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# Preparations and characterizations of homodinuclear complexes containing flyover bridge or cyclopentadienone ligands; X-ray crystal structures of $Co_2(CO)_3(PPh_3)\{\mu\text{-}C(SiMe_3){=}CH{-}CH{=}C(SiMe_3){-}CH{=}C(SiMe_3)\}$, $Co_2(CO)_2(\mu\text{-}CO)_2(\eta^4\text{-}2,5\text{-bistrimethylsilylcyclopentadienone})_2$ and 2,5-bis(trimethylsilanyl)cyclopenta-2,4-dien-1-one

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## Abstract

The reaction of $Co_2(CO)_5(PPh_3)(\mu\text{-}HC{\equiv}C{-}SiMe_3)$ (**1b**) with 2.5 equivalent amount of trimethylsilylacetylene in refluxed THF yielded two homodinuclear complexes containing 'flyover bridge' ligands, $Co_2(CO)_3(PPh_3)\{\mu\text{-}C(SiMe_3){=}CH{-}CH{=}C(SiMe_3){-}CH{=}C(SiMe_3)\}$ (**2a**) and a small amount of $Co_2(CO)_2(\mu\text{-}CO)_2(\eta^4\text{-}2,5\text{-bistrimethylsilylcyclopentadienone})_2$ (**4**). The yield of (**4**) was improved, while using about five equivalent amount of trimethylsilylacetylene. The crystal structures of (**2a**) and (**4**) were determined. The structure of (**2a**) can be regarded as a dimetallic frame contains three linked $HC{\equiv}CSiMe_3$ groups that are arranged in a 'flyover-bridge' geometry. Trimethylsilyl groups are attached to carbon atoms of the flyover bridge ligand at positions 1, 3, and 6. The ligand might be seen as the composition of two allyl groups, C1–C2–C3 and C4–C5–C6, which are joined by a single bond between C3 and C4. Each allyl group is bonded to one cobalt atom. 1,2,4-Tris-trimethysilanylbenzene was obtained from the degradation of the compound (**2a**). The crystal structure of (**4**) shows that two cyclopentadienone ligands, two terminal and two bridged carbonyls were found to be coordinated to both metal centers. The formation of the two cyclopentadienones is believed to take place via the transition metal-mediated cyclization of two alkynes with one carbon monoxide. 2,5-Bis(trimethylsilanyl)cyclopenta-2,4-dien-1-one (**5**) was obtained from the degradation of (**4**) by exposing to air in solution. The formation of (**5**) is believed to take place via the Diels–Alder type cyclization of two released cyclopentadienone ligands from (**4**). © 1999 Elsevier Science S.A. All rights reserved.

*Keywords:* Flyover bridge; Di-cobalt complexes; Homodinuclear complexes; Cyclopentadienone; Benzene

## 1. Introduction

Alkynes are highly reactive building blocks in synthesis. Their interactions with various metal complexes were extensively studied because of its potential in catalysis [1]. The bonding of alkynes with metals using one or both sets of filled π orbitals of the alkynes is well known [2]. Among them, the reactions of $Co_2(CO)_8$ with various alkynes have been widely studied [3]. The alkyne bridged compounds, $Co_2(CO)_6(\mu\text{-alkyne})$, are simply formed from the direct thermal reaction of $Co_2(CO)_8$ with an alkyne. The formation of metallacyclopentadiene rings in reactions with excess alkynes is also well documented. It was via the linkage of two

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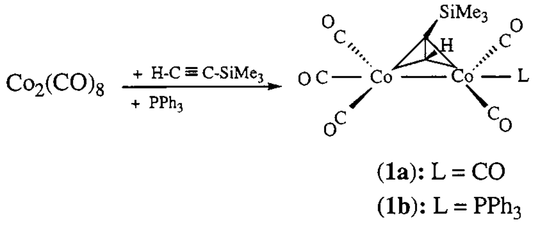


Scheme 1.

alkynes with metal center [4]. In some cases, a dimetallic frame containing three linked acetylenes that are arranged in a 'flyover bridge' geometry can be found in low yield [5]. Corresponding benzene derivatives might be obtained from thermal or chemical degradation of the compound [3c]. There are few structural reports of these type of compounds [6]. Here, we report one more example of the preparation and crystal structure of a 'flyover bridged' homobimetallic compound, $Co_2(CO)_3(PPh_3)\{\mu\text{-}C(SiMe_3){=}CH{-}CH{=}C(SiMe_3){-}CH{=}C(SiMe_3)\}$ (**2a**).

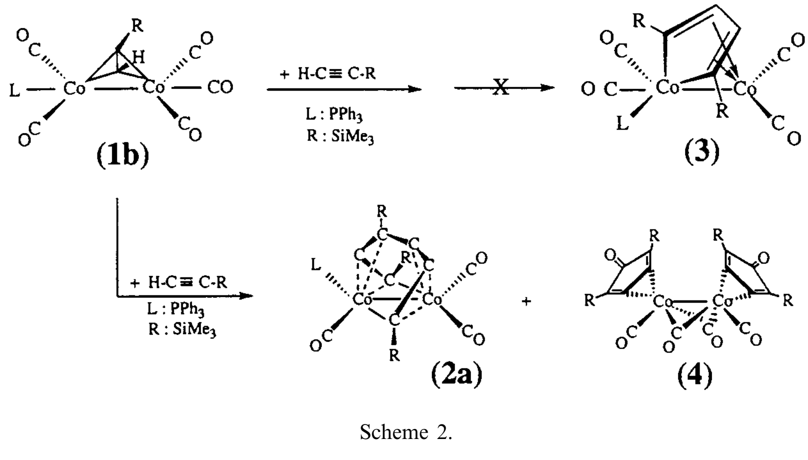
Monomeric substituted cyclopentadienones are not stable and tend to undergo the Diels–Alder reaction to form the dimeric compounds [7]. Here, we report, to our knowledge, the first crystal structure of a cyclopentadienone coordinated dicobalt compound, $Co_2(CO)_2(\mu\text{-}CO)_2(\eta^4\text{-}2,5\text{-bistrimethylsilylcyclopentadienone})_2$ (**4**). An unexpected structure feature was revealed. This compound can be seen as the metal complex containing monomeric cyclopentadienone synthon.

## 2. Results and discussion

An alkyne bridged homobimetallic compound, $Co_2(CO)_5(PPh_3)(\mu\text{-}HC{\equiv}C{-}SiMe_3)$ (**1b**) was obtained with a small amount of $Co_2(CO)_6(\mu\text{-}HC{\equiv}C{-}SiMe_3)$ (**1a**) from the reaction of $Co_2(CO)_8$ with $HC{\equiv}C{-}SiMe_3$ in the presence of one equivalent of $PPh_3$ (Scheme 1). High yields of (**1a**) might be achieved without the presence of $PPh_3$ [8]. Compounds (**1a**) and (**1b**) were characterized by spectroscopic means.

