theory (DFT) calculations on the CpCo-capped cyclopentadienone complex and its O-protonated and O-triflated species.[13] A comparison between the net charges at the cyclopentadienyl ligands of the complexes **A**, **C**, and **D** (Chart 2 and Table 1) shows that the triflate group changes the charge distribution dramatically, which can be explained by interaction between the cyclopentadienyl and the cyclopentadienyloxy fragments, strictly speaking by a transfer of electron density from the Cp fragment to the cyclopentadienyloxy fragment. The charge at the Co

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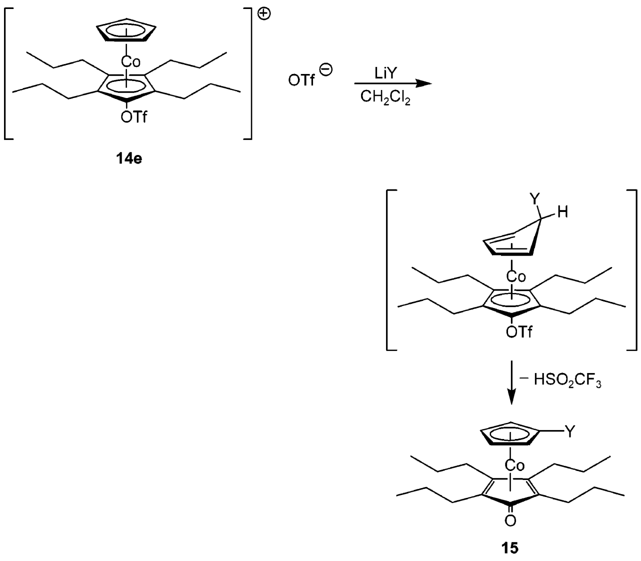
(7) Procedure for the CpCo-capped cyclopentadienone complex **13**: a solution of 6.1 g (34 mmol) of $CpCo(CO)_2$ in 150 mL of decalin was heated at 190 °C. During 8 h 3.3 g (30 mmol) of 4-octyne dissolved in 150 mL of decalin was added. When the addition was completed, the heating was continued for an additional 5 days. The reaction mixture was cooled to room temperature and then filtered through alumina (neutral, grade III). With petroleum ether as eluent the solvent decalin, unreacted $CpCo(CO)_2$, and the benzoic byproducts could be extracted. The cyclopentadienone complex was extracted with 50:1 CH_2Cl_2/MeOH as a broad orange band. After removal of the solvent the crude product was purified by column chromatography on alumina (neutral, grade III, 20:1 CH_2Cl_2/MeOH) to yield 3.01 g (54%) of **13**: Red solid. Mp: 113 °C. ^{1}H NMR (500 MHz, $CDCl_3$; δ/ppm): 0.96−1.00 (m, 12H, CH_3), 1.41−1.45 (m, 6H, CH_2), 1.67−1.68 (m, 2H, CH_2), 1.88−1.93 (m, 2H, CH_2), 2.25−2.49 (m, 6H, CH_2), 4.60 (s, 5H, Cp). ^{13}C NMR (125.76 MHz, $CDCl_3$; δ/ppm): 15.5 (CH_3), 15.6 (CH_3), 23.4 (CH_2), 25.2 (CH_2), 28.5 (CH_2), 29.1 (CH_2), 82.6 (C), 83.0 (Cp C), 92.9 (C), 158.7 (C═O). Exact MS: *m*/*z* calcd for $C_{22}H_{34}CoO$ [$M^+ + H$] 373.1941, found 373.1946. Anal. Calcd for $C_{22}H_{33}CoO$: C, 70.95; H, 8.93. Found: C, 70.84; H, 8.95.

(8) For analytical details see the Supporting Information.

