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Synthesis and reactions of new 1,2- and 1,3-cyclopentadienyl disubstituted cobalt sandwich compounds (η^5-$C_5H_3R_2$)Co(η^4-C_4Ph_4) (R=CH_2OH, CHO, C≡CH, CH_2N_3, CH_2NH_2, CH_2OAc, CH=NPh)

Nem Singh, Bhanu P.R. Metla, Anil J. Elias*

Department of Chemistry, Indian Institute of Technology, Delhi, Hauz Khas, New Delhi 110016, India

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ABSTRACT

Synthesis and characterization of a series of 1,3- and 1,2-cyclopentadienyl disubstituted derivatives of η^5-$C_pCo(\eta^4$-$C_4Ph_4)$ has been described. The 1,3- and 1,2-cyclopentadienyl diester derived cobalt sandwich compounds {η^5-$C_5H_3[C(O)OMe]_2$}Co(η^4-C_4Ph_4) were prepared by literature procedure and were separated by column chromatography. The reduction of these diester derivatives using $LiAlH_4$ gave the bis(hydroxymethyl) derivatives, [1,3-η^5-$C_5H_3(CH_2OH)_2$] Co(η^4-C_4Ph_4) **1** and [1,2-η^5-$C_5H_3(CH_2OH)_2$] Co(η^4-C_4Ph_4) **2** which were oxidized to the dialdehydes [1,3-η^5-$C_5H_3(CHO)_2$]Co(η^4-C_4Ph_4) **3** and [1,2-η^5-$C_5H_3(CHO)_2$]Co(η^4-C_4Ph_4) **4** by using tetrapropylammonium perruthenate along with N-methyl morpholine oxide. Reaction of the dialdehydes with (chloromethyl)triphenylphosphonium chloride/n-BuLi followed by elimination of HCl using n-BuLi resulted in the 1,2- and 1,3-cyclopentadienyl disubstituted dialkynes [1,3-η^5-$C_5H_3(C{\equiv}CH)_2$]Co(η^4-C_4Ph_4) **5** and [1,2-η^5-$C_5H_3(C{\equiv}CH)_2$]Co(η^4-C_4Ph_4) **6**. The reactions of **1** and **2** with NaN_3 in acetic acid resulted in the bis(azidomethyl) derivatives [1,3-η^5-$C_5H_3(CH_2N_3)_2$] Co(η^4-C_4Ph_4) **7** and [1,2-η^5-$C_5H_3(CH_2N_3)_2$]Co(η^4-C_4Ph_4) **8**. Heating of bis(hydroxymethyl) compounds **1** and **2** in acetic acid at 85–90 °C resulted in the formation of bis(2-acetoxymethyl) derivatives [1,3-η^5-$C_5H_3(CH_2OAc)_2$]Co(η^4-C_4Ph_4) **9** and [1,2-η^5-$C_5H_3(CH_2OAc)_2$]Co(η^4-C_4Ph_4) **10**. The reactions of **1** and **2** with thiophenol in the presence of trifluoroacetic acid in dichloromethane gave bis(phenylmethyl thioether) derivatives **11** [1,3-η^5-$C_5H_3(CH_2SPh)_2$]Co(η^4-C_4Ph_4) and [1,2-η^5-$C_5H_3(CH_2SPh)_2$]Co(η^4-C_4Ph_4) **12**. The click reaction of the 1,2-dialkyne **6** with benzyl azide resulted in the 1,2-bis(triazole) derivative **13**. The 1,3-diazide **8** was reduced to bis(aminomethyl) derivative [1,3-η^5-$C_5H_3(CH_2NH_2)_2$]Co(η^4-C_4Ph_4) **14**. Condensation of the 1,3-dialdehyde **3** with aniline resulted in the 1,3-bis(phenylimino) derivative **15**. All the new compounds synthesized in this study were characterized by ^1H and ^{13}C NMR, FT-IR, HRMS, CHN analysis. The compounds **2**–**6**, **8** and **10** have also been structurally characterized by single crystal X-ray diffraction analysis.

