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# Synthesis of Methyl Metallocenecarboxylates [{$\eta^4$-$Ph_{4-n}(SiMe_3)_nC_4$}Co{$\eta^5$-$MeOC(O)C_5H_4$}] ($n$ = 1, 2) and Their Desilylation Reactions: Structural Studies and Conversion to Metallocenecarboxylic Acids and Their Alcohol Derivatives

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The reaction of (2-phenylethynyl)trimethylsilane ($Me_3SiC\equiv CPh$) with [{$\eta^5$-$MeOC(O)C_5H_4$}$Co(PPh_3)_2$] generated in situ results in the exclusive formation of two isomers of methyl metallocenecarboxylates, namely [{*trans*-$\eta^4$-$Ph_2(Me_3Si)_2C_4$}Co{$\eta^5$-$MeOC(O)C_5H_4$}] (**1**) and [{*cis*-$\eta^4$-$Ph_2(Me_3Si)_2C_4$}Co{$\eta^5$-$MeOC(O)C_5H_4$}] (**2**). The reaction of [{$\eta^5$-$MeOC(O)C_5H_4$}$Co(PPh_3)(Me_3SiC\equiv CPh)$] with $PhC\equiv CPh$ yields the methyl metallocenecarboxylate [{$\eta^4$-$Ph_3(Me_3Si)C_4$}Co{$\eta^5$-$MeOC(O)C_5H_4$}] (**3**) along with [{$\eta^4$-$Ph_4C_4$}Co{$\eta^5$-$MeOC(O)C_5H_4$}] (**4**). The reactions of **1**, **2** and **3** with $Bu_4NF$ in dmso results in the desilylated complexes [(*trans*-$\eta^4$-$Ph_2H_2C_4$)Co{$\eta^5$-$MeOC(O)C_5H_4$}] (**5**), [(*cis*-$\eta^4$-$Ph_2H_2C_4$)Co{$\eta^5$-$MeOC(O)C_5H_4$}] (**6**) and [($\eta^4$-$Ph_3HC_4$)Co{$\eta^5$-$MeOC(O)C_5H_4$}] (**7**), respectively. Compounds **5**, **6** and **7** yield the carboxylic acids [(*trans*-$\eta^4$-$Ph_2H_2C_4$)Co{$\eta^5$-$HOC(O)C_5H_4$}] (**8**), [(*cis*-$\eta^4$-$Ph_2H_2C_4$)Co{$\eta^5$-$HOC(O)C_5H_4$}] (**9**) and [($\eta^4$-$Ph_3HC_4$)Co{$\eta^5$-$HOC(O)C_5H_4$}] (**10**) upon treatment with KO*t*Bu in dmso. Reduction of **5** and **7** with $LiAlH_4$ in thf gives the alcohol complexes [(*trans*-$\eta^4$-$Ph_2H_2C_4$)Co($\eta^5$-$HOCH_2C_5H_4$)] (**11**) and [($\eta^4$-$Ph_3HC_4$)Co($\eta^5$-$HOCH_2C_5H_4$)] (**12**) in good yields. Compounds **1**–**7** and **11** were characterized structurally. These structural studies show interesting variations in the orientations of the cyclobutadiene-bound phenyl groups when the silyl groups are systematically removed from the cyclobutadiene moiety.

## Introduction

Stable metallocenecarboxylic acids and their alcohol derivatives are excellent precursors for a host of organometallic molecules with a wide range of potential applications. The most well-known among these is ferrocenecarboxylic acid, which, for example, is widely used in the design and development of electrochemical biosensors for monitoring of glucose and lactate,[1] in electrochemical DNA sensors,[2] in the design of stable electroactive multi(ferrocenyl)stannoxane clusters,[3] and as a reagent for the synthesis of prochiral ferrocene catalysts bearing oxazoline substituents.[4] Unlike ferrocenecarboxylic acid, whose rich chemistry has been well documented, the chemistry of other metallocenecarboxylic acids is still being developed. Among these, ($\eta^5$-carboxycyclopentadienyl)($\eta^4$-tetraphenylcyclobutadiene)cobalt, a highly stable cyclobutadienylcobaltocenecarboxylic acid, has shown great promise in terms of stability and reactivity.[5,6] Cobalt(I) oxazoline palladacycles (COP) such as COP-OAc and COP-Cl, which are commercially available and are prepared from this carboxylic acid, effectively promote the asymmetric rearrangement of allylic trichloroacetimidates and *N*-(4-methoxyphenyl)trifluoroacetimidates, which provides easy access to allylic amines and allylic alcohols of high enantiomeric purity.[7,8] Pioneering work by Richards and co-worker has simplified the preparation of this carboxylic acid by the generation of [{$MeOC(O)C_5H_4$}$Co(PPh_3)_2$] in situ instead of the older and more expensive method involving [$CpCo(CO)_2$].[9,10] However, it has been observed that the steric bulkiness of the tetraphenylcyclobutadiene moiety of [($\eta^4$-$Ph_4C_4$)Co($\eta^5$-$C_5H_4COOH$)] significantly influences the nature of the products formed from its reactions, often reducing its reactivity in comparison to ferrocenecarboxylic acid.[11] We were interested in reducing the steric bulkiness of the tetraphenylcyclobutadiene part of this complex by systematically replacing the phenyl substituents with hydrogen atoms so as to fine-tune its reactivity while maintaining its high stability and accessibility. The method adopted was to initially make metallocenes containing a varying number of phenyl and trimethylsilyl groups on the cyclobutadiene moiety and then removing the silyl groups.

An added interest in this study stems from the difference in reactivity of the cobalt-bound cyclopentadienyl and cyclobutadienyl groups. Rosenblum and co-workers have shown that for the parent complex, ($\eta^5$-cyclopentadienyl)($\eta^4$-cyclobutadiene)cobalt, the hydrogen atoms of the

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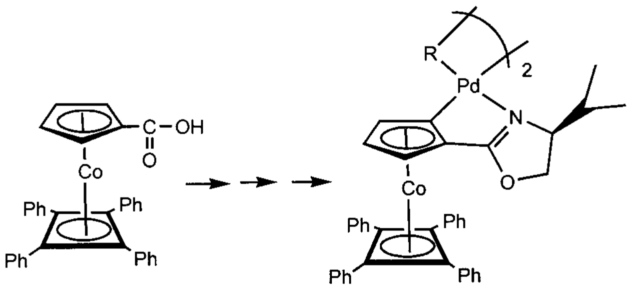


(+)-(*S*)-COP-OAc ( R= OAc)
(+)-(*S*)-COP-Cl (R = Cl)

cyclobutadiene ring are more reactive towards electrophilic substitution reactions than those of the cyclopentadiene ring.[12] In this paper we describe our efforts to prepare examples of sterically less hindered ($\eta^5$-cyclopentadienyl)($\eta^4$-phenylcyclobutadiene)cobalt-based carboxylic esters, carboxylic acids and their alcohols derivatives with varying numbers of hydrogen atoms and phenyl groups bound to the cyclobutadiene unit. Structural studies on the silylated and desilylated metallocenes indicate interesting orientational changes of the phenyl groups around the cyclobutadiene moiety upon removal of the trimethylsilyl groups.

## Results and Discussion

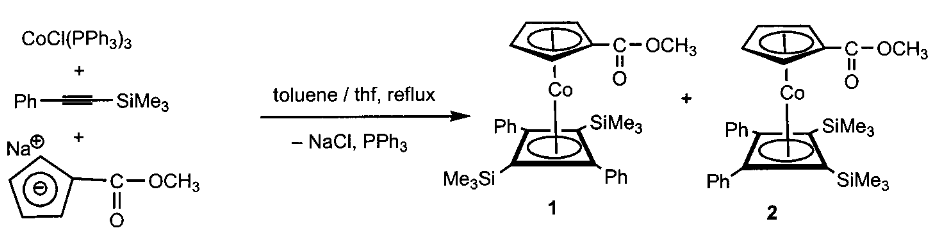
The generation of [$\eta^5$-MeOC(O)C$_5$H$_4$]Co(PPh$_3$)$_2$ in situ was carried out by the preparation of [(methoxycarbonyl)cyclopentadienyl]sodium from cyclopentadienylsodium and dimethyl carbonate followed by the reaction with chloridotris(triphenylphosphane)cobalt. The alkyne, (2-phenylethynyl)trimethylsilane, was then added to this solution of [{$\eta^5$-MeOC(O)C$_5$H$_4$}Co(PPh$_3$)$_2$] in the required molar ratio.

