Tricarbonyl[.eta.5-(1-5)-pentakis(propyn-1-yl)cyclopentadienyl]manganese

Uwe H. F. Bunz, Volker Enkelmann, and J. Raeder

Organometallics, **1993**, 12 (12), 4745-4747• DOI: 10.1021/om00036a012 • Publication Date (Web): 01 May 2002

Organometallics is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Organometallics **1993,** *12,* 4745–4747

Tricarbonyl[η^5-1,2,3,4,5-pentakis(propyn-1-yl)cyclopentadienyl]manganese

Uwe H. F. Bunz,* Volker Enkelmann, and Joachim Räder

Max-Planck-Institut für Polymerforschung, Ackermannweg 10, 55021 Mainz, FRG

Received September 14, 1993[⊗]

Summary: The title compound tricarbonyl[η^5-1,2,3,4,5-pentakis(propyn-1-yl)cyclopentadienyl]manganese (**1b**) *was prepared in two steps from tricarbonylcyclopentadienylmanganese. The key step involves a 5-fold Stille coupling of tricarbonyl(η^5-1,2,3,4,5-pentaiodocyclopentadienyl)manganese with 1-(trimethylstannyl)prop-1-yne.*

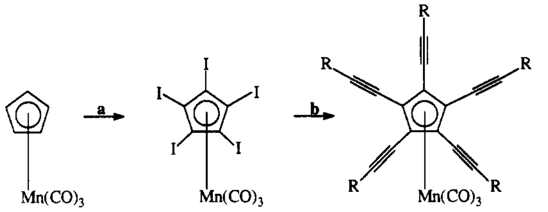
The cyclopentadiene (Cp) ligand is perhaps the most important ligand in organometallic chemistry. Cp complexes of a large number of elements have been prepared.[1] Organometallic compounds containing substituted cyclopentadienyls, on the other hand, often show differing stabilities and reactivities compared to the unsubstituted Cp analogs, and some are useful reagents and/or attractive synthetic goals.[1,2]

Despite the successful preparation of peralkylated and perarylated cyclopentadienyl complexes[2] no (pentaalkynylcyclopentadienyl)metal complex has been described in the literature, probably due to the lack of suitable starting materials for their preparation. We were interested in such compounds because they possess the potential for the buildup of larger cluster systems through multiple complexation of the alkyne groups. This might lead in turn to an enhanced catalytic activity or unusual reactivity imparted by the close proximity of several metal fragments.

Monoalkynyl-substituted[3] Cp complexes have been prepared by reaction of iodoalkynes with the appropriate ring-derived cuprates,[4] by Stille coupling of iodocyclopentadienyl complexes with alkynylstannanes,[5a] or by conversion of acetyl-substituted Cp complexes.[3b] In an extension of this methodology, it should be possible to prepare pentaalkynyl-substituted Cp complexes by reaction of suitable pentaiodo-substituted Cp complexes with alkynylstannanes using Pd catalysts.[6]

When we started our investigation, the only complex with an η^5-C_5I_5 ligand (besides decaiodoferrocene[7d]) described in the literature was Cp*RuC$_5$I$_5$.[7a] Attempts to couple this compound under Stille conditions with alkynylstannanes failed. Even after reaction times of 2 weeks in a sealed NMR tube we could detect only starting material by ^{13}C NMR spectroscopy. We assume (*vide infra*) that the steric bulk of the Cp* substituent inhibits the coupling reaction rather than electronic effects.

Scheme I[a]



3 **2** **1a**, R = CH(CH$_3$)$_2$
b, R = CH$_3$

[a] Legend: (**a**) 5 equiv of Hg(OAc)$_2$, EtOH, ΔT, then NaI$_3$ (**2**, 20%); (**b**) Me$_3$SnC≡CR (**4a**, R = *i*Pr; **4b**, R = Me), 4 mol % PdCl$_2$(CH$_3$CN)$_2$ in dimethylformamide, 40 h, 20 °C, chromatography over flash silica gel (**1a**, R = *i*Pr; 17%; **1b**, R = Me; 38%).

