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Journal of Organometallic Chemistry 692 (2007) 4281–4286

Journal of Organometallic Chemistry

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# Photolysis of dicarbonyl(cyclopentadiene)rhodium complexes with a pendent alkyne unit

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Received 19 March 2007; received in revised form 23 June 2007; accepted 28 June 2007
Available online 4 July 2007

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**Abstract**

The syntheses of dicarbonyl[1-(5,5-dimethylhex-3-inyl)-3-phenylcyclopentadienyl]rhodium (**7**) and its congeners **8** and **9** are reported. Photolysis of **8** and **9** leads to a replacement of one CO ligand by the tethered alkyne unit, yielding **16**, and to the dirhodium complexes **17** and **18**. The structural assignment of **17** and **18** is based on X-ray studies. The photolysis of **9** leads to **19** and **20**.

*Keywords:* Rhodiumdicarbonyl complexes; Alkynes; Dirhodium carbon clusters; Photolysis

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## 1. Introduction

Endohedral metal complexes of cyclophanes, *D*, are usually prepared either from an uncomplexed cyclophane, *A*, by reaction with a metal or metal ion, or by adding tethers to a metallocene, *B*, (Scheme 1) [1]. Recently, we proposed a third path by using an intramolecular ring closure of a metal-π-complex, *C*, containing two or more pendent alkyne units and a metal template $ML_n$ [2–4]. The latter protocol enabled us to synthesize new endohedral cobalt and rhodium complexes. In the cases of two pendent alkyne groups and cobalt dicarbonyl as metal fragment we generated cyclophanes with cyclobutadiene (**1** and **2**) or cyclopentadienone (**3** and **4**) as second ring. When the metal fragment was rhodium dicarbonyl, only cyclopentadienone rings were built from the alkyne units (**5** and **6**) (Fig. 1). The yields of these intramolecular template reactions turned out to be low, especially when heavier transition metals than cobalt were employed [3,4]. This reflects the increased tendency of the heavier metal centers to form bimetallic or cluster compounds [5]. Nevertheless, we have previously found that when Cp ligands with two pendent alkyne groups were involved apart from the endohedral metal complexes no discrete products with more than one metal center could be isolated [2–4]. In this paper we report photochemical experiments of the [phenylcyclopentadienyl]rhodium dicarbonyl complexes **7**–**9** (Chart 1).

## 2. Results and discussion

### 2.1. Synthesis

In order to decrease the reaction possibilities of the substituted Cp ligand and to facilitate the formation of higher molecular products we synthesized Cp rhodium dicarbonyl complexes with only one pendent alkyne group. The synthesis of the corresponding cyclopentadiene ligands **13**–**15** started with the addition of phenyllithium to the monosubstituted cyclopentenones **10**–**12** [4] followed by acidic work-up to generate the cyclopentadiene ligands **13**–**15**. These ligands were deprotonated by butyllithium and treated with $[RhCl(CO)_2]_2$ to yield the corresponding rhodium dicarbonyl complexes **7**–**9** (Scheme 2).

The obtained dicarbonyl complexes **7**–**9** were then reacted by irradiating a hexane solution with UV light. We regarded these reaction conditions to be milder than the pyrolytic reaction conditions used for the synthesis of the previously described endohedral complexes and therefore more likely to yield complexes with more than one

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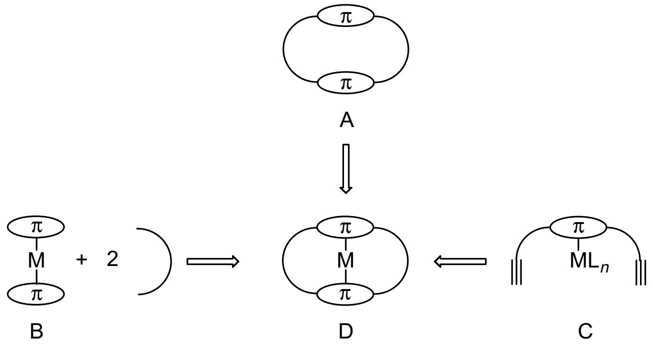
doi:10.1016/j.jorganchem.2007.06.053



Scheme 1. Possible approaches to generate endohedral cyclophanes.

metal center. In the case of the photolytic reaction of **7** we could only observe decomposition. However, in the cases of **8** and **9** we were able to isolate defined products (Schemes 3 and 4).

