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A simple route to (tetraethynylcyclobutadiene)cyclopentadienylcobalt

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Abstract

Reaction of 2-(trimethylsilylethynyl)-1,3-dioxane with $CpCo(CO)_2$ followed by reaction with Me_4NF in and NaH furnishes 1,2- and [1,3-bis[2-dioxanyl]cyclobutadienecyclopentadienylcobalt in an overall combined yield of 95% in a 3.5:1 ratio. Metalation of the 1,2-complex or the 1,3-complex by BuLi is followed by formylation. Transformation of the resulting aldehyde into an alkyne by $CH_3C{=}O(C{=}N_2)P{=}O(OEt)_2$ and repetition of the reaction sequence furnishes the 1,2-diethynyl- or [1,3-diethynyl(2-dioxanyl)cyclobutadiene]cyclopentadienylcobalt. Deketalization and subsequent Ohira reaction transforms these precursors into a host of different tetraethynylated CpCo-stabilized cyclobutadienes. The synthetic method is solution-phase based and circumvents the cumbersome flash-vacuum pyrolysis step hitherto necessary for the preparation of tetraethynylated CpCo-stabilized cyclobutadiene complexes. © 2002 Published by Elsevier Science B.V.

Keywords: Cyclobutadiene complexes; Alkynes; Ohira-alkynylation

1. Introduction

Alkynylated and functionalized cyclobutadiene complexes are fascinating modules that allow the construction of increasingly complex organometallic architectures and materials such as **A**–**C**, (Fig. 1) as we and others have demonstrated [1–4]. While both (tetraethynylcyclobutadiene)cyclopentadienyl cobalt (**1**) [2] and (tetraethynylcyclobutadiene)tricarbonyliron (**2**) [3] have been reported, their synthesis is not facile, but for different reasons. While the bottleneck in the preparation of **2** is the use of expensive cyclooctatetraene in the first transformation, the last step in the synthesis of **1** is a flash vacuum pyrolysis that restricts the amount of **1b** that can be obtained to ca. 20–50 mg per day. In addition this approach invariably produces the *ortho*–*ortho* substituent pattern displayed in **1b**, while the *para*–*para* pattern **1c** cannot be realized utilizing hitherto published methods (Fig. 2).

Herein, we report an effective and flexible wet-chemical method for the synthesis of **1a** and **1b** [1c]. The synthetic approach is based upon the consecutive introduction of aldehyde groups onto the cyclobutadiene nucleus and their effective transformation into alkynes by the Ohira protocol utilizing the Seyferth–Gilbert reagent [5].

2. Results and discussion

The synthetic sequence commences with the preparation of **3** that is obtained by metalation, formylation, and subsequent acetalization of commercially available 2-trimethylsilylacetylene [6]. The alkyne **3** reacts smoothly with $CpCo(CO)_2$ to furnish *ortho* and *para*-**4a**,**b** in a combined yield of 95%. Removal of the trimethylsilyl groups from the cyclobutadiene nuclei by tetramethylammonium fluoride in DMSO with sodium hydride (Scheme 1) furnishes *ortho* and *para*-**5a** and **5b**. The combined yield of **5a** and **5b** exceeds 95% and are available on a 20-g-scale.

Metalation of **5a**,**b** with BuLi in THF followed by workup with *N*,*N*-dimethylformamide results in the isolation of the aldehydes **6a**,**b** even though in the case of **5a** formation of aldehyde **7** is consistently observed (Scheme 2). The competing metalation of the five-membered ring seems to be an unavoidable side reaction for **5a** but not for **5b**.

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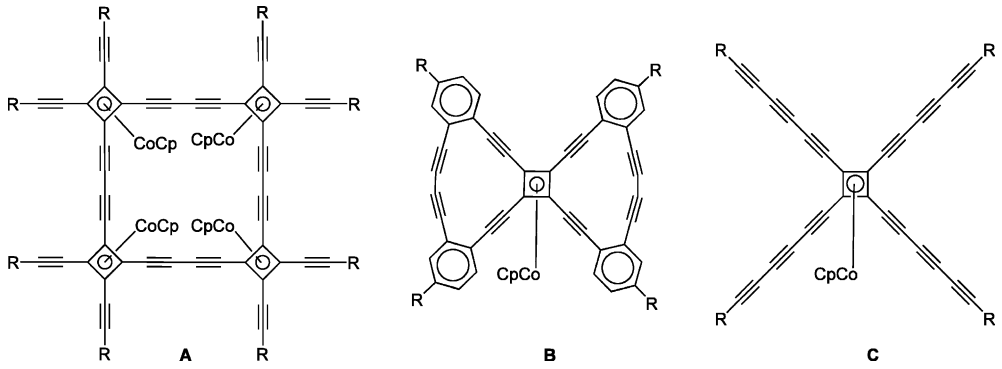


Fig. 1.

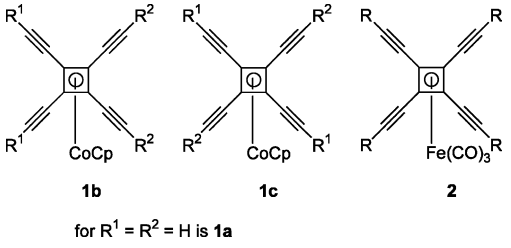


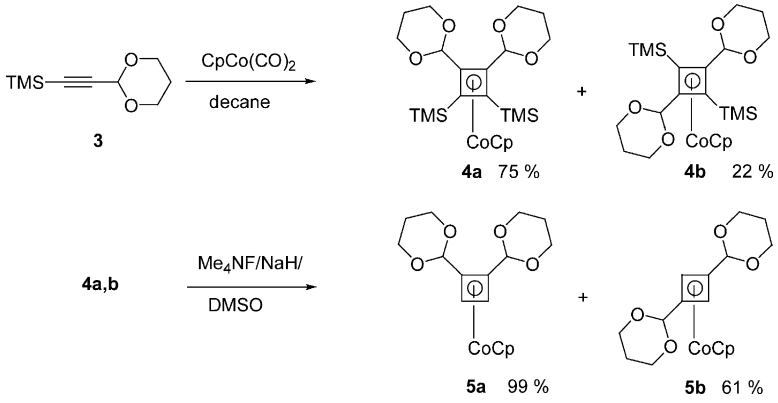
Fig. 2.

Ohira alkynylation of **6a**,**b** with phosphonate **8** followed by silylation of the alkyne leads to **10a**,**b** in high yield (Scheme 3). Attempts to metalate **10a** with BuLi led to a high percentage of deprotonation of the cyclopentadienyl ring. However, lithium diisopropylamide (LDA) selectively removed a proton from the four membered ring. Workup with *N*,*N*-dimethylformamide gave **11a** selectively in a 56% yield. In the case of **10b** metalation with BuLi gives only the desired product **11b** after reaction with DMF. The significantly increased acidity of the four-membered ring in **10a** must be attributed to the presence of the electron-withdrawing alkyne in combination with the *ortho*-chelating effect of the acetal unit [7]. The alkyne seems to play a critical role in the activation towards metalation of the cyclobutadiene nucleus. Attempts to metalate **5** with LDA, however, were unsuccessful and show that the presence of an alkyne is necessary to increase the acidity sufficiently.

