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Journal of Organometallic Chemistry 570 (1998) 121–127

Journal of Organometallic Chemistry

Organometallic chemistry in supercritical water: metallorganic products of the CpCo-catalyzed cyclotrimerization of acetylenes

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Received 5 June 1998; received in revised form 26 June 1998

Abstract

Cyclotrimerization of *t*-butylacetylene or phenylacetylene with $CpCo(CO)_2$ as catalyst in supercritical water yields the isomeric 1,3,5-tris-substituted- (**1**: R = Ph, **1a**: R = bu^t) and 1,2,4-tris-substituted benzene derivatives (**2**: R = Ph, **2a**: R = bu^t). The identification of the organometallic products obtained under these conditions is described. The formation of all possible isomers of the corresponding CpCo(bis-substituted-cyclobutadiene) (**3**, **4**), CpCo(bis-substituted-CpCobaltacyclopentadiene) (**5**, **6**, **7**) and CpCo(bis-substituted-cyclopentadienone) (**8**, **9**, **10**) via GC-MS is reported. Two of three isomers of CpCo(bis-substituted-cyclopentadienone) (**8**, **9** (R = Ph), **8a**, **9a** (R = bu^t)) were separated and characterized in substance. The structures of **8**, **9**, **8a** and **9a** were elucidated by single crystal X-ray diffraction. **8** crystallizes in the orthorhombic space group $P2_12_12_1$ (No.19) with $a = 840.5(1)$, $b = 1105.9(2)$, $c = 1767.2(3)$ pm, $V = 1642.8(1) \times 10^6$ pm^3, $Z = 4$, $D_{calc} = 1.441$ g cm^{-3}, $R_1 = 0.0501$ ($I > 3\sigma$), $wR_1 = 0.0529$ ($I > 3\sigma$). **9** crystallizes in the orthorhombic space group $Pna2_1$ (No.33) with $a = 1086.7(1)$, $b = 4726.0(1)$, $c = 1668.5(1)$ pm, $V = 8427.3(1) \times 10^6$ pm^3, $Z = 20$, $D_{calc} = 1.404$ g cm^{-3}, $R_1 = 0.0705$ ($I > 2\sigma$), $Rw = 0.1321$ (all data on F^2). **8a** crystallizes in the monoclinic space group $P2_1/c$ (No. 14) with $a = 1441.6(3)$, $b = 1241.3(1)$, $c = 3672.6(6)$ pm, $\beta = 92.39(2)°$, $V = 6566(2) \times 10^6$ pm^3, $Z = 16$, $D_{calc} = 1.280$ g cm^{-3}, $R_1 = 0.082$ ($I > 2\sigma$), $Rw = 0.144$ (all data on F^2). **9a** crystallizes in the monoclinic space group $P2_1/c$ (No. 14) with $a = 669.3(1)$, $b = 1335.7(1)$, $c = 1843.1(1)$ pm, $\beta = 94.78(1)°$, $V = 1641.9(1) \times 10^6$ pm^3, $Z = 4$, $D_{calc} = 1.28$ g cm^{-3}, $R_1 = 0.0622$ ($I > 2\sigma$), $Rw = 0.1185$ (all data on F^2).

Keywords: Cyclopentadienyl-Co-complexes; Co-cyclopentadienone-complexes; Supercritical water; Cyclotrimerization of acetylenes

1. Introduction

Supercritical water (SCW, water above 374°C and 221 bar) possesses good solvent properties and has been used as a non polar extractant for coal [1]. About synthesis or reactions of organometallics in SCW only few is reported [2]. $CpCo(CO)_2$ [3–7] is known to catalyze several reactions, as C–C coupling [8] or C–N coupling [9,10] agent. E.O. Fischer described $CpCo(CO)_2$ as a very sensitive compound towards oxidation but quite stable in water, even at elevated temperatures [11]. After treatment with refluxing desoxygenated water for several hours more than 98% $CpCo(CO)_2$ can be recovered.

Jerome and Parsons have shown that cyclotrimerization of monosubstituted acetylenes in SCW is catalyzed by $CpCo(CO)_2$ [2]. We report here the reactions of monosubstituted acetylenes (R = Ph or bu^t) in SCW, catalyzed by $CpCo(CO)_2$ in metallic reactors. The main interest of this work was the isolation, characterization and quantification of the metallorganic products, formed in the catalysis in SCW. Further we compare our results with the mechanism known from the catalysis in organic solvents [12–18].