The sterically less hindered and hitherto unknown (η^5-C$_5$I$_5$)Mn(CO)$_3$ (**2**) seemed to be a better coupling partner to perform a multiple Stille reaction.[6] The synthesis of **2** (Scheme 1) was achieved in 20% yield by refluxing **3** with 5 equiv of Hg(OAc)$_2$ in ethanol for 48 h to give presumably pentakis(acetoxymercurio)cymantrene,[7e] which subsequently was transformed to the pentaiodide **2** by reaction with sodium triiodide.[8] Cymantrene (**3**) is thus the first example for which we can show that pentamercuration[7e] and subsequent functionalization is not

---

[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1993.

(1) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987. (b) Marr, G.; Rockett, B. W. In *The Chemistry of the Functional Groups, The Chemistry of the Metal-Carbon Bond, Part 1*; Hartley, F. R., Patai, S., Eds.; Wiley: New York, 1982; p 443, and references cited therein. (c) Coville, N. J.; du Plooy, K. E.; Pickl, W. *Coord. Chem. Rev.* **1992,** *116,* 1.

(2) (a) Janiak, C.; Schumann, H. *Adv. Organomet. Chem.* **1991,** *33,* 291. (b) Gloaguen, B.; Astruc, D. *J. Am. Chem. Soc.* **1990,** *112,* 4607. (c) Okuda, J. *Top. Curr. Chem.* **1991,** *160,* 99.

(3) (a) Bunel, E. E.; Valle, L.; Jones, N. L.; Caroll, P. J.; Gonzalez, M.; Munoz, N.; Manriquez, J. M. *Organometallics* **1988,** *7,* 789. (b) Schlögl, K.; Steyrer, W. *Monatsh. Chemie* **1965,** *96,* 1520. (c) Rausch, M. D.; Siegel, A.; Kleman, L. P. *J. Org. Chem.* **1969,** *31,* 2703.

(4) (a) Buchmeiser, M.; Schottenberger, H. *J. Organomet. Chem.* **1992,** *441,* 457. Buchmeiser, M.; Schottenberger, H. *J. Organomet. Chem.* **1992,** *436,* 223 and references cited therein. (b) Doisneau, G.; Balvoine, G.; Fillebeen-Khan, T. *J. Organomet. Chem.* **1992,** *425,* 113. (c) Wiegelmann, J. E. C.; Bunz, U. H. F. *Organometallics* **1993,** *12,* 3792.

(5) (a) Lo Sterzo, C.; Stille, J. K. *Organometallics* **1990,** *9,* 687 and references cited therein. (b) Pudelski, J. K.; Callstrom, M. R. *Organometallics* **1992,** *11,* 2757.

(6) (a) Hexaethynylbenzene: Diercks, R.; Armstrong, J. C.; Boese, R.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1986,** *25,* 268. Hexabutadiynylbenzene: Boese, R.; Green, J. R.; Mittendorf, J.; Mohler, D. L.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1992,** *31,* 1643. (b) Other examples of polyethynylated arenes: Neenan, T. X.; Whitesides, G. M. *J. Org. Chem.* **1988,** *53,* 2489. Rutherford, D. R.; Stille, J. K. *Macromolecules* **1988,** *21,* 3530. Hyatt, J. A. *Org. Prep. Proced. Int.* **1992,** *23,* 460. Präfcke, K.; Kohne, B.; Singer, D. *Angew. Chem., Int. Ed. Engl.* **1990,** *29,* 177. Bunz, U. H. F.; Enkelmann, V. *Angew. Chem., Int. Ed. Engl.*, in press. Laschewsky, A. *Angew. Chem., Int. Ed. Engl.* **1989,** *28,* 1574.

(7) (a) Winter, C. H.; Han, Y.-H.; Heeg, M. J. *Organometallics* **1992,** *11,* 3169. (b) Winter, C. H.; Han, Y.-H.; Ostrander, R. L.; Rheingold, A. L. *Angew. Chem., Int. Ed. Engl.*, in press. (c) Synthesis of (η^5-C$_5$Br$_5$)Mn(CO)$_3$: Hermann, W. A.; Huber, M. *J. Organomet. Chem.* **1977,** *140,* 55. (d) Synthesis of decaiodoferrocene: Boev, V. I.; Dombrovskii, A. V. *Zh. Obshch. Khim.* **1977,** *47,* 727. (e) Kuzmina, L. G.; Ginzburg, A. G.; Struchkov, Y. T.; Kursanov, D. N. *J. Organomet. Chem.* **1983,** *253,* 329.