(9) Procedure for the synthesis of the cobaltocenium salts **14e** and **16**: to a cooled (−50 °C) solution of 2.8 g (10.1 mmol) of trifluoromethanesulfonic anhydride in 70 mL of methylene chloride was added over a period of 15 min 2.5 g (6.7 mmol) of the cyclopentadienone complex dissolved in 20 mL of methylene chloride. The mixture was warmed slowly and stirred for 12 h at room temperature. After evaporation of the solvent 100 mL of ether was added. The precipitate was filtered and recrystallized from CH_2Cl_2/Et_2O. Data for **14e** are as follows. Yield: 85%. Yellow solid. Mp: 161 °C. ^{1}H NMR (300 MHz, CD_2Cl_2; δ/ppm): 1.05 (t, 6H, CH_3), 1.08 (t, 6H, CH_3), 1.43−1.62 (m, 8H, CH_2), 2.47−2.68 (m, 8H, CH_2), 5.54 (s, 5H, Cp). ^{13}C NMR (75.47 MHz, CD_2Cl_2; δ/ppm): 14.4 (CH_3), 14.7 (CH_3), 24.2 (CH_2), 25.2 (CH_2), 26.4 (CH_2), 27.7 (CH_2), 88.2 (Cp), 95.9 (C═C), 99.1 (C═C), 118.4 (C−OTf). Exact MS: *m*/*z* calcd for $[C_{23}H_{33}CoF_3O_3S]^+$ [M^+] 505.1434, found 505.1455. Anal. Calcd for $C_{24}H_{33}CoF_6O_6S_2$: C, 44.04; H, 5.08. Found: C, 44.21; H, 5.26. Data for **16** are as follows. Yield: 76%. Yellow solid. Mp: 146 °C. ^{1}H NMR (500 MHz, CD_2Cl_2; δ/ppm): 0.90 (t, 3H, CH_3), 1.06 (t, 6H, CH_3), 1.08 (t, 6H, CH_3), 1.30−1.37 (m, 2H, CH_2), 1.48−1.57 (m, 10H, CH_2), 2.25 (t, 2H, CH_2), 2.42−2.61 (m, 8H, CH_2), 5.23 (m, 2H, Cp-H), 5.46 (m, 2H, Cp-H). ^{13}C NMR (125 MHz, CD_2Cl_2, δ/ppm): 13.7 (CH_3), 14.4 (CH_3), 14.7 (CH_3), 22.5 (CH_2), 24.2 (CH_2), 25.2 (CH_2), 26.1 (CH_2), 26.3 (CH_2), 27.5 (CH_2), 32.5 (CH_2), 86.7 (Cp C), 88.0 (Cp C), 95.5 (C), 98.6 (C), 108.2 (Cp−CBu), 117.7 (C−OTf). Exact MS: *m*/*z* calcd for $[C_{27}H_{41}CoF_3O_3S]^+$ [M^+] 561.2060, found 561.2078. Anal. Calcd for $C_{28}H_{41}CoF_6O_6S_2$: C, 47.32,; H, 5.81. Found: C, 47.46; H, 5.83.