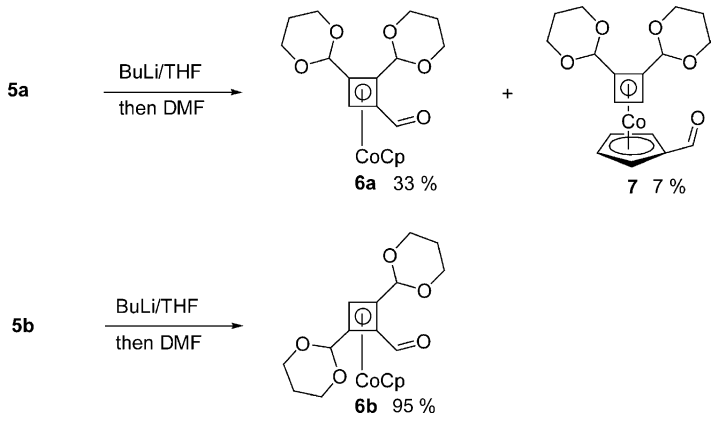
The aldehydes **11a**,**b** are transformed into **13a**,**b** by the Ohira method in 85 and 66% yields, respectively (Scheme 4). Crystallization of **13b** from CH_2Cl_2 afforded yellow–orange, plate-shaped specimen suitable for X-ray structure analysis (Fig. 3). The alkyne groups are nearly planar with respect to the cyclobutadiene segment of the structure and bond lengths and angles are in excellent agreement with literature values [2a,3b].

Desilylation followed by deprotection of the acetal group in **11a** gives **12** (Scheme 5) in a 76% yield. The trialdehyde **12** is unstable and turned dark after several hours at 0° even under exclusion of light. Similarly, deprotection of **13a** furnishes **14a** in acceptable yields. This dialdehyde (**14**) can be handled without any precautions and is stable for several days in air at room temperature.

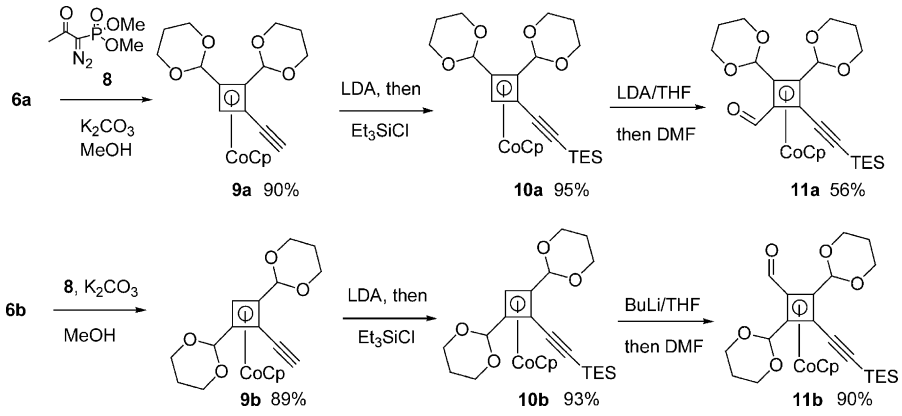
Metalation of the terminal alkynes of **13a** with LDA followed by a copper based Cadiot–Chodkiewicz coupling and workup with 1-bromo-2-triisopropylsilylacetylene in propylamine furnished **15** in good yields (Scheme 6). Deprotection of **15** is facile and followed by the Ohira reaction to give **16**. Polyyne **16** is a nice example of a butadiynylated cyclobutadiene complex that could be useful for further elaboration into organometallic nano-archictures.



Scheme 1.

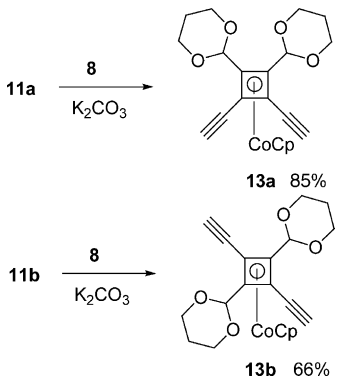


Scheme 2.



Scheme 3.

By utilizing the Sonogashira coupling of **13b** with 4-iodo-*tert*-butylbenzene **17** (Scheme 7) is obtained. Deprotection of **17** followed by the Ohira reaction gives **18**, the first reported tetraethynylcyclobutadiene complex with a pairwise *para* substitutent pattern. Crystallization of **18** from CH_2Cl_2 led to a coffin-shaped specimen, which was used for single crystal X-ray structure determination (Fig. 4). All four alkyne units are bent away from the Cp-Co unit. This is a feature generally observed for tetraethynylated cyclobutadiene complexes and has been attributed to electronic effects; bond lengths and bond angles are in excellent agreement with literature values [2a,3b].



Scheme 4.

3. Conclusions

We have developed a solution-phase synthesis of tetraethynylated CpCo-stabilized cyclobutadiene complexes starting from the dioxane-substituted organometallic substrates **5a** and **5b**. And while a solution-phase synthesis of **1a** was the primary goal of this project, the facile access to **14**, and its surprising stability, may

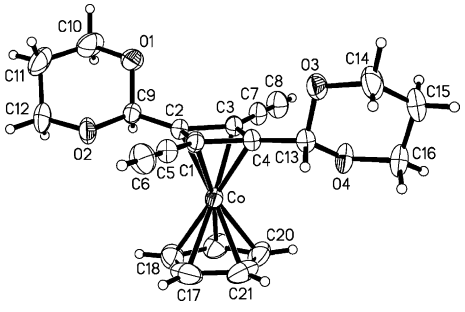
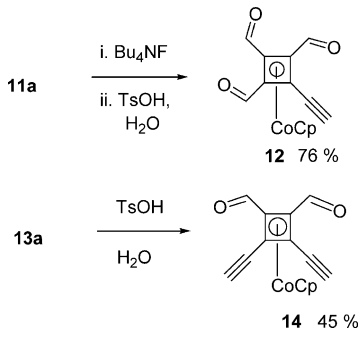


Fig. 3. ORTEP-view of **13b**.



Scheme 5.

actually turn out to be more valuable. Diacetals **13** and aldehyde **14** can be utilized as a synthon for **1** that not only will allow the preparation of novel tetraethynylated cyclobutadiene complexes, but as well may serve as precursor for cyclobutadieno-fused heterocycles, alkynylated cyclobutadiene dicarboxylic acids, and mixed alkynyl–vinyl-substituted cyclobutadiene complexes, upon which we will report in due course.

