Endohedral Metallocenophanes of Rhodium and Cobalt

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Dedicated to Professor Paul von Ragué Schleyer on the occasion of his 75th birthday

Keywords: Cage compounds / Sandwich complexes / Alkynes / Rhodium / Cobalt

The synthesis of seven endohedral metallocenophanes of rhodium (**7b**, **8b**) and cobalt (**1d**–**h**) with a cyclopentadienyl unit as one of the π-systems and a cyclobutadiene or cyclopentadienone unit as the second π-system is described, including the synthesis of the unsubstituted parent compound of the [CpCo(cbd)]-derived endohedral phanes, [3.3]-η^5-(1,1′,3,3′)-cyclopentadienyl–η^4-(cyclobutadienophane)cobalt(I) (**1h**). This compound could be obtained by deprotection of the corresponding trimethylsilyl-substituted endohedral phane **1g**. The X-ray structures of **7b**, **1e**, **1g** and **1h** could be obtained. This paper compares their structural properties to the complexes reported in previous short communications. (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2005)

Introduction

In [*n.n*]phanes[1–4] the cyclic conjugated π-systems which are held in place by at least two bridges, such as hydrocarbon chains, offer a variety of bonding modes for metal centres. The cage structures of these phanes exhibit an inside and an outside face leading to two binding modes for a metal atom or metal fragment to the π-systems: inside the cage (endohedral, **A**) or outside the cage (exohedral, **B**) as shown in Figure 1.[5]

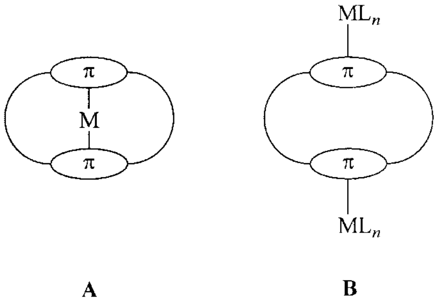
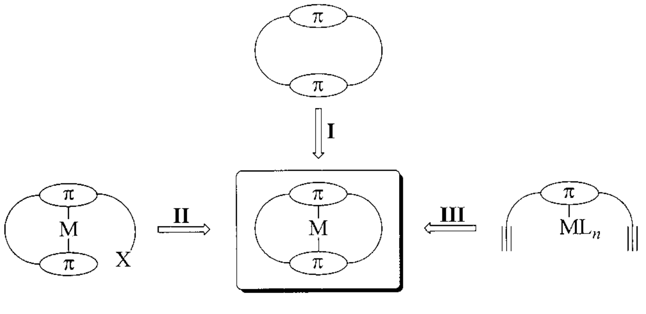


Figure 1. Endohedral (**A**) and exohedral (**B**) bonding modes of metallocenophanes.

In comparison to the numerous examples of the exohedral metallocenophanes reports of endohedral phanes are much rarer because of their limited accessibility. However, they deserve special interest because the hydrocarbon cage is able to stabilize low oxidation states of the incorporated metals. This has been demonstrated by complexing Ga^I and Ge^{II} in [2.2.2]paracyclophane.[6] In the literature there are reports of two protocols for the synthesis of endohedral metallocenophanes:

Either by reacting metal atoms or metal ions directly with the appropriate cyclophanes (path **I** in Scheme 1),[6,7] or by building the tethers on a metallocene in a stepwise fashion (path **II**).[8] Recently, we developed a third path (**III**) by utilizing substituted half-sandwich complexes which are able to form the second π-system by an intramolecular metal mediated cyclization of alkyne units (Scheme 1).[9]



Scheme 1. Protocols **I**–**III** for the synthesis of endohedral metallocenophanes.

Using this third synthetic pathway we were able to synthesize the cobalt and rhodium complexes **1a**–**h**, **2c**, **3a**–**b**, **4a**–**b**, **5a**, and **6a** (Figure 2), of which **1a**, **1b**, **1e**, **1g**, **1h**, **5a**, and **6a** were investigated by X-ray diffraction.[9,10]

In this paper we report the synthesis of two endohedral rhodium phanes **7b** and **8b** (Figure 3), four endohedral co-

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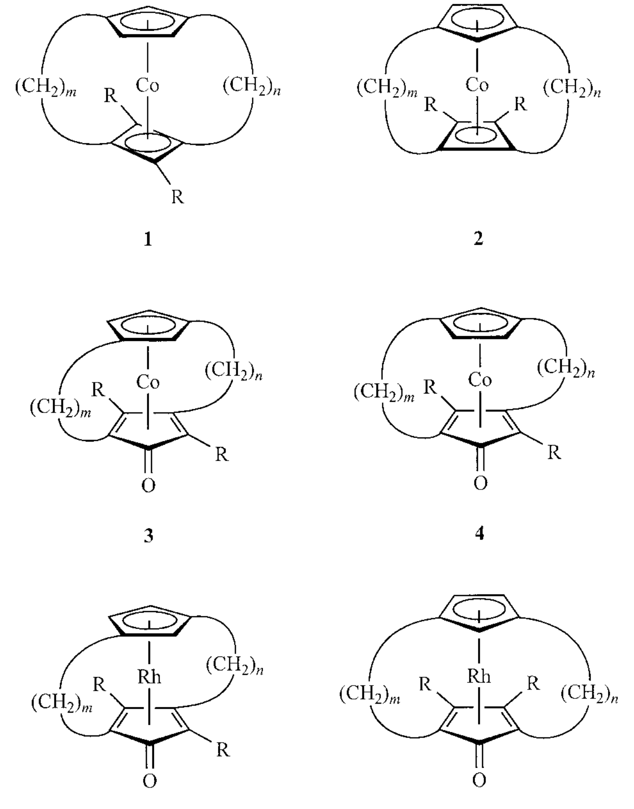


Figure 2. Endohedral metallocenophanes **1a**–**h**, **2c**, **3a**–**b**, **4a**–**b**, **5a**, and **6a** synthesized by route **III** [$m = n = 3$, R = *t*Bu (**a**); $m = n = 4$, R = *t*Bu (**b**); $m = n = 5$, R = *t*Bu (**c**); $m = 3$, $n = 4$, R = *t*Bu (**d**); $m = 3$, $n = 5$, R = *t*Bu (**e**); $m = 4$, $n = 5$, R = *t*Bu (**f**); $m = n = 3$, R = $SiMe_3$ (**g**); $m = n = 3$, R = H (**h**)].

balt phanes **1d**–**g** (Figure 2) and of the unsubstituted parent compound **1h** of phane **1a**.

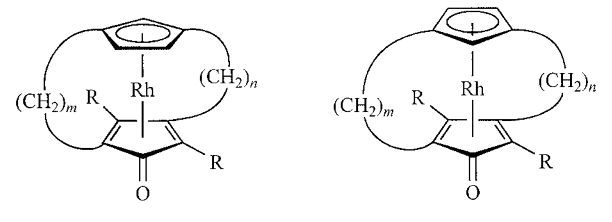
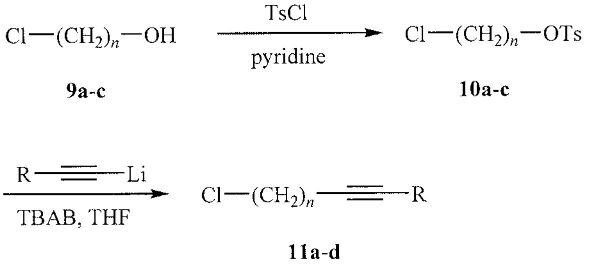


Figure 3. Isomeric rhodium phanes **7b** and **8b** ($m = n = 4$, R = *t*Bu).