The irradiation of **8** yielded a mono-alkyne complex **16** and two dirhodium complexes, **17** and **18** (Scheme 3).

Complex **16** was obtained in a 6% yield as a very air sensitive solid. It was identified by mass spectrometry and shows a strong IR band at 1963 cm$^{-1}$. Similar intermediates with an alkyne unit bound to a $CpM(CO)_n$ fragment are reported in the literature for $M = Co$, $n = 1$ [6,7], and $M = Mn$, $n = 2$ [8,9]. Also complexes of the type $ArCr(CO)_2(alkyne)$ have been reported [8,10–12]. However, most of them proved to be rather unstable [13] whereas the species **17** and **18** were dark red colored air-stable solids. The assigned structures are based on their analytical data and their structures in the solid state.

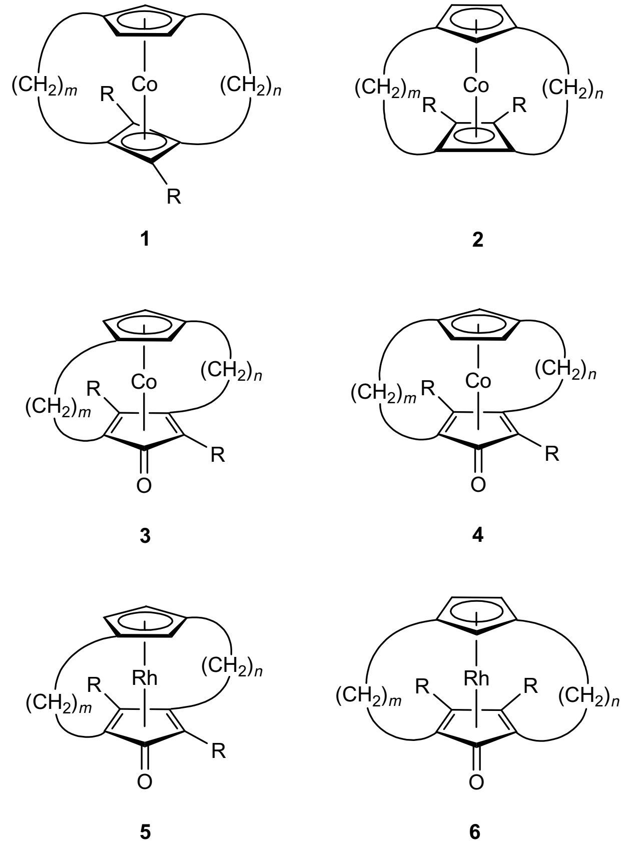


Fig. 1. Endohedral cyclophanes obtained by intramolecular reaction of alkyne units with Co and Rh as metal.

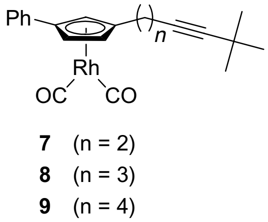
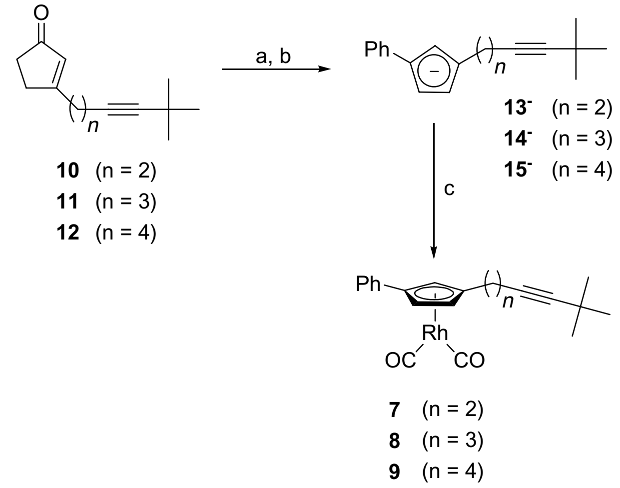
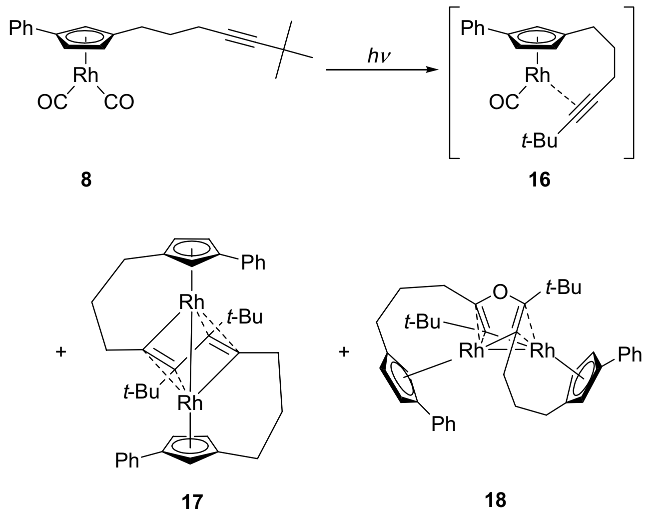