(10) Procedure for the RCpCo-capped cyclopentadienone complexes **15a**−**d** and **17**: a solution of 1.68 mmol of the lithium salt was slowly added to a solution of 1.53 mmol of the cobaltocenium salts of **14e** and of **16**, respectively, in 100 mL of THF at −30 °C. After the mixture was warmed overnight, the mixture was hydrolyzed with 30 mL of saturated NH_4Cl solution, the layers were separated, and the aqueous layer was washed three times with ether. After drying (Na_2SO_4) of the combined organic layers, the solvent was removed and the crude mixture was purified by column chromatography on silica gel with 30:1 CH_2Cl_2/MeOH. Data for **15a** are as follows. Yield: 77%. Red solid. Mp: 104 °C. ^{1}H NMR (500 MHz, CD_2Cl_2; δ/ppm): 0.97 (t, 6H, CH_3), 1.00 (t, 6H, CH_3), 1.31−1.49 (m, 6H, CH_2), 1.59−1.67 (m, 2H, CH_2), 1.83 (s, 3H, Cp−CH_3), 1.82−1.88 (m, 2H, CH_2), 2.23−2.29 (m, 2H, CH_2), 2.35−2.42 (m, 4H, CH_2), 4.32−4.33 (m, 2H, Cp H), 4.42−4.43 (m, 2H, Cp H). ^{13}C NMR (125.76 MHz, CD_2Cl_2; δ/ppm): 10.1 (Cp−CH_3), 14.9 (CH_3), 15.0 (CH_3), 23.0 (CH_2), 25.0 (CH_2), 27.8 (CH_2), 28.6 (CH_2), 81.8 (Cp C), 82.6 (Cp−CCH_3), 83.4 (Cp C), 92.1 (C), 95.5 (C), 156.2 (C═O). Exact MS: *m*/*z* calcd for $C_{23}H_{36}CoO$ [$M^+ + H$] 387.2098, found 387.2107. Anal. Calcd for $C_{23}H_{36}CoO$: C, 71.48; H, 9.13. Found: C, 71.35; H 9.02. Data for **15b** are as follows. Yield: 58%. Dark red solid. Mp: 156 °C. ^{1}H NMR (500 MHz, CD_2Cl_2; δ/ppm): 0.90 (t, 6H, CH_3), 0.91 (t, 6H, CH_3), 1.25−1.40 (m, 8H, CH_2), 1.55−1.67 (m, 4H, CH_2), 1.95−2.01 (m, 2H, CH_2), 2.08−2.15 (m, 2H, CH_2), 2.19−2.25 (m, 2H, CH_2), 4.76−4.77 (m, 2H, Cp H), 4.98−4.99 (m, 2H, Cp H), 7.28−7.31 (m, 1H, Ph H), 7.37−7.42 (m, 4H, Ph H). ^{13}C NMR (125.76 MHz, CD_2Cl_2; δ/ppm): 14.5 (CH_3), 14.6 (CH_3), 22.4 (CH_2), 24.3 (CH_2), 27.2 (CH_2), 27.7 (CH_2), 78.6 (Cp), 81.4 (C), 83.8 (Cp), 92.1 (C), 97.0 (C), 125.9 (Ph CH), 127.4 (Ph CH), 128.6 (Ph CH), 132.2 (C), 157.8 (C═O). Exact MS: *m*/*z* calcd for $C_{28}H_{38}CoO$ [$M^+ + H$] 449.2255, found 449.2280. Anal. Calcd for $C_{28}H_{37}CoO$: C, 74.98; H, 8.31. Found: C, 74.8; H, 8.31. Data for **15c** are as follows. Yield: 79%. Red solid. Mp: 81 °C. ^{1}H NMR (500 MHz, $CDCl_3$; δ/ppm): 0.77 (t, 3H, CH_3), 0.85 (t, 6H, CH_3), 0.88 (t, 6H, CH_3), 1.14−1.22 (m, 2H, CH_2), 1.24−1.38 (m, 8H, CH_2), 1.54−1.65 (m, 2H, CH_2), 1.70−1.76 (dt, 2H, CH_2), 2.06−2.16 (m, 4H, CH_2), 2.21−2.27 (m, 2H, CH_2), 2.30−2.36 (dt, 2H, CH_2), 4.24−4.25 (m, 2H, Cp H), 4.34−4.35 (m, 2H, Cp H). ^{13}C NMR (125.76 MHz, $CDCl_3$; δ/ppm): 14.0 (CH_3), 15.0 (CH_3), 15.1 (CH_3), 22.3 (CH_2), 22.8 (CH_2), 24.7 (CH_2), 25.7 (CH_2), 27.7 (CH_2), 28.4 (CH_2), 33.1 (CH_2), 81.8 (Cp C), 82.1 (Cp C), 91.6 (C), 100.4 (C), 156.4 (C═O). Exact MS: *m*/*z* calcd for $C_{26}H_{42}CoO$ [$M^+ + H$] 429.2567, found 429.2595. Anal. Calcd for $C_{26}H_{42}CoO$: C, 73.0; H, 9.43. Found: C, 72.8; H, 9.50. Data for **15d** are as follows. Yield: 65%. Red solid. Mp: 149 °C. ^{1}H NMR (500 MHz, CD_2Cl_2; δ/ppm): 0.97 (t, 6H, CH_3), 1.01 (t, 6H, CH_3), 1.23 (s, 9H, CH_3), 1.28−1.36 (m, 2H, CH_2), 1.40−1.48 (m, 4H, CH_2), 1.61−1.69 (m, 2H, CH_2), 1.88−1.94 (m, 2H, CH_2), 2.29−2.35 (m, 2H, CH_2), 2.43−2.54 (m, 4H, CH_2), 4.33 (m, 2H, Cp H), 4.50 (m, 2H, Cp H). ^{13}C NMR (125.76 MHz, CD_2Cl_2; δ/ppm): 14.9 (CH_3), 15.1 (CH_3), 23.0 (CH_2), 25.0 (CH_2), 28.4 (CH_2), 29.2 (CH_2), 30.6 (CH_3), 31.8 (C), 79.0 (CH), 81.9 (CH), 92.1 (C), 157.6 (C). Exact MS: *m*/*z* calcd for $C_{26}H_{42}CoO$ [$M^+ + H$] 429.2568, found 429.2547. Anal. Calcd for $C_{26}H_{42}CoO$: C, 72.87; H, 9.64. Found: C, 72.75; H, 9.62. Data for **17** are as follows. Yield: 82%. Red solid. Mp: 58 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ/ppm): 0.87 (t, 6H, CH_3), 0.95 (t, 6H, CH_3), 0.98 (t, 6H, CH_3), 1.22−1.46 (m, 14H, CH_2), 1.68−1.76 (m, 4H, CH_2), 2.09−2.41 (m, 10H, CH_2), 4.10 (m, 1H, Cp H), 4.18 (m, 2H, Cp H). ^{13}C NMR (75 MHz, $CDCl_3$, δ/ppm): 14.0 (CH_3), 15.0 (CH_3), 15.1 (CH_3), 22.4 (CH_2), 22.7 (CH_2), 24.6 (CH_2), 26.0 (CH_2), 27.4 (CH_2), 28.2 (CH_2), 33.1 (CH_2), 81.3 (Cp C), 81.7 (C), 81.8 (Cp C), 90.6 (C), 99.6 (C), 154.8 (C═O). Exact MS: *m*/*z* calcd for $C_{30}H_{50}CoO$ [$M^+ + H$] 485.3194, found 485.3168. Anal. Calcd for $C_{30}H_{49}CoO$: C, 74.35; H, 10.19. Found: C, 74.20; H, 9.93.