Results and Discussion

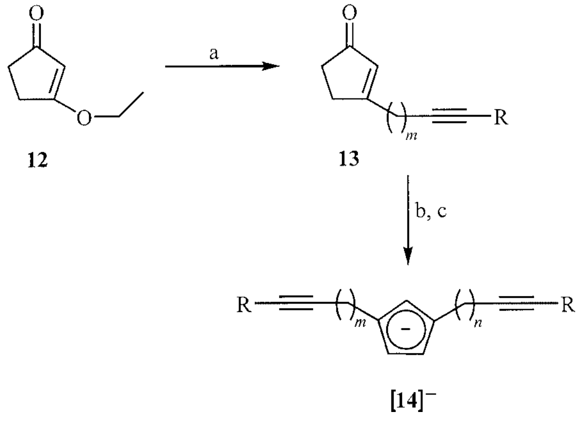
Synthesis

The synthesis of the ω-haloalkynes **11a**–**d** necessary as building blocks for the tethers in the endohedral phanes was achieved by the substitution of tosylated ω-chloro alcohols **10a**–**c** by lithiated *tert*-butylacetylene or (trimethylsilyl)acetylene, respectively (Scheme 2).



Scheme 2. Synthesis of ω-haloalkynes **11a**–**d** [$n = 3$, R = *t*Bu (**a**); $n = 4$, R = *t*Bu (**b**); $n = 5$, R = *t*Bu (**c**); $n = 3$, R = $SiMe_3$ (**d**)] from ω-hydroxy alcohols **9a**–**c** [$n = 3$, R = *t*Bu (**a**); $n = 4$, R = *t*Bu (**b**); $n = 5$, R = *t*Bu (**c**)].

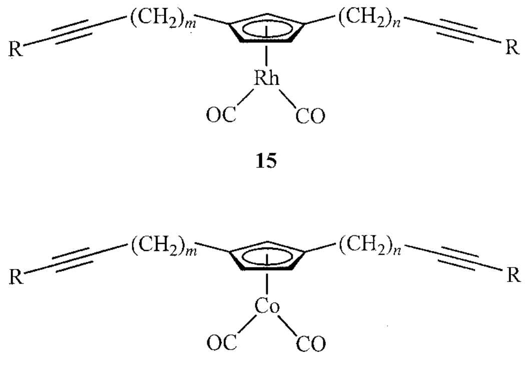
The disubstituted cyclopentadiene derivatives that we used as ligands for the half-sandwich complexes were synthesized by a two step procedure (Scheme 3).[9] In the first step the first alkyne substituent was introduced by treatment of 3-ethoxycyclopent-2-ene-1-one (**12**) with a Grignard reagent of an ω-chloroalkyne **11**. Acidic workup of the reaction mixture yielded the respective 3-alkynylcyclopent-2-enones **13**. The second alkyne substituent was introduced in a similar reaction and again acidic workup led to the desired disubstituted cyclopentadienes. The resulting cyclopentadiene derivatives were deprotonated with *n*-butyllithium in THF shortly before their complexation with metal dicarbonyl fragments.



Scheme 3. Two step synthesis of 1,3-difunctionalized cyclopentadienyllithium salts [**14b**]$^-$ ($n = m = 4$, R = *t*Bu) and [**14d**–**g**]$^-$ [$n = 3$, $m = 4$, R = *t*Bu (**d**); $n = 3$, $m = 5$, R = *t*Bu (**e**); $n = 4$, $m = 5$, R = *t*Bu (**f**); $m = n = 3$, R = $SiMe_3$ (**g**)]. Reagents: (a) ClMg–$(CH_2)_m$C≡CR in THF, then HCl (aq); (b) ClMg–$(CH_2)_n$C≡R in THF, then HCl (aq); (c) *n*-butyllithium in THF.

In the case of the rhodium complexes, the lithium salt [**14b**]$^-$ was treated with the dicarbonyl(chloro)rhodium dimer in THF to yield the dicarbonyl rhodium complex **15b** (Scheme 4) as an orange oil in 77% yield.

The thermolytic reaction of the dicarbonyl rhodium complex **15b** in refluxing cyclooctane yielded two isomeric endohedral products, **7b** and **8b** (Figure 3). While **7b** was formed in an acceptable yield of 16%, **8b** was only produced in minor quantities (0.5% yield). We were able to grow single crystals of **7b** which were suitable for X-ray diffraction analysis. This allowed us to confirm the structure



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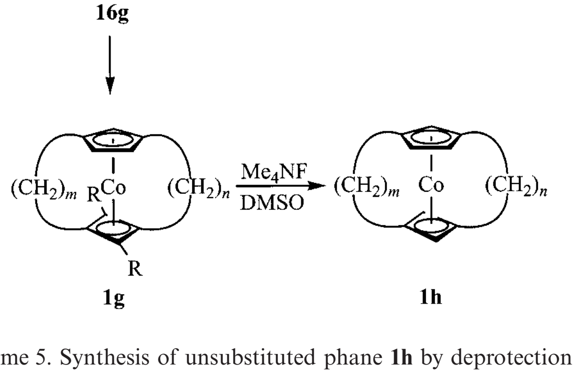
Scheme 4. Synthesized dicarbonyl metal complexes **15b** ($n = m = 4$, R = *t*Bu) and **16d−g** [$n = 3$, $m = 4$, R = *t*Bu (**d**); $n = 3$, $m = 5$, R = *t*Bu (**e**); $n = 4$, $m = 5$, R = *t*Bu (**f**); $m = n = 3$, R = $SiMe_3$ (**g**)].

of **7b** and also to assign the structure of **8b**. For the isomeric endohedral products six isomers are possible, of which four are C_s and two C_1 symmetric. The NMR spectroscopic data for **7b** and **8b** prove the C_1 symmetry of both isolated complexes **7b** and **8b**. As we were able to confirm the structure of **7b** by X-ray analysis the structure of **8b** could also be assigned unambiguously.

Until now only endohedral cobalt phanes bearing alkyl chains of the same length ($m = n$) had been synthesized.[9,10] To investigate the amount of distortion resulting from two different alkyl chains, the endohedral cobalt phanes **1d** ($m = 3$, $n = 4$, R = *t*Bu), **1e** ($m = 3$, $n = 5$, R = *t*Bu), **1f** ($m = 4$, $n = 5$, R = *t*Bu) were envisaged. To obtain the dicarbonyl cobalt complexes **16d–f** we reacted the deprotonated cyclopentadiene derivatives [**14d–f**]$^-$ with $[Co_2(CO)_8]/I_2$. The thermolytic reaction of these half-sandwich complexes in refluxing cyclooctane resulted in the formation of the endohedral complexes **1d–f** in 5% (**1d**), 30% (**1e**) and 15% (**1f**) yield.

For the synthesis of the parent compound **1h** of the recently published endohedral [3.3]phane **1a** we made use of TMS as protecting groups on the cyclobutadiene unit (Scheme 5).[11] The twofold TMS substituted phane **1g** was obtained in 35% yield analogously to **1a** by refluxing the dicarbonyl cobalt complex **16g** in cyclooctane. The removal of the TMS groups was achieved in 74% yield by stirring a solution of **1g** with Me_4NF at 80 °C.

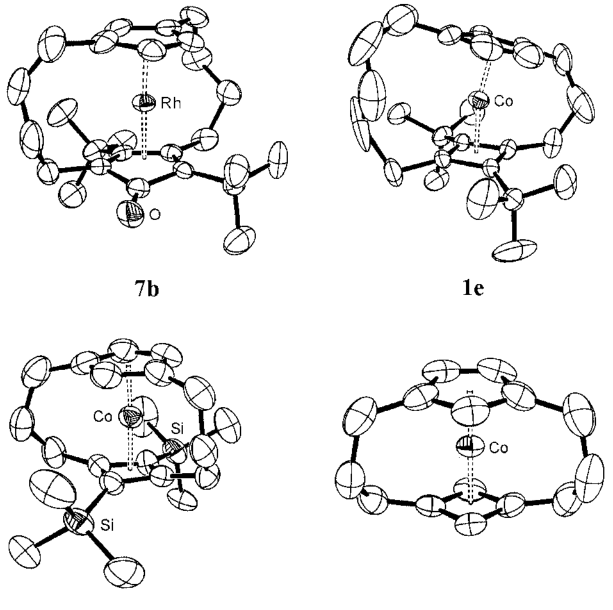


1g **1h**

Scheme 5. Synthesis of unsubstituted phane **1h** by deprotection.

