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Synthesis, reactivity and structural studies of (η^5-methylcyclopentadienyl)(η^4-tetraphenylcyclobutadiene)cobalt and its derivatives

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ABSTRACT

(η^5-methylcyclopentadienyl)(η^4-tetraphenylcyclobutadiene)cobalt (**1**) and its derivatives, [(1-acetyl-2-methyl)η^5-cyclopentadienyl](η^4-tetraphenylcyclobutadiene)cobalt (**2**) [(1-acetyl-3-methyl)η^5-cyclopentadienyl](η^4-tetraphenylcyclobutadiene)cobalt (**3**) [(1-carbomethoxy-2-methyl)η^5-cyclopentadienyl](η^4-tetraphenylcyclobutadiene)cobalt (**4**) and [(1-carbomethoxy-3-methyl)η^5-cyclopentadienyl](η^4-tetraphenylcyclobutadiene) cobalt (**5**) have been prepared in yields varying from 11% to 28% by introducing the substituents on the cyclopentadienyl ring of methylcyclopentadienyl sodium and then reacting with diphenylacetylene and $CoCl(PPh_3)_3$. The carboxylic acids [(1-carboxy-2-methyl)η^5-cyclopentadienyl](η^4-tetraphenylcyclobutadiene)cobalt (**6**), [(1-carboxy-3-methyl)η^5-cyclopentadienyl](η^4-tetraphenylcyclobutadiene)cobalt (**7**) have been prepared after ester hydrolysis of compounds **4** and **5** using KOH/ethanol. [(1-dimethylaminomethyl-3-methyl)η^5-cyclopentadienyl](η^4-tetraphenylcyclobutadiene) cobalt (**8**), was prepared selectively by direct substitution on the cyclopentadienyl ring of (η^5-methylcyclopentadienyl)(η^4-tetraphenylcyclobutadiene)cobalt in 65% yield. The 1,2-isomer was formed only in traces in this reaction. Reactivity of (η^5-methylcyclopentadienyl)(η^4-tetraphenylcyclobutadiene)cobalt and its carbomethoxy derivative have been compared with (η^5-cyclopentadienyl)(η^4-tetraphenylcyclobutadiene)cobalt. All new compounds were characterized by ^1H and ^{13}C NMR, FT-IR, mass spectra and CHN analysis. Compounds **2**, **4**, **6** and **8** have also been structurally characterized by single crystal X-ray structural analysis.

1. Introduction

Planar chirality, a unique property of metal sandwich compounds and particularly of ferrocene has been utilized in realizing a variety of chiral ferrocene based chelating ligands such as Josiphos, bppfa, Walphos and Mandyphos which are used even in industrial organic catalysis [1]. Such compounds are obtained mostly by introducing two different substituents at 1,2 or 1,3 positions of a cyclopentadienyl ring of ferrocene and many synthetic strategies have been evolved for the same [2]. The promise shown by ferrocene in realizing such chiral molecules have evoked interest in extending such studies to other chemically robust metal sandwich compounds as well. The cobalt based sandwich compound, (η^5-Cp)Co(η^4-C_4Ph_4), show similarity to ferrocene in many ways [3]. The high air and moisture stability of this compound which often surpass ferrocene and the relative ease of its synthesis makes this molecule a potential alternative to ferrocene in many reactions. A few examples of planar chiral derivatives of (η^5-Cp)Co(η^4-C_4Ph_4) have already shown promise in enantioselective catalysis such as palladium catalyzed allylic substitutions and rearrangements of allylic trichloroacetimidates and *N*-(4-methoxyphenyl) trifluoroacetimidates [4–7].

The major impediment in developing substitution reactions of (η^5-Cp)Co(η^4-C_4Ph_4) has been the poor reactivity of the cyclopentadienyl ring of this compound and conventional electrophilic substitution reactions which work readily on the cyclopentadienyl ring of ferrocene often do not proceed or occur with poor yields on the cyclopentadienyl ring of this molecule [8,9]. Disubstitution on the cyclopentadienyl ring of (η^5-Cp)Co(η^4-C_4Ph_4) has been restricted to only a few examples of 1,2 and one 1,3 substituted compound prepared by complex multistep methods [9–11]. With a view to explore the possibility of synthesizing 1,2 and 1,3 cyclopentadienyl substituted derivatives of the type [η^5-(R_1)(R_2)C_5H_3]Co(η^4-C_4Ph_4), where R_1 is methyl and R_2 is a well utilized and functionally modifiable group such as –C(O)CH_3, –C(O)OMe, –COOH and –CH_2NMe_2 and also to determine if any selectivity is possible in such disubstitution reactions, we have carried out the preparation of a series of disubstituted derivatives of (η^5-Cp)Co(η^4-C_4Ph_4). Herein we report the results obtained from this study and compare the same with analogous reactions of ferrocene.

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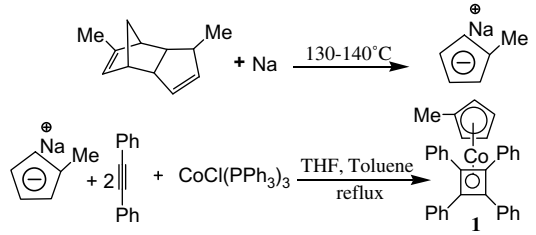
2. Results and discussion

Reaction of sodium salt of methylcyclopentadienyl, $CoCl(PPh_3)_3$ and diphenylacetylene in refluxing toluene/THF mixture resulted in the formation of (η^5-MeCp)Co(η^4-C_4Ph_4) (**1**) (Scheme 1). This relatively simple method to realize the methylated (η^5-Cp)Co(η^4-C_4Ph_4) also indicated a higher yield of the cobalt sandwich compound **1** (64% isolated yield) compared to the synthesis of (η^5-Cp)Co(η^4-C_4Ph_4) by the same method which gave only a maximum of 40% isolated yield [12]. The possible reason for the higher yield is the increased reactivity of sodium salt of methylcyclopentadienyl compared to that of sodium cyclopentadienyl. A different approach was also made to prepare compound **1** by exhaustive reduction of the methoxyester derivative of (η^5-Cp)Co(η^4-C_4Ph_4) using lithium aluminium hydride in THF. The reaction ended in a mixture of products and hence the method was abandoned.