Further reaction of $Co_2(CO)_5(PPh_3)(\mu\text{-}HC{\equiv}C{-}SiMe_3)$ (**1b**) with 2.5 equivalents of trimethylsilylacetylene in refluxed THF yielded two homobinuclear complexes containing flyover bridge ligands, $Co_2(CO)_3(PPh_3)\{\mu\text{-}C(SiMe_3){=}CH{-}CH{=}C(SiMe_3){-}CH{=}C(SiMe_3)\}$ (**2a**) and a small amount of $Co_2(CO)_2(\mu\text{-}CO)_2(\eta^4\text{-}2,5\text{-bistrimethylsilylcyclopentadienone})_2$ (**4**). The yield of the latter might be improved while (**1a**) was allowed to react with about five equivalents of trimethylsilylacetylene. There was no sign of forming $Co_2(CO)_3(PPh_3)\{\mu\text{-}C(SiMe_3){=}CH{-}C(SiMe_3){=}CH{-}C(SiMe_3){=}CH\}$ (**2b**), presumably an isomer of (**2a**) (Scheme 2). The fact that the metallapentadiene type compound, such as (**3**), was not observed is noteworthy. The metallapentadiene type of structure is generally regarded as the possible intermediate while forming flyover bridge compounds.

Compound (**2a**) was characterized by spectroscopic means as well as structural determination. The principal structure of (**2a**) can be regarded as a dimetallic frame contains three linked $HC{\equiv}CSiMe_3$ groups that are arranged in a 'flyover bridge' geometry (Fig. 1). Three trimethylsilyl groups are attached to the six-carbon ligand chain at positions 1, 3, and 6, respectively. The ligand can be seen as the composition of two allyl groups C1–C2–C3 and C4–C5–C6 which are joined by a single bond between C3 and C4. The bond length of C3–C4 is 1.506 Å which is longer than other bonds (Table 2). The dihedral angle between the two allylic planes is 59°. Each of the allyl groups are bonded to both cobalt atoms. This ligand can be seen as a 6-π electron donor, three to each metal center. The only triphenylphosphine ligand is attached to one of the cobalt atoms. Each cobalt atom obeys the EAN rule.



Scheme 2.

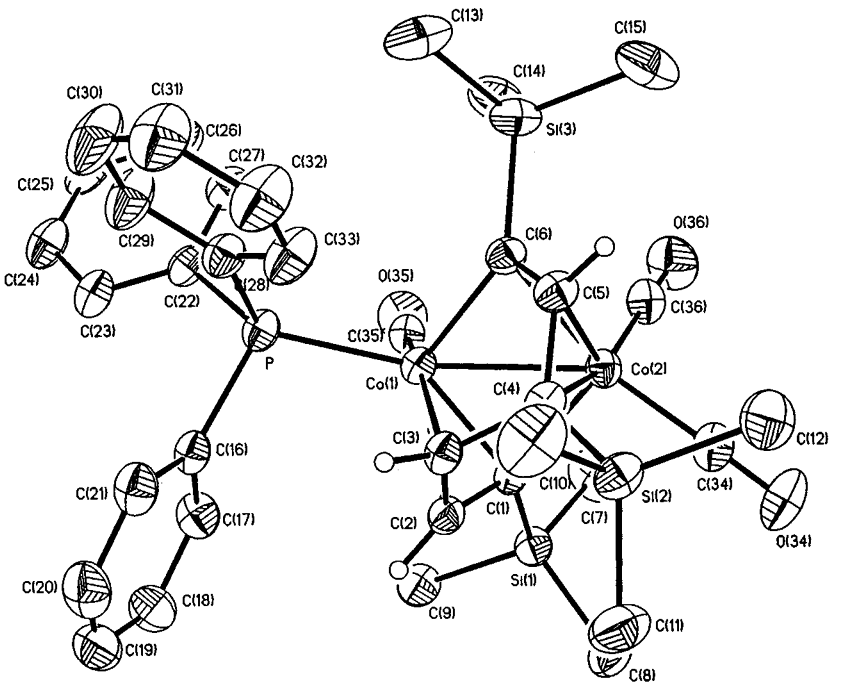


Fig. 1. ORTEP drawing with the numbering scheme of (**2a**). Hydrogen atoms were omitted for clarity.

Four atoms, Co(1), C(1), Co(2), C(6) are almost coplanar. The bond lengths from C(6) to both cobalts are rather small (Table 2). This is also true for C(1) to both metals (Fig. 2). The structure of (**2a**) can be regarded as a flyover bridge ligand wrapping the cobalt–cobalt bond from one side of the molecule. The other side of the molecule is relatively open and further reaction presumably could take place there. The presence of the triphenylphosphine ligand on one of the cobalt atoms does not seem to alter the structure particularly. However, the presence of the $PPh_3$ ligand might play a role in the crystallization of this compound. We observed that these type of compounds are frequently oily and difficult to crystallize without the presence of the $PPh_3$ ligand.

A complicated coupling pattern and relatively larger coupling constants for the protons on the flyover bridge ligand were observed in the $^1$H-NMR of (**2a**). This is probably due to the coupling effect from both vincinal HC–CH protons as well as the triphenylphosphine ligand. It is also supported by the fact that a much more simpler coupling pattern was observed for (**2c**) in which the triphenylphosphine ligand of (**2a**) was replaced by a carbonyl ligand (Scheme 3). In the reaction, the $PPh_3$ ligand, presumably, was pulled out by the Lewis acid, $BH_3$ and the activated species picked up one CO from some decomposed species thus resulting in the formation of (**2c**). Two doublets at 6.16 and 5.88 ppm, with the coupling constants of 6.4 Hz as well as one singlet at 3.20 ppm were observed in $^1$H-NMR of (**2c**). This indicates that the vincinal HC–CH protons are present and the phosphine ligand is absent. Compound (**2a**) also showed one broad $^{31}$P signal around 53.3 ppm. The broad peak is due to the coupling between phosphine and its attached cobalt ($I = 7/2$).

An organic compound, which was characterized as 1,2,4-tris-trimethysilanylbenzene was obtained from the degradation of the compound (**2a**) [8a]. This is also evidence that confirms the observed $^1$H-NMR of (**2a**). The formation of this benzene derivative may have resulted from the breaking of two Co–C σ-bonds from both metal centers and which then rejoined both ends together. Similar observations were reported [9].

The preparation of (**4**)-like compounds from the reaction of $Co_2(CO)_8$ with corresponding acetylenes had been reported [10]. However, the yields of the reactions were quite low and the crystal structures were not available. In our case, (**4**) (Table 3) was obtained as the major product in high yields while about five equivalent amounts of trimethylsilylacetylene was used in the reaction as shown in Scheme 1. The compound was characterized by spectroscopic means. Red crystals of (**4**) were grown in $CH_2Cl_2$ at 10°C and were sampled and subjected to X-ray crystal structural determination (Fig. 3). It was identified as a cyclopentadienone ligand coordinated dicobalt compound. Interestingly, two cyclopentadienone ligands, as well as two bridged carbonyls were found to coordinate to both metal centers. It is believed that the cyclopentadienone was formed by head-to-head coupling of two trimethylsilylacetylenes with a carbonyl through the metal-mediated cyclization. There are two molecules in an asymmetry unit of