Structural Investigations

Crystals suitable for X-ray crystallographic studies could be obtained for the complexes **7b**, **1e**, **1g** and **1h**. In Figure 4, the molecular structures of these endohedral phanes are shown.



7b **1e**

1g **1h**

Figure 4. ORTEP plots (50% ellipsoid probability) of the molecular structures of **7b**, **1g** (left), **1e** and **1h** (right).

Including the previously described molecular structures,[9,10] a total number of eight crystallographically studied endohedral phanes synthesized with our protocol are available and can now be compared. Selected structural properties of these complexes are listed in Table 1.

Table 1. Structural properties of endohedral metallocenophanes **1a**, **1b**, **1g**, **1h**, **5a**, **6a** and **7b**.[a]

	Interplanar angle α [°]	Angle β [°]	(η^5-Cp)−M distance [Å]	M−(η^4-ligand) distance [Å]
1a[9]	6.6	174.2	1.604	1.645
1b[9]	4.0	178.3	1.670	1.692
1e	13.6	166.9	1.677	1.678
1 g[b]	6.8/7.2	173.6/173.1	1.609/1.604	1.645/1.650
1h	9.9	170.8	1.590	1.631
5a[10]	4.3	175.6	1.777	1.742
6a[10]	22.2	170.9	1.806	1.751
7b	5.1	174.8	1.857	1.791

[a] For the calculation of angles and centroids, all five C atoms of the Cp rings were used, but only the four coordinated C atoms of the η^4-ligands (cyclopentadienone or cyclobutadiene). [b] The two different values refer to two independent molecules in the unit cell.

The larger atomic radius of rhodium results in larger distances between the metal centre and the coordinated η^5-Cp ligand as well as the η^4-coordinated unit. While these distances for the rhodium complexes range from 1.78–1.86 Å [(η^5-Cp)···M distance] and 1.74–1.79 Å [M···(η^4-ligand) distance], the cobalt complexes show values of 1.59–1.68 Å [(η^5-Cp)···M distance] and 1.63–1.69 Å [M···(η^4-ligand) distance]. Within these limits the distances vary according to the lengths of the alkyl chains and to the substitution pattern. First, the structural features of the rhodium complexes shall be compared. Generally there exist six possible isomers for endohedral [*n.n*]phanes with a Cp and a cyclopentadienone unit, namely two C_1- and four C_s-symmetric. Of these six isomers three are represented by the complexes **5a** (C_1), **6a** (C_s) and **7b** (C_1). Because of the shorter alkyl bridges the two [3.3]phanes **5a** and **6a** are more strained than the [4.4]phane **7b**, which has the largest distances between the rhodium centre and the π-ligands. The two [3.3]phanes also differ in the strain of the carbon cage. The substitution pattern of the π-ligands in the C_s-symmetric phane **6a** allows the molecule to reduce the strain by increasing the interplanar angle α (22.2°), which is the largest of all the investigated complexes (Figure 5). The C_1-symmetric [3.3]phane **5a** does not have that much flexibility to reduce strain because of the substitution pattern of the alkyl chains and, therefore, shows a small interplanar angle (α = 4.3°) as well as the shortest rhodium···π-ligand distances.

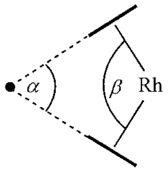


Figure 5. Illustration of the interplanar angle α and angle β.

In the row of the cobalt complexes the shortest bonding lengths between the cobalt centre and the π-ligands are found in the unsubstituted [3.3]phane **1h** [1.590 Å (η^5-Cp)−M distance, 1.631 Å M−(η^4-ligand) distance]. These distances are shorter than those reported for the unbridged species [(η^5-Cp)−M 1.660 Å and M−(η^4-ligand) 1.681 Å].[12] Addition of sterically demanding substituents on the cbd-unit increases these distances, with TMS groups [1.609/1.604 Å (η^5-Cp)−M distance, 1.645/1.650 Å M−(η^4-ligand) distance] having practically the same effect as *t*Bu groups [1.604 Å (η^5-Cp)−M distance, 1.645 Å M−(η^4-ligand) distance]. The metal-ligand distances for **1b** and **1e** are rather close to the parent system.[12] All the symmetrically bridged endohedral cobalt phanes ($n = m$) **1a**, **1b**, **1g** and **1h** show nearly parallel π-systems, with the interplanar angles α ranging from 4.0 to 9.9°. In the unsymmetrically bridged **1e** the distortion leads to an enlarged interplanar angle α (13.6°) and to a remarkably small angle β (166.9°), the smallest in all investigated phanes.

Conclusions

Our method of synthesizing metallocenophanes in situ by generating one ligand out of tethered precursors provided us with endohedral complexes of cobalt and rhodium. The yields were low (5%) to moderate (35%). In the case of the cobalt complexes, the generation of a cyclobutadiene or a cyclopentadienone ring is dependent on the reaction temperature. From the dicarbonyl rhodium complexes only the cyclopentadienone ligand was generated. A comparison of five endohedral (η^5-Cp)Co(η^4-Cbd) metallocenophanes revealed the anticipated shortest metal–ligand distances for the [3.3]cyclophane, whereas the other bridges led to metal−ligand distances close to the unbridged species. The relatively short metal−ligand distances for the [3.3]bridged species are also encountered in the case of the rhodium species **5a** and **6a**.

Experimental Section

General Remarks: All melting points are uncorrected. Elemental analyses were carried out by the Mikroanalytisches Laboratorium der Universität Heidelberg. UV/Vis absorption data were recorded with a Hewlett Packard HP 8452A Diode Array-spectrometer. IR spectra were recorded with a Bruker Vector 22 FT-IR spectrometer. The NMR spectra were measured with a Bruker WH 300 or Avance 500 spectrometer (^{1}H NMR at 300 or 500 MHz and ^{13}C NMR at 75 or 125 MHz) using the solvent as internal standard (δ). Standard symbols for signal multiplicities are used; p = pseudo. FAB and FD mass spectra refer to data from a Jeol JMS-700 instrument. All reactions were carried out in dried glassware under argon using dried and oxygen-free solvents.

X-ray Crystallographic Study: Data were collected with a Bruker Smart CCD-diffractometer at 200 K (**7b** and **1e**) and a Bruker Smart Apex-diffractometer at 295 K (**1g** and **1h**). Relevant crystal and data collection parameters are given in Table 2. The structures were solved by direct methods and refined against F^2 with a full-matrix least-square algorithm by using SHELXTL[13] software. In all cases an absorption correction was applied by using SADABS,[14] based on the Laue symmetry of the reciprocal space.

CCDC-249232 (for **1e**), -249234 (for **1g**), -249233 (for **1h**), and -249231 (for **7b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

General Procedure for the Preparation of ω-Chloroalkynes 11a−d: A dry 100-mL flask was charged with the respective 4-toluenesulfonate, dry THF and *tert*-butylammonium bromide (TBAB) and the mixture was cooled to 0 °C. Alkynyllithium (prepared by the addition of *n*-butyllithium to 1-alkyne in THF) was then added with a cannula. The mixture was stirred at 0 °C (1 h) then allowed to reach room temp. overnight. The solvent was removed, water was added to the residue and the solution was extracted with diethyl ether. The organic layer was washed with brine, dried ($MgSO_4$), filtered and the solvent was evaporated under reduced pressure. The products were purified by distillation.