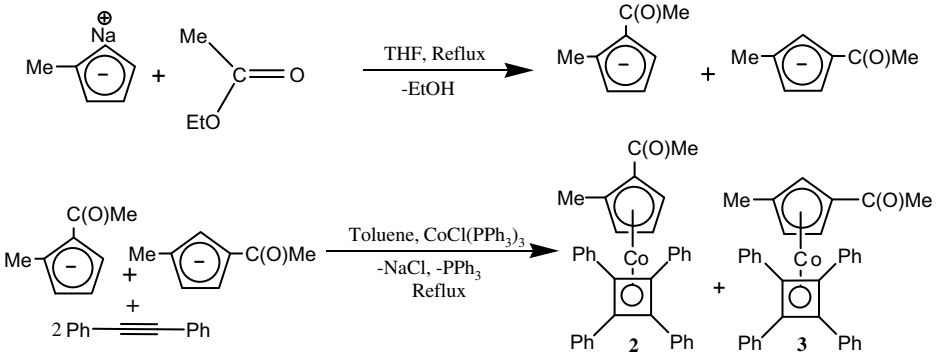
The formation of compound **1** in good yield enabled us to explore the chemistry on its methyl functionalized cyclopentadienyl unit. Our attempts to lithiate the Cp ring using *n*-BuLi or *n*-BuLi/K-Bu^t or acetylation of the Cp ring using Ac_2O and H_3PO_4 were found to be unsuccessful. The steric hindrance of the tetraphenylcyclobutadiene moiety in coming in the way of the reactivity of the Cp ring as indicated in the attempted lithiation of the non-methylated analogue of **1** [13]. The preparation of the acetyl derivative was therefore carried out by introducing the acetyl group on the sodium salt of methylcyclopentadienyl [14–16] and then reacting it with $CoCl(PPh_3)_3$ and diphenylacetylene (Scheme 2).

Two positional isomers (1,2 and 1,3) of the acetyl derivative (**2** and **3**) of **1** were found to form in 11% and 28% yield, respectively. The 1,3-isomer has been found to form in higher yields indicating selectivity towards the formation of a particular isomer to avoid steric hindrance, a trend which has also been observed for other Cp disubstituted derivatives prepared in this study. The isomers were separated on an alumina column. The overall yield of the acetylated products is slightly higher compared to the yields reported for the non-methylated analogue (26% and 33%) [14,16]. Compounds **2** and **3** show significant differences in their IR and NMR spectra which have been discussed later. Attempted reduction of the acetyl derivatives **2** and **3,** with sodium borohydride was not found to proceed. Identity of compound **2** was further confirmed by single crystal X-ray diffraction studies.

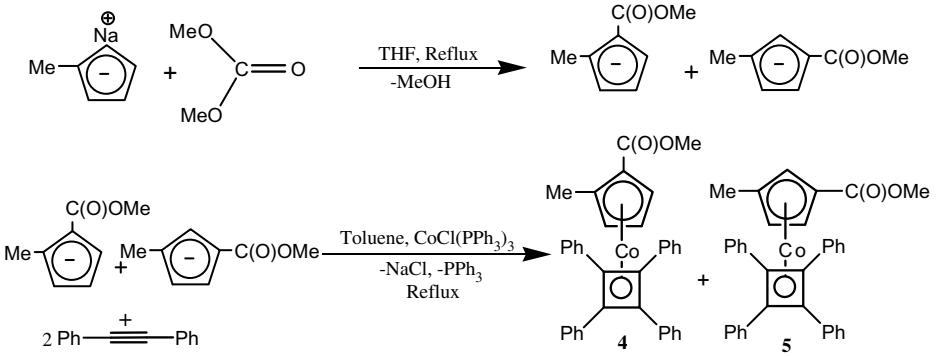
The carbomethoxy derivatives of the compound **1** were prepared following a similar strategy to the acetylation reaction using dimethyl carbonate instead of ethylacetate. These compounds are good precursors for the synthesis of many other derivatives such as carboxylic acids, alcohols, aldehyde etc. [15]. The yields of the compounds were found to be 11% for 1,2-isomer (**4**) and 19% for 1,3-isomer (**5**) (Scheme 3). The main reason for the low yields of these compounds is due to the fact that $RCpCo(PPh_3)_2$ is made *in situ* and utilized and the formation of this compound is only in moderate yields in the one pot reaction. Both compounds were



Scheme 1.



Scheme 2.



Scheme 3.

characterized by a host of spectral and analytical techniques and the crystal structure of **4** has also been determined.

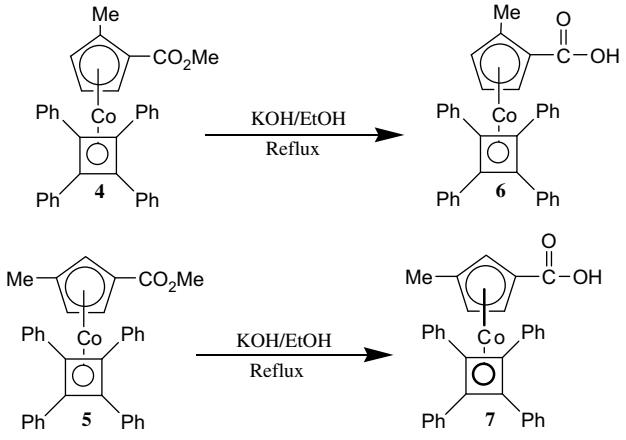
As stable metallocene carboxylic acids are excellent precursors for a host of organometallic molecules with a wide range of potential applications, preparation of the acid derivatives starting from carbomethoxy derivatives were attempted by the reaction with KO^{t}Bu in dry DMSO which has been the procedure reported for preparing [η^5-C_5H_4(COOH)]Co(η^4-C_4Ph_4). However, the reaction was not successful in this case. An ester hydrolysis method using KOH/ethanol was found to proceed readily giving the acid derivatives **6** and **7** of both 1,2 and 1,3 carbomethoxy esters (Scheme 4). The two derivatives have been characterized by ^{1}H NMR, ^{13}C NMR, mass spectra and FT-IR. The crystal structure of the 1,2-derivative **6** has also been determined.