(8) **2**: Compound **3** (500 mg, 2.45 mmol) and mercuric acetate (3.90 g, 12.3 mmol) were dissolved in ca. 100 mL of ethanol, and the solution was refluxed for 48 h. The volatiles were removed at 30 °C/0.01 mmHg. The residue was dissolved in ca. 50 mL of methanol, and this solution was treated with a solution of sodium triiodide (iodine (3.19 g, 12.3 mmol) and sodium iodide (3.75 g, 25.0 mmol) in ca. 25 mL of water) and stirred for 3 h at 0 °C. Removal of all volatiles (rotary evaporator, 35–40 °C), extraction of the black residue with chloroform, and column chromatography (flash silica, pentane as eluent) yielded 407 mg (20%) of **2**. Physical data are given in ref 11.

0276-7333/93/2312-4745$04.00/0

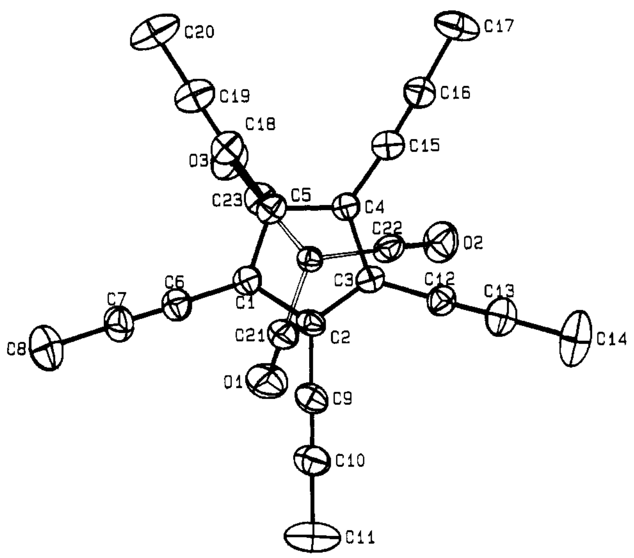


Figure 1. ORTEP drawing of **1b**. All hydrogens are omitted.[13] Important bond lengths (averaged; Å): C—C ring, 1.43(1); C≡C alkyne, 1.17(1); C_{ring}—C_{alkyne}, 1.43(1); C_{alkyne}—CH_3, 1.47(1); Mn—CO 1.80(9).

confined to a metallocene type of substrate but also is possible with less electron-rich half-sandwich complexes.[7b]

Preliminary experiments to couple **2** with alkynylstannanes under conditions described by Farina[9a] (2.5 mol % tris(benzylidene)dipalladium, 10 mol % triphenylarsine in dimethylformamide) did not proceed to our satisfaction. We obtained an inseparable mixture containing the desired coupling product in small amounts, as shown by TLC and ^{13}C NMR spectroscopy. Treating **2** with 3-methyl-1-(trimethylstannyl)but-1-yne (**4a**) and Beletskaya's catalyst[9b] ($PdCl_2(NCCH_3)_2$) in dimethylformamide gave rise to a plethora of different compounds from which only **1a** could be isolated in 17% yield after flash chromatography[10,11] as a yellow oil displaying the lowest R_f value of all components of the product mixture. Using 1-(trimethylstannyl)prop-1-yne (**4b**) as coupling partner under otherwise identical conditions resulted in the isolation of **1b** as a yellow crystalline powder in 38% yield.[10–12] Attempts to react **2** with 2-(trimethylsilyl)-1-(trimethylstannyl)acetylene under these conditions led only to a complex mixture of substances from which the desired pentaalkynyl species could not be obtained.