It has been observed that the reaction of the half-sandwich complex [CpCo(CO)$_2$] with disubstituted acetylenes differs significantly from that of the phosphane complex [CpCo(PPh$_3$)$_2$].[13] Thus, while the former results in the formation of cobaltocenes having $\eta^5$-cyclopentadienide and $\eta^4$-cyclobutadiene groups often along with another metallocene having a carbonyl-inserted $\eta^4$-cyclopentenone moiety, the latter has often been found to form PPh$_3$-stabilized cobaltocyclopentadiene metallacycles along with ($\eta^5$-cyclopentadienyl)($\eta^4$-cyclobutadiene)cobaltocenes. It is of interest to note that in all the reactions that were carried out in the present study using (2-phenylethynyl)trimethylsilane, no PPh$_3$-stabilized cobaltocyclopentadiene metallacycles were found to form. The reaction of equimolar amounts of [CoCl(PPh$_3$)$_3$] with [(methoxycarbonyl)cyclopentadienyl]sodium in a mixture of thf and toluene followed by the reaction with 2 equiv. of (2-phenylethynyl)trimethylsilane under reflux conditions resulted in the formation of the *cis* and *trans* isomers of [$\eta^5$-(methoxycarbonyl)cyclopentadienyl]($\eta^4$-diphenylbis(trimethylsilyl)cyclobutadiene)cobalt, [{*trans*-$\eta^4$-Ph$_2$(Me$_3$Si)$_2$C$_4$}Co{$\eta^5$-MeOC(O)-C$_5$H$_4$}] (**1**) and [{*cis*-$\eta^4$-Ph$_2$(Me$_3$Si)$_2$C$_4$}Co{$\eta^5$-MeOC(O)-C$_5$H$_4$}] (**2**) (Scheme 1).

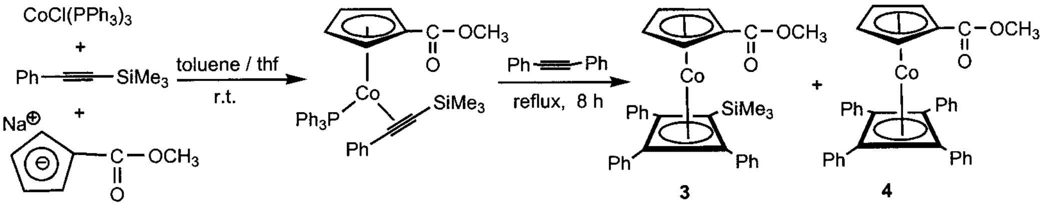
Compounds **1** and **2** were formed in a ca. 3:1 ratio and were purified by column chromatography. While the *trans* isomer crystallized readily from the mixture, purification and crystallization of the *cis* isomer proved time-consuming. Pure crystals of **2** (15%) were isolated by repeated fractional crystallization after removal of **1** (41%) from the mixture. Spectral studies and a crystal-structure analysis of **1** and **2** confirmed their identity.

With a view to preparing complexes having one or three phenyl groups on the cyclobutadiene ring, a different strategy was adopted. The stoichiometry of the reagents and the reaction parameters were controlled so as to synthesize a cobalt complex having only one Me$_3$SiC≡CPh moiety coordinated to it in situ. It was expected that this complex would react with another equivalent of PhC≡CPh or Me$_3$SiC≡CSiMe$_3$ to yield the expected complexes. However, the equimolar reaction of [CoCl(PPh$_3$)$_3$] with [(methoxycarbonyl)cyclopentadienyl]sodium and (2-phenylethynyl)trimethylsilane followed by the reaction with 1 equiv. of diphenylacetylene did not result in the monosilylated product **3**, but gave **1** along with the tetraphenylcyclobutadienyl derivative **4**. From independent studies it was observed that the intermediate complex having one acetylene moiety is formed in only around 50% yield. Changing the stoichiometry of the reactants by halving the amounts of (2-phenylethynyl)trimethylsilane followed by the reaction with diphenylacetylene gave the triphenyl(trimethylsilyl)cyclobutadienyl-substituted complex **3** along with the tetraphenylcyclobutadienyl derivative **4** (Scheme 2). Similar attempts to prepare metallocenes containing three trimethylsilyl groups bound to the cyclobutadiene ring by the reaction of [CpCo(PPh$_3$)(PhC≡CSiMe$_3$)] with Me$_3$SiC≡CSiMe$_3$ were found not to proceed, even under reflux conditions in toluene.

Compounds **1**–**3** were found to readily undergo desilylation when treated with Bu$_4$NF in dmso at 70 °C for 24 h, resulting in *cis* and *trans* isomers of diphenyl- (**5**, **6**) and triphenyl-substituted (**7**) cyclobutadienyl complexes (Scheme 3). The yields of the products varied from 87 to

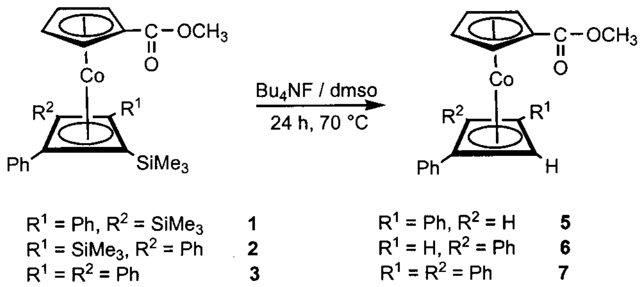


Scheme 1.



Scheme 2.

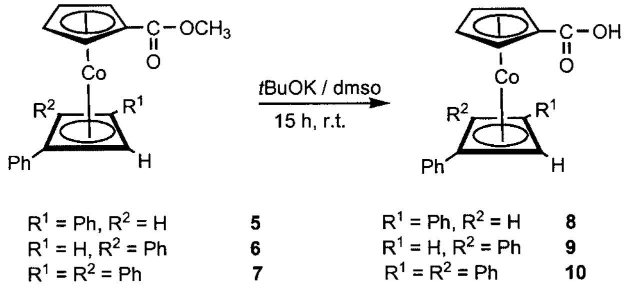
93%. The silylated and desilylated methyl esters have $^{13}C$ NMR chemical shifts in the range $\delta$ = 166.12–167.25 ppm for the ester group.



Scheme 3.

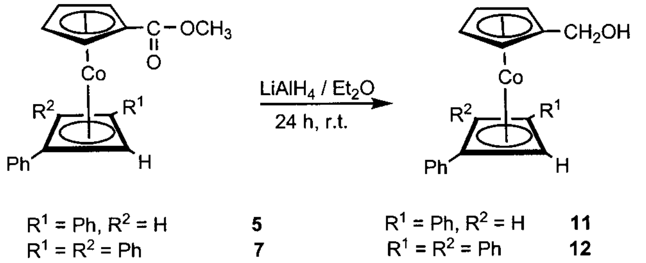
We observed that high yields of desilylated products were obtained by using tetrabutylammonium fluoride as the desilylating reagent. Compounds **5**–**7** are quite stable to hydrolysis and were purified by column chromatography on silica gel. The $^{1}H$ NMR spectra of these complexes clearly show the presence of the cyclobutadienyl protons. For complexes **5** and **7**, for example, the cyclobutadienyl proton signals are observed at $\delta$ = 4.96 and 5.02 ppm, while for the *cis* isomer **6** they are observed at $\delta$ = 4.47 ppm. It is of interest to note that the signal for the cyclobutadiene protons is observed at $\delta$ = 3.66 ppm for the parent unsubstituted complex,[12] and at $\delta$ = 4.04 ppm for tricarbonyl(cyclobutadiene)iron.[14] The deshielding of the cyclobutadiene protons in **5** and **7** is possibly due to the anisotropy effect of the phenyl groups on both sides of the cyclobutadiene-bound hydrogen atoms. The cyclopentadienyl hydrogen atoms appear as a set of two peaks, one in the range $\delta$ = 4.60–4.88 ppm and the other in the range $\delta$ = 5.24–5.33 ppm. The molecular ion peaks in the FAB mass spectra of complexes **5**–**7** also confirm their identity.

Esters **5**–**7** were converted into the corresponding carboxylic acids **8**–**10** by treatment with potassium *tert*-butoxide in dmso at room temperature (Scheme 4). The yields of the carboxylic acids varied from 78 to 85%. The IR spectra of the carboxylic acids **8**–**10** show the acid carbonyl stretching bands at 1658, 1671 and 1674 $cm^{-1}$, respectively, while those for the corresponding esters are observed at 1708, 1706 and 1714 $cm^{-1}$, respectively. The $^{1}H$ NMR spectra also show similar variations in the cyclopentadienyl peaks ($\delta$ = 4.60–4.88 and 5.24–5.33 ppm for the esters and $\delta$ = 4.71–4.75 and 5.18–5.40 ppm for the carboxylic acids). The $^{13}C$ NMR spectra of the complex ($\eta^5$-carboxycyclopentadienyl)($\eta^4$-tetraphenylcyclobutadiene)cobalt show a chemical shift of $\delta$ = 191.1 ppm for the carboxylic acid carbon atom,[9] and the carboxylic acid carbon atoms of the acid complexes **8**, **9** and **10** show $^{13}C$ chemical shifts in the range $\delta$ = 192.26–193.45 ppm. Mass spectral analysis also further confirms the identity of the carboxylic acids. Due to the difficulty in growing suitable crystals, structural analysis of these complexes could not be performed.



Scheme 4.

The carboxylates **5** and **7** were reduced to the corresponding alcohols **11** and **12** by treatment with lithium aluminium hydride in diethyl ether at room temperature (Scheme 5). The stable alcohols were obtained in 69 and 86% yield, respectively, as crystalline solids and were purified by column chromatography. The identity of the *trans*-diphenyl-substituted alcohol **11** was further confirmed by single-crystal X-ray structural analysis. Reduction of the carboxylate **6** could not be carried out as the quantity needed for the reaction was not available due to the poor yield of its precursor complex **2**.