Scheme 4



Y		Yield [%]
Me	**15a**	77
Ph	**15b**	58
n-Bu	**15c**	79
t-Bu	**15d**	65
C≡CSiMe$_3$	**15e**	15
C≡CSiEt$_3$	**15f**	41

Scheme 5

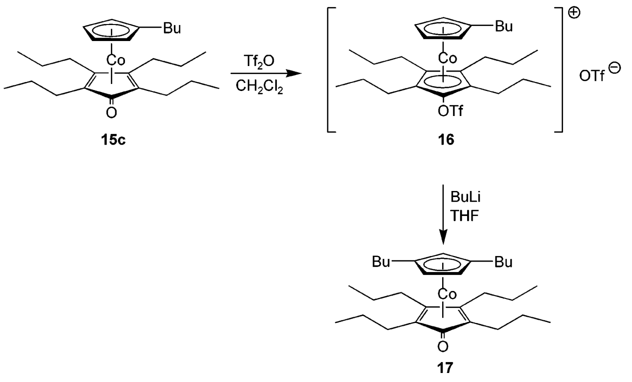


Chart 2

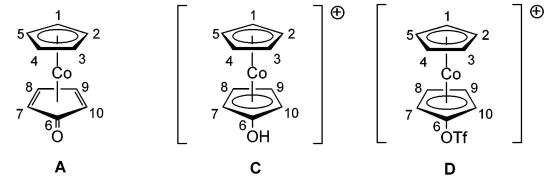


Table 1. Mulliken Net Charges Calculated for A, C, and D

	A	C	D
ΣC1−C5	−0.362	−0.023	+0.028
C6	+0.330	+0.255	+0.204
ΣC7−C10	−0.586	−0.133	−0.017
O	−0.371	−0.064	−0.486
Co	+0.989	+0.964	+0.964

atom remains nearly constant. In **A** the sum of the negative net charges at C1−C5 amounts to −0.362. For the cyclopentadienyl ligand in **C** these net charges sum up to −0.023. For the O-triflated species **D** the sum of the net charges shows even a value of +0.028. These theoretical investigations can be used to rationalize the nucleophilic substitution of Li-organyl species on cobaltocenium ions with subsequent elimination of the sulfinate anion ($SO_2CF_3^-$).