Table 1
Crystal data (**2a**), (**4**) and (**5**)

| | | | |
|---|---|---|---|
| No. of independent reflections | $C_{36}H_{45}Co_2O_3PSi$ | $C_{26}H_{40}Co_2O_6Si$ | $C_{22}H_{40}O_2Si_4$ |
| Empirical formula | $C_{36}H_{45}Co_2O_3PSi_3$ | $C_{26}H_{40}Co_2O_6Si_4$ | $C_{22}H_{40}O_2Si_4$ |
| Formula weight | 758.8 | 678.8 | 448.9 |
| Crystal system | Triclinic | Monoclinic | Monoclinic |
| Space group | $P\bar{1}$ | $P2_1/c$ | $P2_1/n$ |
| Unit cell dimensions | | | |
| $a$ (Å) | 10.365(2) | 26.833(2) | 12.206(2) |
| $b$ (Å) | 11.209(2) | 11.694(1) | 11.053(2) |
| $c$ (Å) | 17.097(2) | 25.343(3) | 20.950(2) |
| $\alpha$ (°) | 80.34(2) | | |
| $\beta$ (°) | 86.44(2) | 117.82(1) | 102.69 |
| $\gamma$ (°) | 87.71(2) | | |
| $V$ (Å$^3$) | 1953.5(6) | 7033.1(16) | 2757.4(7) |
| $Z$ | 2 | 8 | 4 |
| $D_{calc.}$ (Mg m$^{-3}$) | 1.2908 | 1.282 | 1.081 |
| $\lambda$(Mo–K$_\alpha$) (Å) | 0.71073 | 0.71073 | 0.71073 |
| $\mu$ (mm$^{-1}$) | 1.014 | 1.112 | 0.230 |
| Range (°) | 4.0–50.0 | 4.0–48.0 | 4.0–48.0 |
| Scan type | $2\theta/\theta$ | $2\theta/\theta$ | $2\theta/\theta$ |
| No. of reflections collected | 7228 | 11256 | 4527 |
| No. of independent reflections | 6820($R_{int}$ = 1.91%) | 10968 | 4303 |
| No. of observed reflections | 5260($F > 4.0\sigma(F)$) | 6613 | 3329 |
| No. of refined parameters | 406 | 680 | 253 |
| [a]$R_f$ for significant reflections | 0.0369 | 0.0501 | 0.0423 |
| [b]$R_w$ for significant reflections | 0.0497 | 0.0569 | 0.0590 |
| [c]GoF | 1.12 | 1.12 | 1.36 |

[a] $R_f = [\Sigma(F_o - F_c)/\Sigma F_o]$.
[b] $R_w = \Sigma w^{1/2}(F_o - F_c)/\Sigma w^{1/2}F_o$.
[c] $\mathrm{GoF} = [\Sigma w(F_o - F_c)^2/(N_{rflns} - N_{params})]^{1/2}$. $w^{-1} = \sigma^2(F) + 0.0010F^2$.

the cell. The molecule of (**4**) exhibits a pseudo-$C_2$ symmetry. The substituents, $-SiMe_3$, on the cyclopentadienone are pointing away from each other thus preventing steric hindrance. The triphenylphosphine ligand is absent here. Each cyclopentadienone ligand is π-bonded to cobalt and donates four electrons in electron counting. Each cobalt center; therefore, is six coordinated and thus obeys the EAN rule. The bond length between two cobalts is 2.542 Å, which is slightly longer than that of (**2a**). The double bonds, with an average length of 1.40 Å, of the cyclopentadienone ligands are longer than normal one, which is a common observation for a π-bonding olefin. Two bridging carbonyls are found to coordinate to both cobalts about the same distance. $^1$H- and $^{13}$C-NMR of (**4**) exhibit simple patterns due to its symmetrical nature. Only two singlet peaks, 5.47 and 0.32 ppm, were observed for this compound in the $^1$H-NMR.

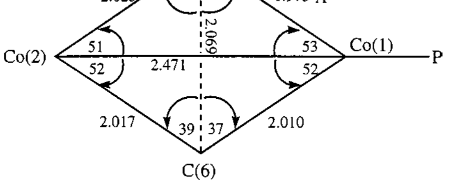
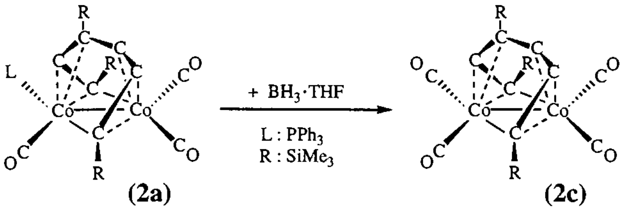


Fig. 2. The symmetrical arrangement of atoms within the Co(1), C(1), C(2), C(6) segment of the molecule.

Substituted cyclopentadienones tend to be dimerized through the Diels–Alder type reaction. Therefore, to find a practical reaction route to generate and stabilize cyclopentadienones through the transition metal-mediated cyclization of two alkynes with one carbon monoxide is of interest to many people [7,11]. Compound (**4**) constitutes useful monomeric cyclopentadienone synthon [12].

The crystal structure of (**4**) has revealed that two cyclopentadienone ligands are on the same side of metal–metal bond, in contrast to previous beliefs. As we know, the shape of a molecule in the solid state does not actually reflect what it has to be in solution. One might expect that (**4**) exhibits fluxional behavior in solution under elevated temperature as does the structural related compound $[CpFe(CO)_2]_2$. The fluxional



Scheme 3.

Table 2
Selected bond lengths (Å) and bond angles (°) for (**2a**)