Scheme 5.

## Electrochemical Studies of Complexes 1–12

Cyclic voltammetric studies on complexes **1**–**12** were carried out using a 0.005 M solution of each complex in 0.1 M tetrabutylammonium perchlorate as supporting electrolyte in dichloromethane solution. Compounds **1**–**3** and **5**–**12** show a quasi-reversible redox couple in the potential range

0.0–1.5 V at a scan rate of 0.1 $V s^{-1}$ in the positive direction. Interestingly, under identical measurement conditions the voltammogram of the tetraphenylcyclobutadienyl ester $[(\eta^4\text{-}Ph_4C_4)Co\{\eta^5\text{-}MeOC(O)C_5H_4\}]$ shows an almost reversible redox couple while that of the tetraphenyl acid $[(\eta^4\text{-}Ph_4C_4)Co\{\eta^5\text{-}HOC(O)C_5H_4\}]$ shows a fully reversible redox couple. The $E_{1/2}$ values given in Table 1 were calculated by averaging the anodic and cathodic potential of the respective redox couple with respect to the ferrocene/ferrocenium redox couple. On increasing the number of cycles, the height of both the anodic and cathodic peaks decreases, although this reduction is minimal after the second cycle; this indicates partial decomposition of the complex at the electrode surface. It is interesting to note that on going from the silylated complexes **1**, **2** and **3** to the desilylated complexes **5**, **6** and **7** there is a negative shift in $E_{1/2}$ values. From the desilylated complexes **5**, **6** and **7** to the carboxylic acids (**8**, **9** and **10**) and alcohols (**11** and **12**) a further negative shift in $E_{1/2}$ values is observed. This indicates that the system is more electroactive towards oxidation on going from silylated complexes through desilylated complexes to carboxylic acids and their alcohol derivatives. The $E_{1/2}$ value for complex **4**, which bears four phenyl rings on the cyclobutadiene ring, is 0.570 V. On removing the phenyl rings one by one, the $E_{1/2}$ values decrease and oxidation becomes easier.

Table 1. Cyclic voltammetric data of complexes **1**–**12**.

| Entry | Complex | $E_{1/2}$ vs. Fc/Fc$^+$ [V] |
|---|---|---|
| 1 | **1** | 0.587 |
| 2 | **2** | 0.589 |
| 3 | **3** | 0.637 |
| 4 | **4** | 0.570 |
| 5 | **5** | 0.433 |
| 6 | **6** | 0.494 |
| 7 | **7** | 0.539 |
| 8 | **8** | 0.368 |
| 9 | **9** | 0.382 |
| 10 | **10** | 0.415 |
| 11 | **11** | 0.287 |
| 12 | **12** | 0.416 |

## Structural Studies on Complexes 1–7 and 11

Detailed structural analysis were carried out on the silylated and desilylated carboxylates **1**–**7** and the alcohol **11** as there is only a preliminary communication available in the literature on the structures of the *cis*- and *trans*-metallocenes $[CpCo\{(Me_3Si)_2Ph_2C_4\}]$, which contain unsubstituted cyclopentadienyl rings.[15] The crystal structures of complexes **1**–**7** and **11** are given in Figures 1, 2, 3, 4, 5, 6, 7 and 8, respectively. Selected bond lengths and angles are given in Tables 2 and 3 and details of data collection, solution and crystal parameters are given in the Experimental Section. The structural studies on complexes **1**–**7** indicate no significant variation in the structure and orientation of the ester-substituted cyclopentadienyl group. However, on comparing structures of complexes **1**–**3** with those of **5**–**7**, the structural changes associated with the cyclobutadiene ring and its substituents were found to be quite significant. As such, the four phenyl rings of the tetraphenylcyclobutadiene ring of **4** are displaced at angles of 37.39°, 48.44°, 29.25° and 60.49° with respect to the cyclobutadiene ring. A comparison of **4** with the corresponding carboxylic acid also shows that the relative orientation of the phenyl rings with

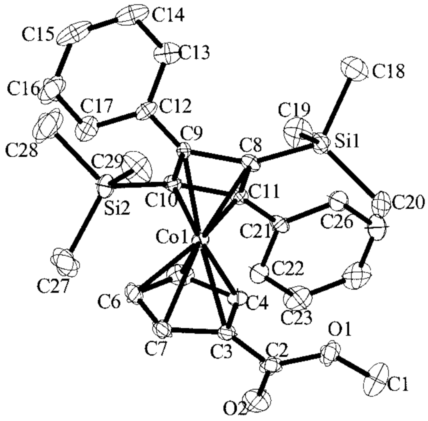


Figure 1. Thermal ellipsoid view of complex **1** with 30% probability ellipsoids (H atoms omitted for clarity).

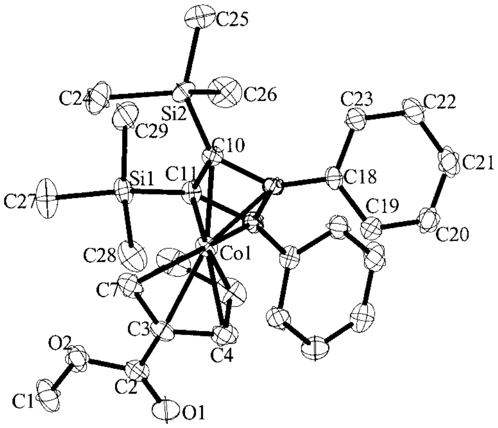


Figure 2. Thermal ellipsoid view of complex **2** with 30% probability ellipsoids (H atoms omitted for clarity).

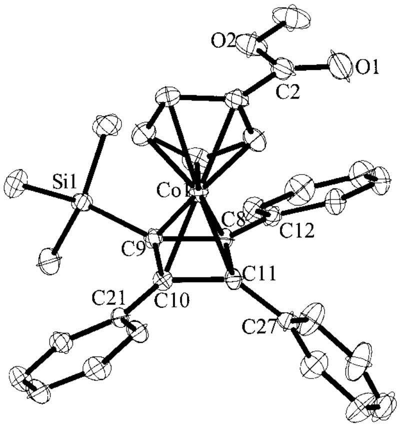


Figure 3. Thermal ellipsoid view of complex **3** with 30% probability ellipsoids (H atoms omitted for clarity).

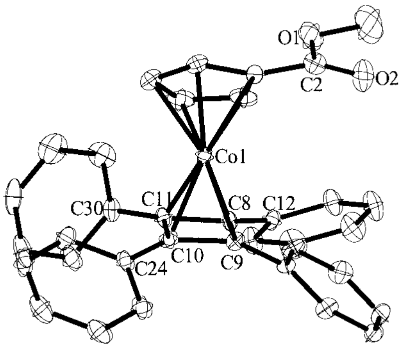


Figure 4. Thermal ellipsoid view of complex **4** with 30% probability ellipsoids (H atoms omitted for clarity).

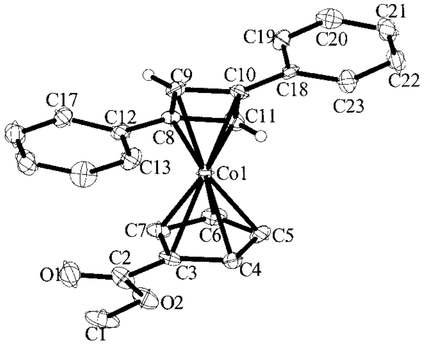


Figure 5. Thermal ellipsoid view of complex **5** with 30% probability ellipsoids (all H atoms, except those of the cyclobutadiene moiety, omitted for clarity).

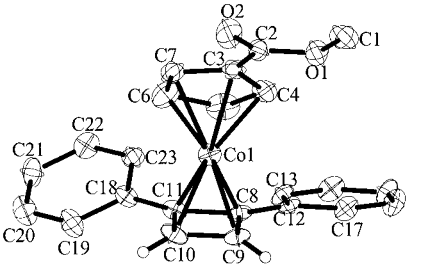


Figure 6. Thermal ellipsoid view of complex **6** with 30% probability ellipsoids (all H atoms, except those of the cyclobutadiene moiety, omitted for clarity).

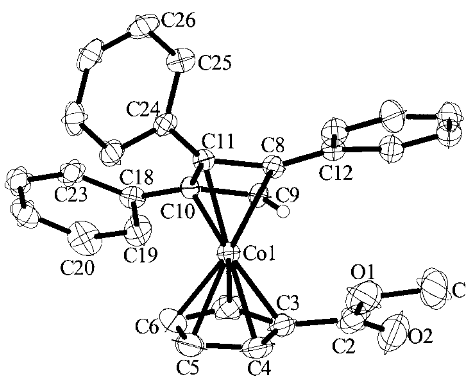


Figure 7. Thermal ellipsoid view of complex **7** with 30% probability ellipsoids (all H atoms, except those of the cyclobutadiene moiety, omitted for clarity).

respect to the cyclobutadiene ring varies significantly from 7.05° to 89.20°.[11] It was therefore of interest to see whether desilylation, which results in lower crowding around the cyclobutadiene ring, will affect the orientation of the phenyl groups in complexes **5**–**7**. In addition, complex **4** is a propeller-type molecule, and such complexes show promise in the design of molecular devices. This study therefore provides information on structural changes at the molecular level accompanying the removal of substituents that are akin to the blades of such propeller-type molecules.