1-Chloro-6,6-dimethylhept-4-yne (11a): Reaction mixture: 3-chloropropyl-1-tosylate (**10a**) (2.49 g, 10 mmol) and TBAB (3.22 g, 10 mmol) in THF (20 mL), 3,3-dimethylbut-1-yne (0.82 g, 10 mmol) and *n*-butyllithium (3.6 mL, 2.8 M) in THF (20 mL). Yield 1.19 g (75%). Colorless liquid, b.p. 49 °C (2 mbar). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.18 (s, 9 H, CH_3), 1.90 (pquint, ^3J = 6.6 Hz, 2 H, CH_2), 2.31 (t, ^3J = 6.8 Hz, 2 H, CH_2), 3.63 (t, ^3J = 6.5 Hz, 2 H, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.9 (CH_2), 28.0 (C), 32.0 (CH_3), 32.6 (CH_2), 44.5 (CH_2), 77.0 (C), 90.8 (C) ppm. IR (film) ṽ = 2968, 2929, 2867, 1477, 1456 cm^{-1}. HRMS (positive EI) calcd. for $C_9H_{15}Cl$ ([M]$^+$), 160.0833; found, 160.0875 (+4.2 mmu).

1-Chloro-7,7-dimethyloct-5-yne (11b): Reaction mixture: 4-chlorobutyl-1-tosylate (**10b**) (2.63 g, 10 mmol) and TBAB (3.22 g,

Table 2. Crystal data and structural refinement for **7b**, **1e**, **1g** and **1h**.

	7b	**1e**	**1g**	**1h**
Empirical formula	$C_{26}H_{37}ORh$	$C_{25}H_{37}Co$	$C_{21}H_{33}CoSi_2$	$C_{15}H_{17}Co$
Formula mass	468.47	396.48	400.58	256.22
Wavelength [Å]	0.71073	0.71073	0.71073	0.71073
Crystal system	tetragonal	monoclinic	monoclinic	orthorhombic
Space group	$I4_1/a$	$P2_1/n$	$P2_1/n$	$Pbca$
Temp. [K]	200	200	295	295
Z	16	4	8	8
a	14.3272(3)	9.1546(2)	8.925(2)	7.5187(8)
b	14.3272(3)	16.4597(3)	25.475(7)	16.561(2)
c	42.901(1)	14.1320(3)	19.307(5)	18.839(2)
α	90	90	90	90
β	90	91.063(1)	94.448(6)	90
γ	90	90	90	90
V [Å^3]	8806.2(4)	2129.07(8)	4377(2)	2345.7(4)
$D_{\text{calcd.}}$ [g/cm^3]	1.413	1.24	1.22	1.45
Abs. coeff. μ [mm^{-1}]	0.789	0.81	0.89	1.43
Max./min. transmission	0.95/0.88	0.93/0.59	0.76/0.97	0.56/0.96
Crystal shape	polyhedron	polyhedron	plate	needle
Crystal size [mm^3]	$0.17 \times 0.15 \times 0.06$	$0.48 \times 0.42 \times 0.10$	$0.33 \times 0.22 \times 0.03$	$0.45 \times 0.11 \times 0.03$
θ range for data collection [°]	1.5–24.7	1.9–27.5	1.92–28.36	2.16–28.35
Index ranges	$-16 \le h \le 16$ $-16 \le k \le 16$ $-50 \le l \le 50$	$-11 \le h \le 11$ $-21 \le k \le 21$ $-18 \le l \le 18$	$-11 \le h \le 11$ $-34 \le k \le 11$ $-22 \le l \le 25$	$-9 \le h \le 10$ $-10 \le k \le 22$ $-25 \le l \le 25$
Reflections collected	37141	21428	21679	16177
Independent reflections [R(int.)]	3763 (0.108)	4883 (0.035)	10521 (0.173)	2906 (0.046)
Observed reflections	2466 [$I > 2\sigma(I)$]	3835 [$I > 2\sigma(I)$]	5773 [$I > 2\sigma(I)$]	2443 [$I > 2\sigma(I)$]
Data/restraints/parameters	3763/10/278	4883/0/241	10521/0/445	2906/0/213
Goodness-of-fit on F^2	1.02	1.06	1.05	1.26
$R(F)$	0.054	0.078	0.088	0.055
$R_W(F^2)$	0.116	0.209	0.247	0.111
$(\Delta\rho)_{\text{max.}}$, $(\Delta\rho)_{\text{min.}}$ [e·Å^{-3}]	2.70 and –1.39	1.54 and –0.70	0.94 and –1.95	0.34 and –0.46

10 mmol) in THF (20 mL), 3,3-dimethylbut-1-yne (0.82 g, 10 mmol) and *n*-butyllithium (3.6 mL, 2.8 M) in THF (20 mL). Yield 1.21 g (70%). Colorless liquid, b.p. 54 °C (1 mbar). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.18 (s, 9 H, CH_3), 1.62 (pquint, ^3J = 7.2 Hz, 2 H, CH_2), 1.87 (pquint, ^3J = 7.1 Hz, 2 H, CH_2), 2.18 (t, ^3J = 7.0 Hz, 2 H, CH_2), 3.56 (t, ^3J = 6.6 Hz, 2 H, CH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 18.7 (CH_2), 26.9 (CH_2), 28.0 (C), 32.0 (CH_3), 32.3 (CH_2), 45.4 (CH_2), 78.2 (C), 90.4 (C) ppm. IR (film) $\tilde{\nu}$ = 2968, 2866, 1477, 1779, 1476, 1362 cm^{-1}. HRMS (positive EI) calcd. for $C_{10}H_{17}Cl$ ([M]$^+$), 172.1019; found, 172.1023 (+0.4 mmu).

1-Chloro-8,8-dimethylnon-6-yne (11c): Reaction mixture: 5-chloropentyl-1-tosylate (**10c**) (2.77 g, 10 mmol) and TBAB (3.22 g, 10 mmol) in THF (20 mL), 3,3-dimethylbut-1-yne (0.82 g, 10 mmol) and *n*-butyllithium (3.6 mL, 2.8 M) in THF (20 mL). Yield 1.31 g (70%). Colorless liquid, b.p. 63 °C (2 mbar). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.17 (s, 9 H, CH_3), 1.45–1.55 (m, 4 H, CH_2), 1.72–1.85 (m, 2 H, CH_2), 2.13 (t, ^3J = 6.5 Hz, 2 H, CH_2), 3.51 (t, CH_2, ^3J = 6.7 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.2 (CH_2), 26.7 (CH_2), 28.0 (C), 29.0 (CH_2), 32.1 (CH_3), 32.8 (CH_2), 45.6 (CH_2), 78.6 (C), 90.1 (C) ppm. IR (film) $\tilde{\nu}$ = 2968, 2864, 1476, 1361 cm^{-1}. HRMS (positive EI) calcd. for $C_{11}H_{19}Cl$ ([M]$^+$), 186.1175; found, 186.1171 (–0.4 mmu).

5-Chloropent-1-ynyltrimethylsilane (11d): Reaction mixture: 3-chloropropyl-1-tosylate (**10a**) (2.49 g, 10 mmol) and TBAB (3.22 g, 10 mmol) in THF (20 mL), (trimethylsilyl)acetylene (0.98 g, 10 mmol) and *n*-butyllithium (3.6 mL, 2.8 M) in THF (20 mL). Yield 1.36 g (78%). Colorless liquid, b.p. 80 °C (28 mbar). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.14 (s, 9 H, CH_3), 1.95 (pquint, ^3J = 6.6 Hz, 2 H, CH_2), 2.40 (t, ^3J = 6.9 Hz, 2 H, CH_2), 3.63 (t, ^3J = 6.4 Hz, 2 H, CH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 0.2 (CH_3), 17.4 (CH_2), 31.5 (CH_2), 43.7 (CH_2), 85.8 (C), 105.3 (C) ppm. IR (film) $\tilde{\nu}$ = 2960, 2176, 1431, 1361 cm^{-1}. HRMS (positive EI) calcd. for $C_8H_{15}ClSi$ ([M]$^+$), 174.0632; found, 174.0567 (–6.5 mmu).

General Procedure for the Synthesis of Cyclopent-2-enones 13a–c: In a dry 50-mL flask a Grignard reagent was prepared from chloroalkyne and magnesium in dry THF. The resulting solution was cooled to 0 °C and 3-ethoxycyclopent-2-enone, dissolved in dry THF, was added dropwise. The reaction mixture was stirred at 0 °C (1 h) and then warmed to room temp. overnight. The reaction mixture was poured into ice, and the solution was acidified with 5% hydrochloric acid to pH 5. After extraction with diethyl ether the organic layer was washed with brine, dried ($MgSO_4$), filtered and the solvent was evaporated under reduced pressure. The products were purified by flash column chromatography (silica gel, petroleum ether/diethyl ether, 3:1).