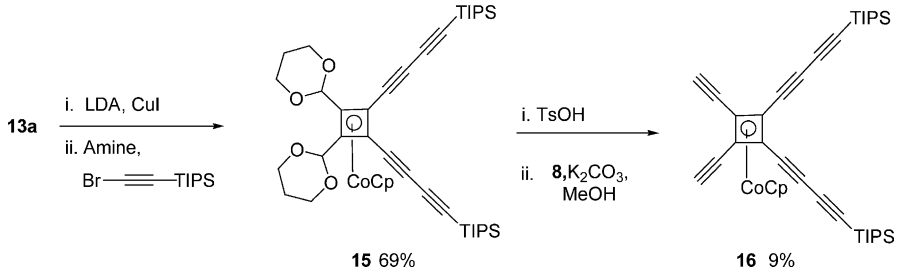
4. Experimental

4.1. General

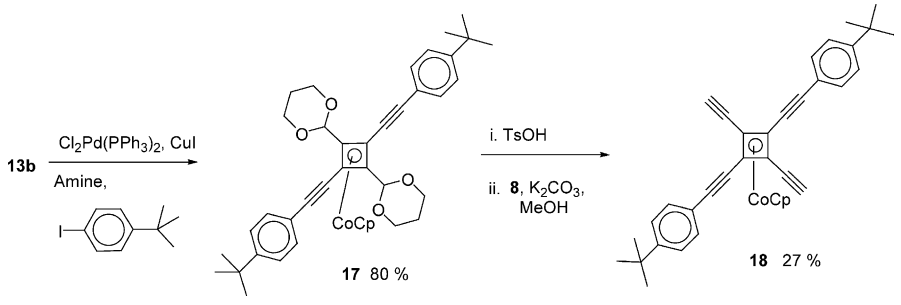
THF was freshly distilled from potassium and benzophenone. All other reagents were of commercial grade and used as obtained. Trimethylsilylacetylene was purchased from Strem Chemicals. Sodium hydride, tetramethylammoniumfluoride, DMF and BuLi were purchased from Sigma–Aldrich. ^{1}H- and ^{13}C-NMR spectra were recorded in $CDCl_3$ on a Bruker AM 300 or a Varian Mercury 400 spectrometer. The mass spectra were measured on a VG 70SQ. IR spectra were obtained using a Perkin–Elmer FTIR 1600 on NaCl plates. X-ray structure analysis of all were measured at 293 K using a Bruker SMART APEX CCD-based diffractometer system equipped with a Mo target X-ray tube.

4.2. Synthesis of *4*

Trimethylsilylethynyl-1,3-dioxane [6], **3** (18.3 g, 99.5 mmol) and $CpCo(CO)_2$ (8.82 g, 49.0 mmol) are dissolved in 250 ml of decane and refluxed for 4 h. A constant flow of nitrogen is bubbled through the solution. Following removal of the solvent by distillation (10^{-1} Torr, 40 °C) the residue is redissolved in hexanes and doubly chromatoghraphed on Celite–silica gel to furnish **4a** (17.0 g, 75%) and **4b** (4.49 g, 20%) as yellow crystalline solids. **4a**: M.p.: 110 °C. IR (cm^{-1}): ν 2958, 2838, 1241, 1093, 1003, 839. ^{1}H-NMR ($CDCl_3$): δ 5.00 (s, 2H, CH acetal), 4.86 (s, 5H, Cp–H), 4.10–4.03 (m, 2H, CH_2 acetal), 3.71 (t, $^{3}J(H,H) = 12.08$ Hz, 2H, CH_2 acetal), 2.03–1.93 (m, 1H, CH_2 acetal), 1.25–1.21 (m, 1H, CH_2 acetal). ^{13}C-NMR ($CDCl_3$): δ 99.59 (acetal-C), 84.66 (Cb–C), 79.79 (Cp–C), 66.92, 66.69 (acetal-C), 64.72 (Cb–C), 25.81 (acetal-C), 1.09 (Me_4Si–C). UV–vis ($CHCl_3$): λ 278 ($\varepsilon = 5503$ cm^{-1} M^{-1}). MS (EI) m/z Calc. for $[M]^+$ ($C_{23}H_{37}CoO_4Si_2$) 492.1562, Found: 492.1562 ($E = 0.0$ ppm). **4b**: M.p.: 95 °C. IR (cm^{-1}): ν 2957, 2846, 1239, 1105, 1000, 838. ^{1}H-NMR ($CDCl_3$): δ 4.81 (s, 5H, Cp–H), 4.79 (s, 2H, CH acetal), 4.01–3.96 (m, 2H, CH_2 acetal), 3.64 (t, $^{3}J(H,H) = 12.35$



Scheme 6.



Scheme 7.

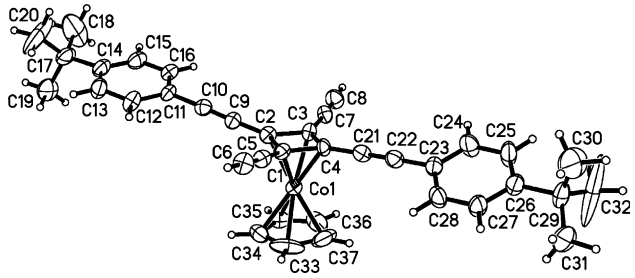


Fig. 4. ORTEP-view of **18**.

Hz, 2H, CH_2 acetal), 1.94–1.90 (m, 1H, CH_2 acetal), 1.22–1.17 (m, 1H, CH_2 acetal). ^{13}C-NMR ($CDCl_3$): δ 100.06 (acetal-C), 84.36 (Cb–C), 79.71 (Cp–C), 66.59 (acetal-C), 66.66 (Cb–C), 25.83 (acetal-C), 0.58 (Me_4Si–C). UV–vis ($CHCl_3$): λ 276 ($\varepsilon = 13656\ cm^{-1}\ M^{-1}$). MS (EI) *m/z* Calc. for $[M]^+$ ($C_{23}H_{37}CoO_4Si_2$) 492.1562, Found: 492.1560 ($E = 0.3$ ppm).

4.3. Synthesis of **5**

Compound **4a** or **4b** (10.0 g, 20.3 mmol), NaH (0.200 g, 8.33 mmol) and Me_4NF (15.0 g, 161 mmol) are placed in a 250 ml oven-dried Schlenk flask and dissolved in 50 ml of dry Me_2SO under an inert atmosphere. The solution is heated to 50 °C overnight. Aqueous workup with ethyl ether followed by chromatography on silica gel (SiO_2; hexanes–ethyl acetate (1:1) to yield **5a** (6.92 g, 99%) as a yellow–brown crystalline solid or **5b** (6.78 g, 97%) as a light yellow powder. **5a**: M.p.: 115 °C. IR (cm^{-1}): ν 2961, 2847, 1517, 1439, 1236, 1097, 990. ^{1}H-NMR ($CDCl_3$): δ 4.97 (s, 2H, CH acetal), 4.93 (s, 5H, Cp–H), 4.08–4.04 (m, 2H, CH_2 acetal), 3.88 (s, 2H, Cb–H), 3.71 (q, $^3J(H,H) = 10.43$ Hz, 2H, CH_2 acetal), 2.08–1.95 (m, 2H, CH_2 acetal), 1.29–1.21 (m, 2H, CH_2 acetal). ^{13}C-NMR ($CDCl_3$): δ 98.65 (acetal-C), 80.23 (Cb–C), 79.79 (Cp–C), 67.10 (Cb–C), 66.95, 66.92 (acetal-C), 25.86 (acetal-C). UV–vis ($CHCl_3$): λ 264 ($\varepsilon = 11539\ cm^{-1}\ M^{-1}$). MS (EI) *m/z* Calc. for $[M]^+$ ($C_{17}H_{21}CoO_4$) 348.0772, Found: 348.0775 ($E = 1.2$ ppm). **5b**: M.p.: 160 °C. IR (cm^{-1}): ν 2959, 2848, 1517, 1439, 1097, 988. ^{1}H-NMR ($CDCl_3$): δ 4.96 (s, 5H, Cp–H), 4.89 (s, 2H, CH acetal), 4.10–4.05 (m, 2H, CH_2 acetal), 4.08 (s, 2H, Cb–H), 3.79–3.70 (m, 2H, CH_2 acetal), 2.09–1.96 (m, 2H, CH_2 acetal), 1.53–1.28 (m, 2H, CH_2 acetal). ^{13}C-NMR ($CDCl_3$): δ 98.58 (acetal-C), 79.79 (Cp–C), 79.67 (Cb–C), 73.47 (Cb–C), 66.83, 54.53, 25.70 (acetal-C). UV–vis ($CHCl_3$): λ 263 ($\varepsilon =$ 9631 $cm^{-1}\ M^{-1}$). MS (EI) *m/z* Calc. for $[M]^+$ ($C_{17}H_{21}CoO_4$) 348.0772, Found: 348.0777 ($E = 1.0$ ppm).