The dimethylaminomethyl derivatives of compound **1** were prepared by using bis(dimethylamino)methane and phosphoric acid [3] (Scheme 5). In this reaction the 1,3-isomer was formed almost exclusively (65% isolated yield) and only a trace amount of 1,2-isomer was formed whose identity was confirmed by mass spectrometry. The steric effect of the tetraphenylcyclobutadiene moiety has possibly played a major role towards the exclusive formation of the 1,3-isomer. It is interesting to note that the analogous reaction reported on monomethyl ferrocene yielded the 1,2 and 1,3-isomers in 14% and 25%, respectively [17].

2.1. Molecular structures of compounds *2*, *4*, *6* and *8*

Suitable crystals of compounds **2, 4, 6** and **8** for single crystal X-ray study were obtained by slow evaporation of their respective solutions in a mixture of hexane/ethylacetate. All the four compounds were found to crystallize in the monoclinic system. Single-crystal diffraction studies were carried out on a Bruker SMART APEX CCD diffractometer with a Mo Kα (λ = 0.71073 Å) sealed tube. Crystal structures of compound **2**, **4** and **8** were solved by direct methods and crystal structure of **6** was solved by Patterson method. 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 [18]. The crystal structures were solved and refined using the SHELXTL (version 6.12) package [19]. All hydrogen atoms were included in idealized positions, and a riding model was used. Non-hydrogen atoms were refined with anisotropic displacement parameters. In order to bring down the value of residual factor, we have omitted the higher 2θ reflections in case of compound **8**. Tables 1–4 lists the selected bond lengths and angles of compounds **2, 4, 6** and **8**.

In compound **2** the cobalt atom is at a distance of 1.680(1) Å from the centroid of the Cp ring and makes a distance of 1.693(1) Å with the centroid of the cyclobutadiene ring. The mean planes containing the four phenyl rings make angles of 24.81°, 28.08°, 37.03° and 54.03° with the cyclobutadiene ring. The cobalt to ring-carbon distances of compound **2** average 2.071(4) Å with



Scheme 4.

Table 1
Selected bond lengths and angles of compound **2**

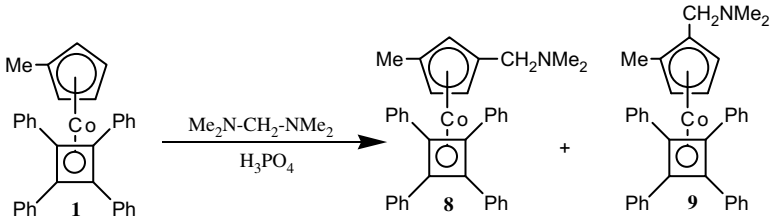
Bonds	Bond length (Å)	Bonds	Bond angles (°)
C2–O1	1.209(11)	O1–C2–C1	123(10)
C7–C8	1.505(11)	C8–C7–C3	127.2(8)
Co1–C3	2.082(8)	C3–Co1–C12	125.3(3)
Co1–C7	2.083(7)	C5–Co1–C11	122.4(3)
Co1–C12	1.994(7)	C9–C12–C31	136.1(6)
Co1–C11	1.983(7)	C2–C3–C4	126.2(9)
C1–C2	1.496(13)	C9–C10–C11	90.1(6)

Table 2
Selected bond lengths and angles of compound **4**

Bonds	Bond length (Å)	Bonds	Bond angles (°)
Co1–C7	2.062(4)	C4–Co1–C9	133.47(17)
Co1–C3	2.055(4)	O1–C2–O2	123.1(5)
Co1–C9	2.018(4)	C8–C7–C3	128.5(5)
Co1–C12	1.985(4)	C10–C19–C20	122.7(4)
C2–O1	1.348(7)	C11–C25–C26	120.57(39)
C2–O2	1.21(7)	C11–C12–C9	89.7(3)
C9–C13	1.458(6)	O2–C2–O1	123.1(5)

Table 3
Selected bond lengths and angles of compound **6**

Bonds	Bond lengths (Å)	Bonds	Bond angles (°)
Co1–C2	2.086(4)	C10–Co1–C9	43.31(13)
Co1–C8	1.998(3)	C8–C11–C30	134.3(3)
C8–C11	1.453(4)	C11–C10–C9	89.7(2)
C1–C2	1.450(6)	C3–C4–C5	108.1(4)
C2–C3	1.453(6)	C2–C3–Co1	70.6(2)
O1–C1	1.270(5)	C7–C6–C2	128.4(4)
O2–C1	1.266(5)	C6–C2–C1	127.4(4)
O1–H1	0.819(5)	C2–C1–O1	116.3(4)
C11–C30	1.461(5)	O1–C1–O2	122.7(4)



Scheme 5.