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0022-328X/98/$ - see front matter
PII S0022-328X(98)00844-4

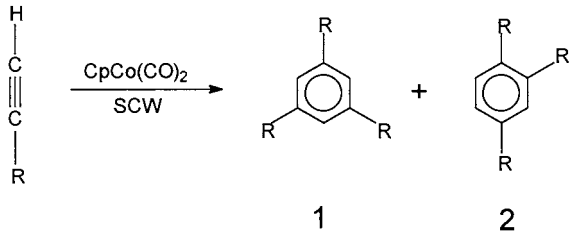

Fig. 1. Cyclotrimerization of acetylenes (**1**, **2** R = Ph, **1a**, **2a** R = bu^t).

2. Results and discussion

Cyclotrimerization of acetylenes under homogeneous catalysis in organic solvents has been investigated first under catalysis of $Ni(CO)_2(P(Ph)_3)_2$ [19]. Under CpCo-catalysis we achieved the conversion of acetylenes to aromats in SCW after heating for 2 h (Fig. 1). The yields and the relative amounts of the both benzene isomers are comparable to published results of catalysis in organic solvents (Table 1) [8,9,12–14]. In the absence of the catalyst no formation of aromatic ring systems is observed.

The mechanism of the cyclotrimerization of acetylenes in organic solvents has been discussed [12–18]. The analysis of the organic and metallorganic products, found for the cyclotrimerization of acetylenes in SCW, leads to a mechanism in SCW according to that known from catalysis in organic solvents.

Under heating $CpCo(CO)_2$, **a**, may loose a carbonyl ligand and after coordination of an acetylene unit **b** can be formed (Fig. 2). Further cleavage of a Co–CO bond forms **c** and coordination of a second acetylene leads to **d**. Oxidative coupling submits the CpCobalta-cyclopentadiene, **e**, which builds **f** coordinating another acetylene unit (Fig. 2). Under insertion of the acetylene-unit and reductive elimination the benzene derivatives **1** and **2** are formed leaving the remaining CpCo-fragment, **g**, which is able to close the catalytic cycle by coordination of a new acetylene unit (Fig. 2).

The central metallorganic compound in the catalytic cycle is **e**, because its formation explains all identified metallorganic products. So **e** can coordinate a carbon monoxide, forming **h**, and further insertion and following reductive elimination forms the CpCo-cyclopentadienones **8, 9** and **10**. These three isomers could also be formed by reaction of **b** with further acetylene under oxidative coupling followed by reductive elimination. Reductive elimination of **e** forms the CpCo-cyclobutadiene complexes **3** and **4**. Coordination of free CpCo-fragments to **e** forms the three isomers **5**, **6**, **7** of CpCo-cobaltacyclopentadiene complexes.

In detail for the $CpCo(CO)_2$ catalyzed cyclotrimerization of phenylacetylene or *t*-butylacetylene, we identified the following metallorganic compounds (Fig. 3).

The formation of the metallorganic compounds **3**–**10** seems to be irreversible, as they do not show catalytic activity based on the catalytic cycle (Fig. 2). This assumption is supported by the observation that in the mixture of the organic products none of the ligands, coordinated to the CpCo-fragment, or their Diels–Alder products were found.

The composition of the mixture of the metallorganic products (Fig. 3) has been analyzed by GC-MS and the characteristic peak for all compounds is the $m^+/z =$ 124, corresponding to the $CpCo^+$-cation which can be generated by fragmentation from **3**–**10** (Table 2).

Generally the catalytic cyclotrimerizations of the monosubstituted acetylenes were carried out in the presence of 3 mol% of $CpCo(CO)_2$. To obtain higher amounts of the metallorganic products for their isolation special experiments were carried out using two equivalents of acetylene for one equivalent $CpCo(CO)_2$. From these experiments first we isolated preparative yields of the metallorganic compounds **8**, **8a**, **9**, and **9a**. Then quantification occurred by adding a certain amount of CpCo(butadiene) as external standard and then via GCMS referring all the peaks of the gas-chromatogramm to the peak of the CpCo(butadiene) (Table 2). So for the cyclotrimerization of phenylacetylene 5% of the $CpCo(CO)_2$ were recovered, and 10% of the metallorganic compounds were lost because of technical reasons and 5% reacted to not exactly identified metallorganic compounds. In the case of *t*-butylacetylene 12% of $CpCo(CO)_2$ were recovered, 10% of metallorganic compounds were lost and 17% of the $CpCo(CO)_2$ reacted to unidentified metallorganic compounds.

