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A Short Synthesis of Donor-Acceptor Substituted CpCo-Capped Cyclobutadiene-Superphanes

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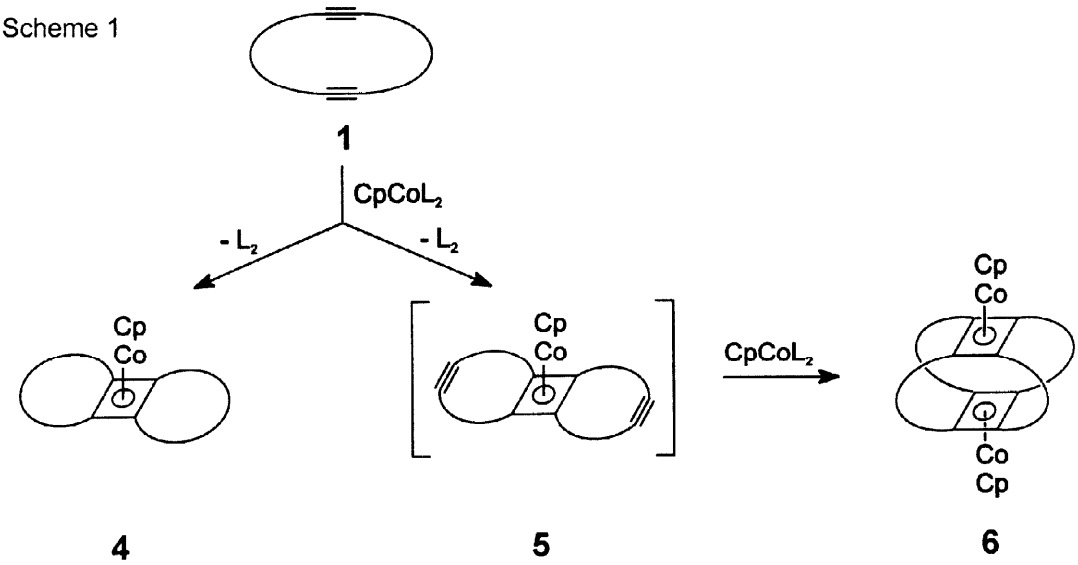
Abstract: The reaction of 1,1,3,3-tetramethyl-1,3-disilanona-4,8-diyne (**7**) and 1,1,4,4-tetramethyl-1,4-disiladeca-5,9-diyne (**8**) with R-CpCo$(CO)_2$ (R=H, CH_3) allowed to stop the reaction at the stage of tricyclic intermediates, the latter could be reacted again with R-CpCoL_2(L_2=COD,$(CO)_2$) to yield CpCo-capped cyclobutadiene-superphanes with different substituents in the two Cp ligands.

The carbon-carbon triple bond shows a large variety of reactions due to its relative high energy content. 50 years ago Reppe et al.[1] who showed that acetylene can be cyclotetramerized to cyclooctatetraene and alkynes can be cyclotrimerized to benzene derivatives by various nickel catalysts.[1,2] Among the metal compounds which catalyze the cyclotrimerization of alkynes to aromatics, cobalt complexes of the type $CpCoL_2$ are among the most efficient ones. Synthetically useful methods for the preparation of new benzene derivatives[3] and six-ring heterocycles have emerged.[4] Open chain diynes can either be transformed to aromatic species or cyclobutadiene derivatives, depending on the reaction conditions.[3,5]