Table 4
Selected bond lengths and angles of compound **8**

Bonds	Bond length (Å)	Bonds	Bond angles (°)
Co1–C4	2.068(6)	C4–Co1–C9	122.5(2)
Co1–C7	2.060(7)	C4–C3–N1	112.7(5)
C3–N1	1.445(7)	C6–Co1–C12	124.6(4)
C9–C13	1.471(8)	C7–Co1–C12	112.5(3)
C7–C37	1.474(17)	C11–C25–C26	120.7(6)
Co1–C9	1.988(5)	C9–C10–C11	90.3(4)
C3–C4	1.459(8)	C1–N1–C2	110.5(6)
N1–C1	1.437(9)	C37–C7–C8	124.4(15)
C12–C31	1.458(7)	C3–C4–C8	127.6(6)
C11–C25	1.463(8)	C5–C6–C7	107.1(9)

cyclopentadienyl ring and 1.984(7) Å with cyclobutadiene ring. These values are in good agreement with the values reported for the acetyl derivative of (η^5-Cp)Co(η^4-C_4Ph_4), where the Co–C distance average 2.070(2) Å to the cyclopentadienyl ring and 1.982(2) Å to the cyclobutadiene ring. The results indicate that the introduction of one methyl group does not have any influence on the distances between the Co atom and two rings. The phenyl groups adopt a propeller like orientation with dihedral angles ranging from 21° to 42°, and are bent in an exo fashion out of the plane of the cyclobutadiene ring by 7.5 Å [14] (see Fig. 1).

In compound **4** (Fig. 2) the cobalt atom makes a distance of 1.680(1) Å with the centroid of the Cp ring and is at a distance of 1.700(1) Å from the centroid of cyclobutadiene ring which is similar to the distances for the carbomethoxy derivative of (η^5-Cp)Co(η^4-C_4Ph_4) of 1.679(1) Å and 1.689(1) Å, respectively [20]. The four phenyl rings of compound **4** make angles of 25.29°, 32.23°, 38.84° and 44.84° with the cyclobutadiene ring. The distances between C2–O1, C2–O2 and O1–C1 are 1.349(7), 1.210(7) and 1.461(7) Å, respectively, whereas the same distances for the methoxyester derivative of (η^5-Cp)Co(η^4-C_4Ph_4) are 1.343(4), 1.195(4) and 1.446(5) Å.

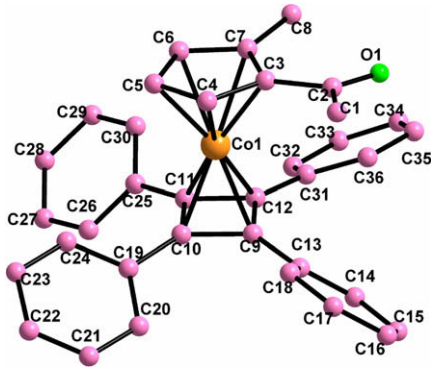


Fig. 1. X-ray crystal structure of compound **2**.

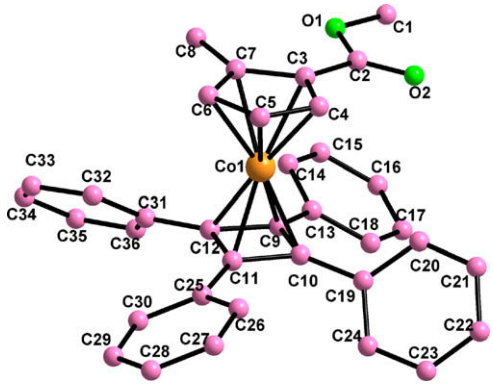


Fig. 2. X-ray crystal structure of compound **4**.

It is interesting to note that compound **6** exists as a dimer with two molecules linked through symmetrical hydrogen bonding interaction between the carboxylic groups. The carboxylic groups have formed a six membered ring through hydrogen bonding where the length of hydrogen bond is 1.852 (9) Å. The hydrogen bonds are formed in such a way that the two metal sandwich moieties orient themselves in trans orientation to avoid steric repulsion between the phenyl rings and the two cyclopentadienyl rings of the dimer are almost in the same plane (angle between the Cp planes is 1.01°). The closely related structure observed for the non-methylated system shows that it exists as a dimer and the carboxylic acid group is hydrogen bonded unsymmetrically where the hydrogen bond lengths are 1.844(7) Å and 1.861(7) Å [21]. In the crystal structure of **6**, the cobalt atom is at a distance of 1.686(1) Å with the centroid of the Cp ring and is at a distance of 1.696(1) Å with the centroid of cyclobutadiene ring whereas the distances for the non-methylated case are 1.694(15) Å and 1.706(16) Å, respectively. The four phenyl rings of the tetraphenyl cyclobutadiene rings of **6** are displaced at angles of 29.07°, 30.36°, 38.75° and 40.96° with respect to the cyclobutadiene ring (see Fig. 3).

To the best of our knowledge no crystal structures of dimethylaminomethyl derivatives of (η^5-Cp)Co(η^4-C_4Ph_4) have been reported yet and we have carried out the single crystal X-ray structure determination of [(1-dimethylaminomethyl-3-methyl)η^5-cyclopentadienyl](η^4-tetraphenylcyclobutadiene) cobalt (**8**). Suitable crystals of **8** for X-ray study were obtained by slow evaporation of its solution in hexane/ethyl acetate mixture. In the structure of compound **8,** the cobalt atom is at a distance of 1.691(1) Å from the centroid of the Cp ring and is at a distance of 1.695(1) Å from the centroid of cyclobutadiene ring. The four phenyl rings of the tetraphenyl cyclobutadiene rings of **8** are displaced at angles of 42.50°, 32.47°, 30.80° and 40.87° with respect to the cyclobutadiene ring. Some selected bond lengths and bond angles are given in Table 4. To decrease steric hindrance, the –NMe_2 group of the compound **8** is oriented in such a way that the methyl groups attached to N atom are projected above the average plane of the five carbon atoms of the cyclopentadienyl ring and the N atom bound to the –CH_2 group is also above the same plane**.** The N atom of the –CH_2NMe_2 group makes a deviation of 1.449 Å from the plane of the five carbon atoms of cyclopentadienyl ring (see Fig. 4).