1. Introduction

Aryl rings with functional groups at the 1,2 and 1,3 positions and heteroaryl rings with functional groups flanking the heteroatom are excellent precursors for preparing a wide variety of chelating and multidentate ligands. The classic examples for such bidentate ligands are the chiral *box* (bis oxazoline) ligands which, along with metal compounds have been used extensively in asymmetric catalysis [1–5]. Achiral bidentate ligands have also been prepared from 1,2 to 1,3-disubstituted aryl rings, the latter being used extensively for the preparation of pincer type complexes [6–8]. Recently there has been a surge of activity in preparing such bidentate ligands using stable metal sandwich compounds, especially with ferrocene as the substrate [9–14]. 1,2- and 1,3-disubstitution of a Cp ring of ferrocene can be achieved with relative ease and many examples of multiple phosphine, amine and heterocycle derived ferrocenes are available in the literature [15–19]. Such compounds have shown promising activity in diverse areas such as antitubercular agents, as receptors for recognition of barbiturates and glucose sensors [20–22]. Apart from realizing bidentate ligands, the ferrocene scaffold has also been derivatized with terminal alkyne units at the 1 and 2 positions to prepare novel alkyne linked multiferrocenyl assemblies [23–28].

Among non-ferrocenyl, highly stable and easily accessible sandwich compounds, (η^5-Cp)Co(η^4-C_4Ph_4) has attracted considerable interest especially for the synthesis of chiral and sterically

* Corresponding author. Tel.: +91 11 26591504.
E-mail address: eliasanil@gmail.com (A.J. Elias).

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bulky derivatives [29–38]. Unlike ferrocene, only a handful of examples having 1,2 and 1,3-disubstitution on the Cp ring of $(\eta^5\text{-Cp})Co(\eta^4\text{-}C_4Ph_4)$ has been reported so far and most of these have methyl group as one of the Cp substituents which limits their usefulness as bidentate ligands [39–41]. Recently, using methyl chloroformate, we have reported an easy way of synthesizing the 1,2- and 1,3-cyclopentadienyl diester derivatives of $(\eta^5\text{-Cp})Co(\eta^4\text{-}C_4Ph_4)$. A chiral 1,3-bis(oxazoline) and a 1,2-acenequinone having both iron and cobalt sandwich units in the molecule were also prepared from the diesters [42]. In this paper we report the easy synthesis and characterization of a range of hitherto unknown 1,2- and 1,3-difunctional derivatives of this cobalt based sandwich compound $(\eta^5\text{-Cp})Co(\eta^4\text{-}C_4Ph_4)$.