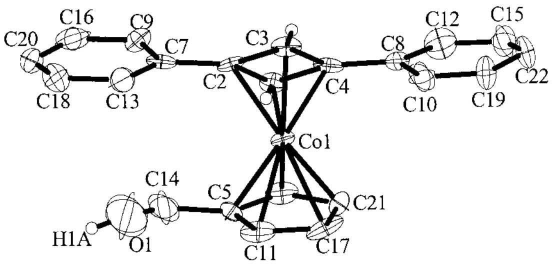


Figure 8. Thermal ellipsoid view of complex **11** with 30% probability ellipsoids (all H atoms, except those of the cyclobutadiene moiety, omitted for clarity).

On comparing the structures of complexes **1**–**3** with their desilylated analogues **5**–**7** it can be seen that, basically, two noticeable structural changes occur. The phenyl groups, which are pushed away from the plane of the cyclobutadienyl ring in complexes **1**–**3**, tend to come close to the plane of the cyclobutadiene ring in complexes **5**–**7**. More interestingly, however, the phenyl groups rotate and take up orientations which tend to align with the planarity of the cyclobutadiene ring. Both these structural changes indicate a tendency to gain better π-delocalization of the phenyl groups with the metal-coordinated cyclobutadiene ring (Scheme 6).

The angle ($\theta$) between the mean plane of the cyclobutadiene ring and the mean plane of a substituted phenyl ring represents the extent of deviation of the phenyl rings from the plane of the cyclobutadiene ring. For complex **1**, which has a *trans* orientation of two phenyl substituents, the values of $\theta$ are 32.68° and 43.97°. The corresponding desilylated complex **5** has $\theta$ reduced to 5.34° and 3.09° (5.45° and 2.15° for the other crystallographically independent structure in the unit cell). For the *cis*-oriented complex **2**, the values of $\theta$ are 63.14° and 43.98°, which are reduced to 24.75° and 12.45° for the desilylated complex **6**. Similarly for the triphenyl(trimethylsilyl)cyclobutadiene complex **3**, the $\theta$ values are 34. 26°, 31.47° and 64.19°, which are reduced in complex **7** to 14.14°, 12.26° and 54.13° respectively (13.97°, 12.26° and 53.98° for the other crystallographically independent structure in the unit cell). These results clearly indicate that removing the steric crowding around the cyclobutadiene unit tends to make the phenyl groups become more aligned to the cyclobutadiene ring.

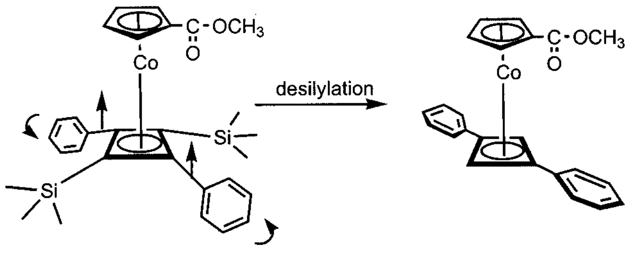
The other interesting difference observed on comparing complexes **1**–**3** with complexes **5**–**7** is the distortion from planarity observed for the exocyclic cyclobutadiene–phenyl bonds. Although the bond connecting the phenyl ring to the cyclobutadiene ring should ideally lie in the same plane

Table 2. Selected bond lengths [Å] and angles [°] for complexes **1**–**4**.

| | | | |
|---|---|---|---|
| Compound **1** | | | |
| Co(1)–C(9) | 1.972(5) | Co(1)–C(8) | 2.005(5) |
| Co(1)–C(3) | 2.069(5) | Si(1)–C(8) | 1.866(6) |
| Si(1)–C(20) | 1.868(8) | O(1)–C(1) | 1.446(10) |
| O(1)–C(2) | 1.336(7) | O(2)–C(2) | 1.195(9) |
| C(2)–C(3) | 1.47(1) | C(3)–C(7) | 1.418(9) |
| C(9)–C(12) | 1.458(9) | C(12)–C(13) | 1.379(10) |
| C(11)–C(12) | 1.467(9) | | |
| C(17)–C(12)–C(13) | 117.5(7) | C(13)–C(12)–C(9) | 120.9(6) |
| C(12)–C(9)–C(8) | 133.3(5) | C(8)–Si(1)–C(18) | 109.4(4) |
| C(9)–C(8)–C(11) | 88.2(5) | C(10)–Co(1)–C(6) | 117.9(3) |
| C(6)–C(7)–C(3) | 107.9(6) | C(7)–C(3)–C(2) | 123.0(6) |
| O(2)–C(2)–O(1) | 123.1(7) | C(2)–O(1)–C(1) | 115.2(6) |
| Compound **2** | | | |
| Co(1)–C(9) | 1.999(4) | Co(1)–C(11) | 1.982(3) |
| Co(1)–C(3) | 2.069(6) | Si(1)–C(11) | 1.864(5) |
| Si(1)–C(27) | 1.863(4) | C(1)–O(2) | 1.447(4) |
| C(2)–O(1) | 1.199(3) | C(2)–O(2) | 1.331(4) |
| C(2)–C(3) | 1.467(4) | C(3)–C(4) | 1.426(4) |
| C(11)–C(10) | 1.487(4) | C(9)–C(18) | 1.473(4) |
| C(8)–C(12) | 1.481(3) | | |
| C(25)–Si(2)–C(26) | 108.92(11) | C(26)–Si(2)–C(10) | 110.23(8) |
| Si(2)–C(10)–C(9) | 131.81(12) | C(10)–C(9)–C(18) | 135.28(14) |
| C(9)–C(18)–C(23) | 120.57(15) | C(11)–C(10)–C(9) | 89.36(12) |
| C(11)–Co(1)–C(7) | 118.31(7) | C(7)–C(3)–C(2) | 127.75(16) |
| C(7)–C(3)–C(4) | 108.29(16) | O(2)–C(2)–O(1) | 123.40(17) |
| Compound **3** | | | |
| Co(1)–C(8) | 2.000(3) | Co(1)–C(3) | 2.073(4) |
| Si(1)–C(18) | 1.866(2) | Si(2)–C(9) | 1.868(4) |
| C(9)–C(10) | 1.475(3) | C(10)–C(21) | 1.468(3) |
| C(3)–C(7) | 1.421(3) | C(3)–C(2) | 1.464(4) |
| O(2)–C(2) | 1.337(4) | O(2)–C(1) | 1.448(4) |
| C(2)–O(1) | 1.208(4) | C(21)–C(22) | 1.395(3) |
| C(8)–C(12) | 1.465(3) | C(11)–C(27) | 1.501(3) |
| C(1)–O(2)–C(2) | 116.77(18) | O(2)–C(2)–O(1) | 124.57(21) |
| O(2)–C(2)–C(3) | 111.31(18) | C(2)–C(3)–C(7) | 127.12(18) |
| C(7)–C(3)–C(4) | 107.60(16) | C(7)–C(3)–C(4) | 107.60(16) |
| C(7)–Co(1)–C(9) | 112.25(7) | C(10)–C(9)–C(8) | 88.32(12) |
| C(10)–C(9)–Si(1) | 135.06(12) | C(9)–C(10)–C(21) | 135.46(14) |
| Compound **4** | | | |
| Co(1)–C(8) | 1.994(3) | Co(1)–C(3) | 2.074(3) |
| O(1)–C(1) | 1.446(6) | O(1)–C(2) | 1.343(4) |
| O(2)–C(20) | 1.194(4) | C(2)–C(3) | 1.450(4) |
| C(3)–C(4) | 1.420(4) | C(10)–C(11) | 1.462(3) |
| C(11)–C(30) | 1.472(3) | C(31)–C(32) | 1.375(5) |
| C(8)–C(12) | 1.458(3) | C(10)–C(24) | 1.375(5) |
| C(9)–C(18) | 1.473(3) | | 1.458(3) |
| C(1)–O(1)–C(2) | 115.81(31) | O(1)–C(2)–O(2) | 123.13(29) |
| O(1)–C(2)–C(3) | 111.12(25) | C(2)–C(3)–C(7) | 128.05(24) |
| C(7)–C(3)–C(4) | 107.23(22) | C(7)–Co(1)–C(8) | 122.97(10) |
| C(11)–C(8)–C(9) | 90.07(18) | C(30)–C(11)–C(10) | 134.06(21) |

Table 3. Selected bond lengths [Å] and angles [°] for complexes **5**–**7** and **11**.