The observation of $CpCo(CO)_2$ at the end of the reaction is due to the unability of the CO to leave the reactor during the experiment, so it can always be

Table 1
Quantified GC-MS data of the aromats

Products	Yield (%)	Ret. Time (min)[a]	m^+/z (%)
1	24	34.58	306, 199 (M^+); 228, 18 (M^+-C_6H_6); 153, 8 (M^{2+}); 77, 17 (Ph^+); 78, 13 ($C_6H_6^+$)
2	71	32.70	306, 100 (M^+); 228, 84 (M^+-C_6H_6); 77, 90 (Ph^+); 51, 88 ($C_4H_3^+$)
1a	64	22.21	246, 11 (M^+); 231, 34 (M^+-CH_3); 189 8 (M^+-$C(CH_3)_3$); 57, 100 ($C(CH_3)_3^+$)
2a	21	19.75	246, 11 (M^+); 231, 100 (M^+-CH_3); 57, 91 ($C(CH_3)_3^+$)

1, **2** R = Ph, **1a**, **2a** R = bu^t. M^+symbolizes the the molecule ion.
[a] Further informations see Section 4.

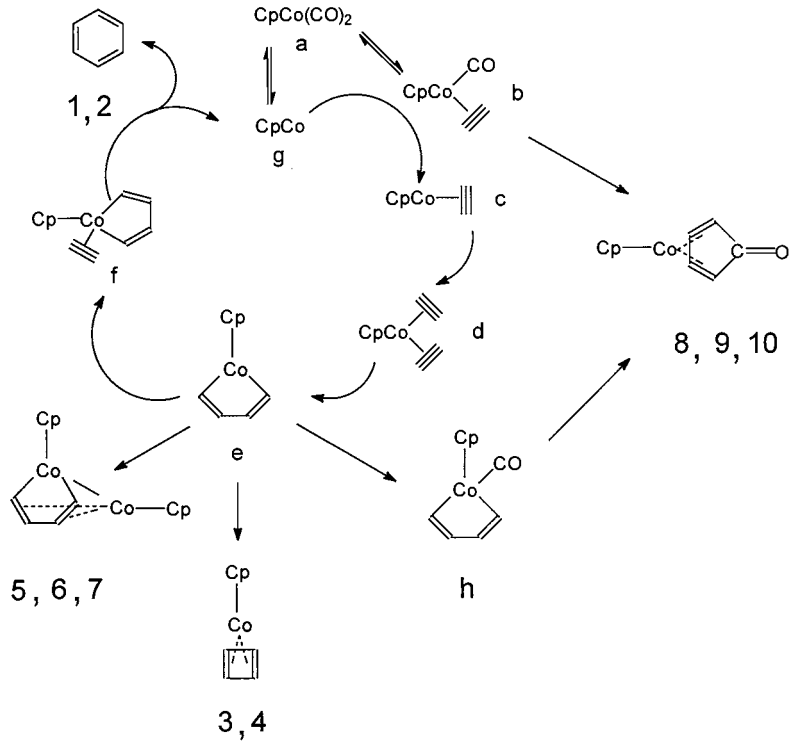

Fig. 2. Mechanism of the reaction of $CpCo(CO)_2$ with acetylenes. For reasons of clarity the substituents of the monosubstituted acetylenes (R = Ph or bu^t) are omitted.

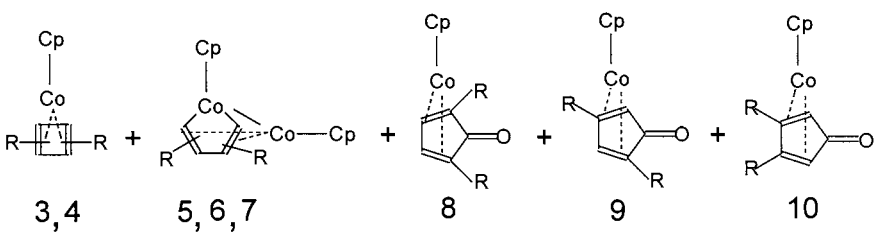

Fig. 3. Metallorganic compounds built in the reaction of $CpCo(CO)_2$ with monosubstituted acetylenes. For **3–10** R = Ph, for **3a–10a** R = bu^t.

rebuilt by recombination of e.g. CpCo with carbon monoxide.