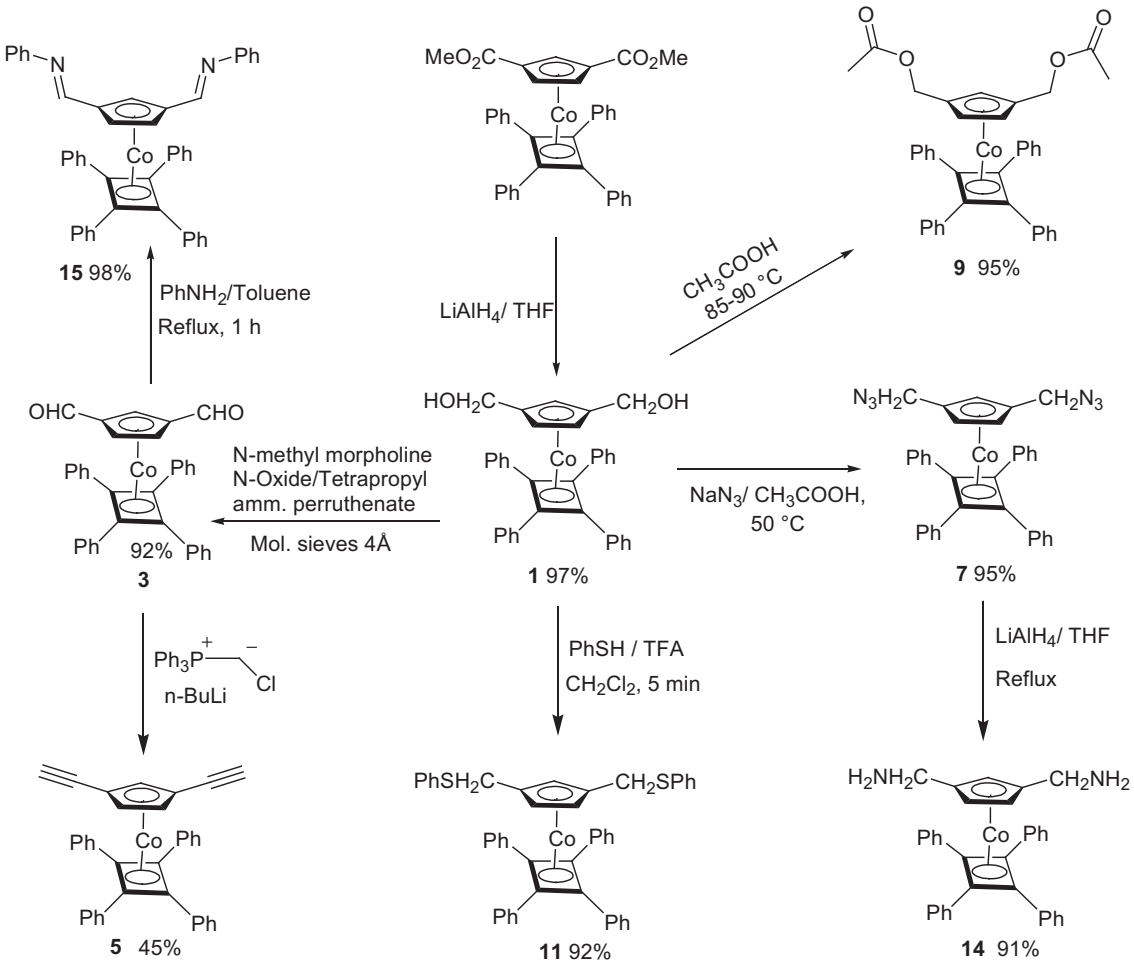
2. Results and discussion

Recently we have reported the synthesis of a palladium complex based on the bidentate 1,3-bis oxazoline derived $(\eta^5\text{-Cp})Co(\eta^4\text{-}C_4Ph_4)$ which has been found to be an excellent catalyst for conversion of achiral trichloroacetimidates to chiral trichloroacetamides in good enantiomeric excess [42]. This finding prompted us to explore the possibility of preparing analogous cyclopentadienyl disubstituted derivatives of $(\eta^5\text{-Cp})Co(\eta^4\text{-}C_4Ph_4)$ with a range of functionalities which can function as bidentate ligands or can be precursors for realizing the same.