Chart 1.

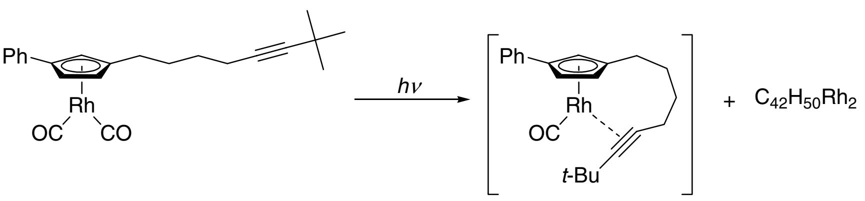


Scheme 2. Synthesis of $CpRh(CO)_2$ complexes **7**–**9**. (a) PhLi, THF, −78°C to r.t.; HCl (aq). (b) *n*-BuLi, THF, −78°C to r.t. (c) $[RhCl(CO)_2]_2$, THF, r.t.



Scheme 3. Photolysis of **8** to generate **16**–**18**.

Photolysis of **9** yielded an air-sensitive yellow oil to which we assign the structure of **19** based on its strong IR band at 1967 cm$^{-1}$. Besides, we isolated a dark red



**9** **19** **20**

Scheme 4. Photolysis of **9** to generate **19** and **20**.

solid, **20** (26%), whose high resolution mass spectrum gave a formula of $C_{42}H_{50}Rh_2$. This suggests a structure analogous to **17** with tetramethylene bridges (Scheme 4). Thus, loss of the first CO ligand leads to a coordination of the alkyne bond whereas on loss of the second CO ligand a dimerization to **17**, **18**, and **20** occurs. Probably the *syn* configuration of the Cp-rings in **18** requires an additional group or atom between the $sp^2$ centers for steric reasons. The presence of the oxygen atom in **18** we attribute to traces of oxygen in the reaction vessel.

## 2.2. Structural investigations

We were able to isolate singe crystals of **17** and **18** which allowed X-ray diffraction studies. Both molecular structures are shown in Fig. 2.

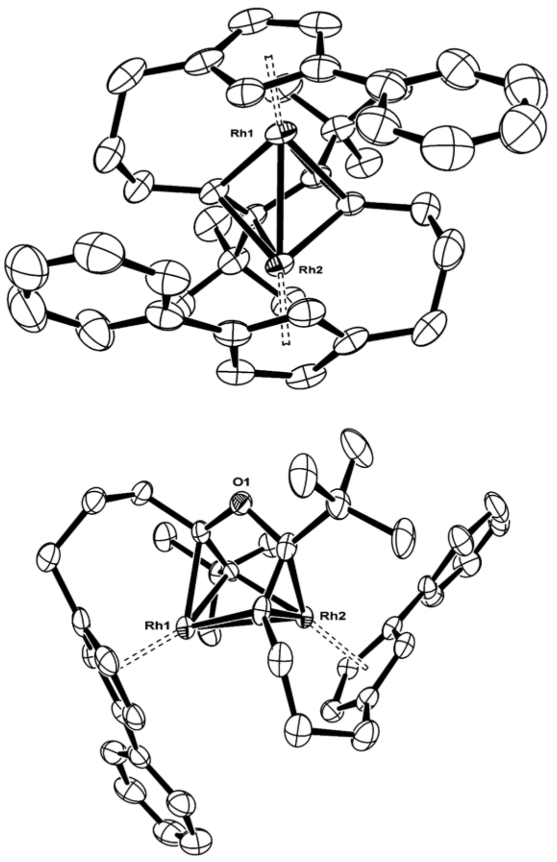
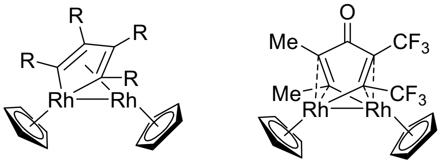