4.4. Synthesis of **6**, **7**

Compound **5a** or **5b** (12.6 g, 36.2 mmol) is placed in an oven-dried 500 ml Schlenk flask and dissolved in 200 ml of absorbate. THF under an inert atmosphere. The solution is cooled to −78 °C and BuLi (26.1 ml, 1.54 M) is added dropwise. After 20 min, the temperature is increased to −10 °C for 1 h. To this solution is added 4.25 ml (54.7 mmol) of dry DMF after cooling the reaction to −78 °C. Upon warming to ambient temperature and quenching with brine, the reaction mixture takes on a deep red color. The water layer is separated and washed with 50 ml of hexanes. The combined organic layers are dried over magnesium sulfate and the solvent is removed in vacuo. Column chromatography (SiO_2; hexanes–CH_2Cl_2 3:1 + 10% NEt_3) furnishes **6a** (4.50 g, 33%) as a red–orange crystalline solid, **7** (0.915 g, 7%) as a red oil or **6b** (12.9 g, 95%) as a deep red oil. **6a**: M.p.: 125 °C. IR (cm^{-1}): ν 2962, 2923, 2846, 1654, 1100, 1000. ^{1}H-NMR ($CDCl_3$): δ 9.71 (s, 1H, ald-H), 5.25 (s, 1H, CH acetal), 5.01 (s, 5H, Cp–H), 4.96 (s, 1H, Cb–H), 4.68 (s, 1H, CH acetal), 4.13–4.07 (m, 2H, CH_2 acetal), 3.88–3.74 (m, 2H, CH_2 acetal), 2.10–2.03 (m, 1H, CH_2 acetal), 1.36–1.24 (m, 1H, CH_2 acetal). ^{13}C-NMR ($CDCl_3$): δ 192.53 (ald-C), 97.83, 96.86 (acetal-C), 80.56 (Cp–C), 79.80, 78.16 (Cb–C), 66.74, 66.63 (acetal-C), 63.23, 55.85 (Cb–C), 25.52 (acetal-C). UV–vis ($CHCl_3$): λ 256 ($\varepsilon = 14513\ cm^{-1}\ M^{-1}$), 280 ($\varepsilon =$ 9157 $cm^{-1}\ M^{-1}$), 332 ($\varepsilon = 4395\ cm^{-1}\ M^{-1}$). MS (EI) *m/z* Calc. for $[M]^+$ ($C_{18}H_{21}CoO_5$) 376.0721, Found: 376.0710 ($E = 2.9$ ppm). **6b**: IR (cm^{-1}): ν 2963, 2921, 2846, 1654, 1100, 999. ^{1}H-NMR ($CDCl_3$): δ 9.71 (s, 1H, ald-H), 5.26 (s, 1H, Cb–H), 5.20 (s, 1H, CH acetal), 5.00 (s, 5H, Cp–H), 4.35 (s, 1H, CH acetal), 4.13–4.06 (m, 2H, CH_2 acetal), 3.87–3.78 (m, 2H, CH_2 acetal), 2.12–2.00 (m, 1H, CH_2 acetal), 1.35–1.30 (m, 1H, CH_2 acetal). ^{13}C-NMR ($CDCl_3$): δ 191.98 (ald-C), 97.15 (acetal-C), 80.36 (Cp–C), 77.52 (Cb–C), 66.53 (acetal-C), 63.81, 60.26 (Cb–C), 25.29 (acetal-C). UV–vis ($CHCl_3$): λ 242 ($\varepsilon = 2934\ cm^{-1}\ M^{-1}$), 281 ($\varepsilon = 1020$ $cm^{-1}\ M^{-1}$), 331 ($\varepsilon = 316\ cm^{-1}\ M^{-1}$). MS (EI) *m/z* Calc. for $[M]^+$ ($C_{18}H_{21}CoO_5$) 376.0721, Found: 376.0708 ($E = 2.7$ ppm). **7**: IR (cm^{-1}): ν 2962, 2923, 2846, 1654, 1100, 1000. ^{1}H-NMR ($CDCl_3$): δ 9.80 (s, 1H, ald-H), 5.50 (d, $^3J(H,H) = 2.20$ Hz, 2H, Cp–H), 5.23 (t, $^3J(H,H) = 2.20$ Hz, 2H, Cp–H), 4.88 (s, 2H, CH acetal), 4.06 (s, 1H, Cb–H), 4.10–4.04 (s, 2H, CH acetal), 3.84–3.71 (m, 4H, CH_2 acetal), 2.25–1.97 (m, 2H, CH_2 acetal), 1.32–1.12 (m, 2H, CH_2 acetal). ^{13}C-NMR ($CDCl_3$): δ 191.75 (ald-C), 97.51 (acetal-C), 84.04 (Cb–C), 81.59 (Cp–C), 66.93 (Cp–C), 57.27 (Cb–C), 29.67, 25.74 (acetal-C). UV–vis ($CHCl_3$): λ 268 ($\varepsilon =$ 5413 $cm^{-1}\ M^{-1}$). MS (EI) *m/z* Calc. for $[M]^+$ ($C_{18}H_{21}CoO_5$) 376.0721, Found: 376.0720 ($E = 0.2$ ppm).