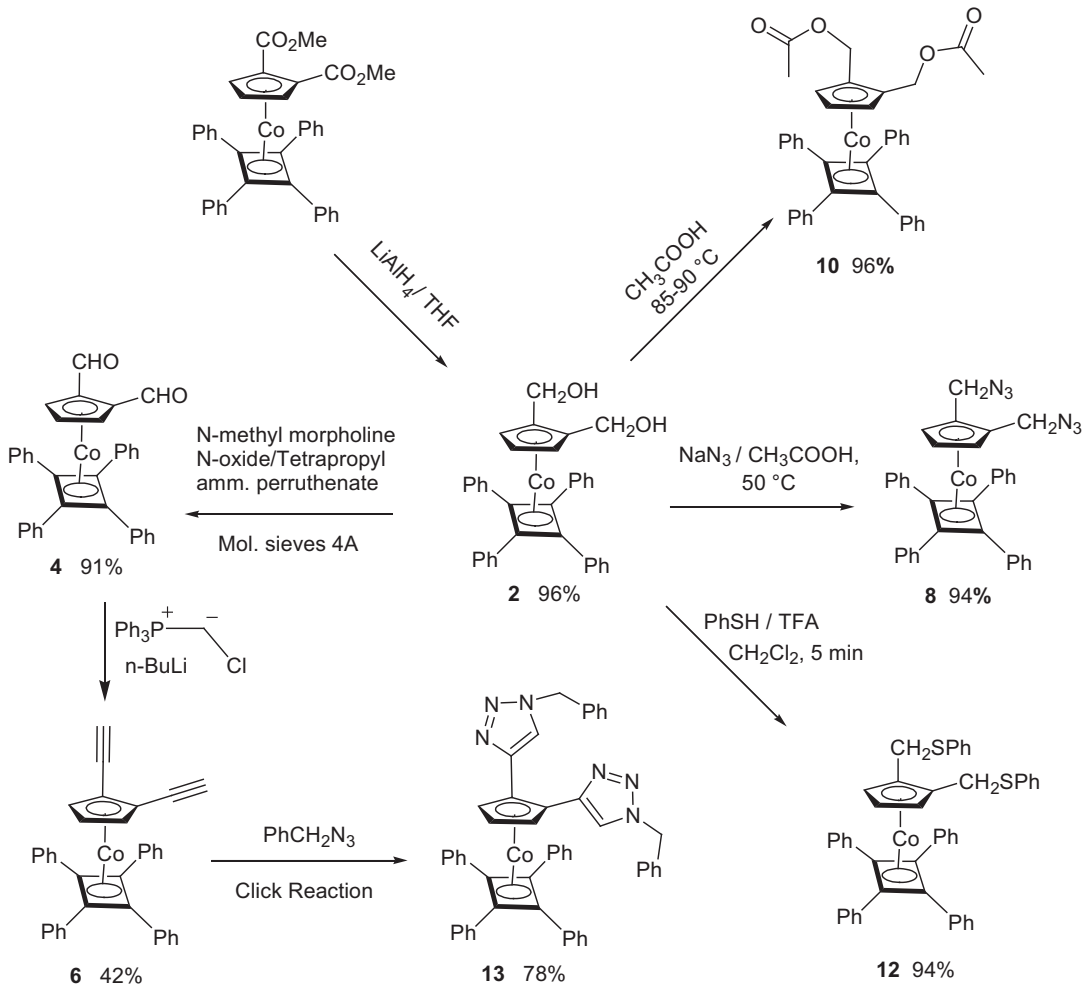
The reduction of 1,2- and 1,3-cyclopentadienyl diester derived cobalt sandwich compounds with $LiAlH_4$ gave almost quantitative yields of the bis(hydroxymethyl) derivatives **1** and **2**. These were readily converted to the dialdehydes **3** and **4** by catalytic amounts of tetrapropylammonium perruthenate along with N-methyl morpholine oxide as oxidant (Schemes 1 and 2), a method which results in high yields of the aldehyde [38].

Reaction of the dialdehydes **3** and **4** with (chloromethyl)triphenylphosphonium chloride/n-BuLi followed by elimination of HCl by n-BuLi resulted in the 1,2 and 1,3 Cp disubstituted dialkynes, **5** and **6** [38]. The bis(hydroxymethyl) derived cobalt sandwich compounds **1** and **2** were converted to bis(azidomethyl) derivatives **7** and **8** by the reaction with NaN_3 in acetic acid at 50 °C, similar to the procedure reported by Francisco and coworkers for the synthesis of azidomethylferrocene [43].