| | | | |
|---|---|---|---|
| *Bond distances* | | | |
| Co(1)–Co(2) | 2.471(1) | Co(1)–P | 2.202(1) |
| Co(1)–C(35) | 1.766(3) | Co(1)–C(1) | 1.975(3) |
| Co(1)–C(2) | 2.069(3) | Co(1)–C(3) | 2.086(3) |
| Co(1)–C(6) | 2.010(3) | Co(2)–C(34) | 1.766(3) |
| Co(2)–C(36) | 1.779(4) | Co(2)–C(1) | 2.025(3) |
| Co(2)–C(4) | 2.116(3) | Co(2)–C(5) | 2.044(3) |
| Co(2)–C(6) | 2.017(3) | P–C(16) | 1.828(3) |
| P–C(22) | 1.838(3) | P–C(28) | 1.842(3) |
| Si(1)–C(1) | 1.876(3) | Si(1)–C(7) | 1.865(5) |
| Si(1)–C(8) | 1.871(4) | Si(1)–C(9) | 1.868(3) |
| Si(2)–C(4) | 1.885(3) | Si(2)–C(10) | 1.874(5) |
| Si(2)–C(11) | 1.842(4) | Si(2)–C(12) | 1.866(4) |
| Si(3)–C(6) | 1.876(3) | Si(3)–C(13) | 1.864(5) |
| Si(3)–C(14) | 1.862(4) | Si(3)–C(15) | 1.869(5) |
| C(34)–O(34) | 1.135(4) | C(35)–O(35) | 1.146(4) |
| C(36)–O(36) | 1.136(5) | C(1)–C(2) | 1.409(4) |
| C(2)–C(3) | 1.418(4) | C(3)–C(4) | 1.506(4) |
| C(4)–C(5) | 1.406(4) | C(5)–C(6) | 1.416(4) |
| *Bond angles* | | | |
| Co(2)–Co(1)–P | 152.8(1) | Co(2)–Co(1)–C(35) | 104.2(1) |
| P–Co(1)–C(35) | 97.1(1) | Co(2)–Co(1)–C(1) | 52.8(1) |
| P–Co(1)–C(1) | 143.3(1) | C(35)–Co(1)–C(1) | 93.0(1) |
| Co(2)–Co(1)–C(2) | 76.5(1) | P–Co(1)–C(2) | 106.3(1) |
| C(35)–Co(1)–C(2) | 122.0(1) | C(1)–Co(1)–C(2) | 40.7(1) |
| Co(2)–Co(1)–C(3) | 73.3(1) | P–Co(1)–C(3) | 91.4(1) |
| C(35)–Co(1)–C(3) | 161.8(1) | C(1)–Co(1)–C(3) | 71.0(1) |
| C(2)–Co(1)–C(3) | 39.9(1) | Co(2)–Co(1)–C(6) | 52.3(1) |
| P–Co(1)–C(6) | 105.5(1) | C(35)–Co(1)–C(6) | 106.7(1) |
| C(1)–Co(1)–C(6) | 105.0(1) | C(2)–Co(1)–C(6) | 116.3(1) |
| C(3)–Co(1)–C(6) | 86.2(1) | Co(1)–Co(2)–C(34) | 145.4(1) |
| Co(1)–Co(2)–C(36) | 104.7(1) | C(34)–Co(2)–C(36) | 95.9(2) |
| Co(1)–Co(2)–C(1) | 50.9(1) | C(34)–Co(2)–C(1) | 96.7(1) |
| C(36)–Co(2)–C(1) | 107.3(1) | Co(1)–Co(2)–C(4) | 74.7(1) |
| C(34)–Co(2)–C(4) | 94.5(1) | C(36)–Co(2)–C(4) | 160.8(1) |
| C(1)–Co(2)–C(4) | 87.4(1) | Co(1)–Co(2)–C(5) | 76.7(1) |
| C(34)–Co(2)–C(5) | 115.6(1) | C(36)–Co(2)–C(5) | 121.4(1) |
| C(1)–Co(2)–C(5) | 115.7(1) | C(4)–Co(2)–C(5) | 39.5(1) |
| Co(1)–Co(2)–C(6) | 52.0(1) | C(34)–Co(2)–C(6) | 154.7(1) |
| C(36)–Co(2)–C(6) | 93.4(1) | C(1)–Co(2)–C(6) | 102.9(1) |
| C(4)–Co(2)–C(6) | 70.9(1) | C(5)–Co(2)–C(6) | 40.8(1) |
| Co(1)–P–C(16) | 107.7(1) | Co(1)–P–C(22) | 118.4(1) |
| C(16)–P–C(22) | 102.2(1) | Co(1)–P–C(28) | 121.3(1) |
| C(16)–P–C(28) | 103.6(2) | C(22)–P–C(28) | 101.3(1) |
| Co(1)–C(1)–Co(2) | 76.3(1) | Co(1)–C(1)–C(2) | 73.3(2) |
| Co(2)–C(1)–C(2) | 109.6(2) | Co(1)–C(2)–C(1) | 66.0(2) |
| Co(1)–C(2)–C(3) | 70.7(2) | C(1)–C(2)–C(3) | 113.1(3) |
| Co(1)–C(3)–C(2) | 69.4(2) | Co(1)–C(3)–C(4) | 101.1(2) |
| C(2)–C(3)–C(4) | 120.1(3) | Co(2)–C(4)–C(3) | 96.8(2) |
| Co(2)–C(4)–C(5) | 67.5(2) | C(3)–C(4)–C(5) | 116.6(2) |
| Co(2)–C(5)–C(4) | 73.0(2) | Co(2)–C(5)–C(6) | 68.6(2) |
| C(4)–C(5)–C(6) | 116.3(3) | Co(1)–C(6)–Co(2) | 75.7(1) |
| Co(1)–C(6)–C(5) | 109.6(2) | Co(2)–C(6)–C(5) | 70.6(2) |

manner of $[CpFe(CO)_2]_2$ in solution was frozen at −31°C [13].

A variable-temperature $^1$H-NMR experiment was carried out for (**4**) in THF-$d_8$. The experiment was conducted in the range of −100 to 40°C. Each measurement was taken at increments of 10°C. There was no significant change judged by the appearance of the spectra. It indicates that there is no fluxional for (**4**) under our investigated temperature range, which is quite different from the case of $[CpFe(CO)_2]_2$ (Scheme 4).

The preparation of 2,5-bis(trimethylsilanyl)cyclopenta-2,4-dien-1-one (**5**) (Table 4) had been reported. The compound was the organic products following the oxidation of ($\eta^4$-cyclopentadienone)($\eta^5$-$C_5H_5$)Co which is the result of the catalytic reaction of trimethylsilyacetylene with ($\eta^5$-$C_5H_5$)$Co(CO)_2$ [14]. In our case, it was obtained from the degradation of (**4**) by exposing it to air in solution. The conversion is quantitatively. The crystal structure of (**5**) was determined. Two $-SiMe_3$ groups are adjacent in (**5**). Nevertheless, no strong repulsion is observed. The formation of (**5**) is believed to take place via the Diels–Alder type of cyclization of the two released cyclopentadienone ligands from (**4**) (Scheme 5, Fig. 4).

With respect to the so called ‘flyover-bridged’ complexes, crystal structures of several closely related compounds had been reported [6]. The arrangement of the substituents on the flyover bridge ligand are at 1,3,6 carbon atoms while $HC\equiv CCMe_3$ or $HC\equiv CCF_3$ were used as alkyne sources. In contrast, it was a head-to-tail trimerization of the alkyne while $PhC\equiv CC(O)CH_3$ was used. Steric effect may play an important role here. It is obvious that the former arrangement prevailed while the bulky substituent was used. Since the $-SiMe_3$ groups are rather bulky, (**2a**) can be proved. The preparation of a closely related heterobimetallic compound, $MoCo(CO)_4\{\mu$-CPh=CH–CH=CPh–CH=CPh–$\}(\eta^5$-$C_5H_5)$ (**6**), was reported without crystal structure [5c]. Unobservable coupling among the three protons of the flyover bridge ligand in the $^1$H-NMR indicates that there are no vincinal HC–CH protons in (**6**). It indicates that the phenyl ring is not regarded as a very bulky group and each of the three –Ph groups are attached to 1,3,6 carbon atoms. In this way, the steric

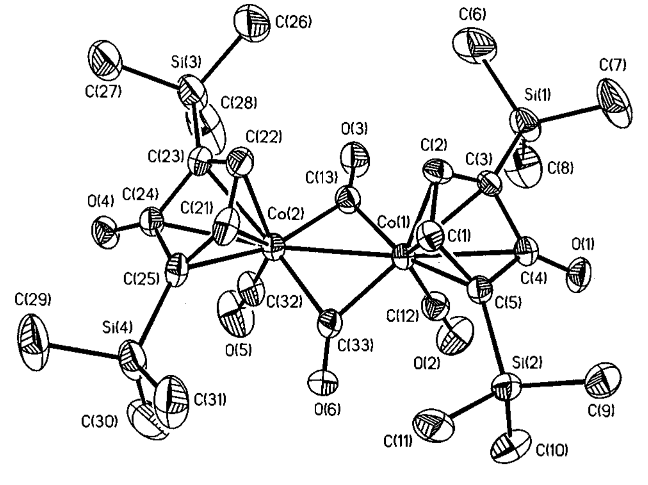
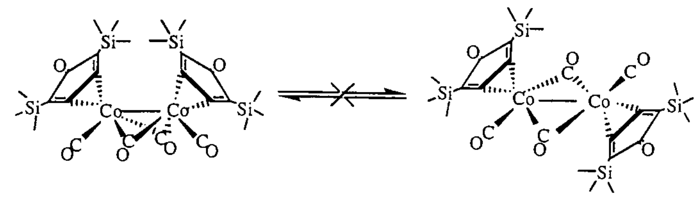
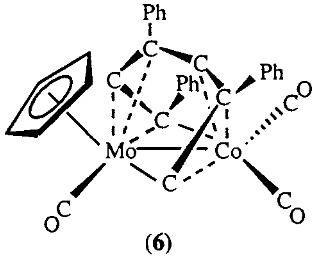


Fig. 3. ORTEP drawing with the numbering scheme of (**4**). Hydrogen atoms were omitted for clarity.