4.5. Synthesis of **9**

Compound **6a** or **6b** (1.91 g, 5.08 mmol) is placed in a 100 ml round bottom flask and dissolved in 50 ml of

MeOH. The solution is cooled to 0 °C and diethyl-(1-diazo-2-oxopropyl)phosphonate (2.81 g, 12.8 mmol) and K_2CO_3 (1.76 g, 12.8 mmol) are added successively. The reaction mixture is stirred for 24 h and allowed to warm to ambient temperature. Partitioning between saturated aq. $NaHCO_3$ and CH_2Cl_2 leads after chromatography on silica gel (SiO_2; hexanes–CH_2Cl_2 3:1 + 10% NEt_3) to **9a** (1.70 g, 90%) as a yellow crystalline solid or **9b** (1.68 g, 89%) as a yellow oil. **9a**: M.p.: 98 °C. IR (cm^{-1}): ν 2961, 2838, 2092, 1237, 1097, 1002, 807. ^{1}H-NMR ($CDCl_3$): δ 5.28 (s, 1H, Cb–H), 5.13 (s, 1H, CH acetal), 4.98 (s, 5H, Cp–H), 4.31 (s, 1H, CH acetal), 4.18–4.04 (m, 2H, CH_2 acetal), 3.87–3.60 (m, 2H, CH_2 acetal), 3.01 (alkyne-H), 2.15–1.97 (m, 1H, CH_2 acetal), 1.36–1.25 (m, 1H, CH_2 acetal). ^{13}C-NMR ($CDCl_3$): δ 98.22, 97.90 (acetal-C), 81.11 (Cp–C), 80.30 (Cb–C), 78.17 (alkyne-C), 74.04 (Cb–C), 66.92, 66.87 (acetal-C), 63.54, 63.45 (Cb–C), 57.82 (alkyne-C), 25.82, 25.67 (acetal-C). UV–vis ($CHCl_3$): λ 278 ($\varepsilon = 26214$ cm^{-1} M^{-1}), 318 ($\varepsilon = 4677$ cm^{-1} M^{-1}). MS (EI) m/z Calc. for $[M]^+$ ($C_{19}H_{21}CoO_4$) 372.0772, Found: 372.0760 (E = 3.2 ppm). **9b**: IR (cm^{-1}): ν 2960, 2840, 2092, 1237, 1097, 1001, 809. ^{1}H-NMR ($CDCl_3$): δ 5.03 (s, 1H, CH acetal), 4.97 (s, 5H, Cp–H), 4.15–4.06 (m, 2H, CH_2 acetal), 3.99 (s, 1H, Cb–H), 3.84–3.73 (m, 2H, CH_2 acetal), 3.07 (alkyne-H), 2.07–1.99 (m, 1H, CH_2 acetal), 1.34–1.22 (m, 1H, CH_2 acetal). ^{13}C-NMR ($CDCl_3$): δ 97.47 (acetal-C), 80.68 (Cp–C), 79.88 (alkyne-C), 79.24, 78.70 (Cb–C), 75.76 (alkyne-C), 66.47, 66.48 (acetal-C), 63.54, 63.45 (Cb–C), 25.30 (acetal-C). UV–vis ($CHCl_3$): λ 278 ($\varepsilon = 1869$ cm^{-1} M^{-1}), 319 ($\varepsilon = 325$ cm^{-1} M^{-1}). MS (EI) m/z Calc. for $[M]^+$ ($C_{19}H_{21}CoO_4$) 372.0772, Found: 372.0765 ($E = 2.7$ ppm).

4.6. Synthesis of *10*

Compound **9a** or **9b** (0.100 g, 0.260 mmol) is placed in a 50 ml oven-dried Schlenk flask and dissolved in 20 ml of absolute THF under an inert atmosphere. The solution is cooled to −78 °C and LDA (0.031 g, 0.32 mmol) in THF is added dropwise. After 20 min the temperature is increased to −10 °C for 1 h. To this solution is added triethylchlorosilane (0.05 ml, 0.30 mmol) upon cooling the reaction to −78 °C. The reaction mixture is warmed to ambient temperature and quenched with water. The water layer is separated and washed with 50 ml of ethyl ether, after which the combined organic layers are dried over magnesium sulfate and the solvent removed in vacuo. Filtration through a silica plug with (SiO_2; hexanes–CH_2Cl_2, 1:1) furnishes **10a** (125 mg, 95%) as red–orange oily solid or **10b** (123 mg, 93%) as red oil. **10a**: IR (cm^{-1}): ν 2955, 2869, 2846, 2130, 1238, 1101, 1003, 807. ^{1}H-NMR ($CDCl_3$): δ 5.14 (s, 1H, Cb–H), 4.99 (s, 1H, CH acetal), 4.95 (s, 5H, Cp–H), 4.31 (s, 1H, CH acetal), 4.15–4.05 (m, 2H, CH_2 acetal), 3.85–3.70 (m, 2H, CH_2 acetal), 2.07–1.99 (m, 1H, CH_2 acetal), 1.42–1.25 (m, 1H, CH_2 acetal), 1.01–0.88 (m, 6H, silyl-CH_2), 0.63–0.50 (m, 9H, silyl-CH_3). ^{13}C-NMR ($CDCl_3$): δ 103.02 (alkyne-C), 98.22, 98.06 (acetal-C), 93.55 (Cb–C), 81.19 (Cp–C), 74.29 (Cb–C), 66.87, 66.59 (acetal-C), 57.98 (alkyne-C), 25.88, 25.69 (acetal-C), 7.39, 6.51 (silyl-C). UV–vis ($CHCl_3$): λ 296 ($\varepsilon = 21169$ cm^{-1} M^{-1}). MS (EI) m/z Calc. for $[M]^+$ ($C_{25}H_{35}CoO_4Si$) 486.1637, Found: 486.1627 ($E = 2.1$ ppm). **10b**: IR (cm^{-1}): ν 2957, 2869, 2846, 2130, 1238, 1108, 1003, 807. ^{1}H-NMR ($CDCl_3$): δ 5.04 (s, 1H, CH acetal), 4.93 (s, 5H, Cp–H), 4.14–4.00 (m, 2H, CH_2 acetal), 4.01 (s, 1H, Cb–H), 3.85–3.72 (m, 2H, CH_2 acetal), 2.06–1.97 (m, 1H, CH_2 acetal), 1.41–1.30 (m, 1H, CH_2 acetal), 1.02–0.83 (m, 6H, silyl-CH_2), 0.70–0.48 (m, 9H, silyl-CH_3). ^{13}C-NMR ($CDCl_3$): δ 102.05 (alkyne-C), 97.88 (acetal-C), 94.09 (Cb–C), 81.03 (Cp–C), 76.31 (Cb–C), 66.59, 66.75 (acetal-C), 54.59 (alkyne-C), 25.60 (acetal-C), 7.26, 4.28 (silyl-C). MS (EI) m/z Calc. for $[M]^+$ ($C_{25}H_{35}CoO_4Si$) 486.1637, Found: 486.1634 ($E = 0.6$ ppm).