Interestingly the reactions of **1** and **2** in acetic acid at 85–90 °C resulted in bis(2-acetoxy methyl) derivatives **9** and **10** [44]. A modified procedure reported for the synthesis of thioglycosylated ferrocene was used to convert the bis(hydroxymethyl) derivatives **1** and **2** to the bis(phenyl thioether) derivatives **11** and **12** [43]. Our reaction using phenyl mercaptan and trifluoroacetic acid was considerably faster and was completed in 5 min instead of the 2 h reported for the thioglycosylated ferrocene. Click reaction of the 1,2-dialkyne **6** with benzyl azide resulted in the 1,2-bis(triazole) derivative **13**. The 1,3-bis(azidomethyl) derivative **8** was readily reduced to amino methyl derivative **14** by $LiAlH_4$ in refluxing THF [45]. A novel 1,3-bis(phenylimino) derivative **15** was also prepared in quantitative yield by condensation reaction of aldehyde **3** with aniline using toluene as solvent.



Scheme 1. Synthesis and reactions of 1,3-bis(hydroxymethyl) derived $(\eta^5\text{-Cp})Co(\eta^4\text{-}C_4Ph_4)$.



Scheme 2. Synthesis and reactions of 1,2-bis(hydroxymethyl) derived (η^5-Cp)Co(η^4-C_4Ph_4).

2.1. Spectral studies

The ^{1}H NMR spectrum of 1,2- and 1,3-cyclopentadienyl disubstituted compounds **1**–**15** showed two peaks indicating the presence of two unequal sets of protons on the cyclopentadienyl ring. The spectral data of compounds **1**–**6** is mostly in accord with analogous cyclopentadienyl monosubstituted derivatives of (η^5-Cp)Co(η^4-C_4Ph_4) as reported by Richards and coworkers [38].

The bis(azidomethyl) derivatives **7** and **8** are the first examples of such disubstituted derivatives on a metal sandwich compound. In the ^{1}H NMR spectra of both **7** and **8**, the CH_2 hydrogens were found to be diastereotopic showing two doublets in the range of 3.44–3.70 ppm, ($^2J_{C-H}$ = 13.5 Hz). The infrared spectra of compounds **7** and **8** showed strong azide vibrational bands at 2095 and 2102 cm^{-1} respectively. Although 1, 2-Cp substituted diacetate is known for ferrocene [50] no example of 1,3-Cp substituted diacetates of sandwich compounds are known so far. The diastereotopic CH_2 protons of **9** and **10** were found to be further deshielded (4.37–4.54 ppm, $^2J_{C-H}$ = 12.0 Hz). Compounds **11** and **12** are the first examples of phenylthiomethyl derivatives of (η^4-Cp)Co(η^4-C_4Ph_4). The diastereotopic CH_2 protons of these compounds were found to be shielded compared to azidomethyl and acetate derivatives (3.10–3.37 ppm, $^2J_{C-H}$ = 13.5 Hz). For the novel 1,3-bis(phenylimino) derivative **15**, the imino hydrogens were found to be deshielded as expected and were observed at 7.75 ppm.

2.2. Structural studies

The crystal structure of the 1,2-bis(hydroxymethyl) derivative **2** indicated the two OH groups pointing away from the bulky C_4Ph_4 unit. Although no intramolecular hydrogen bonding was observed in its crystal structure, weak O–H···O intermolecular hydrogen bonding between hydroxyl groups with H–O···O distance 2.837 Å and O–H···O angle 165° were observed linking two molecules into a dimer (Fig. 1).

The crystal structures of dialdehydes **3** and **4** are given in Figs. 2 and 3. The structure of **3** shows one of the two different molecules present within the asymmetric unit. In both the compounds, the aldehyde moiety was found to be coplanar with the cyclopentadienyl ring and the exocyclic C–C bond was found to show partial double bond character with bond distances in the range of 1.445(8) to 1.465(7) Å. Although 1,2- and 1,3-dialkynyl derived ferrocene and $CpMn(CO)_3$ compounds are known [46], crystal structures of terminal dialkyne derived sandwich compounds have not been reported so far.