Acknowledgment. We are grateful to the Deutsche Forschungsgemeinschaft (Grant No. SFB 623), the Fonds der Chemischen Industrie, and the BASF Aktiengesellschaft, Ludwigshafen, Germany, for financial support.

Supporting Information Available: Text giving experimental details of the synthesis and characterization of **14a**−**d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[11] Procedure for the substituted complexes **15e**,**f**: 2.29 mmol of *n*-butyllithium (1.6 M solution) was slowly added to a solution of 3.06 mmol of (trialkylsilyl)acetylene in 60 mL of THF at −30 °C. After the mixture was stirred at this temperature for 90 min, a solution of 1.53 mmol of the cobaltocenium salt **14e** in 30 mL of THF was added over a period of 10 min. After it was warmed overnight and stirred further at room temperature for 48 h, the mixture was hydrolyzed with 30 mL of saturated NH_4Cl solution, the layers were separated, and the aqueous layer was washed three times with ether. After drying (Na_2SO_4) of the combined organic layers, the solvent was removed and the crude mixture was purified by column chromatography on silica with 30:1 CH_2Cl_2/MeOH. Data for **15e** are as follows. Yield: 15%. Dark red oil. ^1H NMR (500 MHz, $CDCl_3$; δ/ppm): 0.25 (s, 9H, $Si(CH_3)_3$), 0.96−1.04 (m, 12H, CH_3), 1.45−1.49 (m, 6H, CH_2), 1.63−1.65 (m, 2H, CH_2), 1.90−1.93 (m, 2H, CH_2), 2.27−2.43 (m, 6H, CH_2), 4.61 (m, 2H, Cp H), 4.73 (m, 2H, Cp H), ^{13}C NMR (75.47 MHz, $CDCl_3$; δ/ppm): 0.0 ($Si(CH_3)_3$), 15.0 (CH_3), 15.0 (CH_3), 22.9 (CH_2), 24.5 (CH_2), 27.5 (CH_2), 27.5 (CH_2), 77.5 (C), 78.8 (C), 84.5 (Cp C), 85.2 (Cp C), 92.9 (C), 94.7 (C), 99.1 (C), 158.6 (C=O). Exact MS: *m*/*z* calcd for $C_{27}H_{42}CoOSi$ [$M^+ + H$] 469.2337, found 469.2339. Data for **15f** are as follows. Yield: 41%. Dark red oil. ^1H NMR (500 MHz, CD_2Cl_2; δ/ppm): 0.87 (q, 6H, $SiCH_2$), 1.15 (t, 9H, $SiCH_2CH_3$), 1.20 (t, 6H, CH_3), 1.24 (t, 6H, CH_3), 1.56−1.70 (m, 6H, CH_2), 1.78−1.87 (m, 2H, CH_2), 2.08−2.14 (m, 2H, CH_2), 2.45−2.52 (m, 2H, CH_2), 2.56−2.64 (m, 4H, CH_2), 4.85−4.86 (m, 2H, Cp H), 4.92−4.93 (m, 2H, Cp H). ^{13}C NMR (125.76, CD_2Cl_2; δ/ppm): 4.7 ($SiCH_2CH_3$), 7.7 ($SiCH_2$), 14.9 (CH_3), 15.0 (CH_3), 22.9 (CH_2), 24.6 (CH_2), 27.5 (CH_2), 27.6 (CH_2), 79.1 (C), 82.3 (C), 84.5 (Cp C), 85.2 (Cp C), 92.3 (C), 92.9 (C), 100.2 (C), 158.9 (C=O). Exact MS: *m*/*z* calcd for $C_{30}H_{47}CoOSi$ [$M^+ + H$] 511.2806, found 511.2823. Anal. Calcd for $C_{30}H_{47}CoOSi$: C, 70.55; H, 9.28. Found: C, 70.49; H, 9.30.

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