2.2. Spectral studies

The ^{1}H NMR spectrum of compound **1** shows two peaks (4.44 and 4.51 ppm) indicating the presence of two unequal sets of protons on the cyclopentadienyl ring, ortho and meta with respect to methyl group. In contrast, the protons of the methylcyclopentadienyl ring of methylferrocene have been reported to appear as a singlet at 4.12 ppm [22]. 1,2 and 1,3-isomers of the functionalized derivatives of **1** show significant differences both in their ^{1}H NMR chemical shifts and splitting pattern in all the cases. The chemical shifts of cyclopentadienyl protons of the disubstituted derivatives are complex and vary from 4.37 to 5.16 ppm depending on the type of substituent on the cyclopentadienyl ring. The ^{1}H NMR chemical shift differences are only marginal when compared to the mono substituted non-methylated analogues except for the 1,2 acetyl derivative (**2**) [8,14,15]. The protons of the acetyl group of η^5-CpC(O)CH_3]Co(η^4-C_4Ph_4) appear at 1.65 ppm [14] whereas in compounds **2** and **3** it appears at 1.66 and 1.87 ppm, respectively. The methyl protons of all the derivatives appear in the range of 1.45–1.90 ppm. The positional isomers of the derivatives show

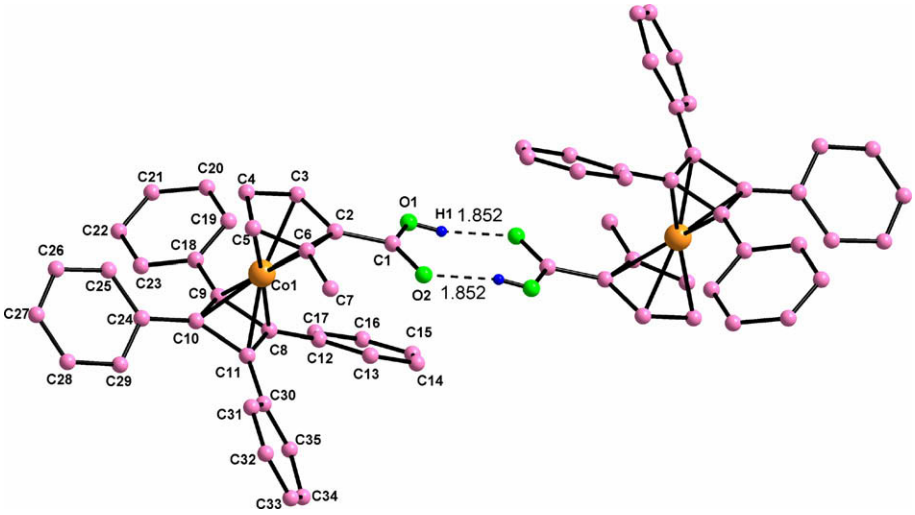


Fig. 3. X-ray crystal structure of compound **6** showing symmetrical hydrogen bonding.

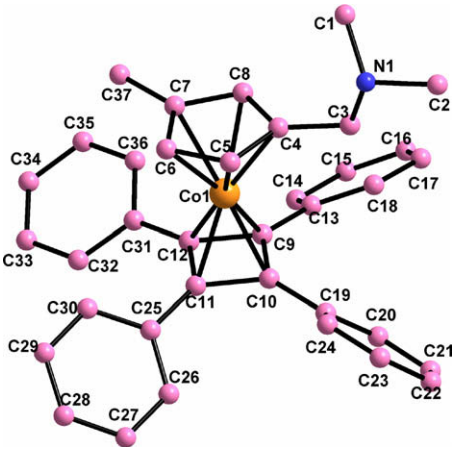


Fig. 4. X-ray crystal structure of compound **8**.

differences not only in the ^{1}H NMR spectra but also in other spectral studies. Compounds **4** and **5** show a difference of $\sim 4\ cm^{-1}$ in their carbonyl stretching frequency whereas compounds **2** and **3** differs by only $\sim 2\ cm^{-1}$. ^{13}C NMR studies also help to identify substitution especially from the chemical shifts of the ipso carbon atoms of the Cp ring. The ipso carbon atom of MeC_5H_4 unit of **1** appears at 94.57 ppm while the rest of the ring-carbon atoms appear at 82.74 and 83.56 ppm. This shift is similar to the trends shown by monoacetyl (93.80 ppm) and monocarboxylic acid (92.90 ppm) derivatives of $(\eta^5\text{-Cp})Co(\eta^4\text{-}C_4Ph_4)$ [14,21]. Moving from 1,2 to 1,3 derivative, significant changes in the ^{13}C NMR chemical shift values of the ipso carbon atoms are observed. For example, in acetyl derivatives of **1**, the chemical shifts of the ipso carbon atoms are 99.44 and 93.03 ppm for the 1,2-isomer (compound **2**) and 96.58 and 90.55 ppm for the 1,3-isomer (compound **3**). Similarly, differences are also shown by carbomethoxy and carboxylic acid derivatives. The positions of the substituents in the new derivatives have been further confirmed by X-ray crystallography.

3. Conclusions

A simple synthetic method for the preparation of methylcyclopentadienyl derived cobalt sandwich compound, $(\eta^5\text{-MeCp})Co(\eta^4\text{-}C_4Ph_4)$, and preparation and characterization of a host of its derivatives (acetyl, carbomethoxy, carboxylic acid and aminomethyl) are described. The study critically evaluates the scope and utility of disubstitution on the cyclopentadienyl ring of $(\eta^5\text{-Cp})Co(\eta^4\text{-}C_4Ph_4)$. Two different positional isomers (1,2 and 1,3) of the derivatives of $(\eta^5\text{-MeCp})Co(\eta^4\text{-}C_4Ph_4)$ were found to form. In all the reactions, the relative yields of the 1,3-isomer was higher than that of the 1,2-isomer and in the case of dimethylaminomethyl derivative, **8** the 1,3-isomer was formed almost exclusively. It was observed that both 1,2 and 1,3 carbomethoxy derivatives of $(\eta^5\text{-MeCp})Co(\eta^4\text{-}C_4Ph_4)$ gave the corresponding acid derivatives after ester hydrolysis reaction with KOH/ethanol. X-ray crystal structure of compounds **2**, **4**, **6** and **8** have been determined and the orientation of four phenyl rings with respect to the cyclopentadienyl ring are also reported. The increase in yield of the 1,3-isomer on going from carbomethoxy to acetyl to aminomethyl derivative, possibly indicates a substituent effect in controlling the formation of a particular positional isomer. All the new compounds reported are highly stable to air and moisture, are high melting and are important precursors for the synthesis of a host of useful derivatives of $(\eta^5\text{-MeCp})Co(\eta^4\text{-}C_4Ph_4)$.