Fig. 2. ORTEP drawing for **17** (top) and **18** (bottom) (50% probability ellipsoids). Hydrogen atoms are omitted for clarity.



**21** R = $Ph_f$
**22** R = $CF_3$

**23**

Fig. 3. Binuclear rhodium complexes found in the literature.

The structures of **17** and **18** reveal a Rh-Rh single bond with a length of 2.562 Å (**17**) and 2.617 Å (**18**). The distances between the carbon atoms of the former triple bonds amount to 1.41 Å (**17**) and 1.42 Å (**18**). Both show double bond character as indicated in the respective formulae in Scheme 3.

Binuclear complexes from reaction of cyclopentadienyl rhodium dicarbonyl complexes with alkynes have been described in the literature (Fig. 3). The structures of complexes **21** and **22** can be described as a rhodacyclopentadiene ring π bonded to a CpRh unit [14–16]. A coordination similar to that found in **17** and **18** can be found in complex **23**, however in this complex a CO unit is inserted between the two coordinated double bonds [17]. More examples with a $(CpRh)_2$ unit with Rh–Rh distances around 2.6 Å and alkyne units coordinated to the metal centers can be found in the literature [18].

## 3. Conclusion

In this paper we report the synthesis and photochemical reactions of the cyclopentadienyl rhodium dicarbonyl complexes **7**–**9**. The photolysis of **7** did not yield any isolable products, possibly due to the short dimethylene tether. However, complexes **8** and **9** bearing trimethylene and tetramethylene tethers respectively, yielded the mono-alkyne complexes **16** and **19** and the dirhodium complexes **17**, **18** and **20**. We were able to investigate species **17** and **18** by X-ray diffraction methods revealing Rh–Rh bonds in both cases.

## 4. Experimental

### 4.1. 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 using 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 ($\delta$). FAB and FD mass spectra refer to data from a Jeol JMS-700 instrument. All reactions were carried out in dried glassware under argon atmospheres using dried and oxygen-free solvents. The investigated crystals were obtained by evaporating solvent from the respective column chromatography fractions. X-ray diffraction data were collected on a Bruker Smart CCD-diffractometer at 200 K. Relevant crystal and data collection parameters are given in Table 1. The structures were solved by direct methods and refined against $F^2$ with a full-matrix least-square algorithm by using the SHELXTL [19] package. In both cases an empirical absorption correction was applied by using SADABS [20], based on the Laue symmetry of the reciprocal space.

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 638944 for compound **17** and CCDC No. 638945 for compound **18**.