The bond angles of the alkynyl group in compounds **5** and **6** (Figs. 4 and 5) were appearing in the range of 177.5(5) to 179.1(7)° which were similar to the bond angle [178.1(3)°] of the alkynyl group in the crystal structure of monoalkynyl cobalt sandwich compound [η^5-(C_5H_4(C≡CH)]Co(η^4-C_4Ph_4) [35]. These values were also found to be closer to the alkynyl bond angles reported for cyclopentadienyl 1,2 and 1,3-bis(trimethylsilylalkynyl) derived $CpMn(CO)_3$ compounds [46].

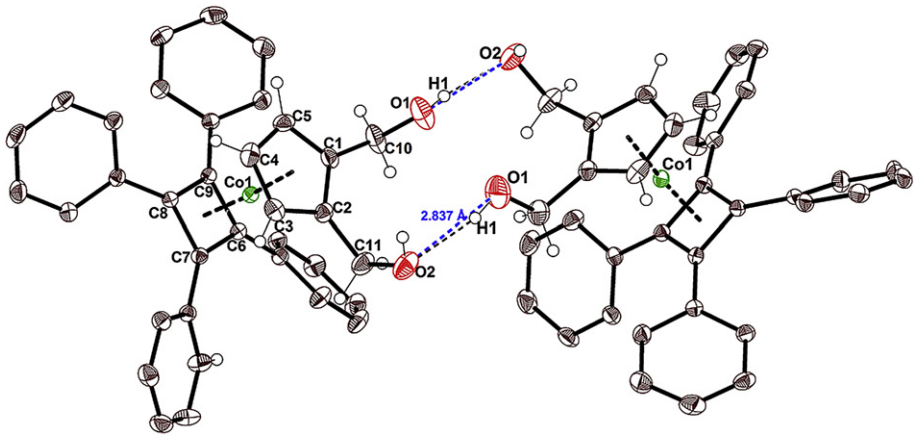


Fig. 1. ORTEP diagram of **2** (showing intermolecular hydrogen bonding) with thermal ellipsoids at the 30% probability level. Phenyl hydrogen atoms have been omitted for clarity. Selected bond lengths (Å), Co(1)–C(1) 2.072(3), O(1)–C(10) 1.431(4), C(1)–C(2) 1.425(4), C(2)–C(3) 1.419(4), C(1)–C(10) 1.500(5). Selected bond angles (°) O(1)–C(10)–C(1) 109.2(3), C(2)–C(1)–C(10) 127.9(3), C(5)–C(1)–C(10) 125.0(3).

The structure of the 1,2-bis(azidomethyl) derivative **8** (Fig. 6) is the first crystal structure of an azidomethyl substituted metal sandwich compound. The two azidomethyl groups are oriented away from each other and the N–N–N angles are almost linear in the range of 171.8(7) to 173.4(6)°. Although cyclopentadienyl 1,2-bis(2-acetoxymethyl) derived ferrocene is known [47], analogous derivatives were so far unknown for (η^4-Cp)Co(η^4-C_4Ph_4). The crystal structure of compound **10** (Fig. 7) shows the two acetoxymethyl groups oriented upwards away from the bulky C_4Ph_4 unit.