Scheme 4.

hindrance between phenyl rings can be reduced to a minimum.



(**6**)

The reaction of [MoCo(CO)$_6$(PPh$_3$)(η$^5$-C$_5$H$_5$)] (**7**) [15] with an excess of trimethylsilylacetylene in THF at 60°C yielded two heterobinuclear complexes containing flyover bridge ligands, CpMoCo(CO)$_3${μ- C(SiMe$_3$)=CH–CH=C(SiMe$_3$)–CH=C(SiMe$_3$)} (**8a**), and (**8b**). The compound (**8b**) was presumably an isomer of (**8a**) (Scheme 6).

Interestingly, a small amount of (**1b**) was also observed. It was believed that the Mo–Co bond of (**6**) was broken down and two cobalt fragments were joined together to pick up one acetylene and form the bridged structure [16]. The isomers of (**8a**) and (**8b**) had very close $R_f$ values. It was rather difficult to thoroughly separate them from CTLC. However, we were managed to get a small amount of reasonably pure (**8a**) from the front part of mixed band. $^1$H-, $^{13}$C-NMR and mass of (**8a**) had been recorded. The $^1$H-NMR pattern of the flyover bridge ligand of (**8a**) is similar to that of (**2a**). This indicates that the arrangement of the substituents on the flyover bridge ligand are at 1,3,6 carbon atoms as in the case of (**2a**). The only triphenylphosphine ligand came off from the metal center during the reaction. The corresponding peaks of PPh$_3$ in the $^1$H-NMR were absent. This was also confirmed by the $^{13}$C-NMR. Unfortunately, the attempt to grow crystals from (**8a**) resulted in failure. Further characterization of (**8a**) was not carried out due to the instability and small quantity obtained from this compound. 1,2,4-Tris-trimethysilanylbenzene had been obtained again from the degradation of compound (**8a**). This was also a confirmation of the observed $^1$H-NMR of (**8a**).

To stabilize the flyover bridge structure, the importance of the electronegative substituent is emphasized [9]. It was believed that the backbonding from the metal centers to the bridged ligand would be enhanced and the whole bonding strengthened while the strong electron-withdrawing substituents are present in the ligand. The –CF$_3$ is a strong electron-withdrawing substituent and is regarded as an important factor in stabilizing the flyover bridge structure of Co$_2$(CO)$_4${μ-C(CF$_3$)=CH–CH=C(CF$_3$)–CH=C(CF$_3$)}. However, in the case of (**2a**) the –SiMe$_3$ is not an electron-withdrawing substituent at all. However, the flyover bridged structure of (**2a**) is stable. One might argue that the presence of the triphenylphosphine ligand provides the necessary electron density which flows to the metal centers thus enhancing the backbonding as a result.

In summary, the preparation and crystal structure determination of (**2a**), another example of a dimetallic frame containing a ‘flyover bridge’ ligand, was reported. In complex (**4**), substituted cyclopentadienone was formed by the metal-mediated coupling of two alkynes and one carbon monoxide, and it can be seen as a monomeric cyclopentadienone synthon.

## 3. Experimental

### *3.1. Apparatus and materials*

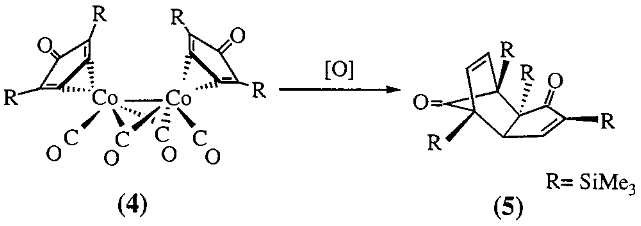
All preparations were performed in a nitrogen-flushed glove box or in a vacuum system. Freshly distilled solvents were used. All processes of separation of the products were performed by Centrifugal Thin-Layer Chromatography (TLC, Chromatotron, Harrison model 8924). $^1$H-, $^{31}$P- and $^{13}$C-NMR spectra were recorded (Varian-VXR-300S spectrometer) at 300.00, 121.44 and 75.46 MHz, respectively; chemical shifts are reported in ppm relative to internal TMS. $^1$H-NMR spectra of variable temperature experiments were recorded by the same machine. IR spectra of solution in CH$_2$Cl$_2$ were recorded on a Hitachi 270-30 spectrometer. Mass spectra were recorded on JOEL JMS-SX/SX 102A GC/MS/MS spectrometer. Elementary analysis was recorded on a Heraeus CHN-O-S-Rapid.

### *3.1.1. Preparation of (**1a**)*

Into a 100 cm$^3$ flask was placed Co$_2$(CO)$_8$ (400 mg, 1.17 mmol) and trimethylsilylacetylene (0.25 ml, 1.75 mmol) with 30 cm$^3$ of THF. The solution was stirred under 30°C during the following 3 h.

Table 3
Selected bond lengths (Å) and bond angles (°) for (**4**)