After chromatographic purification **8**, **9**, **8a**, and **9a** could be isolated and characterized by ^{1}H-NMR- and IR-spectroscopy.

All ^{1}H-NMR-spectra show the characteristic signal at $\delta = 4.65–5.00$ for the resonance frequency of the protons of the Cp-ring (Table 3). All IR-spectra show a shouldered peak at 1560–1590 cm^{-1} which is characteristic for the C=O vibration in CpCo-cyclopentadienones [21,23] (Table 3). The characteristic C–H-valence vibration of the aromatic rings appears for all four compounds in the region 3057–3092 cm^{-1}. In **8a** and **9a** the C–H valence vibration for the bu^t-residue is found between 2954 and 2960 cm^{-1} (Table 3).

The four CpCo-cyclopentadienone derivatives (**8**, **8a**, **9**, **9a**) were crystallized and characterized by single crystal X-ray diffractometry.

The results of the X-ray analyses are shown in Fig. 4. Table 4 summarizes the crystallographic data [24]. For **8a** four molecules are found in the crystallographic independent unit of the elementary cell, as for **9** five, respectively. As the independent molecules for **8a** and **9** differ mainly in the rotation positions of the residues bound to the Cyclopentadienone only one is shown in Fig. 4 as example. The corresponding distances and angles are listed for all molecules in Table 5.

The substituted cyclopentadienones are in all the structures bound to the CpCo-fragment in the same way (Fig. 4). The Co–C(C2, C5)-distances are found to be in the array of 204–207 pm (Table 5). For the C-atoms in meta position to the carbonyl group (C3, C4) slightly shorter Co–C-distances are found (198–202 pm, Table 5) according to a back bonding from the metal atom in antibonding orbitals of the butadiene unit of the cyclopentadienone.

Table 2
GC-MS data of the metallorganic compounds [20–22]

Products	Yield (%)	Ret. time (min)[a]	m^+/z (%)
3–4	25	31.36, 31.72	328, 90 (M^+); 226, 40 (M^+-C_8H_6); 124, 100 ($CpCo^+$); 59, 37 (Co^+)
5–7	37	39.30, 40.16, 41.25	452, 100 (M^+); 328, 2 (M^+-CpCo); 189, 24 (Cp_2Co^+); 124, 21 ($CpCo^+$); 59, 13 (Co^+)
8–10	18	37.61, 37.65, 37.70	356, 100 (M^+); 328, 67 (M^+-CO); 226, 9 (M^+-CO-C_8H_6); 124, 43 ($CpCo^+$); 59, 35 (Co^+)
3a–4a	26	21.92, 23.34	288, 100 (M^+); 273, 84 (M^+-CH_3); 258, 66 (M^+-$(CH_3)_2$); 243, 20 (M^+-$(CH_3)_3$); 231, 6 (M^+-$C(CH_3)_3$); 124, 58 ($CpCo^+$); 59, 44 (Co^+)
5a–7a	31	30.63, 32.27, 32.30	412 100 (M^+); 397, 5 (M^+-CH_3); 382, 11 (M^+-$(CH_3)_2$); 288, 6 (M^+-CpCo); 189, 24 (Cp_2Co^+); 124, 3 ($CpCo^+$)
8a–10a	4	27.40, 27.80, 27.90	316, 11 (M^+); 301, 43 (M^+-CH_3); 274, 65 (M^+-C_3H_6); 259, 48 (M^+-57); 124, 77 (CpCo); 59, 100 (Co^+); 57, 28 ($C(CH_3)_3^+$)

For **3–10** R = Ph, for **3a–10a** R = bu^t. M^+ symbolizes the molecule ion.
[a] Isomers of compounds with same mass show similar mass spectra. The retention times are only related to moieties with same mass, their constitution is not identified.