| | | | |
|---|---|---|---|
| Compound **5** | | | |
| Co(1)–C(11) | 1.969(8) | Co(1)–C(10) | 1.978(6) |
| Co(1)–C(3) | 2.062(5) | O(2)–C(1) | 1.452(8) |
| C(2)–O(2) | 1.326(8) | C(2)–O(1) | 1.201(8) |
| C(2)–C(3) | 1.471(7) | C(11)–C(8) | 1.434(8) |
| C(8)–C(12) | 1.478(7) | C(4)–C(5) | 1.430(8) |
| C(10)–C(18) | 1.446(6) | C(10)–C(11) | 1.446(9) |
| C(1)–O(2)–C(2) | 115.67(5) | O(2)–C(2)–O(1) | 123.5(5) |
| O(1)–C(2)–C(3) | 125.1(5) | C(7)–C(3)–C(4) | 108.6(5) |
| C(3)–Co(1)–C(8) | 115.0(2) | C(9)–C(8)–C(11) | 90.2(4) |
| C(13)–C(12)–C(8) | 120.3(5) | C(17)–C(12)–C(13) | 119.0(5) |
| Compound **6** | | | |
| Co(1)–C(9) | 1.968(3) | Co(1)–C(8) | 1.981(2) |
| Co(1)–C(3) | 2.045(3) | O(1)–C(1) | 1.445(4) |
| O(1)–C(2) | 1.335(4) | O(2)–C(2) | 1.196(4) |
| C(2)–C(3) | 1.464(4) | C(3)–C(7) | 1.422(4) |
| C(9)–C(10) | 1.430(4) | C(11)–C(18) | 1.471(4) |
| C(8)–C(9) | 1.458(4) | C(8)–C(12) | 1.453(3) |
| C(1)–O(1)–C(2) | 115.77(23) | O(1)–C(2)–O(2) | 123.12(26) |
| O(2)–C(2)–C(3) | 124.58(28) | C(2)–C(3)–C(7) | 124.16(27) |
| C(7)–C(3)–C(4) | 107.33(25) | C(7)–Co(1)–C(11) | 112.59(12) |
| C(10)–C(11)–C(8) | 88.97(22) | C(18)–C(11)–C(10) | 131.98(25) |
| Compound **7** | | | |
| C(1)–O(1) | 1.474(6) | O(1)–C(2) | 1.294(5) |
| O(2)–C(2) | 1.187(5) | C(3)–C(2) | 1.497(5) |
| C(3)–C(4) | 1.406(4) | Co(1)–C(3) | 2.050(3) |
| Co(1)–C(8) | 1.992(3) | C(11)–C(8) | 1.463(3) |
| C(9)–C(8) | 1.444(4) | C(10)–C(18) | 1.452(3) |
| C(11)–C(24) | 1.473(3) | | |
| C(1)–O(1)–C(2) | 111.69(34) | O(1)–C(2)–O(2) | 126.69(41) |
| O(2)–C(2)–C(3) | 123.43(35) | C(2)–C(3)–C(7) | 130.33(30) |
| C(4)–C(3)–C(7) | 108.19(29) | C(10)–C(11)–C(8) | 89.42(19) |
| C(10)–C(9)–C(8) | 91.03(20) | C(9)–C(8)–C(12) | 134.00(26) |
| C(9)–C(10)–C(18) | 132.96(22) | C(10)C(18)C(19) | 120.56(21) |
| Compound **11** | | | |
| O(1)–C(14) | 1.231(34) | C(14)–C(5) | 1.548(24) |
| C(11)–C(5) | 1.441(22) | Co(1)–C(5) | 2.066(14) |
| Co(1)–C(4) | 1.966(12) | C(1)–C(4) | 1.486(14) |
| C(4)–C(8) | 1.467(16) | C(2)–C(7) | 1.470(15) |
| O(1)–C(14)–C(5) | 105.4(17) | C(14)–C(5)–C(11) | 136.2(14) |
| C(6)–C(5)–C(11) | 106.3(10) | C(5)–Co(1)–C(2) | 113.37(44) |
| C(4)–C(1)–C(2) | 89.4(8) | C(3)–C(4)–C(1) | 89.2(8) |
| C(2)–C(7)–C(13) | 121.0(10) | | |



Scheme 6.

as that of the cyclobutadiene ring, what is observed is that all the exocyclic bonds from the cyclobutadiene ring to the phenyl groups are displaced at an angle ($\phi$) to the plane of the cyclobutadiene ring with the displacement directed away from the cyclopentadienylcobalt moiety. The value of $\phi$ varies from 167.50° to 177.11° for the phenyl substituents. A comparison of the silylated metallocenes **1**–**3** and desilylated metallocenes **5**–**7** indicates that this distortion decreases upon desilylation, with the angles coming closer to 180°. The values of $\phi$ for complex **1** are 172.54° and 175.48° which become 176.14° and 177.11° in **5** upon desilylation. For **2**, the values of $\phi$ are 174.36° and 167.50°, which increases to 174.56° and 173.44° for complex **6**. A similar, while minor, increase is seen when $\phi$ is compared for complexes **3** and **7**.

Both these structural variations clearly indicate that, in the absence of steric repulsion, the phenyl groups would prefer to lie aligned with the plane of the cyclobutadiene ring, which possibly helps to extend the aromatic conjugation between the phenyl rings and the cobalt-bound cyclobutadienyl ring. We have also observed that these variations in structural parameters are not affected by the orientation of the ester groups on this ring. This study provides a good comparison to the structure of biphenyl.[16] In the case of biphenyl, the two phenyl groups do not lie in the same plane due to the *ortho* effect of the hydrogen atoms. Such an effect does not exist in the case of complexes such as **5**. It has also been reported that the C–C bond connecting the two phenyl rings in biphenyl is 1.507 Å. In the case of complexes **1**–**4**, the bond length between the cyclobutadiene and phenyl groups varies from 1.458(3) to 1.501(3) Å, while for complexes **5**–**7** and **11** the same distance varies from 1.444(7) to 1.486(8) Å, which is between those of a carbon–carbon single and double bond.

The crystal structure of the alcohol complex **11** is quite similar to that of complex **5**, with the values of $\theta$ being 1.19° and 6.01°. This indicates that both the phenyl groups and the cyclobutadiene ring are almost in the same plane, further increasing their aromatic conjugation. The hydroxy group of the complex is disordered and the oxygen atom has two independent crystallographic positions (occupancy factors of 0.8 and 0.2).

## Conclusions

In conclusion, we have described a method to prepare examples of sterically less hindered and stable carboxylic acid analogues of [($\eta^5$-Cp)Co($\eta^4$-$C_4Ph_4$)] and their alcohol derivatives by desilyation, de-esterification and reduction of the trimethylsilyl-derived metallocenecarboxylates. The carboxylic acids are potential reagents for preparing catalysts such as cobalt(I) oxazoline palladacycles and a host of other similar catalysts and reagents with less steric bulkiness than [($\eta^5$-Cp)Co($\eta^4$-$C_4Ph_4$)] on the cyclobutadiene ring. The silylated and desilylated carboxylates have been structurally characterized and this study provides an opportunity to compare structural changes around the cyclobutadiene moiety accompanying the desilylation reactions. It has been observed that two major structural changes occur upon desilylation of the silylated esters: the phenyl groups rotate around their bonds to the cyclobutadiene ring and also bend towards the plane of the cyclobutadiene ring, tending to become more aligned and parallel to its plane. This possibly helps to extend the delocalization of electron density of the phenyl groups to that of the cobalt-bound cyclobutadiene ring. Further work exploring the chemistry of these new metallocenecarboxylic acids and their alcohol derivatives is in progress.

## Experimental Section

**General Remarks:** All manipulations of the complexes were carried out using standard Schlenk techniques under nitrogen. Toluene and thf were freshly distilled from sodium benzophenone ketyl under nitrogen before use. The sodium salt of (methoxycarbonyl)cyclopentadiene,[9] chloridotris(triphenylphosphane)cobalt[17] and (2-phenylethynyl)trimethylsilane[18] were prepared according to literature procedures. Diphenylacetylene, dimethyl carbonate and triphenylphosphane (Aldrich) were used as received. $^1$H and $^{13}$C{$^1$H} NMR spectra were recorded with a Bruker Spectrospin DPX-300 NMR spectrometer at 300 and 75.47 MHz, respectively. IR spectra in the range 4000–250 cm$^{-1}$ were recorded with a Nicolet Protége 460 FT-IR spectrometer as KBr pellets. Elemental analyses were carried out with a Carlo Erba CHNSO 1108 elemental analyzer. Mass spectra were recorded in the FAB mode using a JEOL SX 102/DA-6000 mass spectrometer and in the electrospray mode with a Micromass Quattro II triple quadrupole mass spectrometer.

**Electrochemical Studies:** All electrochemical measurements were performed with a basic electrochemistry system CHI 604A, using a three-electrode configuration of a Pt working electrode (0.1 mm diameter), a commercially available Ag/AgCl electrode as the reference electrode and a Pt mesh electrode as the counter electrode. Half-wave potentials were measured as the average of the cathodic and anodic peak potentials. The voltammograms were recorded in $CH_2Cl_2$ containing 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte, and the potential was scanned from 0 to +1.5 V at various scan rates. Ferrocene gave a reversible single redox couple with $E_{1/2}$ at 652 mV under the same experimental conditions.