| | | | |
|---|---|---|---|
| *Bond lengths* | | | |
| Co(1)–Co(2) | 2.542(1) | Co(1)–C(1) | 2.074(7) |
| Co(1)–C(2) | 2.074(7) | Co(1)–C(3) | 2.165(5) |
| Co(1)–C(4) | 2.390(5) | Co(1)–C(5) | 2.179(6) |
| Co(1)–C(12) | 1.809(9) | Co(1)–C(13) | 1.902(6) |
| Co(1)–C(33) | 1.932(6) | Co(2)–C(13) | 1.916(6) |
| Co(2)–C(21) | 2.062(8) | Co(2)–C(22) | 2.060(8) |
| Co(2)–C(23) | 2.181(7) | Co(2)–C(24) | 2.398(5) |
| Co(2)–C(25) | 2.166(6) | Co(2)–C(32) | 1.792(9) |
| Co(2)–C(33) | 1.927(6) | Si(1)–C(3) | 1.869(6) |
| Si(1)–C(6) | 1.849(9) | Si(1)–C(7) | 1.842(7) |
| Si(1)–C(8) | 1.835(12) | Si(2)–C(5) | 1.881(6) |
| Si(2)–C(9) | 1.845(7) | Si(2)–C(10) | 1.837(11) |
| Si(2)–C(11) | 1.859(7) | Si(3)–C(23) | 1.870(7) |
| Si(3)–C(26) | 1.849(9) | Si(3)–C(27) | 1.852(10) |
| Si(3)–C(28) | 1.773(15) | Si(4)–C(25) | 1.860(6) |
| Si(4)–C(29) | 1.822(7) | Si(4)–C(30) | 1.824(13) |
| Si(4)–C(31) | 1.852(9) | O(1)–C(4) | 1.223(7) |
| O(2)–C(12) | 1.124(11) | O(3)–C(13) | 1.159(8) |
| O(4)–C(24) | 1.220(7) | O(5)–C(32) | 1.132(12) |
| O(6)–C(33) | 1.152(8) | C(1)–C(2) | 1.446(8) |
| C(1)–C(5) | 1.395(9) | C(2)–C(3) | 1.400(10) |
| C(3)–C(4) | 1.491(8) | C(4)–C(5) | 1.510(8) |
| C(21)–C(22) | 1.396(11) | C(21)–C(25) | 1.426(10) |
| C(22)–C(23) | 1.405(10) | C(23)–C(24) | 1.500(9) |
| C(24)–C(25) | 1.504(9) | | |
| *Bond angles* | | | |
| Co(2)–Co(1)–C(1) | 106.8(1) | Co(2)–Co(1)–C(2) | 107.0(2) |
| C(1)–Co(1)–C(2) | 40.8(2) | Co(2)–Co(1)–C(3) | 135.8(2) |
| C(1)–Co(1)–C(3) | 66.6(2) | C(2)–Co(1)–C(3) | 38.5(3) |
| Co(2)–Co(1)–C(4) | 168.1(2) | C(1)–Co(1)–C(4) | 62.2(2) |
| C(2)–Co(1)–C(4) | 62.0(2) | C(3)–Co(1)–C(4) | 37.8(2) |
| Co(2)–Co(1)–C(5) | 135.3(2) | C(1)–Co(1)–C(5) | 38.2(2) |
| C(2)–Co(1)–C(5) | 66.2(2) | C(3)–Co(1)–C(5) | 66.9(2) |
| C(4)–Co(1)–C(5) | 38.2(2) | Co(2)–Co(1)–C(12) | 109.7(2) |
| C(1)–Co(1)–C(12) | 137.7(3) | C(2)–Co(1)–C(12) | 137.9(2) |
| C(3)–Co(1)–C(12) | 99.4(3) | C(4)–Co(1)–C(12) | 82.1(3) |
| C(5)–Co(1)–C(12) | 99.6(3) | Co(2)–Co(1)–C(13) | 48.5(2) |
| C(1)–Co(1)–C(13) | 124.2(3) | C(2)–Co(1)–C(13) | 92.9(3) |
| C(3)–Co(1)–C(13) | 97.2(2) | C(4)–Co(1)–C(13) | 132.4(2) |
| C(5)–Co(1)–C(13) | 159.1(3) | C(12)–Co(1)–C(13) | 96.2(3) |
| Co(2)–Co(1)–C(33) | 48.7(2) | C(1)–Co(1)–C(33) | 94.2(3) |
| C(2)–Co(1)–C(33) | 126.0(3) | C(3)–Co(1)–C(33) | 160.7(3) |
| C(4)–Co(1)–C(33) | 132.7(2) | C(5)–Co(1)–C(33) | 97.5(2) |
| C(12)–Co(1)–C(33) | 94.1(3) | C(13)–Co(1)–C(33) | 94.9(3) |
| C(3)–Si(1)–C(6) | 109.6(3) | C(3)–Si(1)–C(7) | 106.7(3) |
| C(6)–Si(1)–C(7) | 110.0(4) | C(3)–Si(1)–C(8) | 110.9(4) |
| C(6)–Si(1)–C(8) | 109.3(5) | C(7)–Si(1)–C(8) | 110.3(4) |
| C(2)–C(1)–C(5) | 109.9(5) | C(1)–C(2)–C(3) | 109.8(5) |
| Co(1)–C(3)–Si(1) | 130.9(4) | O(1)–C(4)–C(3) | 127.9(5) |
| O(1)–C(4)–C(5) | 126.2(5) | C(3)–C(4)–C(5) | 105.8(5) |
| C(1)–C(5)–C(4) | 106.1(5) | Co(1)–C(12)–O(2) | 178.4(5) |
| Co(1)–C(13)–Co(2) | 83.5(3) | Co(1)–C(13)–O(3) | 138.6(4) |
| Co(2)–C(13)–O(3) | 137.9(4) | Co(2)–C(32)–O(5) | 177.2(6) |
| Co(1)–C(33)–Co(2) | 82.4(3) | Co(1)–C(33)–O(6) | 138.8(4) |
| C(13)–Co(2)–C(33) | 94.6(2) | | |



Scheme 5.

Subsequently, the resulting dark red solution was filtered through a silica gel column. A dark red band was collected and was identified as (**1a**). The yield was 94% (424 mg, 1.10 mmol).

### 3.1.2. *Characterization of (1b)*

$^1$H-NMR (CDCl$_3$, $\delta$/ppm): 0.29 (s, 9H, –SiMe$_3$), 6.37 (s, 1H, CH); $^{13}$C-NMR (CDCl$_3$, $\delta$/ppm): 0.80 (s, 3C, –SiMe$_3$), 85.27 (s, 1C, ≡CH), 77.44 (s, 1C, ≡C–SiMe$_3$), 200.49 (Co–CO's); IR (CH$_2$Cl$_2$): $\nu_{(CO)}$ 2063(s), 2005(b) cm$^{-1}$; MS $m/z$ 384 (P$^+$).

### 3.1.3. *Preparation of (1b)*

Into a 100 cm$^3$ flask was placed Co$_2$(CO)$_8$ (200 mg, 0.58 mmol), triphenylphosphine (153 mg, 0.58 mmol) and trimethylsilylacetylene (0.13 ml, 0.88 mmol) with 30 cm$^3$ of THF. The solution was stirred at 55°C during the following 5 h.

Subsequently, the resulting dark red solution was filtered through a small amount of silica gel. The filtrate was evaporated under reduced pressure to yield the crude product. Purification with centrifugal thin-layer chromatography (eluent:hexane/CH$_2$Cl$_2$), a dark red band was collected and was identified as (**1b**). The yield was 40% (138 mg, 0.22 mmol).

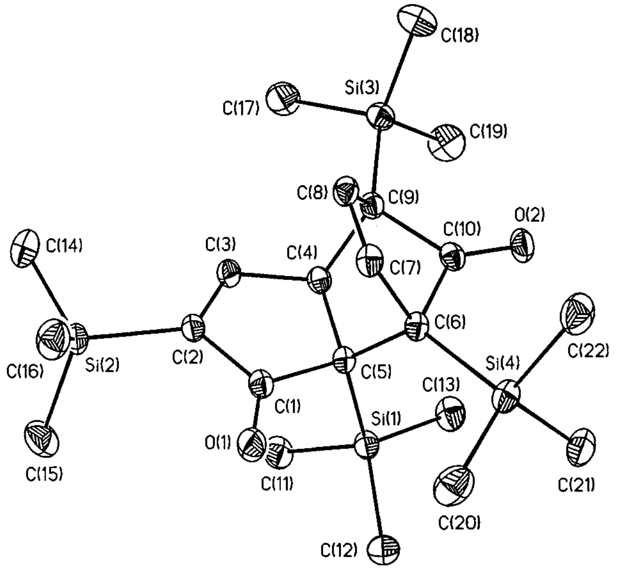
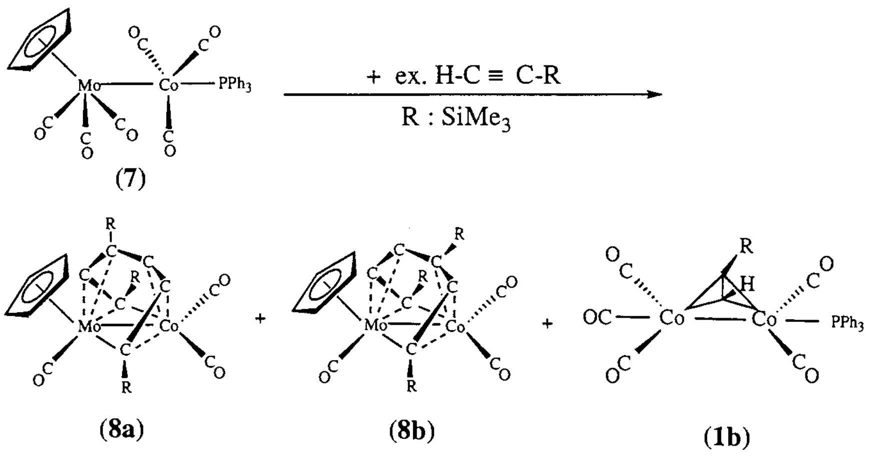


Fig. 4. ORTEP drawing with the numbering scheme of (**5**). Hydrogen atoms were omitted for clarity.