Scheme 1



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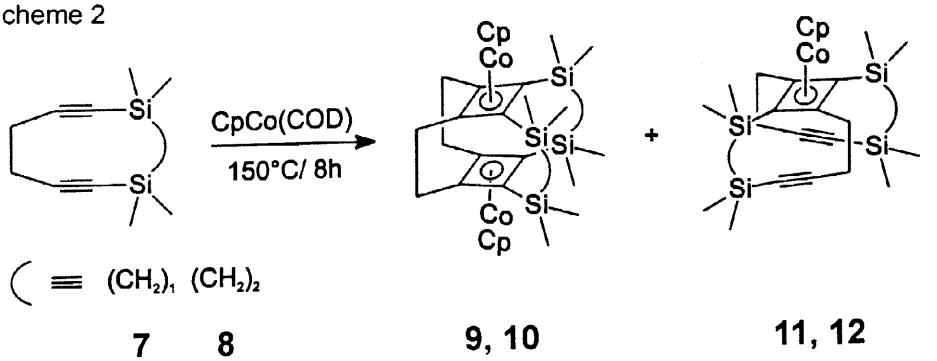
The reactions of cyclic diynes **1** with dicarbonyl(η^5-cyclopentadienyl)cobalt ($CpCo(CO)_2$, **2**) or (η^4-cyclooctadiene-1,5)(η^5-cyclopentadienyl)cobalt (CpCo(COD), **3**) yielded only CpCo-stabilized cyclobutadiene complexes.[6] In an intramolecular pathway tricyclic cyclobutadiene complexes **4**, and in an intermolecular pathway CpCo-capped cyclobutadiene superphanes **6** could be generated (Scheme 1).[7] For the superphane formation one assumes a tricyclic diyne, **5** as intermediate.[7] This assumption is corroborated by two observations: In the case of the reaction of 4,9-diisopropylidene-1,6-cyclodecadiyne with **2** we were able to isolate such an intermediate.[8] The independent stepwise synthesis of **5** revealed that such species react much faster with **2** or **3** to superphanes **6** than the corresponding cyclic diynes **1**.[9]

We reasoned that the isolation of intermediates should be possible if the chains of **1** are short and/or bulky. In order to check this hypothesis we investigated the reaction of 1,1,3,3-tetramethyl-1,3-disilanona-4,8-diyne (**7**)[10] and 1,1,4,4-tetramethyl-1,4-disiladeca-5,9-diyne (**8**)[10] with $CpCoL_2$.

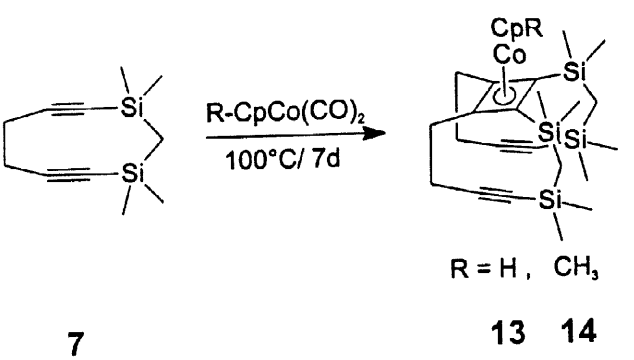
Scheme 2



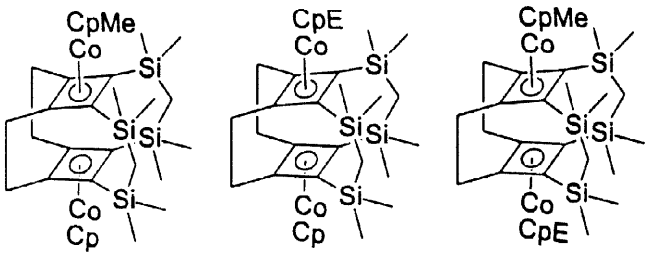
Heating of **7** and **8** with CpCo(COD) at 150 °C in toluene for 8 h gave as main products the superphanes **9** and **10**[11] in 60 - 70% yield (Scheme 2). As side products we isolated the tricyclic diynes **11** and **12**.[11] An X-ray study on **12** reveals[12] that the two triple bonds are tilted with respect to each other by 77°. This is very likely the reason why further reaction to a superphane is prevented under the conditions used.