3-(6,6-Dimethylhept-4-ynyl)cyclopent-2-enone (13a): Reaction mixture: 1-chloro-6,6-dimethylhept-4-yne (**11a**) (6.03 g, 38 mmol) and magnesium (0.92 g, 38 mmol) in THF (10 mL), 3-ethoxycyclopent-2-enone (3.0 g, 23.8 mmol) in THF (10 mL). Yield 3.11 g (64%). Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.17 (s, 9 H, CH_3), 1.68–1.76 (pquint, ^3J = 7.1 Hz, 2 H, CH_2), 2.19 (t, ^3J = 6.9 Hz, 2 H, CH_2), 2.38 (m, 2 H, CH_2), 2.47–2.52 (m, 2 H, CH_2), 5.94 (s, 1 H, CH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 18.3 (CH_2), 26.4 (CH_2), 27.3 (C), 31.3 (CH_3), 31.5 (CH_2), 32.3 (CH_2), 35.2 (CH_2), 77.3 (C), 90.1 (C), 129.6 (CH), 182.3 (C), 210.0 (C) ppm. IR (film) $\tilde{\nu}$ = 2967, 2866, 1710, 1675, 1616, 1437, 1361 cm^{-1}. HRMS (positive

EI) calcd. for $C_{14}H_{20}O$ ($[M]^+$), 204.1514; found, 204.1511 (–0.3 mmu). $C_{14}H_{20}O$ (204.31): calcd. C 82.30, H 9.87, found C 82.02, H 10.32.

3-(7,7-Dimethyloct-5-ynyl)cyclopent-2-enone (13b): Reaction mixture: 1-chloro-7,7-dimethyloct-5-yne (**11b**) (6.56 g, 38 mmol) and magnesium (0.92 g, 38 mmol) in THF (10 mL), 3-ethoxycyclopent-2-enone (3.0 g, 23.8 mmol) in THF (10 mL). Yield 2.65 g (51%). Colorless oil. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.14$ (s, 9 H, CH_3), 1.44–1.49 (m, 2 H, CH_2), 1.62–1.68 (m, 2 H, CH_2), 2.13 (t, $^3J =$ 6.9 Hz, 2 H, CH_2), 2.34–2.41 (m, 4 H, CH_2), 2.53–2.55 (m, 2 H, CH_2), 5.91–5.92 (m, 1 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 19.0$ (CH_2), 26.6 (CH_2), 27.9 (C), 29.2 (CH_2), 32.0 (CH_3), 32.1 (CH_2), 33.6 (CH_2), 35.9 (CH_2), 78.2 (C), 90.2 (C), 130.2 (CH), 183.4 (C), 210.7 (C) ppm. IR (film) $\tilde{\nu} = 2966$, 2930, 2864, 1710, 1675, 1616, 1437, 1361 cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (log ε) = 276 (2.56), 310 (1.82) nm. HRMS (positive EI) calcd. for $C_{15}H_{22}O$ ($[M]^+$), 218.1671; found, 218.1672 (+0.1 mmu). $C_{15}H_{22}O$ (218.33): calcd. C 82.52, H 10.16; found C 82.11, H 10.36.

3-[5-(Trimethylsilyl)pent-4-ynyl]cyclopent-2-enone (13g): Reaction mixture: (5-chloropent-1-ynyl)trimethylsilane (**11d**) (6.64 g, 38 mmol) and magnesium (0.92 g, 38 mmol) in THF (10 mL), 3-ethoxycyclopent-2-enone (3.0 g, 23.8 mmol) in THF (10 mL). Yield 4.14 g (79%). Colorless oil. ^1H NMR (500 MHz, $CDCl_3$): $\delta = 0.14$ (s, 9 H, CH_3), 1.79 (pquint, $^3J = 7.3$ Hz, 2 H, CH_2), 2.28 (t, $^3J =$ 6.9 Hz, 2 H, CH_2), 2.39–2.41 (m, 2 H, CH_2), 2.51 (t, $^3J = 7.7$ Hz, 2 H, CH_2), 2.57–2.59 (m, 2 H, CH_2), 5.94–5.96 (m, 1 H, CH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 0.2$ (CH_3), 19.6 (CH_2), 26.0 (CH_2), 31.7 (CH_2), 32.5 (CH_2), 35.4 (CH_2), 85.9 (C), 106.0 (C), 129.9 (CH), 181.9 (C), 210.0 (C) ppm. HRMS (positive EI) calcd. for $C_{13}H_{20}OSi$ ($[M]^+$), 220.1283; found, 220.1283 (±0.0 mmu). IR (film) $\tilde{\nu} = 2957$, 2174, 1710, 1675, 1616, 1438, 1409, 1249, 1183, 842, 760 cm^{-1}. $C_{13}H_{20}OSi$ (220.38): calcd. C 70.85, H 9.15; found C 70.91, H 9.32.

General Procedure for the Synthesis of Cyclopentadienes 14b and 14d–g: In a dry 50-mL flask a Grignard reagent was prepared from chloroalkyne and magnesium in dry THF. The resulting solution was cooled to 0 °C, cyclopent-2-enone dissolved in dry THF, was added. The mixture was stirred at 0 °C (1 h) and then allowed to reach room temp. overnight. The reaction mixture was poured into ice, the solution was acidified with 5% hydrochloric acid to pH 5 and extracted with diethyl ether. The organic layer was washed with brine, dried ($MgSO_4$), filtered and the solvent was evaporated under reduced pressure. The product was purified by flash column chromatography [alox III (neutral), petroleum ether] and used directly for the complexation after the removal of solvent.

1,3-Bis(7,7-dimethyloct-5-ynyl)cyclopentadiene (14b): Reaction mixture: 1-chloro-7,7-dimethyloct-5-yne (**11b**) (5.01 g, 29 mmol) and magnesium (0.70 g, 29 mmol) in THF (6 mL), 3-(7,7-dimethyloct-5-ynyl)cyclopent-2-enone (**13b**) (3.21 g, 14.7 mmol) in THF (10 mL). Yield 3.19 g (64%).

1-(6,6-Dimethylhept-4-ynyl)-3-(7,7-dimethyloct-5-ynyl)cyclopentadiene (14d): Reaction mixture: 1-chloro-7,7-dimethyloct-5-yne (**11b**) (5.01 g, 29 mmol) and magnesium (0.70 g, 29 mmol) in THF (6 mL), 3-(7,7-dimethylhept-4-ynyl)cyclopent-2-enone (**13a**) (3.00 g, 14.7 mmol) in THF (10 mL). Yield 0.91 g (19%).

1-(6,6-Dimethylhept-4-ynyl)-3-(8,8-dimethylnon-6-ynyl)cyclopentadiene (14e): Reaction mixture: 1-chloro-8,8-dimethylnon-6-yne (**11c**) (5.41 g, 29 mmol) and magnesium (0.70 g, 29 mmol) in THF (6 mL), 3-(7,7-dimethylhept-4-ynyl)cyclopent-2-enone (**13a**) (3.00 g, 14.7 mmol) in THF (10 mL). Yield 3.53 g (71%).

1-(7,7-Dimethyloct-5-ynyl)-3-(8,8-dimethylnon-6-ynyl)cyclopentadiene (14f): 1-Chloro-8,8-dimethylnon-5-yne (**11c**) (5.41 g, 29 mmol) and magnesium (0.70 g, 29 mmol) in THF (6 mL), 3-(7,7-dimethyloct-5-ynyl)cyclopent-2-enone (**13b**) (3.21 g, 14.7 mmol) in THF (10 mL). Yield 2.44 g (47%).