The coordination of the cyclopentadienone to the metal causes a folding of the former planar cyclopentadienone, as the interaction of the CpCo-fragment with the butadiene-unit is stronger than with the CO-part. The folding angles (angles between the planes once built from the four carbon-atoms of the butadiene unit of the cyclopentadienone (C2, C3, C4, C5) and once built from the oxygen atom and C1, C2, C5 are in the range of 9–11°.

Table 3
^{1}H-NMR- and IR-data of disubstituted CpCo-cyclopentadienones **8**, **9**, **8a**, **9a**

Compound	^{1}H-NMR (δ)	IR (cm^{-1})
$C_{22}H_{17}CoO$	8.14 (m, 4H, Ph–H, orth)	3062 m (C–H_{aromat})
	7.35 (m, 6H, Ph–H, m, p)	1574 vs (C=O)
8	5.53 (s, 2H, Cpon–H)	1446 m (C=C)
	4.65 (s, 5H, Cp)	771 s (Cp)
$C_{18}H_{25}Co$	1.29 (s, 18H, bu^t–H)	3086 w (C–H_{aromat})
	4.79 (s, 2H, Cpon–H)	2954 s (C–H, bu^t)
8a	5.03 (s, 5H, Cp–H)	1577 vs (C=O)
$C_{22}H_{17}CoO$	8.11 (m, 2H, Ph–H, orth)	3058 m (C–H_{aromat})
	7.55 (m, 2H, Ph–H, orth)	1585 vs (C=O)
9	7.36 (m, 6H, Ph–H, m, p)	1452 s (C=C)
	6.02 (s, 1H, Cpon–H)	772 s (Cp)
	5.13 (s, 1H, Cpon–H)	
	4.70 (s, 5H, Cp)	
$C_{18}H_{25}CoO$	1.18 (s, 9H, bu^t–H)	3092 w (C–H_{aromat})
	1.31 (s, 9H, bu^t–H)	2960 s (C–H, bu^t)
9a	4.29 (s, 1H, Cpon–H)	1558 vs (C=O)
	4.81 (s, 1H, Cpon–H)	
	5.01 (s, 5H, Cp)	

For **8, 9** R = Ph, for **8a, 9a** R = bu^t.

The folding of the cyclopentadienone-rings is further expressed in the longer Co–C-distances for the carbonyl-C-atoms, which are determined between 223 and 229 pm (Table 5).

The bonding feature of the cyclopentadienone to the CpCo-fragment is for all the complexes identical to other compounds of this type [28].

3. Conclusions

We showed here the evidence that metallorganic chemistry is also possible under extreme conditions as they are in SCW.

For the cyclotrimerization of monosubstituted acetylenes in SCW under $CpCo(CO)_2$ catalysis we identified and quantified the metallorganic products and the results confirm a mechanism, working in SCW, similar to that in organic solvents.

The possibility to use SCW as a solvent for metallorganic reactions or for catalysis involving metallorganic compounds is opening the catalytic field for interesting research on the influence of SCW on these reactions.

4. Experimental details

Reagents and analytic details: $CpCo(CO)_2$ (Sigma–Aldrich) was distilled and stored under Argon in a Schlenk tube. The monosubstituted acetylenes (Sigma Aldrich) (R = Ph, bu^t), pentane and dichloromethane (Merck) were dried using standard methods and all preparations were carried out using Schlenk techniques. To get reproducible results the water was heated to reflux under argon for 48 h prior its use. Alumina, used for chromatography, was heated (500°C) under vacuum. After cooling at room temperature 4% water has been added to get alumina II.