When we carried out the reaction of **7** with **2** or (dicarbonyl)(methylcyclopentadienyl)cobalt **15** under milder

Scheme 3



conditions (100°C, 7d) we were able to isolate the tricyclic diynes **13** and **14** in about 30 - 35% yields (Scheme 3). The diynes were used for further reactions with **2**, **15** and (dicarbonyl)(methoxycarbonylcyclopentadienyl)cobalt (**16**) to yield the superphanes **17** - **19** in which the Cp-ligands are substituted differently.



17 **18** **19**

The use of cyclic diynes with short chains and bulky groups enabled us to separate and identify the intermediates **11** - **14**. The isolation of these species allows to substantiate the mechanism of the superphane formation as shown schematically in Scheme 1. Furthermore, it provides a simple way of synthesizing donor-acceptor substituted CpCo-capped cyclobutadiene-superphanes.

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References

1 Reppe, W.; Schlichting, O.; Klager, K.; Toepel, T. *Liebigs Ann. Chem.* **1948**, *560*, 1.

2 Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, Mill Valley, Calif. **1987**.

3 Vollhardt, K. P. C. *Acc. Chem. Res.* **1977**, *10*, 1; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 539.

4 Bönnemann, H. *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 248; Bönnemann, H.; Goddard, R.; Grub, J.; Mynott, R.; Raabe, E.; Wendel, S. *Organometallics* **1989**, *8*, 1941.

5 Shore, N. E. *Chem. Rev.* **1988**, *88*, 1081.

6 King, R. B.; Efraty, A. *J. Am. Chem. Soc.* **1970**, *92*, 6071; *ibid* **1972**, *94*, 3021.

7 Gleiter, R. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 27; Gleiter, R.; Merger, M. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2426.

8 Gleiter, R.; Merger, R.; Irngartinger, H.; Nuber, B. *J. Org. Chem.* **1993**, *58*, 2025.

9 Gleiter, R.; Langer, H.; Schehlmann, V.; Nuber, B. *Organometallics* **1995**, *14*, 975.

10 Haberhauer, G.; Roers, R.; Gleiter, R. *Tetrahedron Lett.* **1997**, *38*, 8679.

[11] **9**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = -0.22 (d, 2H), -0.19 (d, 2H), 0.1 (s, 24H), 2.0 (m, 4H), 2.2 (m, 4H), 4.7 (s, 10H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 0.7 (q), 3.0 (q), 7.1 (t), 24.6 (t), 64.4 (s), 77.9 (d), 90.1 (s); HRMS (EI): m/z calcd. 660.1340, found 660.1340.

10: ^{1}H NMR (200 MHz, $CDCl_3$): δ = -0.1 (s, 12H), 0.0 (s, 12H), 0.4 (s, 8H), 2.0 (m, 4H), 2.3 (m, 4H), 4.6 (s, 10H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = -0.4 (q), 1.5 (q), 8.6 (t), 26.7 (t), 64.3 (s), 79.0 (d), 90.5 (s); HRMS (EI): m/z calcd. 688.1654, found 688.1659.

11: ^{1}H NMR (300 MHz, $CDCl_3$): δ = -0.1 (d, 2H), 0.0 (d, 2H), 0.13 (s, 6H), 0.15 (s, 6H), 0.22 (s, 6H), 0.35 (s, 6H), 2.3 (m, 8H), 4.8 (s, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 0.5 (q), 1.4 (q), 2.1 (q), 4.5 (q), 7.2 (t), 22.1 (t), 31.2 (t), 73.1 (s), 80.5 (d), 88.5 (s), 89.2 (s), 110.8 (s); HRMS (FAB^+): m/z calcd. 536.1618, found 536.1619.