4.7. Synthesis of *11a*

Compound **10a** (0.113 g, 0.260 mmol) is placed in a 50 ml oven-dried Schlenk flask and dissolved in 25 ml of absolute THF under an inert atmosphere. The solution is cooled to −78 °C and LDA (0.030 g, 0.32 mmol) in THF added dropwise. After 20 min the temperature is increased to −10 °C for 1 h. To this solution is added 0.030 ml (0.39 mmol) of dry DMF after cooling the reaction to −78 °C. The reaction mixture is warmed to ambient temperature and quenched with brine at which time the mixture turned deep red. The water layer is separated and washed with 50 ml hexanes. The combined organic layers are dried over magnesium sulfate and the solvent removed in vacuo. Column chromatography (SiO_2; hexanes–CH_2Cl_2 2:1 + 10% NEt_3) furnishes **11a** (66 mg, 56%) as a red oil. IR (cm^{-1}): ν 2953, 2915, 2861, 2139, 1653, 1100, 1007. ^{1}H-NMR ($CDCl_3$): δ 9.82 (s, 1H, ald-H), 5.22, 5.16 (s, 2H, CH acetal), 4.98 (s, 5H, Cp–H), 4.13–4.07 (m, 2H, CH_2 acetal), 3.82–3.75 (m, 2H, CH_2 acetal), 2.05–1.98 (m, 1H, CH_2 acetal), 1.37–1.24 (m, 1H, CH_2 acetal), 0.98 (t, 6H, ^3J(H,H) = 7.88 Hz, silyl-CH_2), 0.58 (q, 9H, ^3J(H,H) = 7.88 Hz, silyl-CH_3). ^{13}C-NMR ($CDCl_3$): δ 191.67 (ald-C), 100.23 (alkyne-C), 97.86, 97.19 (acetal-C), 93.55 (Cb–C), 82.24 (Cp–C), 80.97 (alkyne-C), 77.60, 66.69 (Cb–C), 66.70, 66.76 (acetal-C), 25.26 (alkyne-C), 25.83, 25.78 (acetal-C), 7.46, 4.37 (silyl-C). UV–vis ($CHCl_3$): λ 265 ($\varepsilon = 10590$ cm^{-1} M^{-1}), 302 ($\varepsilon = 10654$ cm^{-1} M^{-1}), 341 ($\varepsilon = 2969$ cm^{-1} M^{-1}). MS (EI) m/z Calc. for $[M]^+$ ($C_{26}H_{35}CoO_5Si$) 514.1586, Found: 514.1598 ($E = 2.3$ ppm).

4.8. Synthesis of **11b**

Compound **10b** (0.314 g, 0.640 mmol) is placed in a 100 ml oven-dried Schlenk flask and dissolved in 50 ml of absolute THF under an inert atmosphere. The solution is cooled to −78 °C and BuLi (0.55 ml, 1.30 mol dm^{-3}) is added dropwise. After 20 min the temperature is increased to −10 °C for 1 h. To this solution is added 0.080 ml (0.98 mmol) of dry DMF after cooling the reaction to −78 ° C. Upon warming to ambient temperature and quenching with brine, the reaction mixture takes on a deep red color. The water layer is separated and washed with 50 ml hexanes. The combined organic layers are dried over magnesium sulfate and the solvent removed in vacuo. Column chromatography (SiO_2; hexanes–CH_2Cl_2 4:1 + 10% NEt_3) furnishes **11b** (0.288 g, 90%) as a red–orange oil. IR (cm^{-1}): ν 2953, 2917, 2863, 2136, 1653, 1100, 1003. ^{1}H-NMR ($CDCl_3$): δ 9.70 (s, 1H, ald-H), 5.29 (s, 2H, CH acetal), 4.97 (s, 5H, Cp–H), 4.15–4.09 (m, 2H, CH_2 acetal), 3.88–3.79 (m, 2H, CH_2 acetal), 2.13–2.00 (m, 1H, CH_2 acetal), 1.36–1.22 (m, 1H, CH_2 acetal), 0.98 (t, 6H, ^3J(H,H) = 7.69 Hz, silyl-CH_2), 0.57 (q, 9H, ^3J(H,H) = 7.69 Hz, silyl-CH_3). ^{13}C-NMR ($CDCl_3$): δ 192.62 (ald-C), 99.99 (alkyne-C), 97.47 (acetal-C), 95.95 (Cb–C), 82.22 (Cp–C), 79.51 (alkyne-C), 66.88, 66.85 (acetal-C), 63.52, 58.76 (Cb–C), 25.72 (acetal-C), 7.32, 4.30 (silyl-C). UV–vis ($CHCl_3$): λ 264 (ε = 4327 cm^{-1} M^{-1}), 363 (ε = 420 cm^{-1} M^{-1}). MS (EI) m/z Calc. for $[M]^+$ ($C_{26}H_{35}CoO_5Si$) 514.1586, Found: 514.1599 (E = 0.7 ppm).

4.9. Synthesis of **12**

Compound **11a** (60 mg, 0.12 mmol) is placed in a 50 ml round bottom flask and dissolved in 25 ml THF. Bu_4NF (0.20 ml, 1 M in THF) is added and the resulting mixture stirred at ambient temperature for 15 min. The reaction mixture is quenched with water, then washed with 50 ml of Et_2O and the organic layer separated. After drying the organic layer over magnesium sulfate the solvent is removed in vacuo to give a dark oil. To the oil is added (0.200 g, 1.05 mmol) of *p*-toluenesulfonic acid, 1 ml of water, and 10 ml of THF. The resulting solution is stirred for 12 h at ambient temperature under the exclusion of light. Aqueous workup followed by chromatography (SiO_2; hexanes–CH_2Cl_2 1:1) furnishes **12** (25 mg, 76%) as red crystalline solid. M.p. unable to determine, rapid decomp. IR (cm^{-1}): ν 2959, 2923, 2852, 2099, 1660, 1410, 1101. ^{1}H-NMR ($CDCl_3$): δ 10.18 (s, 1H, ald-H), 10.05 (s, 1H, ald-H), 5.18 (s, 5H, Cp–H), 3.41 (s, 1H, alkyne-H). ^{13}C-NMR ($CDCl_3$): δ 190.60 (ald-C), 189.22 (ald-C), 84.58 (alkyne-C), 83.21 (Cp–C), 82.69 (Cb–C), 74.94 (alkyne-C), 73.56, 69.32 (Cb–C). UV–vis ($CHCl_3$): λ 286 (ε = 590 cm^{-1} M^{-1}). MS (EI) m/z Calc. for $[M]^+$ ($C_{14}H_9CoO_3$) 283.9884, Found: 283.9890 (E = 2.1 ppm).