4. Experimental

4.1. General procedures

All manipulations were carried out using standard Schlenk techniques under a nitrogen atmosphere. THF and toluene were freshly distilled from sodium benzophenone ketyl and hexane was distilled and dried over sodium and used. Tris(triphenylphosphine)cobalt chloride was prepared according to reported procedure [23]. Diphenylacetylene, triphenylphosphine and methylcyclopentadiene dimer procured from Aldrich were used as such. ^{1}H and $^{13}C\{^{1}H\}$ spectra were recorded on 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 on a Nicolet Protége 460 FT-IR spectrometer as KBr pellets. Elemental analyses were carried out on a Carlo Erba CHNSO 1108 elemental analyzer. Mass spectra were recorded in the EI and TOF mode using a JEOL SX 102/DA-6000 and MALDI-TOF Q-Star Micromass.

4.2. Preparation of methylcyclopentadienyl sodium

Freshly cut sodium 0.50 g (21.74 mmol) was added to 16.5 mL of methylcyclopentadiene dimer at room temperature. On slow

heating, the solution turned blue (~35–40 °C) then to deep orange and later to brown (~75–80 °C). The mixture was heated to reflux at 140 °C until all the sodium got dissolved. During heating, a light yellow solid was found to precipitate out. After the hydrogen evolution stopped, the reaction mixture was further refluxed for 2 h. The mixture was allowed to cool to room temperature under nitrogen atmosphere. The excess methylcyclopentadiene dimer was partially removed using a syringe. The wet solid was washed with dry hexane (3 × 60 mL) under nitrogen atmosphere. The air and moisture sensitive solid obtained was dried and kept under nitrogen at 0 °C. The compound was directly used for further reactions. Yield: 1.85 g (84%).

4.3. Preparation of (η^5-MeCp)Co(η^4-C_4Ph_4) (**1**)

A solution of 0.62 g (6.08 mmol) of methylcyclopentadienyl sodium in 30 mL of dry THF was stirred at room temperature for 15 min. 5.35 g (6.08 mmol) of chlorotris(triphenylphosphine)cobalt(I), 1.50 g (8.43 mmol) of diphenylacetylene and 50 mL of dry toluene were added to the THF solution of the sodium salt. The resulting solution was refluxed for 24 h and then allowed to cool to room temperature. The reaction mixture was filtered using a Büchner funnel and washed with hexane–ethylacetate mixture (50%). The colored solution obtained was concentrated and a slurry was made with silica gel and this was chromatographed with hexane–ethylacetate (98:2) mixture to get red crystals of (η^5-methylcyclopentadienyl)(η^4-tetraphenylcyclobutadiene)cobalt, (η^5-MeCp)Co(η^4-C_4Ph_4) (**1**) Yield: 1.33 g (64%). m.p: 160–162 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.53 (s, 3H), 4.43 (s, 2H), 4.50 (s, 2H), 7.22 (t, 12H, m, m+p-Ph-H, J_1 = 3.6 Hz, J_2 = 1.5), 7.43 (t, 8H, m+o-Ph-H, J_1 = 3.6 Hz, J_2 = 3.6 Hz) ppm. ^{13}C NMR (75 MHz $CDCl_3$): δ = 11.47, 74.50, 82.74, 83.58, 94.57, 125.99, 127.89, 128.81, 136.48 ppm. IR(KBr, ν/cm^{-1}): 3053(m), 2920(w), 2362(w), 1598(vs), 1497(vs), 1445(s), 699(vs), 564(s), 408(s). Mass (ES^+) *m*/*e* (fragment): 494(M^+), 495(M+1), 496(M+3), 415(M−MeCp). Anal. Calc.: C, 82.58; H, 5.50. Found: C, 82.47; H, 5.53%.

4.4. Preparation of {η^5-1-[(MeC(O)], 2-MeC_5H_3}Co(η^4-C_4Ph_4) (**2**) and {η^5-1-[MeC(O)], 3-MeC_5H_3}Co(η^4-C_4Ph_4) (**3**)