Scheme 6.

### 3.1.4. *Characterization of (**1b**)*

$^1$H-NMR ($CDCl_3$, $\delta$/ppm): 0.06 (s, 9H, $-SiMe_3$), 5.52 (d, 1H, $J_{PH} = 6.6$ Hz), 7.38 ~ 7.49 (m, 15H, $PPh_3$); $^{13}$C-NMR ($CDCl_3$, $\delta$/ppm): 1.52 (3C, $Me_3Si-$), 134.96 (d, $J_{PC} = 40$ Hz), 132.84 (d, $J_{PC} = 11$ Hz), 129.85 (d, $J_{PC} = 1$ Hz), 128.16 (d, $J_{PC} = 10$ Hz), 86.00, 72.67 (2C), 201.38, 205.82 (3C, Co–CO's); IR ($CH_2Cl_2$): $\nu_{(CO)}$ 2058(s), 2000(s), 1955(sh) cm$^{-1}$; MS $m/z$ 643 ($P^+$).

### 3.1.5. *Preparation of (**2a**)*

Into a 100 cm$^3$ flask was placed (**1b**) (138 mg, 0.22 mmol) and trimethylsilylacetylene (1.46 mmol) with 30 cm$^3$ of THF. The solution was stirred at 65°C during the following 17 h.

Subsequently, the resulting orange solution was filtered through a small amount of silica gel. The filtrate was evaporated under reduced pressure to yield the crude product. Purification with centrifugal thin-layer chromatography (eluent:hexane/$CH_2Cl_2$), a purple band was collected and was identified as (**2a**). The yield was 35% (59 mg, 0.077 mmol).

### 3.1.6. *Characterization of (**2a**)*

$^1$H-NMR ($CDCl_3$, $\delta$/ppm): 0.07 (s, 9H, $-SiMe_3$), 0.21 (s, 9H, $-SiMe_3$), 0.32 (s, 9H, $-SiMe_3$), 3.58 (dd, 1H, $J_{HH} = 17$, 3 Hz), 4.66 (b, 1H), 6.08 (b, 1H), 7.2 ~ 7.4 (m, 15H, $PPh_3$); $^{13}$C-NMR ($CDCl_3$, $\delta$/ppm): $-1.64$, 0.66, 1.79 (9C, $-SiMe_3$), 83.82, 97.88, 122.33, 127.63, 127.95 (6C, $PPh_3$, d, $J_{PC} = 9.4$ Hz), 129.81 (3C, $PPh_3$), 133.49 (6C, $PPh_3$, d, $J_{PC} = 10.0$ Hz), 134.63 (3C, $PPh_3$, d, $J_{PC} = 39.6$ Hz), 204.24, 203.89, 214.43 (3C, 3CO); $^{31}$P-NMR ($CDCl_3$, $\delta$/ppm): $\delta$ 53.3 (b, 1P); IR ($CH_2Cl_2$): $\nu_{(CO)}$ 2010.3, 1962.5 cm$^{-1}$; MS $m/z$ 758 ($P^+$); Anal. Calc. for (**2a**): C, 56.98; H, 5.98. Found: C, 57.00; H, 6.03.

### 3.1.7. *Preparation of (**4**)*

Into a 100 cm$^3$ flask was placed (**1a**) (491 mg, 1.28 mmol) and trimethylsilylacetylene (0.90 ml, 6.39 mmol) with 30 cm$^3$ of THF. The solution was stirred at 40°C during the following 15 h.

Subsequently, the resulting orange solution was filtered through a small amount of silica gel. The filtrate was evaporated under reduced pressure to yield the crude product. Purification with centrifugal thin-layer chromatography (eluent:hexane/$CH_2Cl_2$), a dark red and an orange–red band were collected. The first band was characterized as unreacted (**1a**) and the second band was identified as (**4**). The yield of (**4**) was 25% (220 mg, 0.324 mmol).

### 3.1.8. *Characterization of (**4**)*

$^1$H-NMR ($CDCl_3$, $\delta$/ppm): 0.32 (s, 36H, $SiMe_3$), 5.47 (s, 4H, CH); $^1$H-NMR (THF-$d_8$, $\delta$/ppm): 0.31 (s, 36H, $SiMe_3$), 5.93 (s, 4H, CH); $^{13}$C-NMR (d-THF, $\delta$/ppm): $-0.77$ (12C, $SiMe_3$), 90.00 (4C, $C(SiMe_3)$), 103.22 (4C, CH), 185.06 (2C, CO), 200.70 (2C, CO), 239.18 (2C, CO); IR ($CH_2Cl_2$): $\nu_{(CO)}$2068, 1842, 1629 cm$^{-1}$; MS $m/z$ 678.8 ($P^+$); Anal. Calc. for (**4**): C, 45.96; H, 5.89. Found: C, 49.52; H, 6.24.

### 3.1.9. *Characterization of (**5**)*

$^1$H-NMR (THF-$d_8$, $\delta$/ppm): 0.07 (m, 9H, $-SiMe_3$), 0.11 (m, 9H, $SiMe_3$), 0.20 (m, 9H, $SiMe_3$), 0.26 (m, 9H, $SiMe_3$), 3.31 (d, 1H, CH, $J_{HH} = 2.4$ Hz), 5.99 (d, 1H, CH, $J_{HH} = 6.4$ Hz), 6.20 (d, 1H, CH, $J_{HH} = 6.4$ Hz), 7.40(d, 1H, CH, $J_{HH} = 2.4$ Hz); $^{13}$C-NMR (THF-$d_8$, $\delta$/ppm): $-2.31$ (3C, $SiMe_3$), $-1.29$ (3C, $SiMe_3$), $-0.83$ (3C, $SiMe_3$), 0.05 (3C, $SiMe_3$), 51.00 (1C, $C(SiMe_3)$), 53.77 (1C, $C(SiMe_3)$), 55.12 (1C, $C(SiMe_3)$), 72.01 (1C, CH), 130.73 (1C, CH), 137.90 (1C, CH), 156.30 (1C, $C(SiMe_3)$), 167.52 (1C, CH), 206.00 (1C,

Table 4
Selected bond lengths (Å) and bond angles (°) for (**5**)