**Preparation of [{*trans*-$\eta^4$-$Ph_2(Me_3Si)_2C_4$}Co{$\eta^5$-MeOC(O)$C_5H_4$}] (1) and [{*cis*-$\eta^4$-$Ph_2(Me_3Si)_2C_4$}Co{$\eta^5$-MeOC(O)$C_5H_4$}] (2):** A solution of chloridotris(triphenylphosphane)cobalt(I) (5.06 g, 5.73 mmol) in toluene (30 mL) was added to a solution of [(methoxycarbonyl)cyclopentadienyl]sodium (0.84 g, 5.73 mmol) in thf (10 mL). The resulting red solution was stirred for 0.5 h and then added to (2-phenylethynyl)trimethylsilane (2.00 g, 11.5 mmol). The solution turned dark brown on stirring at room temperature for 0.5 h. The resulting mixture was heated at reflux for 8 h and then cooled to room temperature. The solvent was removed in vacuo and the residue dissolved in hexane and filtered to give a yellow filtrate. This was concentrated and cooled to partially remove triphenylphosphane by fractional crystallization. The residue was chromatographed on silica gel using a mixture of hexane and ethyl acetate as eluent to give a mixture of **1** and **2**. Compound **1** (1.20 g, 41 %) crystallized readily upon cooling the solution and complex **2** (0.42 g 15 %) was isolated by repeated fractional crystallization of the remaining solution.

**[{*trans*-$\eta^4$-$Ph_2(Me_3Si)_2C_4$}Co{$\eta^5$-MeOC(O)$C_5H_4$}] (1):** M.p. 95 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 3.18 (s, 3 H, $CH_3$), 4.77 (s, 2 H, CpH), 5.41 (s, 2 H, CpH), 7.07 (m, 6 H, PhH), 7.16 (m, 4 H, PhH), 0.02 (s, 18 H, $SiMe_3$) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 0.8 ($SiMe_3$), 60.0 (COMe), 69.8, 82.0 ($C_4$ ring), 82.7, 86.6, 90.9 (CpC), 126.3, 127.5, 128.9, 137.3 (Ph-C), 166.1 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 3396 m, 3095 w, 2951 s, 2896 m, 1706 vs, 1596 w, 1495 vs, 1467 s, 1362 s, 1288 vs, 1245 vs, 1194 s, 1140 vs, 1068 m, 1026 m, 969 m, 843 vs, 761 vs, 694 vs, 602 w, 560 w, 509 w, 443 w cm$^{-1}$. MS (FAB): $m/z$ = 530 [M$^+$], 531 [M + 1], 499 [M$^+$ – $OCH_3$], 407 [M$^+$ – $CpCo_2Me$] 515 [M$^+$ – $CH_3$], 356 [M$^+$ – $PhCCSiMe_3$]. $C_{29}H_{35}CoO_2Si_2$ (530.15): calcd. C 65.63, H 6.65; found C 65.59, H 6.52.

**[*cis*-$\eta^4$-$Ph_2(Me_3Si)_2C_4$]Co{$\eta^5$-MeOC(O)$C_5H_4$}] (2):** M.p. 80 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 3.10 (s, 3 H, $CH_3$), 4.81 (s, 2 H, CpH), 5.14 (s, 2 H, CpH), 6.97 (m, 6 H, PhH), 7.03 (m, 4 H, PhH), 0.01 (SiMe$_3$) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 0.8 (SiMe$_3$C), 51.0 (COOMeC), 67.9, 82.0 (C$_4$ ring), 82.7, 87.1, 90.4 (CpC), 126.4, 127.5, 129.0, 135.7 (PhC), 166.2 (C=O) ppm. IR, (KBr): $\tilde{\nu}$ = 3054 m, 3021 w, 2954 s, 2896 m, 1710 vs, 1599 w, 1467 vs, 1439 s, 1369 s, 1287 vs, 1248 vs, 1192 s, 1147 vs, 1064 m, 1028 m, 970 m, 839 vs, 772 vs, 695 vs, 633 w, 616 w, 509 w cm$^{-1}$. MS (FAB): *m*/*z* = 530 [M$^+$], 531 [M$^+$ + 1], 529 [M$^+$ – 1], 498 [M$^+$ – OCH$_3$], 514 [M$^+$ – CH$_3$], 457 [M$^+$ – SiMe$_3$], 356 [M$^+$ – PhCCSiMe$_3$], 407 [M$^+$ – CpCO$_2$Me]. C$_{29}$H$_{35}$CoO$_2$Si$_2$ (530.15): calcd. C 65.63, H 6.65; found C 65.57, H 6.60.

**Preparation of [{$\eta^4$-Ph$_3$(Me$_3$Si)C$_4$}Co{$\eta^5$-MeOC(O)C$_5$H$_4$}] (3) and [($\eta^4$-Ph$_4$C$_4$)Co{$\eta^5$-MeOC(O)C$_5$H$_4$}] (4):** A solution of chloridotris(triphenylphosphane)cobalt(I) (5.16 g, 5.84 mmol) in toluene (30 mL) was added to a solution of [(methoxycarbonyl)cyclopentadienyl]sodium (0.86 g, 5.85 mmol) in thf (5 mL). The resulting red solution was stirred at room temperature for 0.5 h and then a solution of (2-phenylethynyl)trimethylsilane (0.61 g, 3.50 mmol) in toluene was added and stirred at room temperature for 1 h to give a brown solution. A solution of diphenylacetylene (1.04 g, 5.85 mmol) in toluene was added and the resulting mixture was stirred at room temperature for 10 min and thereafter refluxed for 8 h and cooled to room temperature. The solvent was removed in vacuo and the residue suspended in 20% ethyl acetate in hexane and filtered. The filtrate was concentrated and chromatographed on silica gel, eluting with a hexane/ethyl acetate mixture (2% ethyl acetate) to give a yellow solution, which upon slow cooling gave crystals of **3** (0.52 g, 29%). On increasing the polarity of the eluent (10% ethyl acetate) a dark yellow solution was obtained, which on cooling gave crystals of **4** (0.76 g, 24%). The physical and spectral properties of **4** were found to agree well with those reported in the literature.[9]

**[{$\eta^4$-Ph$_3$(Me$_3$Si)C$_4$}Co{$\eta^5$-MeOC(O)C$_5$H$_4$}] (3):** M.p. 75 °C. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 0.27 (s, 9 H, SiMe$_3$), 3.33 (s, 3 H, CH$_3$), 4.94 (s, 2 H, CpH), 5.37 (s, 2 H, CpH), 7.28–7.34 (m, 9 H, PhH), 7.47–7.48 (m, 6 H, PhH) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 1.1 (SiMe$_3$), 51.1 (CO$_2$Me), 63.1, 82.5 (C$_4$ ring), 83.6, 84.3, 86.9 (CpC), 135.9, 135.1, 129.6, 129.0, 128.0, 127.7, 126.7, 126.5 (PhC), 167.2 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 3051 m, 3020 w, 2950 m, 1717 vs, 1596 m, 1495 m, 1469 m, 1444 m, 1364 m, 1280 vs, 1250 s, 1229 m, 1145 s, 1066 w, 826 s, 768 s, 694 s, 585 s cm$^{-1}$. MS (FAB): *m*/*z* = 534 [M$^+$], 335 [M$^+$ + 1], 356 [M$^+$ – PhCCPh], 411 [M$^+$ – CpCO$_2$Me], 360 [M$^+$ – PhCCSiMe$_3$], 503 [M$^+$ – OCH$_3$]. C$_{32}$H$_{31}$CoO$_2$Si (534.14): calcd. C 71.89, H 5.84; found C 71.80, H 5.90.

**General Procedure for the Desilylation of Compounds 1–3:** The silylated cobalt complex (1.0 mmol) and a slight excess of tetrabutylammonium fluoride (1 M solution in thf) were dissolved in dmso (10 mL) and the mixture was stirred at 70 °C under nitrogen for 24 h. The product was extracted with ethyl acetate, and the solution was washed repeatedly with water to remove any trace of dmso. The ethyl acetate solution was dried with anhydrous MgSO$_4$ and concentrated to give a dark yellow powder, which was chromatographed on silica gel with an appropriate eluent.

**[{*trans*-$\eta^4$-Ph$_2$H$_2$C$_4$}Co{$\eta^5$-MeOC(O)C$_5$H$_4$}] (5):** Chromatographed on silica gel with hexane as eluent to give 0.36 g (93%) of **5**. M.p. 122 °C. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 3.20 (s, 3 H, CH$_3$), 4.96 (s, 2 H, C$_4$ ring), 4.60 (s, 2 H, CpH), 5.39 (s, 2 H, CpH), 7.19 (m, 6 H, PhH), 7.17 (m, 4 H, PhH) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 51.1 (OMeC), 54.8, 76.1 (C$_4$ ring), 81.7, 84.1, 86.1 (CpC), 124.5, 126.1, 128.4, 136.3 (PhC), 166.7 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 3086 w, 3055 m, 2952 m, 1708 vs, 1594 s, 1501 s, 1468 vs, 1393 m 1358 m, 1282 vs, 1197 s, 1143 vs, 1067 m, 1022 s, 967 s, 902 s, 817 s, 764 vs, 691 vs. 663 m, 538 m, 480 s cm$^{-1}$. MS (FAB): *m*/*z* = 386 [M$^+$], 387[M$^+$ + 1], 355 [M$^+$ – OCH$_3$], 263 [M$^+$ – CpCO$_2$Me]. C$_{23}$H$_{19}$CoO$_2$ (386.07): calcd. C 71.51, H 4.96; found C 71.63, H 4.92.