Table 1
Crystal data and structural refinement for **17** and **18**

| | **17** | **18** |
|---|---|---|
| Empirical formula | $C_{40}H_{46}Rh_2$ | $C_{40}H_{46}ORh_2$ |
| Molecular weight | 732.59 | 748.59 |
| Wavelength (Å) | 0.71073 | 0.71073 |
| Crystal system | Monoclinic | Orthorhombic |
| Space group | $C2/c$ | $P2_12_12_1$ |
| Temperature (K) | 200 | 200 |
| $Z$ | 8 | 4 |
| $a$ | 34.4254(5) | 10.5933(2) |
| $b$ | 11.9626(1) | 15.5095(2) |
| $c$ | 16.4381(2) | 20.0712(3) |
| $\beta$ | 102.540(1) | 90 |
| $V$ (Å$^3$) | 6608.00(14) | 3297.63(9) |
| $D_{calcd}$ (g/cm$^3$) | 1.473 | 1.508 |
| Absorption coefficient μ [mm$^{-1}$] | 1.025 | 1.031 |
| Maximum and minimum transmission | 0.87 and 0.71 | 0.94 and 0.77 |
| Crystal shape | Polyhedron | Polyhedron |
| Crystal size (mm$^3$) | $0.36 \times 0.18 \times 0.14$ | $0.27 \times 0.11 \times 0.06$ |
| $\theta$ Range for data coll [deg] | 1.81 to 27.49 | 1.7 to 26.4 |
| Index ranges | $-44 \leqslant h \leqslant 44$<br>$-15 \leqslant k \leqslant 15$<br>$-21 \leqslant l \leqslant 21$ | $-12 \leqslant h \leqslant 13$<br>$-19 \leqslant k \leqslant 19$<br>$-24 \leqslant l \leqslant 25$ |
| Reflections collected | 33883 | 31769 |
| Independent reflections [$R$(int)] | 7592 (0.0438) | 6749 (0.0540) |
| Observed reflections | 6045 [$I > 2\sigma(I)$] | 5963 [$I > 2\sigma(I)$] |
| Data/restraints/parameters | 7592 / 0 / 385 | 6749 / 0 / 394 |
| Goodness-of-fit on $F^2$ | 1.02 | 1.03 |
| $R(F)$ | 0.025 | 0.027 |
| $R_W(F^2)$ | 0.085 | 0.049 |
| $(\Delta\rho)$max, $(\Delta\rho)$min (e Å$^{-3}$) | 0.87 and −0.50 | 0.28 and −0.41 |

### 4.2. General procedure for the preparation of CpRh complexes 7–9

The corresponding cyclopentenones **10–12**, respectively, were dissolved in THF and cooled to −78 °C. Then the phenyllithium solution was added via syringe and the resulting mixture was stirred for one hour keeping the solution at −78 °C. After warming up to room temperature the mixture was poured on ice. The mixture was acidified by addition of aqueous HCl and extracted with diethylether. The elimination to the cyclopentadiene was monitored by TLC. Then the organic phase was washed with aqueous $NaHCO_3$ and brine, solvent removed by rotary evaporation and the residue was purified by flash column chromatography on alox III (neutral) using pentanes as eluent.

The purified ligand was immediately subjected to the next reaction step: *n*-butyllithium was added to a solution of the cyclopentadiene ligand in THF at −78 °C. After warming up to room temperature the solution was added to a solution of dicarbonylchlororhodium(I)dimer in 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 as eluent.

#### 4.2.1. Dicarbonyl-$\eta^5$-[1-(5,5-dimethylhex-3-ynyl)-3-phenylcyclopentadienyl]rhodium(I) (7)

Reaction mixture in the first reaction step: Cyclopentenone **10** (816 mg, 4.86 mmol) in THF (10 ml), phenyllithium (20% in $n$-$Bu_2O$, 2.00 g, 4.76 mmol). Reaction mixture in the second reaction step: Cyclopentadiene **13** in THF (25 ml), *n*-butyllithium (1.6 M in hexanes, 2.68 ml, 4.29 mmol), dicarbonylchlororhodium(I)dimer (500 mg, 1.29 mmol) in THF (100 ml). Yield 708 mg (67%) of **7** as an orange oil. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 1.24 (s, 9H, $CH_3$), 2.40 (m, 2H, $CH_2$), 2.54 (s, 2H, $CH_2$), 5.55 (ps, 1H, CH), 5.77 (ps, 1H, CH), 5.97 (ps, 1H, CH), 7.20–7.46 (m, 5H, CH). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 22.5 ($CH_2$), 27.4 (C), 28.2 ($CH_2$), 31.4 ($CH_3$), 77.55 (C), 83.4 (CH, $J_{Rh,C} = 3.4$ Hz), 86.5 (CH, $J_{Rh,C} = 3.4$ Hz), 88.0 (CH, $J_{Rh,C} = 3.8$ Hz), 90.2 (C), 109.4 (C, $J_{Rh,C} = 3.3$ Hz), 111.2 (C, $J_{Rh,C} = 3.8$ Hz), 125.8 (CH), 127.4 (CH), 128.7 (CH), 133.5 (C), 191.4 (CO, $J_{Rh,C} = 83.9$ Hz). IR (Film) $\tilde{\nu}$ = 2968, 2865, 2034, 1968, 1476, 1452, 1362, 1267 cm$^{-1}$. UV/Vis ($CH_2Cl_2$) (log $\varepsilon$) $\lambda_{max} = 256$ (4.01), 314 (3.83), 420 (2.51) nm. MS (positive FAB): $m/z = 380$ ([M−CO]$^+$), 352 ([M−2CO]$^+$). HRMS (positive FAB) calcd. for $C_{20}H_{21}ORh$ ([M−CO]$^+$), 380.0647; 380.0629 found, (−1.8 mmu).