0.62 g (6.08 mmol) of the sodium salt of **1** was taken in a two necked R.B flask under nitrogen. 30 mL of dry THF was added and the resulting solution was stirred for 15 min. Dry ethylacetate (1.5 mL, 15.03 mmol) was then added to the reaction mixture and it was stirred at reflux for 5–6 h. During this time a red color developed. After cooling the solution to room temperature, $CoCl(PPh_3)_3$ (5.35 g, 6.08 mmol) was added followed by dry toluene (50 mL). Diphenylacetylene (1.00 g, 5.62 mmol) was then added and the resulting mixture was heated at reflux overnight. The mixture was cooled to room temperature, filtered, concentrated and chromatographed on neutral alumina column. After removal of triphenylphosphine and its oxide from the column, compound **2** was eluted out with 96:5 hexane–ethylacetate mixture as the first fraction followed by compound **3** (93:7 hexane–ethylacetate). {η^5-1-[(MeC(O)], 2-MeC_5H_3}Co(η^4-C_4Ph_4) (**2**). Yield: 0.17 g (11%). m.p: 181–184 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.69 (s, 3H), 1.87 (s, 3H), 4.54 (brs, 1H), 4.69 (t, 1H, J_1 = 2.7 Hz, J_2 = 2.7 Hz), 4.99 (q, 1H, J_1 = 1.8 Hz, J_2 = 1.2 Hz, J_3 = 1.5 Hz), 7.263 (brs, 12H, m, m+p-Ph-H), 7.38 (brs, 8H,m+o-Ph-H) ppm. ^{13}C NMR (75 MHz $CDCl_3$): δ = 11.40, 26.86, 76.29, 82.86, 83.32, 87.99, 93.03, 99.44, 126.77, 128.21, 128.68, 135.13, 198.3 ppm. IR (KBr ν/cm^{-1}): 1659(vs, C=O), 1597(m), 1495(m), 1419(m), 1350(m), 1271(m), 1213(w), 1176(w),1069(w),1024(w), 926(w), 775(s), 744(s), 699(vs), 561(m). MS (TOF MS ES^+) *m*/*e* (fragment): 536(M^+). Anal. Calc.: C, 80.59; H, 5.45. Found: C, 79.87, H, 5.62%. {η^5-1-[MeC(O)], 3-MeC_5H_3}Co(η^4-C_4Ph_4) (**3**). Yield: 0.42 g (28%). m.p: 151–153 °C. ^{1}H NMR (300 MHz $CDCl_3$): δ = 1.58 (s, 3H), 1.66(s, 3H), 4.64(brs, 1H), 5.09 (t, 2H, J_1 = 1.8 Hz, J_2 = 9.6 Hz), 7.25(bs, 12H, m, m+p-Ph-H), 7.42 (bs, 8H, m+o-Ph-H) ppm. ^{13}C NMR (75 MHz $CDCl_3$): δ = 12.49, 28.14, 75.75, 84.73, 85.4, 89.77, 90.55, 96.58, 126.71, 128.14, 128.67, 135.04, 198.9 ppm IR (KBr ν/cm^{-1}): 1662(C=O, vs), 1597(m), 1493(s), 1436(s), 1354(m), 1298(m), 1185(m), 1067(w), 1024(w), 776(m), 743(s), 698(vs), 559(m). MS (ES^+) *m*/*e* (fragment): 537 (M+1), 538 (M+2). Anal. Calc.: C, 80.59; H, 5.45. Found: C, 79.00; H, 5.35%.

4.5. Preparation of {η^5-1-[(MeOC(O)}, 2-MeC_5H_3}Co(η^4-C_4Ph_4) (**4**) and {η^5-1-[(MeOC(O)}, 3-MeC_5H_3)]Co(η^4-C_4Ph_4) (**5**)

0.62 g (6.08 mmol) of the sodium salt was taken in a two necked R.B flask under nitrogen. 30 mL of dry THF was added and the resulting solution was stirred for 15 min. Then dimethylcarbonate (1.00 mL, 9.78 mmol) was added to the reaction mixture and the mixture was stirred at reflux for 5–6 h. During this time a red color developed. After bringing the solution to room temperature, 5.35 g (6.08 mmol) of chlorotris(triphenylphosphine)cobalt, 1.50 g (8.43 mmol) of diphenylacetylene and 50 mL of dry toluene were added to the reaction mixture. The resulting solution was refluxed overnight was then allowed to cool to room temperature. The reaction mixture was filtered using a Büchner funnel and washed with hexane–ethylacetate mixture (50%). The colored solution obtained was concentrated and the residue was chromatographed on a neutral alumina column. After removal of triphenyl phosphine with hexane, compound **4** was eluted as first fraction with 2–3% (v/v) ethyl acetate/hexane mixture and compound **5** with 3–4% (v/v) ethyl acetate/hexane mixture. {η^5-1-[(MeOC(O)}, 2-MeC_5H_3}-Co(η^4-C_4Ph_4) (**4**). Yield: 0.18 g (12%). m.p: 171–173 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.88(s, 3H), 3.28 (s, 3H), 4.65 (brs, 2H), 5.13 (brs, 1H), 7.29 (brs,12H, m, m+p-Ph-H), 7.45 (brs, 8H, m+o-Ph-H) ppm. ^{13}C NMR (75 MHz $CDCl_3$): δ = 11.58, 50.86, 75.71, 83.91, 84.83, 85.21, 88.13, 97.08, 126.55, 128.04, 128.83, 135.09, 167.13 ppm. IR(KBr ν/cm^{-1}): 1708 (vs, C=O), 1597 (w), 1497 (s), 1444 (w), 1283 (s) 1218 (w), 1161(vw), 1089 (w), 1029 (w), 819 (w), 778 (w), 746 (w), 700 (s), 618 (vw), 589 (vw), 562 (vw). MS (ES^+) *m*/*e* (fragment): 553 (M+1), 415 [M−MeO(O)C_5H_3Me]$^+$. Anal. Calc.: C, 78.25; H, 5.29. Found: C, 77.00; H, 5.36%. {η^5-1-[(MeO-C(O)}, 3-MeC_5H_3)]Co(η^4-C_4Ph_4) (**5**). Yield: 0.30 g (19%). m.p: 216–218 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.90 (s, 3H), 3.29 (s, 3H), 4.67 (d, 2H, J = 8.1 Hz), 5.15 (brs, 1H), 7.29 (d,12H, J = 6.3 Hz, m, m+p-Ph-H), 7.47 (d, 8H, J = 6.3 Hz, m+o-Ph-H) ppm. ^{13}C NMR (75 MHz $CDCl_3$): δ = 11.67, 51.14, 83.99, 84.49, 86.34, 86.86, 98.16, 126.66, 128.03, 128.82, 135.18, 166.57 ppm. IR (KBr ν/cm^{-1}): 1712(vs, C=O), 1596(m), 1494(s), 1446(s), 1299(s), 1207(w), 777(m), 741(m), 698(vs), 558(s) MS (ES+) *m*/*e* (fragment): 553 (M+1), 415 [M−MeO(O)C_5H_3Me]$^+$. Anal. Calc.: C, 78.25; H, 5.29. Found: C, 78.54; H, 5.39%.