**[{*cis*-$\eta^4$-Ph$_2$H$_2$C$_4$}Co{$\eta^5$-MeOC(O)C$_5$H$_4$}] (6):** Chromatographed on silica gel with hexane as eluent to give 0.35 g (92%) of **6**. M.p. 70 °C. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 3.36 (s, 3 H, CH$_3$), 4.88 (s, 2 H, CpH), 5.24 (s, 2 H, CpH), 4.46 (s, 2 H, C$_4$ ring), 7.24–7.26 (m, 6 H, PhH), 7.38 (m, 4 H, PhH) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 51.22 (CH$_3$), 58.2, 77.4 (C$_4$ ring), 82.6 (CpC), 83.1, 86.2 (CpC), 124.6, 126.6, 128.3, 136.7 (PhC), 167.2 (C=O) ppm. IR (KBr): 3059 m, 29469 m, 1706 vs, 1597 w, 1567 w, 1499 w, 1458 s, 1359 m, 1278 vs, 1187 m, 1135 vs, 1024 w, 961 m, 893 m, 827 m, 766 vs, 694 vs, 576 vs, 523 m cm$^{-1}$. MS (FAB): *m*/*z* = 386 [M$^+$], 387 [M$^+$ + 1], 355 [M$^+$ – OCH$_3$], 263 [M$^+$ – CpCO$_2$Me]. C$_{23}$H$_{19}$CoO$_2$ (386.07): calcd. C 71.51, H 4.96; found C 71.58, H 4.85.

**[($\eta^4$-Ph$_3$HC$_4$)Co{$\eta^5$-MeOC(O)C$_5$H$_4$}] (7):** Chromatographed on silica gel with hexane as eluent to give 0.33 g (87%) of **7**. M.p. 180 °C. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 3.21 (s, 3 H, CH$_3$), 4.67 (s, 2 H, CpH), 5.02 (s, 1 H, C$_4$ ring), 5.33 (s, 2 H, CpH), 7.7 (m, 2 H, PhH), 7.34 (m, 3 H, PhH), 7.24–7.18 (m, 10 H, PhH) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 51.1 (CH$_3$C), 54.6, 76.1, 77.9 (C$_4$ ring), 85.7, 84.9, 82.9 (CpC), 125.9, 126.3, 127.0, 128.1, 128.3, 130.1, 135.4, 136.2 (PhC), 166.2 (C=O) ppm. IR (KBr): 3080 w, 2948 w, 2362 w, 1714 vs, 1595 m, 1500 s, 1467 s, 1363 m, 1281 vs, 1187 s, 1139 vs, 1067 w, 1026 w, 967 w, 825 w, 764 vs, 692 vs, 608 w, 582 w cm$^{-1}$. MS (FAB): *m*/*z* = 462 [M$^+$], 463 [M$^+$ + 1], 339 [M$^+$ – CpCO$_2$Me]. C$_{29}$H$_{23}$CoO$_2$ (462.40): calcd. C 75.32, H 5.01; found C 75.24, H 5.15.

**General Procedure for the De-esterification of Compounds 5–7:** A mixture of 1.0 mmol of the ester and potassium *tert*-butoxide (1.68 g, 15 mmol) in 10 mL of dmso was stirred at room temperature for 15 h and then quenched with 2 M HCl (20 mL). After extraction with ethyl acetate, the organic phase was separated and dried with MgSO$_4$. The solvent was removed in vacuo and the residue was column-chromatographed on silica gel with an appropriate eluent to give the carboxylic acid complex.

**[*trans*-($\eta^4$-Ph$_2$H$_2$C$_4$)Co($\eta^5$-C$_5$H$_4$COOH)] (8):** Chromatographed on silica gel with 20% EtOAc/chloroform as eluent to give 0.31 g (84%) of **8** as an orange crystalline solid. M.p. 165 °C. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 4.75 (br. s, 2 H, CpH), 5.06 (s, 2 H, C$_4$ ring), 5.40 (br. s, 2 H, CpH), 7.10–7.20 (m, 10 H, PhH) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 54.2, 76.1 (C$_4$ ring), 85.3, 86.8, 92.5 (CpC), 124.8, 126.2, 128.6, 135.9 (PhC), 193.1 (COOH) ppm. IR (KBr): $\tilde{\nu}$ = 3053 m, 3023 m, 2912 m, 1659 vs, 1596 m, 1495 m, 1448 s, 1365 m, 1296 m, 1184 w, 1118 w, 1034 vs, 966 s, 758 vs, 695 vs, 541 s cm$^{-1}$. MS (FAB): *m*/*z* = 371 [M$^+$ – 1], 370 [M$^+$ – 2], 369 [M$^+$ – 3], 263 [M$^+$ – CpCO$_2$Me]. C$_{22}$H$_{17}$CoO$_2$ (372.05): calcd. C 70.97, H 4.60; found C 71.05, H 4.65.

**[*cis*-($\eta^4$-Ph$_2$H$_2$C$_4$)Co($\eta^5$-C$_5$H$_4$COOH)] (9):** Chromatographed on silica gel with 20% EtOAc/chloroform as eluent to give 0.29 g (78%) of **9** as an orange crystalline solid. M.p. 188 °C. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 4.48 (s, 2 H, C$_4$ ring), 4.75 (s, 2 H, CpH), 5.18 (s, 2 H, CpH), 7.21–7.33 (s, 10 H, PhH) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 58.3, 77.4 (C$_4$ ring), 86.4, 87.1, 92.2 (CpC), 126.2, 128.1, 128.6, 136.2 (PhC), 192.2 (COOH) ppm. IR (KBr): $\tilde{\nu}$ = 2927 w, 2625 w, 1674 vs, 1599 m,1480 w, 1421 m, 1354 w, 1295 vs, 1165 w, 1122 w, 1021 w, 947 m, 761 s, 694 s cm$^{-1}$. MS (ESI): *m*/*z* = 371 [M$^+$ – 1], 325 [M$^+$ – COOH]. C$_{22}$H$_{17}$CoO$_2$ (372.30): calcd. C 70.97, H 4.60; found C 71.07, H 4.69.

**[($\eta^4$-Ph$_3$HC$_4$)Co($\eta^5$-C$_5$H$_4$COOH)] (10):** Chromatographed on silica gel with 20% EtOAc/chloroform as eluent to give 0.38 g (85%)

of **10** as an orange crystalline solid. M.p. 180 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 4.71 (br. s, 2 H, CpH), 5.02 (s, 1 H, $C_4$ ring), 5.27 (br. s, 2 H, CpH), 7.10–7.71 (m, 15 H, PhH) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 54.7, 76.0, 78.0 ($C_4$ ring), 86.4, 86.8, 92.2 (CpC), 125.0, 126.1, 127.2, 128.1, 128.5, 130.1, 135.2, 136.3 (PhC), 193.4 (C=O) ppm. IR (KBr): 3053 m, 2634 m, 2561 m, 2360 m, 1671 vs, 1598 m, 1480 vs, 1404 w, 1358 m, 1301 vs, 1166 s, 1023 w, 916 w, 823 w, 753 vs, 690 vs, 572 m cm$^{-1}$. MS (FAB): *m/z* = 448 [M$^+$], 449 [M$^+$ + 1], 431 [M$^+$ – OH], 339 [M$^+$ – $CpCO_2Me$]. $C_{28}H_{21}CoO_2$ (448.08): calcd. C 75.00, H 4.72; found C 75.09, H 4.65.

**General Procedure for the Reduction:** A 50-mL, two necked, round-bottomed flask was charged with $LiAlH_4$ (0.19 g, 5.0 mmol) and 30 mL of dry diethyl ether under nitrogen. The ester complex (1.0 mmol) was then added and the resulting mixture was stirred at room temperature for 24 h. The reaction was quenched by adding 25 mL of ethyl acetate and stirring for 0.5 h. After that solution was filtered through Whatman 40 filter paper, the solvent was evaporated and the residue was chromatographed on silica gel with a suitable eluent.

**[*trans*-($\eta^4$-$Ph_2H_2C_4$)Co($\eta^5$-$C_5H_4CH_2OH$)] (11):** Chromatographed on silica gel with chloroform as eluent to give 0.27 g (69%) of complex **11**. M.p. 95 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 1.48 (s, 1 H, OH), 3.87 (s, 2 H, $OCH_2$), 4.39 (s, 2 H, $C_4$ ring H), 4.72 (s, 2 H, CpH), 4.86 (s, 2 H, CpH), 7.13 (s, 10 H, PhH) ppm. IR (KBr): $\tilde{\nu}$ = 3558 vs, 3056 m, 2921 s, 2856 s, 1592 s, 1499 s, 1447 s, 1394 m, 13639 w, 1262 w,1180 w, 1103 w, 1049 vs,1017 vs, 810 vs, 764 vs, 691 vs cm$^{-1}$. MS (FAB): *m/z* = 358 [M$^+$], 359 [M$^+$ + 1], 341 [M$^+$ – OH], 263 [M$^+$ – $CpCH_2OH$]. $C_{22}H_{19}CoO$ (358.07): calcd. C 73.74, H 5.34; found C 73.69, H 5.45.