4.10. Synthesis of **13**

Compound **11a** or **11b** (2.53 g, 4.92 mmol) is placed in a 250 ml round bottom flask and dissolved in 150 ml of MeOH. The solution is cooled to 0 °C and diethyl-(1-diazo-2-oxopropyl)phosphonate **8** (2.71 g, 12.3 mmol) and K_2CO_3 (1.83 g, 12.3 mmol) are added successively. The reaction mixture is stirred for 24 h and allowed to warm to ambient temperature. Partitioning between saturated aq. $NaHCO_3$ and CH_2Cl_2 leads, after chromatography on silica gel (SiO_2; hexanes–CH_2Cl_2 4:1 + 10% NEt_3), to **13a** (1.62 g, 89%) as a yellow crystalline solid or **13b** (1.26 g, 66%) as a yellow–orange crystalline solid. **13a**: M.p.: 112 °C. IR (cm^{-1}): ν 2964, 2848, 2355, 1517, 1148, 1037, 989, 809. ^{1}H-NMR ($CDCl_3$): δ 5.11 (s, 2H, CH acetal), 5.00 (s, 5H, Cp–H), 4.17–4.11 (m, 2H, CH_2 acetal), 3.84–3.75 (m, 2H, CH_2 acetal), 3.19 (alkyne-H), 2.12–2.03 (m, 1H, CH_2 acetal), 1.54–1.24 (m, 1H, CH_2 acetal). ^{13}C-NMR ($CDCl_3$): δ 97.75, 97.72 (C-acetal), 82.48 (Cp–C), 80.45 (alkyne-C), 80.42, 78.40 (Cb–C), 76.16 (alkyne-C), 66.96 (C-acetal), 25.75 (C-acetal). UV–vis ($CHCl_3$): λ 296 (ε = 14053 cm^{-1} M^{-1}). MS (EI) m/z Calc. for $[M]^+$ ($C_{21}H_{21}CoO_4$) 396.0772, Found: 396.0769 (E = 0.8 ppm). **13b**: M.p.: 180 °C (dec.). IR (cm^{-1}): ν 2964, 2850, 2353, 1517, 1148, 1037, 989, 812. ^{1}H-NMR ($CDCl_3$): δ 5.16 (s, 2H, CH acetal), 5.02 (s, 5H, Cp–H), 4.20–4.16 (m, 2H, CH_2 acetal), 3.87–3.80 (m, 2H, CH_2 acetal), 3.06 (alkyne-H), 2.16–2.07 (m, 1H, CH_2 acetal), 1.67–1.37 (m, 1H, CH_2 acetal). ^{13}C-NMR ($CDCl_3$): δ 97.74, 97.71 (C-acetal), 82.53 (Cp–C), 79.50 (alkyne-C), 79.46, 78.67 (Cb–C), 78.26 (alkyne-C), 67.08 (C-acetal), 25.79 (C-acetal). UV–vis ($CHCl_3$): λ 288 (ε = 261 cm^{-1} M^{-1}). MS (EI) m/z Calc. for $[M]^+$ ($C_{21}H_{21}CoO_4$) 396.0772, Found: 396.0765 (E = 1.9 ppm).

4.11. Synthesis of **14**

Compound **13a** (207 mg, 0.520 mmol) is placed in a 50 ml round bottom flask and *p*-toluenesulfonic acid (0.200 g, 1.05 mmol), 1 ml of water, and 10 ml of THF is added successively. The resulting solution is stirred for 12 h at ambient temperature under the exclusion of light. Aqueous workup followed by chromatography (SiO_2; hexanes–CH_2Cl_2 1:1) furnishes **14** (65 mg, 45%) as red crystalline solid, m.p. 170 °C (decomp). IR (cm^{-1}): ν 2928, 2829, 2098, 1604, 1405, 1032, 834. ^{1}H-NMR ($CDCl_3$): δ 10.01 (ald-H), 5.12 (Cp–H), 3.36 (alkyne-H). ^{13}C-NMR ($CDCl_3$): δ 189.47 (ald-C), 84.58 (alkyne-C), 83.38 (alkyne-C), 83.15 (Cp–C), 74.91 (Cb–C), 68.92 (alkyne-C), 64.00 (Cb–C). UV–vis ($CHCl_3$): λ 284 (ε = 2133 cm^{-1} M^{-1}). MS (EI) m/z Calc. for $[M]^+$ ($C_{15}H_9CoO_2$) 279.9935, Found: 279.9931 (E = 1.4 ppm).

4.12. Synthesis of **15**

Compound **13a** (0.200 g, 0.500 mmol) is placed in a 100 ml oven-dried Schlenk flask and dissolved in 50 ml of absolute THF. To the solution at −78 °C is added LDA (0.043 g, 0.46 mmol) in THF dropwise. After stirring for 30 min the temperature is increased to −10 °C and CuI (0.240 g, 2.10 mmol) is added. Stirring is continued for an additional 15 min, at which point the temperature was decreased to −20 °C and propylamine (6.0 ml) and 1-bromo-2-isopropylsilylacetylene (0.500 g, 1.91 mmol) are added successively. The resulting solution is warmed to ambient temperature and quenched with water. The water layer is washed with 50 ml hexanes and the combined organic layers dried over magnesium sulfate. After the solvent is removed in vacuo, column chromatography (SiO_2; hexanes + 10% NEt_3) furnishes 15 (263 mg, 69%) as a deep red oil. IR (neat): *v* 2945, 2861, 2216, 2084, 1630, 1453, 1238, 1100, 992 [cm^{-1}]. ^{1}H-NMR ($CDCl_3$): δ 5.10 (s, 2H, CH acetal), 5.06 (s, 5H, Cp–H), 4.17–4.10 (m, 4H, CH_2 acetal), 3.83–3.65 (m, 4H, CH_2 acetal), 2.14–2.06 (m, 2H, CH_2 acetal), 1.45–1.28 (m, 2H, CH_2 acetal), 1.07 (2, 42H, TIPS-H). ^{13}C-NMR ($CDCl_3$): δ 97.49 (acetal-C), 97.47 (alkyne-C), 91.04 (alkyne-C), 88.06 (Cb–C), 82.51 (Cp–C), 78.14 (alkyne-C), 78.07 (Cb–C), 71.33 (alkyne-C), 66.98 (acetal-C), 54.53, 25.69 (acetal-C), 18.51 (TIPS-CH), 11.24 (TIPS-CH_3). MS (EI) *m/z* Calc. for $[M]^+$ ($C_{43}H_{61}CoO_4Si_2$) 756.3440, Found: 756.3429 (E = 1.4 ppm).

4.13. Synthesis of **16**

Compound **15** (0.250 g, 0.330 mmol) is placed in a 50 ml round bottom flask and *p*-toluenesulfonic acid (0.200 g, 1.05 mmol), 1 ml of water, and 5 ml of THF are added successively. The resulting solution is stirred for 12 h at ambient temperature under the exclusion of light. Aqueous workup followed by removal of solvent in vacuo furnished a dark red oil. The oil is redissolved in 20 ml of MeOH in a 50 ml round bottom flask. The solution is cooled to 0 °C, diethyl-(1-diazo-2-oxopropyl)phosphonate (0.360 g, 1.64 mmol), and K_2CO_3 (0.230 g, 1.67 mmol) are added successively. The reaction mixture is stirred at for 24 h and allowed to warm to ambient temperature. Partitioning between saturated aq. $NaHCO_3$ and CH_2Cl_2 leads after chromatography on silica gel (SiO_2; hexanes + 10% NEt_3) to **16** (0.175 mg, 79%) as an orange oily solid. IR (cm^{-1}): *v* 2940, 2864, 2355, 2194, 2086, 1540, 1455, 980. ^{1}H-NMR ($CDCl_3$): δ 5.06 (s, 5H, Cp–H), 3.27 (s, 2H, alkyne-H), 1.08 (s, 42H, TIPS-H). ^{13}C-NMR ($CDCl_3$): δ 90.21, 89.99 (alkyne-C), 84.13 (Cp–C), 82.42 (Cb–C), 79.31, 76.71 (alkyne-C), 69.66, 61.07 (alkyne-C), 59.77 (Cb–C), 18.57 (TIPS-CH), 11.27 (TIPS-CH_3). MS (EI) *m/z* Calc. for $[M]^+$ ($C_{39}H_{49}CoSi_2$) 632.2705, Found: 632.2698 (E = 3.2 ppm).