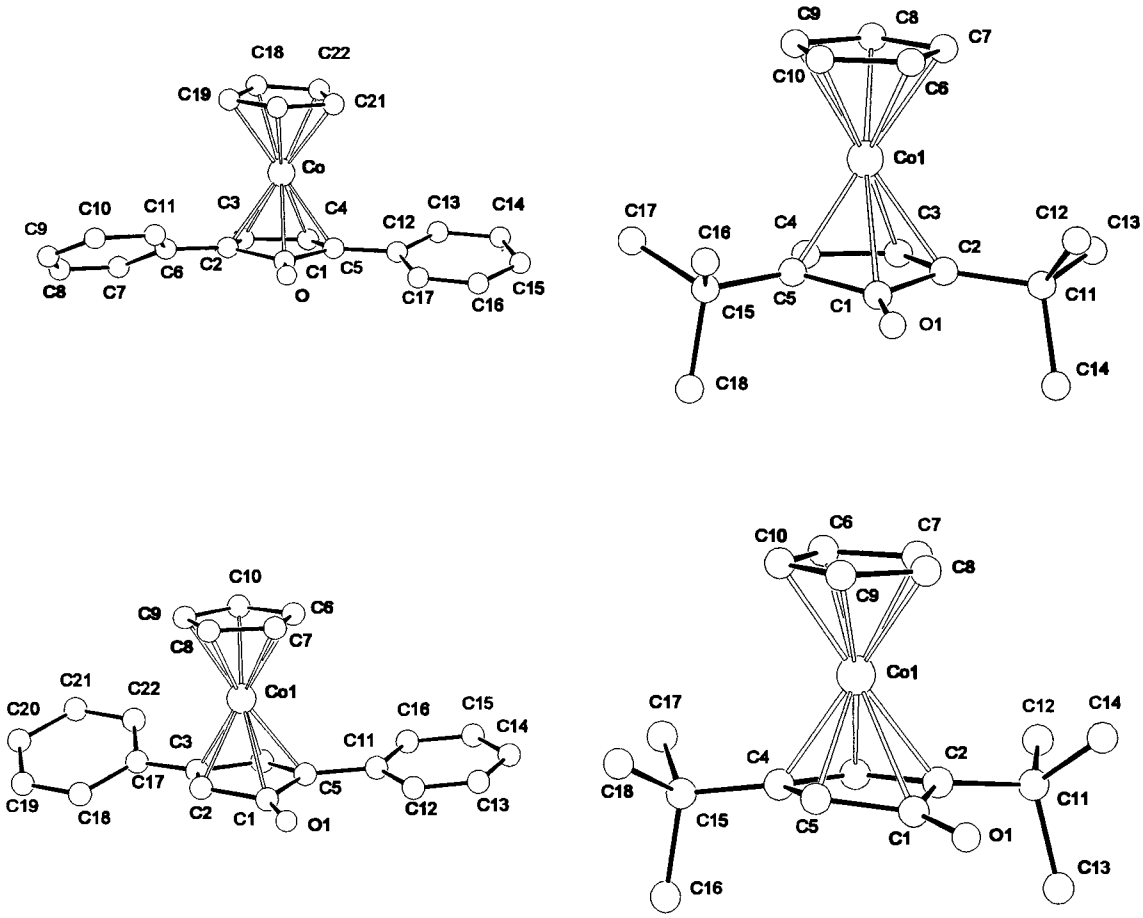

Fig. 4. View to one molecule of **8** (above left), **8a** (above right), **9** (down left), **9a** (down right) in the crystal.

Reaction extracts in dichloromethane were analyzed by GCMS-techniques (Hewlett Packard 5890, column db5, l = 30 m, Inj. temp. 250°C, Det. temperature 310°C, Initial temp. 20°C, Initial time 5 min, Rate 10 °C min^{-1}, final temperature 300°C, final time 30 min). ^{1}H-NMR-spectroscopy of the isolated products were obtained on a Varian Unity Inova spectrometer in $CDCl_3$ solution ($\delta = 7.27$ ppm) at 29°C. The spectra were obtained at the operating frequency of 400 MHz; 45° pulses were used with 5 s repetition time. Infrared spectra were recorded on a BIORAD FT spectrometer in KBr-pellets in the region of 400–4000 cm^{-1}. For the details of the X-ray analysis see Table 4.

All reactions in SCW were carried out in a batch reactor (5 ml) of Inconel 625 under an inert atmosphere of argon.

The 5 ml-autoklav was filled under conditions of standard Schlenk techniques. At the beginning the apparatus was heated with a heat gun under vacuum (Fig. 5). The solvent and the reagents were filled under argon atmosphere and by varying the amount of the solvent (2.5–4.0 ml) the pressure during the experiment can be controlled (normal conditions: 380°C, 250 bar).

For the catalytic reactions the reactor was filled with 0.25 ml (0.24 g, 2.4 mmol) of phenylacetylene or 0.3 ml *t*-butylacetylene (0.2 g, 2.4 mmol) and 0.013 g (0.07 mmol) $CpCo(CO)_2$ (educt:catalyst = 35:1) and 3.96 ml H_2O.