#### 4.2.2. Dicarbonyl-$\eta^5$-[1-(6,6-dimethylhept-4-ynyl)-3-phenylcyclopentadienyl]rhodium(I) (8)

Reaction mixture in the first reaction step: Cyclopentenone **11** (1.05 g, 5.14 mmol) in THF (10 ml), phenyllithium (20% in $n$-$Bu_2O$, 2.40 g, 5.71 mmol). Reaction mixture in the second reaction step: Cyclopentadiene **14** in THF (25 ml), *n*-butyllithium (1.6 M in hexanes, 3.21 ml, 5.14 mmol), dicarbonylchlororhodium(I)dimer (600 mg, 1.54 mmol) in THF (100 ml). Yield 621 mg (48%) of **8** as an orange oil. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 1.21 (s, 9 H, $CH_3$), 1.50 (m, 2 H, $CH_2$), 2.05 (m, 2H, $CH_2$), 2.16 (m, 2H, $CH_2$), 5.02 (ps, 1H, CH), 5.33 (ps, 1H, CH), 5.48 (ps, 1H, CH), 6.96–7.21 (m, 5H, CH). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 18.8 ($CH_2$), 27.5 ($CH_2$), 27.7 (C), 31.7 ($CH_3$), 32.0 ($CH_2$), 78.2 (C), 83.6 (CH, $J_{\mathrm{Rh,C}} = 3.5$ Hz), 86.6 (CH, $J_{\mathrm{Rh,C}} = 3.0$ Hz), 88.1 (CH, $J_{\mathrm{Rh,\ C}} = 3.8$ Hz), 90.0 (C), 109.7 (C), 112.0 (C, $J_{\mathrm{Rh,C}} = 3.8$ Hz), 126.2 (CH), 127.5 (CH), 128.9 (CH), 133.9 (C), 192.4 (CO, $J_{\mathrm{Rh,C}} = 84.0$ Hz). IR (Film) $\tilde{\nu} = 3064$, 2968, 2865, 2033, 1969, 1603, 1475, 1453, 1362, 1329, 1265, 1205 $cm^{-1}$. UV/Vis ($CH_2Cl_2$) (log$\varepsilon$) $\lambda_{max} = 242$ (4.14), 258 (4.10), 312 (3.88), 378 (2.60), 410 (2.50) nm. MS (positive FAB): $m/z = 394$ ($[M-CO]^+$), 366 ($[M-2CO]^+$). HRMS (positive FAB) calcd. for $C_{21}H_{23}ORh$ ($[M-CO]^+$), 394.0804; 394.0805 found, (+0.1 mmu). $C_{22}H_{23}O_2Rh \cdot 1/6\ C_6H_6$ (422.32): calcd. C 63.46, H 5.56, found C 63.69, H 5.58.