4.14. Synthesis of **17**

Compound **13b** (50 mg, 0.13 mmol) is placed in a 25 ml oven-dried Schlenk flask and is dissolved in 5 ml of dry piperdine. To the solution is added $Cl_2Pd(PPh_3)_2$ (2 mg, 0.003 mmol), CuI (1.2 mg, 0.006 mol) and 4-iodo-*tert*-butyl benzene (100 mg, 0.400 mmol). The resulting solution was stirred at ambient temperatures for 24 h. The reaction mixture was quenched with water and extracted twice with ethyl ether. The combined organic layers were dried over magnesium sulfate and the solvent removed in vacuo, and column chromatography (SiO_2; $MeCl_2$–hexanes 2:1 + 10% NEt_3) furnishes **17** (67 mg, 80%) as a red oily solid. IR (cm^{-1}): *v* 2961, 2923, 2854, 2253, 2182, 1700, 1507, 1238, 1108. ^{1}H-NMR ($CDCl_3$): δ 7.36 (d, ^3J(H,H) = 8.43 Hz, 4H, aromatic-H), 7.26 (d, ^3J(H,H) = 8.43 Hz, 4H, aromatic-H), 5.28 (s, 2H, acetal-H), 5.03 (s, 5H, Cp–H), 4.23–4.18 (m, 2H, CH_2 acetal), 3.90–3.65 (m, 2H, CH_2 acetal), 2.14–2.03 (m, 1H, CH_2 acetal), 1.45–1.40 (m, 1H, CH_2 acetal). ^{13}C-NMR ($CDCl_3$): δ 151.11, 131.33, 125.39, 121.64 (aromatic-C), 98.22 (acetal-C), 98.19 (Cb–C), 92.16, 84.81 (alkyne-C), 82.63 (Cp–C), 78.33 (Cb–C), 66.93 (acetal-C), 35.05, 31.44 (alkane-C), 26.23 (acetal-C). MS (EI) *m/z* Calc. for $[M]^+$ ($C_{41}H_{45}CoO_4$) 660.2650, Found: 660.2660 (E = 1.5 ppm).

4.15. Synthesis of **18**

Compound **17** (0.080 g, 0.12 mmol) is placed in a 25 ml round bottom flask and *p*-toluenesulfonic acid (0.100 g, 0.530 mmol), 1 ml of water, and 3 ml of THF are added successively. The resulting solution is stirred for 12 h at ambient temperature under the exclusion of light. Aqueous workup followed by removal of solvent in vacuo furnished a dark red oil. The oil is re-dissolved in 5 ml of MeOH in a 50 ml round bottom flask. The solution is cooled to 0 °C, 8 (0.060 g, 0.31 mmol), and K_2CO_3 (0.06 g, 0.43 mmol) are added. The reaction mixture is stirred for 24 h and allowed to warm to ambient temperature. Partitioning between saturated aq. $NaHCO_3$ and CH_2Cl_2 leads after chromatography on silica gel (hexanes + 10% NEt_3) to **18** (18 mg, 27%) as a red orange crystalline solid. M.p.: 122 °C. IR (cm^{-1}): *v* 2959, 2920, 2253, 2182, 1700, 1507, 1239, 1100. ^{1}H-NMR ($CDCl_3$): δ 7.42 (d, ^3J(H,H) = 8.51 Hz, 4H, aromatic-H), 7.31 (d, ^3J(H,H) = 8.51 Hz, 4H, aromatic-H), 5.02 (s, 5H, Cp–H), 3.29 (s, 2H, alkyne-H), 1.30 (s, 18H, alkane-H). ^{13}C-NMR ($CDCl_3$): δ 151.69, 131.22, 125.33, 120.25 (aromatic-C), 94.21, (alkyne-C), 83.78 (Cp–C), 82.44, 81.60 (alkyne-C), 61.63, 59.09 (Cb–C), 34.85, 31.12 (alkane-C). UV–vis ($CHCl_3$): λ

Table 1
Crystallographic information for **13b** and **18**

	13b	**18**
Empirical formula	$C_{21}H_{21}CoO_4$	$C_{37.25}H_{33.50}Cl_{0.50}Co$
Formula weight	396.31	557.80
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$
Crystal color, habit	Yellow–orange plate	Yellow–orange needle
Unit cell dimensions		
a (Å)	8.9033(4)	23.132(2)
b (Å)	8.3224(4)	18.932(2)
c (Å)	25.0314(11)	29.492(4)
α (°)	90	90
β (°)	91.383(1)	102.163(3)
γ (°)	90	90
V (Å^3)	1854.21(15)	12626(3)
Z	4	16
D_{calc} (g cm^{-3})	1.420	1.174
Absorption coefficient (mm^{-1})	0.948	0.608
Crystal size (mm)	0.48 × 0.32 × 0.12	0.36 × 0.12 × 0.10
Reflections collected	19 079	22 647
Independent reflections	4592	8515
R_{int}	0.0373	0.0989
Absorption correction	Semi-empirical from equivalents	None
Max/min transmission	0.8944 and 0.5834	
Data/restraints/parameters	4592/0/235	8515/27/748
Goodness-of-fit on F^2	1.010	1.009
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0346$ $wR_2 = 0.0758$	$R_1 = 0.0699$ $wR_2 = 0.1379$
R indices (all data)	$R_1 = 0.0443$ $wR_2 = 0.0779$	$R_1 = 0.1344$ $wR_2 = 0.1616$
Largest difference peak and hole (e Å^{-3})	0.308 and −0.271	0.464 and −0.261

302 ($\varepsilon = 823$ cm^{-1} M^{-1}). MS (EI) m/z Calc. for $[M]^+$ ($C_{37}H_{33}Co$) 536.1914, Found: 536.1914 ($E = 1.5$ ppm).

4.16. X-ray single crystal structure determinations of *13b* and *18*

Single crystals suitable for X-ray structure determination were mounted onto glass fibers. X-ray intensity data were measured at 293 K (**13b**) or 190 K (**18**) on a Bruker SMART APEX CCD-based diffractometer (Mo–K_α, $\lambda = 0.71073$ Å). The raw data frames were integrated with the [8] SAINT PLUS program, [8a] which also applied corrections for Lorentz and polarization effects. Final unit cell constants are based on the least-squares refinement of reflections with $I > 5(\sigma)I$ from each data set (9765 for **13b** and 4526 for **18**). An empirical absorption correction based on the multiple measurement of equivalent reflections was applied in the case of **13b**; no absorption correction was made to **18** due to the small size of the crystal. Both structures were solved by a combination of direct methods and difference Fourier syntheses, and refined against F^2 using the SHELXTL software package [8b]. No irregularities were encountered during the solution and refinement of **13b**; however, the t-butylphenyl end of one of the two independent molecules in **18** suffers from severe disorder, with both the phenyl part and the t-butyl group occupying two distinct orientations in equal proportions. Several geometric restraints on these disordered groups were necessary to achieve a stable refinement. With the exception of two methyl carbons in the disordered t-butyl group of **18**, eventually all non-hydrogen atoms in each crystal were refined with anisotropic displacement parameters. Hydrogen atoms were placed in geometrically idealized positions and refined using a riding model. Relevant crystallographic details are given in Table 1.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 172066 for compound **13b** and CCDC no. 171473 for compound **18**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.uk or www: http://www.ccdc.cam.ac.uk).

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