To isolate **8** and **9** (**8a** and **9a**) in preparative yields experiments with higher amounts of $CpCo(CO)_2$ were carried out. In these experiments we gave to the same amount of the acetylenes 0.22 g $CpCo(CO)_2$ (educt: catalyst 2:1) and 3.8 ml H_2O in the reactor.

After heating for 2 h and reaction at 380°C and 250 bar pressure, the reactor was cooled at room temperature and the contents was filled in a Schlenk tube. After cleaning the reactor with 4 ml dichloromethane the organic layer and the water mixture were combined and the water layer were extracted three times with 2 ml dichloromethane. The organic layer was analyzed by GCMS-spectroscopy.

After removal of the solvent in vacuum the brown residue was subjected to chromatography on an aluminia column using dichloromethane/methanol (100:1) mixture as eluant. The eluant has been developed by chromatography on pre-coated plastic sheets (Machery–

Table 4
Crystallographic data

Compound	**8**	**8a**	**9**	**9a**
Empirical formula	$C_{22}H_{17}CoO$	$C_{18}H_{25}CoO$	$C_{22}H_{17}CoO$	$C_{18}H_{25}CoO$
Formula weight	356.3	316.3	356.3	316.3
Crystal size (mm^3)	$0.45\times0.13\times0.10$	$0.30\times0.30\times0.15$	$0.20\times0.30\times0.40$	$0.30\times0.30\times0.30$
Crystal system	Orthorhombic	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$ (No. 19)	$P2_1/c$ (No. 14)	$Pna2_1$ (No. 33)	$P2_1/c$ (No. 14)
Unit cell dimensions				
a (pm)	840.5(1)	1441.6(3)	1086.7(1)	669.3(1)
b (pm)	1105.9(2)	1241.3(1)	4726.0(1)	1335.7(1)
c (pm)	1767.2(3) pm	3672.6(6)	1668.5(1)	1843.1(1)
β (°)	—	92.39(2)	—	94.78(1)
V (pm^3)	$1642.8(1)\times10^6$	$6566(2)\times10^6$	$8427.3(1)\times10^6$	$1641.9(1)\times10^6$
Z	4	16	20	4
D_{calc} (g cm^{-3})	1.441	1.280	1.404	1.28
Diffractometer, wavelength	ENRAF-NONIUS CAD4, Mo–K_α, Graphit-monochromator	Siemens SMART 5000 CCD-Diffractometer, Mo–K_α, Graphit-monochromator		
Temperature (K)	295	200	200	200
Cell parameters on the base of reflections	25 ($4.4\le\theta\le13.0°$)	—	—	—
θ-Range (°)	$2.0\le\theta\le25.0$	$1.73\le\theta\le28.46$	$1.72\le\theta\le28.31$	$1.89\le\theta\le28.27$
ω-Scan	2θ	$\Delta\omega=0.3°$	$\Delta\omega=0.3°$	$\Delta\omega=0.3°$
Index ranges	$-9\le h\le8,\ -13\le k\le0,\ -20\le l\le20$	$-19\le h\le19,\ -16\le k\le16,\ -48\le l\le48$	$-14\le h\le14,\ -62\le k\le62,\ -21\le l\le22$	$-8\le h\le8,\ -17\le k\le17,\ -24\le l\le23$
Reflections measured	4746	65 373	85 182	16 705
Independent reflections	1665	16 156	20 658	4006
Reflections observed	1176 ($I>3\sigma$)	6850 ($I\ge2\sigma$)	15 167 ($I\ge2\sigma$)	2926 ($I\ge2\sigma$)
Number of parameters refined	218	758	1101	191
Residual electron density (e pm^{-3})	0.388×10^{-6}	0.46×10^{-6}	0.748×10^{-6}	0.594×10^{-6}
Corrections	Exp. Absorption correction; ψ-scan	Lorentz and polarisation, exp. absorption correction		
Structure solution	Direct methods	Direct methods		
Structure refinement	Full matrix least square on F	Full matrix least square on F^2		
Programs and weightings used	Enraf-Nonius SDP-Plus [25]	SHELX-97 [26], xpma, zortep [27]		
R indices				
R_1	0.0501 ($I>3\sigma$)	0.082 ($I>2\sigma$)	0.0705 ($I>2\sigma$)	0.0622 ($I>2\sigma$)
Rw	0.0529 ($I>3\sigma$)	0.144 (all data on F^2)	0.1321 (all data on F^2)	0.1185 (all data on F^2)

Standard deviations in parenthesis.