4.6. Preparation of [η^5-1-(COOH), 2-MeC_5H_3]Co(η^4-C_4Ph_4) (**6**)

Compound **4** (0.18 g, 0.32 mmol) was taken in a 100 ml two necked round bottom flask followed by 50 mL of distilled ethanol. Potassium hydroxide (0.40 g, 7.12 mmol) dissolved in 5 mL of distilled water was added to the mixture and it was heated at reflux for 36 h. The orange red solution was poured into a beaker containing 100 ml of distilled water. Concentrated hydrochloric acid was added dropwise to neutralize the solution. A bright yellow precipitate formed immediately. The solution was extracted with dichloromethane. The organic extracts were washed twice with distilled water and concentrated. The solid obtained was purified on a silica gel column (60–120 mesh) using hexane and ethylacetate mixture (93:7) as eluent to get an yellow colored product **6**. Yield: 0.13 g (76%), ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.84 (s, 3H), 4.685 (brs, 2H),

5.16 (brs, 1H), 7.218 (t, 12H, m, m+p-Ph-H, J_1 = 3.3 Hz, J_2 = 2.4), 7.404 (t, 8H, m+o-Ph-H, J_1 = 3.3 Hz, J_2 = 3.6 Hz) ppm. ^{13}C NMR (75 MHz $CDCl_3$): δ = 11.78, 75.98, 83.298, 84.9, 86.04, 88.34, 97.65, 126.58, 128, 128.68,134.85, 172.07 ppm. IR (KBr ν/cm^{-1}): 3053 (vw), 2923 (w), 2607(vw), 2361(vw), 1949(w), 1883(w), 1723(vw), 1761(vs), 1597(s), 1468(w), 1439(w), 1380(w), 1347(w), 1283(s), 1226(s), 1161(w), 1090(m), 1025(s), 819(w), 773(s), 697(vs), 556(s). MS (+TOF) *m*/*e* (fragment): 561 (M+Na$^+$).

4.7. Preparation of [η^5-1-(COOH), 3-MeC_5H_3]Co(η^4-C_4Ph_4) (**7**)

Compound **5** (0.22 g, 0.39 mmol) was taken in a 100 mL two necked round bottom flask followed by 50 mL of distilled ethanol. Potassium hydroxide (0.40 g, 7.12 mmol) dissolved in 5 mL distilled water was added to the mixture and it was heated at reflux for 36 h. The reaction mixture was worked up similar to the procedure used for **6** to yield an yellow colored compound **7**. Yield: 0.15 g (72%), ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.554 (s, 3H), 4.632 (brs, 1H), 5.12 (d, 2H, *J* = 13.2 Hz), 7.214 (brs, 12H, m, m+p-Ph-H), 7.415 (brs, 8H, m+o-Ph-H) ppm. ^{13}C NMR (75 MHz $CDCl_3$): δ = 11.75, 60.37, 84.67, 84.74, 87.21, 87.27, 98.73, 126.66, 128.04, 128.66, 134.93, 171.13 ppm. IR (KBr ν/cm^{-1}): 3053(vw), 2922(s), 2855(w), 2603(w), 1951(w), 1672(vs), 1598(s), 1495(w), 1469(s), 1440(s), 1380(w), 1346(s), 1285(s), 1226(s), 1163(s), 1093(s), 1026(s), 914(w), 849(w), 820(s), 751(vs), 698(vs), 618(w), 588(w), 559(s), 463(s). MS (+TOF) *m*/*e* (fragment): 561(M+Na$^+$).

4.8. Preparation of [η^5-1-(Me_2NCH_2), 3-MeC_5H_3]Co(η^4-C_4Ph_4) (**8**) and [η^5-1-(Me_2NCH_2), 2-MeC_5H_3]Co(η^4-C_4Ph_4) (**9**)

In a 100 ml two necked R.B flask, 0.22 g (0.50 mmol) of **1** and 50 mL of glacial acetic acid were taken. The flask was equipped with a condenser, nitrogen inlet and a magnetic stirrer bar. The suspension was brought to reflux. To the hot solution, 0.5 mL (8.92 mmol) of ortho phosphoric acid followed by 2.3 mL of bis(dimethylamino)methane were added. Refluxing and stirring were continued for 12 h. Reaction mixture was cooled to room temperature and 150 mL of water was added. This was extracted with chloroform and the organic extract was then washed first with 50 ml saturated $NaHCO_3$ solution and then with water. The organic layer was dried over Na_2SO_4. The resultant yellow colored liquid was concentrated and chromatographed on a basic alumina column to obtain the major product **8**. Traces of a minor product was also obtained which was identified as the 1,2-isomer by mass spectrometry. The identity of **8** was further confirmed by X-ray diffraction study. [η^5-1-(Me_2NCH_2), 3-MeC_5H_3]Co(η^4-C_4Ph_4) (**8**). Yield: 0.16 g (65%). m.p: 121–123 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H = 1.45 (s, 3H), 2.05 (s, 6H), 2.66 (d, 2H), 4.369 (s, 1H), 4.475 (t, 2H), 7.24 (bs, 12H, m, m+p-Ph-H), 7.43 (bs, 8H, m+o-Ph-H) ppm. ^{13}C NMR (75 MHz $CDCl_3$): δ = 11.75, 44.81, 56.75, 82.39, 83.83, 84.26, 92.85, 94.79, 126–128.74, 136.34. MS (ES$^+$) *m*/*e* (fragment) 552 (M+1), 553 (M+2), 554 (M+3), 555 (M+4), 507 (M−NMe_2). IR (KBr) cm^{-1}: 1596(s), 1496(s), 1447(s), 1254(w), 1170(w), 1069(w), 1021(s), 844(w), 777(m), 744(m), 699(vs), 562(s). Anal. Calc.: C, 80.56; H, 6.21; N, 2.54. Found: C, 79.79; H, 6.17; N, 2.39%. {η^5-1-[Me_2NCH_2], 2-MeC_5H_3}Co(η^4-C_4Ph_4) (**9**) MS (ES$^+$) *m*/*e* (fragment) 551(M$^+$).

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Appendix A. Supplementary material

CCDC 693176, 693174, 693177 and 693175 contain the supplementary crystallographic data for **2**, **4**, **6** and **8**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.09.030

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