### 4.2.3. Dicarbonyl-$\eta^5$-[1-(7,7-dimethyloct-5-ynyl)-3-phenylcyclopentadienyl]rhodium(I) (9)

Reaction mixture in the first reaction step: Cyclopentenone **12** (936 mg, 4.29 mmol) in THF (10 ml), phenyllithium (20% in *n*-$Bu_2O$, 2.00 g, 4.76 mmol). Reaction mixture in the second reaction step: Cyclopentadiene **15** in THF (25 ml), *n*-butyllithium (1.6 M in hexanes, 2.68 ml, 4.29 mmol), dicarbonylchlororhodium(I)dimer (500 mg, 1.29 mmol) in THF (100 ml). Yield 732 mg (65%) of **9** as an orange solid, m.p. 47 °C. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 1.23 (s, 9 H, $CH_3$), 1.59 (m, 2H, $CH_2$), 1.66 (m, 2H, $CH_2$), 2.20 (m, 2H, $CH_2$), 2.38 (m, 2H, $CH_2$), 5.50 (ps, 1H, CH), 5.76 (ps, 1H, CH), 5.90 (ps, 1H, CH), 7.21–7.46 (m, 5H, CH). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 18.5 ($CH_2$), 27.0 (C), 27.9 ($CH_2$), 28.8 ($CH_2$), 31.5 ($CH_3$), 78.0 (C), 83.2 (CH, $J_{\mathrm{Rh,C}} = 3.6$ Hz), 86.5 (CH, $J_{\mathrm{Rh,C}} = 3.5$ Hz), 88.0 (CH, $J_{\mathrm{Rh,C}} = 3.8$ Hz), 89.5 (C), 109.2 (C, $J_{\mathrm{Rh,C}} = 3.4$ Hz), 112.3 (C, $J_{\mathrm{Rh,C}} = 3.6$ Hz), 125.9 (CH), 127.4 (CH), 128.7 (CH), 133.5 (C), 191.5 (CO, $J_{\mathrm{Rh,C}} = 84.0$ Hz). IR (Film) $\tilde{\nu} = 2967$, 2930, 2862, 2035, 1970, 1603, 1475, 1452, 1361, 1265, 1205 $cm^{-1}$. UV/Vis ($CH_2Cl_2$) (log $\varepsilon$) $\lambda_{max} = 242$ (3.98), 302 (3.94), 314 (3.93), 424 (2.54) nm. MS (positive FAB): $m/z = 408$ ($[M\text{-}CO]^+$), 380 ($[M\text{-}2CO]^+$). HRMS (positive FAB) calcd. for $C_{22}H_{25}ORh$ ($[M\text{-}CO]^+$), 408.0960; 408.0965 found, (+0.5 mmu).

### 4.3. General procedure for the irradiation of CpRh complexes 7–9

A deoxygenated solution of **7**–**9** in hexanes under argon atmosphere was irradiated with UV light (HPK 125 W high pressure mercury vapour lamp in a reactor fitted with a water cooled jacket). The reaction was monitored by IR. The colour of the reaction mixture turned from light orange to dark brownish red. The solvent was removed in vacuo and the residue was chromatographed on alox III (neutral) using pentanes as eluent.

### 4.3.1. Irradiation of dicarbonyl-$\eta^5$-[1-(6,6-dimethylhept-4-ynyl)-3-phenylcyclopentadienyl] rhodium(I) (8)

Reaction mixture: CpRh complex **8** (485 mg, 1.15 mmol), hexane (250 ml). First complex **16** was eluted from the column as a light orange fraction, then a dark red fraction containing complex **17** and finally a light red fraction containing complex **18** was obtained. Yields: 25 mg (6%) of **16**, 64 mg (15%) of **17** and 38 mg (9%) of **18**.

**16:** Yellow oil, very sensitive to air, therefore we were only able to get reliable data from IR and mass spectra. IR (Film) $v = 1963$ $cm^{-1}$. MS (positive FD): $m/z = 394$ ($[M]^+$).

**17:** Dark red solid, m.p. 170 °C (dec.). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 1.16 (s, 18 H, $CH_3$), 1.55 (m, 4H, $CH_2$), 2.23 (m, 8H, $CH_2$), 5.27 (ps, 2H, CH), 5.32 (ps, 2H, CH), 5.51 (ps, 2H, CH), 7.11–7.33 (m, 10H, CH). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 1.2 ($CH_3$), 25.3 ($CH_2$), 30.5 ($CH_2$), 31.5 ($CH_2$), 37.4 (C), 77.5 (CH), 79.3 (C), 85.6 (CH), 87.1 (CH), 100.0 (C), 104.1 (C), 123.3 (CH), 125.3 (CH), 128.8 (CH), 135.4 (C). IR (Film) $\tilde{\nu} = 2993$, 2947, 2913, 2847, 1600, 1517, 1477, 1450, 1436, 1383, 1356, 1190 $cm^{-1}$. UV/Vis ($CH_2Cl_2$) (log $\varepsilon$) $\lambda_{max} = 236$ (4.47), 314 (4.28), 336 (4.28), 456 (3.33), 522 (3.31). MS (positive FAB): $m/z = 732$ ($[M]^+$). HRMS (positive FAB) calcd. for $C_{40}H_{46}Rh_2$ ($[M]^+$), 732.1709, 732.1694 found, (−1.5 mmu). $C_{40}H_{46}Rh_2$ (732.60): calcd. C 65.58, H 6.33, found C 65.54, H 6.33.