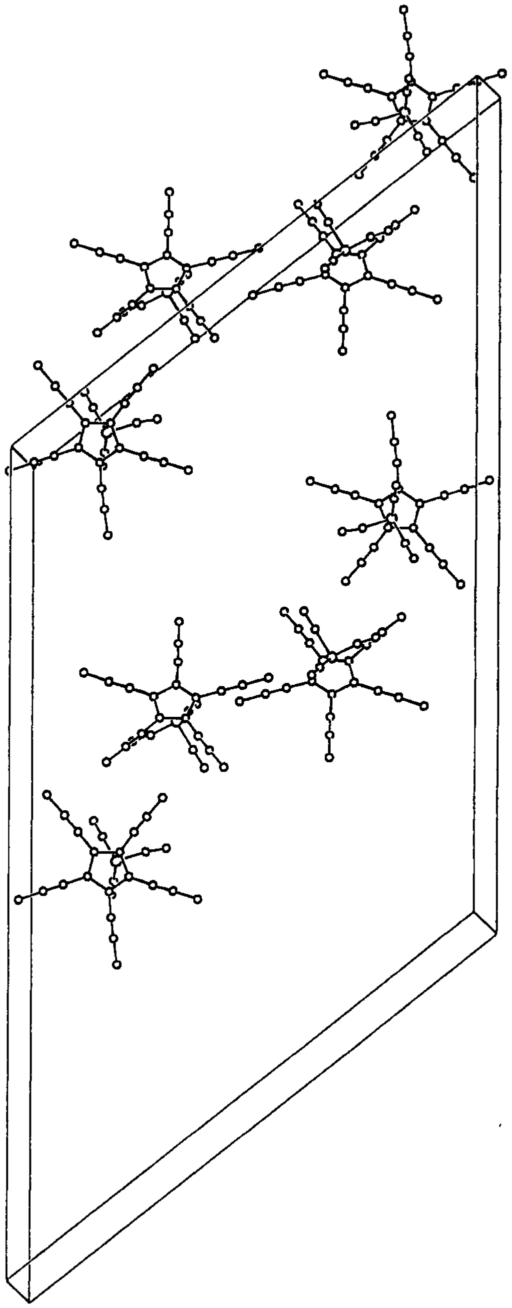


Figure 2. Packing diagram of **1b**.

Due to the high symmetry of the ligand and to prove its topology, an X-ray structure analysis of **1b** was undertaken. Suitable platelets were grown[13] by slow evaporation of an

---

[9] (a) Farina, V.; Krishnan, B. *J. Am. Chem. Soc.* **1991**, *113*, 9585 and references cited therein. (b) Beletskaya, I. P. *J. Organomet. Chem.* **1983**, *250*, 551 and references cited therein.

[10] Stille coupling to **1b**: **3** (351 mg, 0.421 mmol), 1-(trimethylstannyl)-propyne (600 mg, 2.96 mmol), and $PdCl_2(NCCH_3)_2$ (30 mg, 0.116 mmol) were stirred under argon in 10 mL of dry dimethylformamide for 40 h. Removal of volatiles and double chromatography over flash silica gel (85% petroleum ether/15% CH_2Cl_2) yielded 63 mg (38%) of **1b** and 37 mg of a yellow oil as a forerun.[12] By the same procedure **1a** was obtained in 17% yield.