| | | | |
|---|---|---|---|
| *Bond lengths* | | | |
| O(1)–C(1) | 1.220(3) | O(2)–C(10) | 1.199(3) |
| Si(1)–C(5) | 1.914(3) | Si(1)–C(11) | 1.867(4) |
| Si(1)–C(12) | 1.850(3) | Si(1)–C(13) | 1.870(3) |
| Si(2)–C(2) | 1.878(3) | Si(2)–C(14) | 1.862(3) |
| Si(2)–C(15) | 1.861(4) | Si(2)–C(16) | 1.851(4) |
| Si(3)–C(9) | 1.887(2) | Si(3)–C(17) | 1.863(4) |
| Si(3)–C(18) | 1.856(4) | Si(3)–C(19) | 1.857(4) |
| Si(4)–C(6) | 1.902(2) | Si(4)–C(20) | 1.862(3) |
| Si(4)–C(21) | 1.860(3) | Si(4)–C(22) | 1.864(4) |
| C(1)–C(2) | 1.487(3) | C(1)–C(5) | 1.535(3) |
| C(2)–C(3) | 1.322(3) | C(3)–C(4) | 1.499(3) |
| C(4)–C(5) | 1.572(3) | C(4)–C(9) | 1.582(4) |
| C(5)–C(6) | 1.601(4) | C(6)–C(7) | 1.527(4) |
| C(6)–C(10) | 1.549(3) | C(7)–C(8) | 1.321(3) |
| C(8)–C(9) | 1.518(4) | C(9)–C(10) | 1.550(3) |
| *Bond lengths* | | | |
| C(5)–Si(1)–C(11) | 106.6(1) | C(5)–Si(1)–C(11) | 113.2(1) |
| C(11)–Si(1)–C(12) | 106.2(1) | C(5)–Si(1)–C(13) | 110.0(1) |
| C(11)–Si(1)–C(13) | 108.7(2) | C(12)–Si(1)–C(13) | 111.8(1) |
| C(2)–Si(2)–C(14) | 108.0(1) | C(2)–Si(2)–C(15) | 107.9(1) |
| C(14)–Si(2)–C(15) | 109.4(2) | C(2)–Si(2)–C(16) | 108.8(1) |
| C(14)–Si(2)–C(16) | 111.2(1) | C(15)–Si(2)–C(16) | 111.3(2) |
| C(9)–Si(3)–C(17) | 109.1(1) | C(9)–Si(3)–C(18) | 109.2(1) |
| C(17)–Si(3)–C(18) | 109.8(2) | C(9)–Si(3)–C(19) | 110.0(1) |
| C(17)–Si(3)–C(19) | 107.4(2) | C(18)–Si(3)–C(19) | 111.4(2) |
| C(6)–Si(4)–C(20) | 110.6(1) | C(6)–Si(4)–C(21) | 114.2(1) |
| C(20)–Si(4)–C(21) | 111.7(1) | C(6)–Si(4)–C(22) | 105.2(1) |
| C(20)–Si(4)–C(22) | 108.3(2) | C(21)–Si(4)–C(22) | 106.5(2) |
| O(1)–C(1)–C(2) | 125.6(2) | O(1)–C(1)–C(5) | 124.8(2) |
| C(2)–C(1)–C(5) | 109.7(2) | Si(2)–C(2)–C(1) | 124.6(2) |
| Si(2)–C(2)–C(3) | 127.6(2) | C(1)–C(2)–C(3) | 107.8(2) |
| C(2)–C(3)–C(4) | 115.6(2) | C(3)–C(4)–C(5) | 103.8(2) |
| C(3)–C(4)–C(9) | 115.3(2) | C(5)–C(4)–C(9) | 106.0(2) |
| Si(1)–C(5)–C(1) | 107.2(2) | Si(1)–C(5)–C(4) | 109.7(2) |
| C(1)–C(5)–C(4) | 102.6(2) | Si(1)–C(5)–C(6) | 120.7(2) |
| C(1)–C(5)–C(6) | 111.8(2) | C(4)–C(5)–C(6) | 103.4(2) |
| Si(4)–C(6)–C(5) | 127.0(2) | Si(4)–C(6)–C(7) | 112.6(2) |
| C(5)–C(6)–C(7) | 104.5(2) | Si(4)–C(6)–C(10) | 114.6(2) |
| C(5)–C(6)–C(10) | 98.1(2) | C(7)–C(6)–C(10) | 94.6(2) |
| C(6)–C(7)–C(8) | 110.8(2) | C(7)–C(8)–C(9) | 109.9(2) |
| Si(3)–C(9)–C(4) | 116.2(2) | Si(3)–C(9)–C(8) | 119.8(2) |
| C(4)–C(9)–C(8) | 105.8(2) | Si(3)–C(9)–C(10) | 119.0(2) |
| C(4)–C(9)–C(10) | 96.9(2) | C(8)–C(9)–C(10) | 95.1(2) |
| O(2)–C(10)–C(6) | 130.0(2) | O(2)–C(10)–C(9) | 129.7(2) |
| C(6)–C(10)–C(9) | 100.3(2) | | |

CO), 212.22 (1C, CO); MS *m*/*z* 448.9 ($P^+$); Anal. Calc. for (**5**): C, 58.89; H, 8.95. Found: C, 58.72; H, 8.98.

### *3.1.10. Preparation of (8a)*

The synthesis of [MoCo(CO)$_6$(PPh$_3$)($\eta^5$-C$_5$H$_5$)] (**7**) was done according to a procedure in the literature [16].

Into a 50 cm$^3$ flask was placed (**7**) (429 mg, 0.67 mmol) and trimethylsilylacetylene (1 ml, 7.08 mmol) with 30 cm$^3$ of THF. The solution was stirred at 60°C during the following 15 h.

Subsequently, the resulting orange solution was filtered through a small amount of silica gel. The filtrate was evaporated under reduced pressure to yield the crude product. Purification with centrifugal thin-layer chromatography (eluent:hexane), firstly an orange band of mixed (**8a**) and (**8b**) was obtained which was then followed by a reddish brown band of (**1b**). Further purification of (**8a**) from mixture was again carried out by CTLC, with thinner silica coating plates and slower solvent flow speed. The front part of the band was collected.

### *3.1.11. Characterization of (8a)*

$^1$H-NMR(CDCl$_3$, $\delta$/ppm): $\delta$ 0.07, 0.29, 0.35 (s, 18H, Me$_3$Si–), 4.85 (s, 5H, Cp), 4.34 (d, 1H, $J_{HH} = 3.3$ Hz), 5.13 (d, 1H, $J_{HH} = 0.6$ Hz), 6.14 (dd, 1H, $J_{HH} = 3.3$, 0.6 Hz); $^{13}$C-NMR (CDCl$_3$, $\delta$/ppm): 0.19, 1.73, 2.36 (9C, Me$_3$Si–), 86.60 (5C, Cp), 118.95, 106.12, 87.82, 80.18, 77.21, 61.74 (6C), 184.63 (2C, Co–CO's), 224.64 (1C, Mo–CO's); MS *m*/*z* 600 ($P^+ = M + 2$).

### *3.1.12. Characterization of 1,2,4-tris-trimethysilanylbenzene*

$^1$H-NMR(CDCl$_3$): $\delta$ 0.06(s, 9H, Me$_3$Si–), 0.26 (s, 9H, Me$_3$Si–), 0.37 (s, 9H, Me$_3$Si–), 7.84 (s, 1H), 7.66 (d, 1H, $J_{HH} = 7.4$ Hz), 7.49 (d, 1H, $J_{HH} = 7.4$ Hz).

## 4. X-ray crystallographic studies

Suitable crystals of (**2a**), (**4**) and (**5**) were sealed in thin-walled glass capillaries under nitrogen atmosphere and mounted on a Siemens P4 diffractometer. The crystallographic data were collected using a $\theta$–$2\theta$ scan mode with Mo–K$_\alpha$ radiation. The space group determination was based on a check of the Laue symmetry and systematic absences, and was confirmed by the structure solution. The structure was solved by direct methods using Siemens SHELXTL PLUS package [17]. All non-H atoms were located from successive Fourier maps. Anisotropic thermal parameters were used for all non-H atoms and fixed isotropic for H atoms that were refined using riding model [18]. Crystallographic data of (**2a**), (**4**) and (**5**) are summarized in Table 1.

## 5. Supplementary material available

Atomic coordinates of (**2a**), (**4**) and (**5**), tables of thermal parameters, bond lengths and angles, anisotropic thermal parameters, and H atom coordinates have been deposited as supplementary material.

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[18] Hydrogen atoms were ride on carbons or oxygens in their idealized positions and held fixed with C–H distances of 0.96 Å.