**[($\eta^4$-$Ph_3HC_4$)Co($\eta^5$-$C_5H_4CH_2OH$)] (12):** Chromatographed on silica gel with chloroform as eluent to give 0.37 g (86%) of complex **12**. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 1.55 (s, 1 H, OH), 3.9 (s, 2 H, $OCH_2$), 4.97 (s, 2 H, CbH), 4.54 (s, 2 H, CpH), 4.78 (s, 2 H, CpH), 7.1–7.72 (m, 15 H, PhH). IR (KBr): $\tilde{\nu}$ = 3530 s, 3054 m, 2922 m, 1595 s, 1499 s, 1444 m, 1322 w, 1231 m, 1178 w, 1066 w,1000 vs, 818 s, 760 vs, 693 vs, 582 w cm$^{-1}$. MS (FAB): *m/z* = 435[M$^+$ + 1], 417[M$^+$ – OH]. $C_{28}H_{23}CoO$ (434.10): calcd. C 77.41, H 5.34; found C 77.55, H 5.24.

**X-ray Crystallographic Study:** Suitable crystals of complexes **1**–**7** and **11** were obtained by slow concentration of their saturated solutions in ethyl acetate/hexane solvent mixtures. Details of data collection and solution and crystal parameters are given in Tables 4 and 5. Single-crystal diffraction studies were carried out with a Bruker SMART APEX CCD diffractometer with an Mo-$K_\alpha$ ($\lambda$ = 0.71073 Å) sealed-tube radiation source. All crystal structures were solved by direct methods. The program SAINT (version 6.22) was used for integration of the intensity of reflections and scaling. The program SADABS was used for absorption correction.[19] The crystal structures were solved and refined using the SHELXTL (version 6.12) package.[20] All hydrogen atoms were included in idealized positions, and a riding model was used. Non-hydrogen atoms were refined with anisotropic displacement parameters. Because of the poor crystal quality of complex **1**, higher 2$\theta$ reflections were omitted to bring the value of the residual factor down. The oxygen atom of the alcohol group present in the cyclopentadienyl ring of complex **11** shows disorder and occupies two crystallographically independent positions which could be located from the additional residual electron density observed in the difference map. The site occupancy factors were refined with the help of the free variable

Table 4. X-ray crystallographic data for complexes **1**–**4**.

| | **1** | **2** | **3** | **4** |
|---|---|---|---|---|
| Empirical formula | $C_{29}H_{35}CoO_2Si_2$ | $C_{29}H_{35}CoO_2Si_2$ | $C_{32}H_{31}CoO_2Si$ | $C_{35}H_{27}CoO_2$ |
| Formula mass | 530.68 | 530.6 | 534.62 | 538.50 |
| Crystal system | orthorhombic | triclinic | triclinic | monoclinic |
| Space group | *Pbca* | $P\bar{1}$ | $P\bar{1}$ | $P2_1/n$ |
| $T$ [K] | 298(2) | 298(2) | 298(2) | 298(2) |
| $a$ (Å | 10.6624(11) | 9.256(2) | 9.1247(19) | 10.8340(15) |
| $b$ [Å] | 20.098(2) | 9.381(2) | 11.255(2) | 16.982(2) |
| $c$ [Å] | 26.255(3) | 16.219(5) | 13.342(3) | 14.279(2) |
| $\alpha$ [°] | 90 | 96.700(5) | 91.538(3) | 90 |
| $\beta$ [°] | 90 | 98.844(4) | 101.728(3) | 92.587(2) |
| $\gamma$ [°] | 90 | 91.188(3) | 92.523(3) | 90 |
| $V$ [Å$^3$] | 5626.3(10) | 1381.0(6) | 1339.4(5) | 2624.4(6) |
| $Z$ | 8 | 2 | 2 | 4 |
| $D_{calcd.}$ [g cm$^{-3}$] | 1.253 | 1.276 | 1.326 | 1.363 |
| $\mu$ [mm$^{-1}$] | 0.718 | 0.731 | 0.709 | 0.685 |
| $T_{max}/T_{min}$ | 0.927/0.826 | 0.939/0.907 | 0.941/0.849 | 0.929/0.859 |
| $\theta$ range [°] | 2.17–23.25 | 2.23–28.26 | 2.22–24.55 | 2.23–25.38 |
| Index ranges | $-11 \le h \le 11$ | $-11 \le h \le 11$ | $-11 \le h \le 11$ | $-13 \le h \le 13$ |
| | $-21 \le k \le 21$ | $-11 \le k \le 11$ | $-13 \le k \le 13$ | $-20 \le k \le 20$ |
| | $-28 \le l \le 28$ | $-19 \le l \le 19$ | $-16 \le l \le 16$ | $-17 \le l \le 17$ |
| Refl. collected | 40499 | 13657 | 13369 | 25438 |
| Refl. unique | 3690 | 5115 | 4985 | 25438 |
| Refl. observed | 3572 | 4829 | 4602 | 4435 |
| Restraint/parameters | 0/314 | 0/314 | 0/329 | 0/344 |
| Goodness of fit on $F^2$ | 1.446 | 1.076 | 1.065 | 1.199 |
| $R_1[I > 2\sigma(I)]$[a] | 0.0868 | 0.0309 | 0.0318 | 0.0479 |
| $wR_2$ (all data)[b] | 0.2027 | 0.0870 | 0.0882 | 0.1226 |
| $(\Delta\rho)_{max}/(\Delta\rho)_{min}$ | 0.555/–0.662 | 0.239/–0.381 | 0.299/–0.201 | 0.312/–0.392 |
| $\lambda$ [Å] | 0.71073 | 0.71073 | 0.71073 | 0.71073 |

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \Sigma w(F_o^2 - F_c^2)^2/\Sigma[(F_o^2)^2]^{1/2}$.

Table 5. X-ray crystallographic data for complexes **5**–**7** and **11**.

| | **5** | **6** | **7** | **11** |
|---|---|---|---|---|
| Empirical formula | $C_{23}H_{19}CoO_2$ | $C_{23}H_{19}CoO_2$ | $C_{29}H_{23}CoO_2$ | $C_{22}H_{19}CoO$ |
| Formula mass | 386.31 | 386.31 | 462.40 | 358.30 |
| Crystal system | monoclinic | orthorhombic | orthorhombic | monoclinic |
| Space group | $P2_1$ | $P2$ | $Pcca$ | $P2_1$ |
| $T$ [K] | 273(2) | 273(2) | 273(2) | 273(2) |
| $a$ [Å] | 5.818(3) | 8.5776(12) | 41.122(5) | 10.463(5) |
| $b$ [Å] | 27.822(12) | 10.7107(15) | 10.7107(15) | 7.535(4) |
| $c$ [Å] | 10.967(5) | 19.950(3) | 10.0060(13) | 11.911(6) |
| $\alpha$ [°] | 90 | 90 | 90 | 90 |
| $\beta$ [°] | 91.226(8) | 90 | 90 | 113.528(7) |
| $\gamma$ [°] | 90 | 90 | 90 | 90 |
| $V$ [Å$^3$] | 1774.8(14) | 1832.8(5) | 4480.9(10) | 856.0(7) |
| $Z$ | 4 | 4 | 8 | 2 |
| $D_{calcd.}$ [g cm$^{-3}$] | 1.446 | 1.400 | 1.371 | 1.390 |
| $\mu$ [mm$^{-1}$] | 0.975 | 0.950 | 0.790 | 1.006 |
| $T_{max}/T_{min}$ | 0.927/0.888 | 0.872/0.816 | 0.500/0.391 | 0.913/0.863 |
| $\theta$ range [°] | 2.37–25.50 | 2.16–24.49 | 2.81–25.0 | 2.20–25.00 |
| Index ranges | $-7 \le h \le 7$ | $-10 \le h \le 10$ | $-48 \le h \le 48$ | $-12 \le h \le 12$ |
| | $-33 \le k \le 33$ | $-12 \le k \le 12$ | $-12 \le k \le 12$ | $-8 \le k \le 8$ |
| | $-13 \le l \le 13$ | $-24 \le l \le 24$ | $-11 \le l \le 11$ | $-14 \le l \le 14$ |
| Refl. collected | 17235 | 18108 | 39929 | 7793 |
| Refl. unique | 3362 | 3402 | 3936 | 1637 |
| Refl. observed | 3024 | 3208 | 3267 | 1571 |
| Restraint/parameters | 1/471 | 0/236 | 0/290 | 1/217 |
| Goodness of fit on $F^2$ | 1.017 | 1.140 | 1.064 | 1.137 |
| $R_1[I > 2\sigma(I)]$[a] | 0.0517 | 0.0339 | 0.0442 | 0.0974 |
| $wR_2$ (all data)[b] | 0.1194 | 0.0859 | 0.1120 | 0.2344 |
| $(\Delta\rho)_{max}/(\Delta\rho)_{min}$ | 0.653/–0.671 | 0.472/–0.328 | 0.517/–0.241 | 2.135/–1.089 |
| $\lambda$ [Å] | 0.71073 | 0.71073 | 0.71073 | 0.71073 |

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \Sigma w(F_o^2 - F_c^2)^2/\Sigma[(F_o^2)^2]^{1/2}$.

PART instruction.[20] CCDC-614825, -614826, -614827, -614828, -614829, -614830, -614831 and -614832 (**1**–**7** and **11**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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