Table 5
Selected bond lengths (pm) and angles (°)[a]

Selected distances	**8**	**8a**	**9**	**9a**
Co–C(CO)	222.9(7)	228.5(5) 227.3(5) 228.8(5) 228.7(5)	226.1(5), 224.3(5), 227.7(6), 225.6(5), 225.0(5)	227.2(4)
Co–C(C2/C5)	207.3(8)	207.2(6) 207.6(6) 206.9(6) 207.2(6)	204.5(5), 207.1(5), 203.9(5), 205.3(5), 203.8(5)	205.7(3)
	204.3(7)	207.4(5), 207.4(5), 207.5(5), 207.9(5)	206.1(5), 204.6(5), 206.4(5), 203.9(5), 205.7(5)	206.7(3)
Co–C(C3/C4)	198.8(8)	198.6(6) 198.8(5) 198.9(5) 199.5(6)	199.0(5), 200.6(5), 199.0(5), 201.5(5), 197.9 (5)	198.5(3)
	202.8(9)	198.7(5), 199.2(5), 199.3(5), 200.0(5)	199.9(5), 198.2(5), 201.2(5), 199.4(5), 201.5(5)	201.7(3)
Co–C(Cp)	204.6(9)	204.7(6), −206.3(6)	203.6(6), −205.5(6)	202.4(4)
	−210.0(8)	204.9(6), −206.9(6)	201.5(5), −205.2(5)	−204.1(4)
		203.8(6), −206.3(5)	200.8(7), −204.8(8)	
		203.5(6), −206.4(6)	203.9(6), −205.7(5)	
C(CO)–O	126.5(9)	125.6(6), 126.5(6), 123.9(6), 124.6(6)	124.7(6), 125.5(6), 124.1(7), 125.5(7), 127.4(6)	125.5(4)
Selected angles				
C–C(CO)–C	105.1(7)	104.8(5), 105.6(5), 104.5(4), 104.5(4)	104.0(4), 103.9(4), 103.4(5), 104.2(5), 104.5(4)	104.4(3)

[a] Numbers in parentheses are estimated standard deviations in the last significant digit. As for **8a** four crystallographic independent molecules and for **9** five are found in the elementary cell, in the table for **8a** there are four given values as for **9** five, respectively.

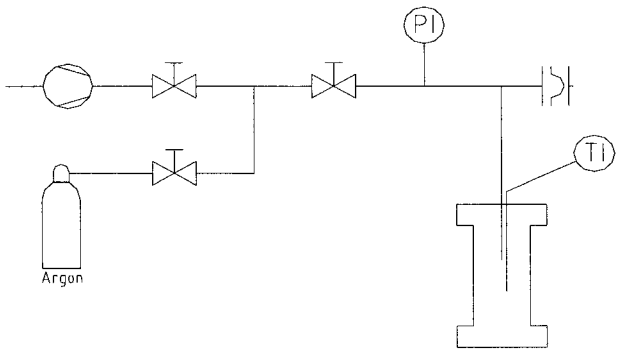

Fig. 5. Schematic view of the batch reactor with thermoelement T1, manometer P1, burst window (392 bar), pump and argon supply.

Nagel, 40×80 mm, polygram alox N/UV_{254}). This procedure yields in case of R = Ph (educt:cat 2:1) the dark red **8** ($R_f = 0.5$; 20 mg, 0.06 mmol, yield 5.6%) and the red **9** ($R_f = 0.25$; 36 mg, 0.1 mmol, yield 9.4%), in case of R = bu^t (educt:cat 2:1) the dark yellow **8a** ($R_f = 0.4$; 3.8 mg, 0.012 mmol, yield 1.2%) and yellow **9a** ($R_f = 0.2$; 5.7 mg, 0.018 mmol, yield 1.8%) [21,23]. **8** and **9** were crystallized under vacuum sublimation to red crystals. For **8a** and **9a** crystals were grown from a pentane solution by slow diffusion of the solvent at r.t.

Acknowledgements

We thank Dr Chr. Apostolitis and E. Dornberger for their help in growing crystals and their support in preparative chemistry. We are also very grateful to R. Will for the GC-MS analytical data and Dr F. Gaßner for the measurement of the NMR spectra.

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