1,3-Bis[5-(trimethylsilyl)pent-4-ynyl]cyclopentadi-ene (14g): (5-Chloropent-1-ynyl)trimethylsilane (**11d**) (5.07 g, 29 mmol) and magnesium (0.70 g, 29 mmol) in THF (6 mL), 3-[5-(trimethylsilyl)pent-4-ynyl]cyclopent-2-enone (**13g**) (3.24 g, 14.7 mmol) in THF (10 mL). Yield 2.37 g (64%).

Dicarbonyl-η^5-[1,3-bis(7,7-dimethyloct-5-ynyl)cyclopentadienyl]rhodium(I) (15b): *n*-Butyllithium (2.6 mL, 1.6 M in hexane, 2.68 mmol) was added to a solution of cyclopentadiene **14b** (1.12 g, 3.30 mmol) in 10 mL of THF at –40 °C. After warming up to room temperature the solution was added to a solution of dicarbonyl(chloro)rhodium(I) dimer (0.50 g, 0.83 mmol) in 100 mL of THF and stirred for 24 h. The solvents were removed under vacuum and the products purified by flash column chromatography on silica gel using pentanes/diethyl ether (20:1) as eluent. Yield 636 mg (77%). Orange oil. ^1H NMR (500 MHz, $CDCl_3$): $\delta = 1.17$ (s, 18 H, CH_3), 1.50 (m, 4 H, CH_2), 1.58 (m, 4 H, CH_2), 2.13 (m, 4 H, CH_2), 2.25 (m, 4 H, CH_2), 5.25 (ps, 2 H, CH), 5.38 (ps, 1 H, CH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 18.5$ (CH_2), 27.4 (C), 27.9 (CH_2), 28.9 (CH_2), 31.4 (CH_2), 31.5 (CH_3), 78.0 (C), 86.0 (CH, $J_{Rh,C} =$ 3.8 Hz), 89.1 (CH, $J_{Rh,C} = 3.8$ Hz), 89.5 (C), 110.6 (C, $J_{Rh,C} =$ 3.8 Hz), 192.7 (CO, $J_{Rh,C} = 83.8$ Hz) ppm. IR (film) $\tilde{\nu} = 2967$, 2862, 2034, 1969, 1476, 1456, 1361 cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (log ε)= 240 (4.18), 296 (3.62) nm. MS (positive FD): *m*/*z* = 468 ($[M - CO]^+$).

General Procedure for the Synthesis of Dicarbonylcobalt Complexes 16d–g: A dry flask was charged with $[Co_2(CO)_8]$ and dry THF, I_2 was added and the green mixture stirred at room temp. for 1 h. The green solution was cooled to 0 °C and a solution of cyclopentadienyllithium (prepared by the addition of *n*-butyllithium to a solution of cyclopentadiene in dry THF at –40 °C) was added. The brown mixture was stirred at 0 °C (1 h), then allowed to warm to room temp. overnight. The solvent was evaporated under reduced pressure and the product was purified by flash column chromatography [alox III (neutral), petroleum ether].

Dicarbonyl-η^5-[1-(6,6-dimethylhept-4-ynyl)-3-(7,7-dimethyloct-5-ynyl)cyclopentadienyl]cobalt(I) (16d): Reaction mixture: $[Co_2(CO)_8]$ (402 mg, 1.2 mmol) and I_2 (299 mg, 1.2 mmol) in THF (25 mL), 1-(6,6-dimethylhept-4-ynyl)-3-(7,7-dimethyloct-5-ynyl)cyclopentadiene (**14d**) (0.9 g, 2.8 mmol) and *n*-butyllithium (2.4 mL, 1.6 M in hexane) in THF (5 mL). Yield 285 mg (55%). Orange oil. ^1H NMR (300 MHz, C_6D_6): $\delta = 1.32$ (s, 9 H, CH_3), 1.34 (s, 9 H, CH_3), 1.50–1.64 (m, 6 H, CH_2), 2.10–2.56 (m, 8 H, CH_2), 4.57 (s, 2 H, CH), 4.70 (s, 1 H, CH) ppm. ^{13}C NMR (75 MHz, C_6D_6): $\delta = 18.7$ (CH_2), 18.9 (CH_2), 27.4 (CH_2), 27.7 (C), 28.0 (CH_2), 29.2 (CH_2), 30.1 (CH_2), 30.3 (CH_2), 31.7 (CH_3), 78.1 (C), 78.5 (C), 83.5 (CH), 83.6 (CH), 85.6 (CH), 89.5 (C), 90.0 (C), 105.4 (C), 106.1 (C) ppm. IR (film) $\tilde{\nu} = 2964$, 2862, 2044, 1952, 1475, 1453, 1360 cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (log ε)= 252 (6.71), 336 (2.76), 360 (2.49).

Dicarbonyl-η^5-[1-(6,6-dimethylhept-4-ynyl)-3-(8,8-dimethylnon-6-ynyl)cyclopentadienyl]cobalt(I) (16e): Reaction mixture: $[Co_2(CO)_8]$ (388 mg, 1.1 mmol) and I_2 (288 mg, 1.1 mmol) in THF (25 mL), 1-(6,6-dimethylhept-4-ynyl)-3-(8,8-dimethylnon-6-ynyl)cyclopentadiene (**14e**) (1.0 g, 3.0 mmol) and *n*-butyllithium (2.6 mL, 1.6 M in hexane) in THF (5 mL).Yield 130 mg (25%). Orange oil. ^1H NMR (500 MHz, C_6D_6): $\delta = 1.20$ (s, 9 H, CH_3), 1.25 (s, 9 H, CH_3), 1.35–1.53 (m, 6 H, CH_2), 2.03–2.40 (m, 10 H, CH_2), 4.49 (s, 1 H, CH), 4.50 (s, 1 H, CH), 4.61 (s, 1 H, CH) ppm. ^{13}C NMR (125 MHz, C_6D_6): $\delta = 18.7$ (CH_2), 19.0 (CH_2), 27.4 (CH_2), 27.7 (C), 28.3 (CH_2), 28.8 (CH_2), 29.2 (CH_2), 30.2 (CH_2), 30.3 (C), 30.6 (CH_2), 31.5 (CH$_3$), 31.6 (CH$_3$), 78.1 (C), 78.8 (C), 83.5 (CH), 83.6 (CH), 85.6 (CH), 89.3 (C), 90.0 (C), 105.3 (C), 106.2 (C) ppm. IR (film) $\tilde{\nu}$ = 2964, 2920, 2850, 2015, 1955, 1474, 1455 cm^{-1}. UV/Vis (CH$_2$Cl$_2$): $\lambda_{max.}$ (log ε) = 250 (3.77), 306 (3.00), 330 (2.85) nm.

Dicarbonyl-η^5-[1-(7,7-dimethyloct-5-ynyl)-3-(8,8-dimethylnon-6-ynyl)cyclopentadienyl]cobalt(I) (16f): Reaction mixture: [Co$_2$(CO)$_8$] (458 mg, 1.3 mmol) and I$_2$ (340 mg, 1.3 mmol) in THF (28 mL), 1-(7,7-dimethyloct-5-ynyl)-3-(8,8-dimethylnon-6-ynyl)cyclopentadiene (**14f**) (1.1 g, 3.2 mmol) and *n*-butyllithium (1.8 mL, 2.5 M in hexane) in THF (6 mL).Yield 250 mg (40%). Orange oil. ^{1}H NMR (300 MHz, C$_6$D$_6$): δ = 0.80–0.87 (m, 4 H, CH$_2$), 1.24 (s, 18 H, CH$_3$), 1.30–1.50 (br., 6 H, CH$_2$), 1.86–1.91 (m, 4 H, CH$_2$), 2.01–2.09 (m, 4 H, CH$_2$), 4.48 (s, 2 H, CH), 4.60 (s, 1 H, CH) ppm. ^{13}C NMR (75 MHz, C$_6$D$_6$): δ = 18.9 (CH$_2$), 19.1 (CH$_2$), 27.7 (C), 28.0 (CH$_2$), 28.4 (CH$_2$), 28.9 (CH$_2$), 29.2 (CH$_2$), 29.3 (CH$_2$), 30.1 (C), 30.3 (CH$_2$), 30.6 (CH$_2$), 31.6 (CH$_3$), 31.7 (CH$_3$), 78.6 (C), 78.8 (C), 83.4 (CH), 83.5 (CH), 85.6 (CH), 89.3 (C), 89.6 (C), 106.0 (C), 106.2 (C) ppm. IR (film) $\tilde{\nu}$ = 2967, 2930, 2860, 2016, 1955, 1475, 1455, 1388 cm^{-1}. UV/Vis (CH$_2$Cl$_2$): $\lambda_{max.}$ (log ε) = 246 (4.27), 294 (2.87) nm.