[11] Physical data for the new compounds are as follows. **2**: mp 171 °C; IR (KBr, cm^{-1}) ν 2030, 1975, 1951, 1295, 1256; ^{13}C NMR ($CDCl_3$) δ 68.24 (s), 223.73 (s, CO); MS (EI; *m/z* (relative intensity, %)) 833 (M^+, 4), 805 (M^+ – CO, 3), 777 (M^+ – 2CO, 20), 749 (M^+ – 3CO, 35). Anal. Calcd: C, 11.53; I, 76.13. Found: C, 11.46; I, 76.22. **1a**: yellow oil; IR (KBr, cm^{-1}) ν 2973, 2931, 2871, 2238, 2024, 1954, 1314; ^1H NMR ($CDCl_3$) δ 1.26 (d, ^3J(H,H) = 6.8 Hz; 30 H, CH(CH_3)$_2$), 2.76 (sept, ^3J(H,H) = 6.8 Hz; 5 H, CH(CH_3)$_2$); ^{13}C NMR ($CDCl_3$) δ 21.30 (d), 22.88 (q), 70.36 (s), 85.92 (s), 100.16 (s), 223.78 (s, CO); MS (FD; *m/z* (relative intensity, %)) 1040 (2M – CO, 8), 534 (M^+, 100), 468 (M^+ – CO, 3); HRMS *m/z* 534.197 08 (calcd M^+, $C_{33}H_{35}MnO_3$: *m/z* 534.196 67). **1b**: dec pt 214 °C; IR (KBr, cm^{-1}) ν 2970, 2960, 2920, 2242, 2019, 1959, 1945, 1913, 1737, 1439; ^1H NMR ($CDCl_3$) δ 2.08 (s, 15 H); ^{13}C NMR ($CDCl_3$) δ 4.75 (q), 70.01 (s), 86.07 (s), 90.53 (s), 222.73 (s, CO); MS (FD; *m/z* (relative intensity, %)) 394 (M^+, 100), 366 (M^+ – CO, 8); HRMS *m/z* 394.0400 (calcd M^+, $C_{23}H_{15}$-MnO_3: *m/z* 394.040 2). All ^1H NMR spectra were recorded at 300 MHz and all ^{13}C NMR spectra at 75 MHz. Spectra were taken at ambient temperature.

[12] We were able to isolate an additional fraction as a forerun. It is composed of two compounds inseparable by TLC. The FD mass spectrum shows two peaks at *m/z* 356 and 370. The ^1H NMR spectrum of the mixture gives rise to three singlets between δ 1.9 and 2.2 where the signal located at δ 2.04 is considerably smaller than the two other resonances. An additional signal is apparent at δ 4.88. Due to these observations we presume this fraction to consist of tricarbonyl(η^5-5-methyl-1,2,3,4-tetrakis(propynyl)cyclopentadienyl)manganese and tricarbonyl(η^5-1,2,3,4-tetrakis(propynyl)cyclopentadienyl)manganese.

[13] Crystallographic data for **1b**: $C_{23}H_{15}MnO_3$, M_r = 394.33; a = 45.790(2) Å, b = 7.2039(14) Å, c = 32.222(2) Å, α = 90°, β = 127.326(4)°, γ = 90°, space group $C2/c$, Z = 16, V = 8452 Å^3, d_{exptl} = 1.239 g cm^{-3}, μ = 52.41 cm^{-1}; 4674 reflections collected, 2970 observed. $|F| > 5.0$, R = 0.045, R_w = 0.051. Data were collected on an Enraf-Nonius CAD4 diffractometer with Cu Kα radiation (λ = 154.05 pm) at 298 K. The structure was solved by the heavy-atom method (Patterson). Positions of the H atoms were geometrically placed and refined using the riding mode. Programs used: DIRDIF, CRYSTALS, Molen.

ethereal solution of the complex: The hydrocarbon ligand of **1b** shows perfect 5-fold symmetry with linearly arranged propynyl groups (Figure 1). The ligand as a whole is approximately planar, and two of the metal-bound CO groups are in a staggered conformation with respect to the propynyl substituents, while the third one is eclipsed in the same sense. The monoclinic unit cell of the space group *C*2/*c* contains 16 molecules; i.e., the asymmetric unit consists of two chemically equivalent but crystallographically different molecules. Figure 2 shows a projection of the unit cell. Both crystallographically inequivalent molecules are connected by a pseudo center of inversion.

As we have demonstrated by our investigation, pentaalkynyl-substituted Cp complexes of the $Mn(CO)_3$ fragment can be prepared from **3** in two steps. We think that this synthetic approach also should be applicable to other Cp-bearing complexes.

Acknowledgment. This work was supported by the BASF and the Stiftung Volkswagenwerk. We wish to thank Prof. Dr. K. Müllen for generous support. U.H.F.B. is the recipient of a Liebig scholarship (1992–1994).

Supplementary Material Available: Tables of bond distances, atomic coordinates, and thermal parameters for **1b** (6 pages). Ordering information is given on any current masthead page.

OM930637+