**18:** Dark red solid, m.p. 155 °C (dec.). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 0.74 (s, 9 H, $CH_3$), 0.84–0.89 (m, 2H, $CH_2$), 1.16 (s, 9H, $CH_3$), 1.44–2.32 (m, 10H, CH), 5.10 (ps, 1H, CH), 5.36 (ps, 1H, CH), 5.42 (ps, 1H, CH), 5.45 (ps, 1H, CH), 5.70 (ps, 1H, CH), 5.96 (ps, 1H, CH), 7.06–7.26 (m, 10H, CH). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 19.6 (C), 22.7 (C), 25.2 ($CH_2$), 26.0 ($CH_2$), 30.6 ($CH_2$), 30.9 ($CH_2$), 31.0 ($CH_3$), 33.7 ($CH_2$), 33.8 ($CH_2$), 37.3 (C), 38.3 (C), 76.2 (CH, $J_{\mathrm{Rh,C}} = 4.2$ Hz), 79.1 (CH, $J_{\mathrm{Rh,C}} = 5.5$ Hz), 82.7 (CH, $J_{\mathrm{Rh,C}} = 6.2$ Hz), 85. 3 (CH, $J_{\mathrm{Rh,\ C}} = 2.1$ Hz), 86.2 (CH, $J_{\mathrm{Rh,C}} = 6.9$ Hz), 87.9 (CH, $J_{\mathrm{Rh,C}} = 3.5$ Hz), 98.5 (C, $J_{\mathrm{Rh,C}} = 5.5$ Hz), 99.8 (C, $J_{\mathrm{Rh,C}} = 4.9$ Hz), 104.6 (C, $J_{\mathrm{Rh,\ C}} = 2.1$ Hz), 107.2 (C, $J_{\mathrm{Rh,C}} = 2.8$ Hz), 123.4 (CH), 125.1 (CH), 125.6 (CH), 126.0 (CH), 128.6 (CH), 128.7 (CH), 135.5 (C), 135.6 (C). IR (KBr) $\tilde{\nu} = 2924$, 2855, 1636 $cm^{-1}$. UV/Vis ($CH_2Cl_2$) (log $\varepsilon$) $\lambda_{max} = 242$ (4.45), 264 (4.40), 300 (4.28), 348 (4.19), 458 (3.49), 526 (3.24), 574 (2.88). MS (positive FAB): $m/z = 748$ ($[M]^+$), 732 ($[M\text{-}O]^+$). HRMS (positive FAB) calcd. for $C_{40}H_{46}ORh_2$ ($[M]^+$), 748.1659, 748.1641 found, (−1.8 mmu).

### 4.3.2. Irradiation of Dicarbonyl-$\eta^5$-[1-(7,7-dimethyloct-5-ynyl)-3-phenylcyclopenta- dienyl]rhodium(I) (9)

Reaction mixture: CpRh complex **9** (250 mg, 0.573 mmol), hexane (250 ml). First complex **19** was eluted from the column as a light orange fraction, then a purple fraction containing complex **20** was obtained. Yields: 76 mg (32%) of **19**, 57 mg (26%) of **20**.

**19:** Yellow oil. IR (Film) $\tilde{\nu} = 1967 cm^{-1}$.

**20:** Dark red solid, m.p. 82 °C. IR (KBr) $\tilde{\nu} = 3060, 2962, 2920, 2857, 2033, 1969, 1876, 1599, 1477, 1446, 1032\ \text{cm}^{-1}$. UV/Vis ($CH_2Cl_2$) (log $\varepsilon$) $\lambda_{max} = 276$ (4.33), 332 (4.11), 516 (3.67). MS (positive FD): $m/z = 760$ ($[M]^+$). HRMS (positive FAB) calcd. for $C_{42}H_{50}Rh_2$ ($[M]^+$), 760.2022, 760.2006 found, (−1.8 mmu).

## Acknowledgement

We are grateful to the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support.

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