Dicarbonyl-η^5-[1,3-bis(5-trimethylsilylpent-4-ynyl)cyclopentadienyl]-cobalt(I) (16g): Reaction mixture: [Co$_2$(CO)$_8$] (1.2 g, 3.5 mmol) and I$_2$ (896 mg, 3.5 mmol) in THF (75 mL), 1,3-bis[5-(trimethylsilyl)pent-4-ynyl]cyclopentadiene (**14g**) (2.7 g, 7.8 mmol) and *n*-butyllithium (6.3 mL, 1.6 M in hexane) in THF (15 mL). Yield 696 mg (57%). Orange oil. ^{1}H NMR (300 MHz, C$_6$D$_6$): δ = 0.17 (s, 18 H, CH$_3$), 1.37–1.46 (m, 4 H, CH$_2$), 1.94–2.07 (m, 8 H, CH$_2$), 4.40 (s, 2 H, CH), 4.48 (s, 1 H, CH) ppm. ^{13}C NMR (75 MHz, C$_6$D$_6$): δ = 0.4 (CH$_3$), 19.8 (CH$_2$), 27.3 (CH$_2$), 29.7 (CH$_2$), 83.5 (CH), 85.4 (CH), 85.5 (C), 105.1 (C), 106.9 (C) ppm. IR (film) $\tilde{\nu}$ = 2858, 2174, 2046, 2016, 1955, 1427, 1326 cm^{-1}. UV/Vis (CH$_2$Cl$_2$): $\lambda_{max.}$ (log ε) = 250 (4.03), 330 (3.21) nm.

Synthesis of Endohedral Rhodium Complexes 7b and 8b: A dry 250-mL flask was charged with cyclopentadienyl(dicarbonyl)rhodium (**15b**, 636 mg, 1.28 mmol) and 120 mL cyclooctane. The solution was refluxed (72 h). The solvent was evaporated under reduced pressure and the products were purified by column chromatography [alox III (neutral)]. After eluting the column with petroleum ether in the beginning, dichloromethane was used to elute first complex **7b** and then complex **8b** as yellow bands.

Complex 7b: Yield 95 mg (16%). Yellow solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 1.49 (s, 9 H, CH$_3$), 1.51 (s, 9 H, CH$_3$), 1.56 (m, 2 H, CH$_2$), 1.73 (m, 2 H, CH$_2$), 1.79 (m, 2 H, CH$_2$), 1.90 (m, 2 H, CH$_2$), 2.19 (m, 2 H, CH$_2$), 2.22 (m, 2 H, CH$_2$), 2.58 (m, 2 H, CH$_2$), 2.71 (m, 2 H, CH$_2$), 5.15 (ps, 1 H, CH), 5.28 (ps, 1 H, CH), 5.35 (ps, 1 H, CH) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 26.0 (CH$_2$), 27.0 (CH$_2$), 27.2 (CH$_2$), 29.1 (CH$_2$), 29.7 (CH$_2$), 30.0 (CH$_2$), 30.8 (CH$_2$), 31.6 (CH$_3$), 32.1 (CH$_2$), 33.4 (C), 33.9 (C), 34.5 (CH$_3$), 83.2 (CH, $J_{\mathrm{Rh,C}}$ = 5.6 Hz), 84.0 (CH, $J_{\mathrm{Rh,C}}$ = 6.5 Hz), 85.7 (C, $J_{\mathrm{Rh,C}}$ = 8.8 Hz), 86.2 (CH, $J_{\mathrm{Rh,C}}$ = 6.8 Hz), 93.5 (C, $J_{\mathrm{Rh,C}}$ = 9.3 Hz), 93.9 (C, $J_{\mathrm{Rh,C}}$ = 10.1 Hz), 106.1 (C, $J_{\mathrm{Rh,C}}$ = 5.5 Hz), 106.4 (C, $J_{\mathrm{Rh,C}}$ = 6.3 Hz), 111.1 (C, $J_{\mathrm{Rh,C}}$ = 11.4 Hz), 163.2 (CO) ppm. MS (positive FAB): m/z = 468 [M]$^+$. IR (KBr) $\tilde{\nu}$ = 2922, 2857, 2232, 1733, 1598, 1485, 1448, 1388 cm^{-1}. UV/Vis (CH$_2$Cl$_2$): $\lambda_{max.}$ (log ε) = 266 (5.05), 348 (4.42) nm. HRMS (positive FAB) calcd. for C$_{26}$H$_{37}$ORhNa ([M + Na]$^+$), 491.1797; 491.1804 found, (+0.7 mmu).

Complex 8b: Yield 3 mg (0.5%). Yellow oil. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 1.41 (s, 9 H, CH$_3$), 1.58 (s, 9 H, CH$_3$), 1.91–2.62 (m, 16 H, CH$_2$), 5.33 (ps, 1 H, CH), 5.38 (ps, 1 H, CH), 5.50 (ps, 1 H, CH) ppm. MS (positive FD): m/z = 468 [M]$^+$. IR (film) $\tilde{\nu}$ = 2925, 2856, 1562, 1446, 1362, 1261, 1029 cm^{-1}. HRMS (positive FAB) calcd. for C$_{26}$H$_{38}$ORh ([M]$^+$), 469.1978; found, 469.1939 (–3.9 mmu).

General Procedure for the Synthesis of Endohedral Cobalt Complexes 1d–g: A dry 250-mL flask was charged with the dicarbonylcobalt complex and cyclooctane. The solution was refluxed (12 h). The solvent was evaporated under reduced pressure and the products were purified by column chromatography (alox III).

[3.4]-η^5-(1,1′,3,3′)-Cyclopentadienyl-η^4-[2,4-bis(*tert*-butyl)cyclobutadienophane]cobalt(I) (1d): Reaction mixture: complex **16d** (140 mg, 0.40 mmol) in cyclooctane (80 mL). Yield 20 mg (5%). Yellow solid, m.p. 110 °C. ^{1}H NMR (500 MHz, C$_6$D$_6$): δ = 1.20 (s, 18 H, CH$_3$), 1.54–1.81 (br., 8 H, CH$_2$), 2.03–2.12 (br., 4 H, CH$_2$), 2.24–2.27 (m, 1 H, CH$_2$), 2.53–2.61 (m, 1 H, CH$_2$), 4.56 (s, 1 H, CH), 4.79 (s, 1 H, CH), 5.00 (s, 1 H, CH) ppm. ^{13}C NMR (125 MHz, C$_6$D$_6$): δ = 23.5 (CH$_2$), 24.3 (CH$_2$), 29.3 (CH$_2$), 29.6 (CH$_2$), 29.7 (CH$_2$), 31.2 (CH$_2$), 31.6 (CH$_3$), 32.4 (C), 32.7 (C), 33.0 (CH$_3$), 39.0 (CH$_2$), 66.1 (C), 80.9 (CH), 81.1 (C), 81.3 (CH), 81.8 (CH), 92.7 (C), 93.2 (C), 95.3 (C), 95.5 (C) ppm. IR (KBr) $\tilde{\nu}$ = 3079, 2953, 2910, 2849, 1622, 1478, 1460, 1442, 1391 cm^{-1}. UV/Vis (CH$_2$Cl$_2$): $\lambda_{max.}$ (log ε) = 268 (4.16), 302 (3.24), 342 (2.80) nm. HRMS (positive EI) calcd. for C$_{24}$H$_{35}$Co ([M]$^+$), 383.2071; found, 383.2057 (–1.4 mmu). C$_{24}$H$_{35}$Co (382.47): calcd. C 75.37, H 9.22; found C 75.47, H 8.99.