12: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.09 (s, 6H), 0.11 (s, 6H), 0.15 (s, 6H), 0.3 (s, 6H), 0.7 (m. 4H), 0.9 (m, 4H), 2.2 (m, 4H), 2.3 (m, 4H), 4.7 (s, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = -1.7 (q), -0.8 (q), -0.2 (q), 1,2 (q), 9.4 (t), 10.3 (t), 22.3 (t), 30.7 (t), 71.7 (s), 80.7 (d), 86.6 (s), 88.8 (s), 108.1 (s); HRMS (EI): m/z calcd. 564.1930 found 564.1936.

13: ^{1}H NMR (300 MHz, $CDCl_3$): δ = -0.2 (d, 2H), 0.0 (d, 2H), 0.1 (s, 12H), 0.2 (s, 6H), 0.3 (s, 6H), 2.1 - 2.3 (m, 8H), 4.7 (s, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 0.5 (q), 0.6 (q), 1.2 (q), 5.1 (q), 5.7 (t), 20.9 (t), 27.5 (t), 68.7 (s), 79.5 (d), 88.7 (s), 89.7 (s), 109.6 (s); HRMS (FAB^+): m/z calcd. 536.1617, found 536.1603.

14: ^{1}H NMR (200 MHz, $CDCl_3$): δ = -0.3 (d, 2H), 0.0 - 0.3 (m, 26H), 1.8 (s, 3H), 2.0 - 2.3 (m, 8H), 4.4 (m, 2H), 4.6 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 0.76 (q), 0.8 (q), 1.4 (q), 5.3 (q), 6.1 (t), 13.3 (q), 21.0 (t), 27.1 (t), 68.2 (s), 78.5 (d), 80.6 (d), 88.6 (s), 88.9 (s), 93.4 (s), 109.8(s); HRMS (FAB^+): m/z calcd. 550.1774, found 550.1804.

17: ^{1}H NMR (300 MHz, $CDCl_3$): δ = -0.2 (m, 4H), 0.09 (s, 12H), 0.1 (s, 12H), 1.9 (s, 3H), 2.0 - 2.3 (m, 8H), 4.56 (m, 2H), 4.6 (m, 2H), 4.7 (s, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 0.4 (q), 3.4 (q), 7.6 (t), 13.8 (q), 24.4 (t), 24.8 (t), 64.3 (s), 64.8 (s), 77.2 (d), 78.3 (d), 79.3 (d), 89.6 (s), 90.5 (s), 93.1 (s); HRMS (FAB^+): m/z calcd. 674.1497, found 674.1490.

18: ^{1}H NMR (300 MHz, $CDCl_3$): δ = -0.2 (m, 4H), 0.1 (m, 24H), 1.9 - 2.2 (m, 8H), 3.7 (s, 3H), 4.7 (s, 5H), 5.3 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 0.0 (q), 0.3 (q), 3.0 (q), 3.4 (q), 7.2 (t), 24.0 (t), 24.6 (t), 51.1 (q), 64.6 (s), 67.7 (s), 78.4 (d), 80.4 (d), 81.6 (d), 83.6 (s), 90.2 (s), 92.6 (s), 168.4 (s); HRMS (FAB^+): m/z calcd. 718.1395, found 718.1371.

19: ^{1}H NMR (300 MHz, $CDCl_3$): δ = -0.2 (m, 4H), 0.1 (m, 24H), 1.9 (s, 3H), 1.9 - 2.2 (m, 8H), 3.7 (s, 3H), 4.5 (m, 2H), 4.6 (m, 2H), 4.9 (m, 2H), 5.3 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 0.0 (q), 0.3 (q), 3.1 (q), 3.3 (q), 7.4 (t), 13.8 (q), 23.9 (t), 24.0 (t), 51.0 (q), 64.1 (s), 67.7 (s), 77.2 (d), 79.3 (d), 80.4 (d), 81.5 (d), 83.7 (s), 89.4 (s), 92.6 (s), 93.2 (s), 168.4(s); HRMS (FAB^+): m/z calcd. 732.1552, found 732.1550.

[12] Haberhauer, G.; Gleiter, R.; Rominger, F. to be published.