[3.5]-η^5-(1,1′,3,3′)-Cyclopentadienyl-η^4-[2,4-bis(*tert*-butyl)cyclobutadienophane]cobalt(I) (1e): Reaction mixture: complex **16e** (130 mg, 0.29 mmol) in cyclooctane (50 mL). Yield 34 mg (30%). Yellow solid, m.p. 140 °C. ^{1}H NMR (300 MHz, C$_6$D$_6$): δ = 1.14 (s, 9 H, CH$_3$), 1.16 (s, 9 H, CH$_3$), 1.37–1.74 (m, 8 H, CH$_2$), 1.82–1.88 (m, 4 H, CH$_2$), 2.19–2.23 (m, 1 H, CH$_2$), 2.39–2.43 (m, 1 H, CH$_2$), 2.59–2.62 (m, 2 H, CH$_2$), 4.58 (s, 1 H, CH), 4.70 (s, 1 H, CH), 4.78 (s, 1 H, CH) ppm. ^{13}C NMR (125 MHz, C$_6$D$_6$): δ = 22.9 (CH$_2$), 23.1 (CH$_2$), 24.0 (CH$_2$), 24.3 (CH$_2$), 25.0 (CH$_2$), 26.1 (CH$_2$), 31.4 (CH$_3$), 32.1 (CH$_3$), 32.4 (C), 32.6 (C), 37.7 (CH$_2$), 66.4 (C), 73.4 (C), 78.8 (CH), 81.0 (CH), 81.3 (CH), 90.7 (C), 92.1 (C) 93.5 (C), 94.2 (C) ppm. IR (KBr) $\tilde{\nu}$ = 2955, 2919, 2855, 1478, 1455, 1372 cm^{-1}. UV/Vis (CH$_2$Cl$_2$): $\lambda_{max.}$ (log ε) = 270 (4.49), 300 (3.54), 374 (3.20) nm. HRMS (positive EI) calcd. for C$_{25}$H$_{37}$Co ([M]$^+$), 396.2227; found, 396.2238 (+1.1 mmu). C$_{25}$H$_{37}$Co (396.49): calcd. C 75.37, H 9.41; found C 75.37, H 9.28.

[4.5]-η^5-(1,1′,3,3′)-Cyclopentadienyl-η^4-[2,4-bis(*tert*-butyl)cyclobutadienophane]cobalt(I) (1f): Reaction mixture: complex **16f** (165 mg, 0.35 mmol) in cyclooctane (60 mL). Yield 22 mg (15%). Yellow solid, m.p. 151 °C. ^{1}H NMR (300 MHz, C$_6$D$_6$): δ = 1.22 (s, 9 H, CH$_3$), 1.23 (s, 9 H, CH$_3$), 1.25–1.56 (m, 4 H, CH$_2$), 1.44–1.61 (m, 4 H, CH$_2$), 1.88–1.89 (m, 1 H, CH$_2$), 1.89–1.95 (m, 2 H, CH$_2$), 2.09–2.14 (m, 1 H, CH$_2$), 2.21–2.28 (m, 1 H, CH$_2$), 2.30–2.34 (m, 1 H, CH$_2$), 2.41–2.49 (m, 1 H, CH$_2$), 2.53–2.55 (m, 2 H, CH$_2$), 2.65–2.71 (m, 1 H, CH$_2$), 4.65 (s, 1 H, CH), 4.76 (s, 1 H, CH), 4.84 (s, 1 H, CH) ppm. ^{13}C NMR (125 MHz, C$_6$D$_6$): δ = 23.4 (CH$_2$), 23.7 (CH$_2$), 23.9 (CH$_2$), 25.3 (CH$_2$), 25.4 (CH$_2$), 27.3 (CH$_2$), 27.5 (CH$_2$), 28.9 (CH$_2$), 31.6 (CH$_2$), 31.8 (CH$_3$), 31.9 (CH$_3$) 32.6 (C), 69.7 (C), 74.1 (C), 77.8 (CH), 79.5 (CH), 79.8 (CH), 87.7 (C), 89.6 (C), 95.4 (C), 95.6 (C) ppm. IR (KBr) $\tilde{\nu}$ = 2957, 2921, 2857, 2026, 1628, 1479, 1458 cm^{-1}. UV/Vis (CH$_2$Cl$_2$): $\lambda_{max.}$ (log ε) = 278 (4.34), 322 (3.18), 372 (2.98) nm. HRMS (positive EI) calcd. for C$_{26}$H$_{39}$Co ([M]$^+$), 410.2384; found, 410.2336 (–4.8 mmu).

[3.3]-η^5-(1,1′,3,3′)-Cyclopentadienyl-η^4-[2,4-bis(trimethylsilyl)cyclobutadienophane]cobalt(I) (1g): Reaction mixture: complex **16g** (665 mg, 360 mmol) in cyclooctane (360 mL). Yield 207 mg (35%). Yellow solid, m.p. 55 °C. ^{1}H NMR (500 MHz, C$_6$D$_6$): δ = 0.14 (s, 9 H, CH$_3$), 0.24 (s, 9 H, CH$_3$), 1.41–1.56 (br., 4 H, CH$_2$), 1.73–1.85 (br., 6 H, CH$_2$), 2.04–2.14 (m, 2 H, CH$_2$), 4.55 (s, 1 H, CH), 4.56

(s, 1 H, CH), 5.13 (s, 1 H, CH) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 1.7 (CH_3), 1.9 (CH_3), 26.0 (CH_2), 26.9 (CH_2), 40.8 (CH_2), 77.3 (C), 79.5 (C), 80.1 (CH), 84.1 (C), 84.3 (CH), 95.0 (C) ppm. IR (KBr) $\tilde{\nu}$ = 2936, 2912, 2849, 1627, 1545, 1421, 1324 cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (log ε)= 266 (4.01), 310 (3.31), 398 (2.71) nm. HRMS (positive EI) calcd. for $C_{21}H_{33}CoSi_2$ ([M]$^+$), 400.1453; found, 400.1477 (+2.4 mmu).

[3.3]-η^5-(1,1′,3,3′)-Cyclopentadienyl-η^4-(cyclobutadienophane)cobalt(I) (1h): A dry 25-mL flask was charged with complex **1g** (126 mg, 0.32 mmol), tetramethylammonium fluoride tetrahydrate (408 mg, 2.47 mmol) and DMSO (10 mL). The solution was stirred at 80 °C (15 h). Then the mixture was extracted with petroleum ether (8×). The organic layer was washed with water and dried ($MgSO_4$). The solvent was removed under reduced pressure and the product was purified by column chromatography [alox III (neutral)]. Yield 61 mg (74%). Yellow solid, m.p. 77 °C. ^{1}H NMR (300 MHz, C_6D_6): δ = 1.09–1.25 (m, 4 H, CH_2), 1.53 (pt, ^2J = 12.7 Hz, 2 H, CH_2), 1.77–1.93 (m, 4 H, CH_2), 2.17 (pd, ^2J = 14.4 Hz, 2 H, CH_2), 3.68 (pd, ^4J = 8.0 Hz, 1 H, CH), 4.45–4.47 (d, ^4J = 8.0 Hz, 1 H, CH), 4.53 (s, 2 H, CH), 4.66 (s, 1 H, CH) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 25.4 (CH_2), 25.9 (CH_2), 37.7 (CH_2), 66.1 (CH), 67.9 (CH), 72.2 (C), 78.7 (CH), 83.2 (CH), 94.9 (C) ppm. IR (KBr) $\tilde{\nu}$ = 3072, 2910, 2867, 2831, 1627, 1428, 1407 cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (log ε) = 254 (4.31), 284 (3.30), 362 (3.01) nm. HRMS (positive EI) calcd. for $C_{15}H_{17}Co$ ([M]$^+$), 265.0662; found, 265.0649 (–1.3 mmu).

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