3. Conclusions

The first synthesis and characterization of 1,2- and 1,3-difunctional derivatives of the cobalt sandwich compound, (η^5-Cp)Co(η^4-C_4Ph_4) with functional groups such as CH_2OH, CHO, C≡CH, CH_2N_3, CH_2SPh, CH_2OAc, CH_2NH_2, CH═NPh has been described. 1,2- and 1,3-bis(hydroxymethyl) compounds [η^5-$C_5H_3(CH_2OH)_2$]Co(η^4-C_4Ph_4) prepared from 1,2- and 1,3-cyclopentadienyl diester derived cobalt sandwich compounds were readily converted to bis(2-acetoxymethyl), bis(azidomethyl) and bis(phenylthiomethyl) derivatives in very high yields. Both bis(hydroxymethyl) derivatives were also oxidized to dialdehydes using tetrapropylammonium perruthenate/N-methyl morpholine N-oxide in the presence of molecular sieves 4 Å in 90–91% yields. The first examples of 1,2- and 1,3-Cp derived terminal dialkynes of (η^5-Cp)Co(η^4-C_4Ph_4) were prepared using these dialdehydes as precursors in 42–45% yields. Click chemistry was used successfully to convert the 1,2-dialkyne derivative **6** to 1,2-triazole derivative **13**. The 1,3-dialdehyde was also converted to a novel bis(phenylimino) derivative in good yield. All the new compounds reported are highly stable to air and moisture and are precursors for the synthesis of a range of basal bulky bidentate chiral and achiral ligands with potential applications in catalysis.

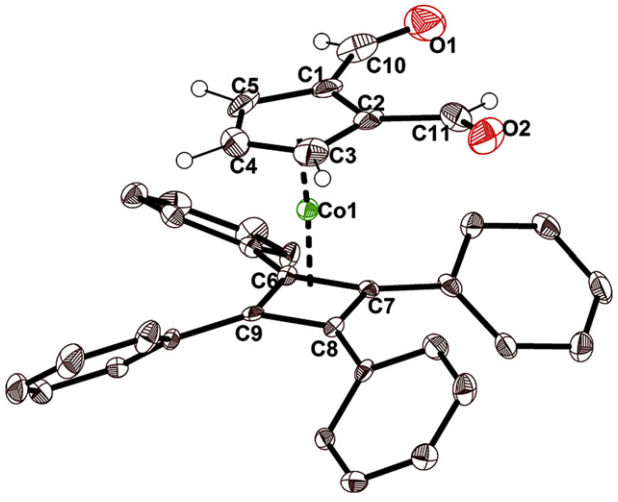


Fig. 2. ORTEP diagram of **4** with thermal ellipsoids at the 50% probability level. Phenyl hydrogen atoms have been omitted for clarity. Selected bond lengths (Å), Co(1)–C(1) 2.072(3), Co(1)–C(6) 1.993(3), O(1)–C(10) 1.431(4), C(1)–C(2) 1.425(4), C(2)–C(3) 1.419(4), C(1)–C(10) 1.500(5). Selected bond angles (°), O(2)–C(11)–C(2) 114.4(3), C(2)–C(1)–C(10) 127.9(3), C(5)–C(1)–C(10) 125.0(3), C(1)–C(2)–C(11) 128.3(3), C(3)–C(2)–C(1) 107.5(3).

4. Experimental

4.1. General procedures

All manipulations were carried out using standard Schlenk techniques under a nitrogen atmosphere. THF and xylene were freshly distilled from sodium benzophenone ketyl and hexane was distilled and dried over sodium and used. [(1,3-dicarbomethoxy) η^5-cyclopentadienyl] (η^4-tetraphenylcyclobutadiene)cobalt and [(1,2-dicarbomethoxy)η^5-cyclopentadienyl](η^4-tetraphenylcyclobutadiene)cobalt [42] were prepared according to reported procedures. Diphenylacetylene, triphenylphosphine, dicyclopentadiene and methyl chloroformate 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. X-ray crystallography

The crystal structures of the **2**–**6**, **8** and **10** were obtained by slow evaporation of their respective solutions in a mixture of hexane/ethylacetate. The compounds **2**, **5**, **6**, **8** and **10** were found to crystallize in the monoclinic system, compounds **3**, **4** crystallized in triclinic and orthorhombic crystal lattices respectively. The data was collected using Bruker AXS SMART Apex CCD diffractometer.

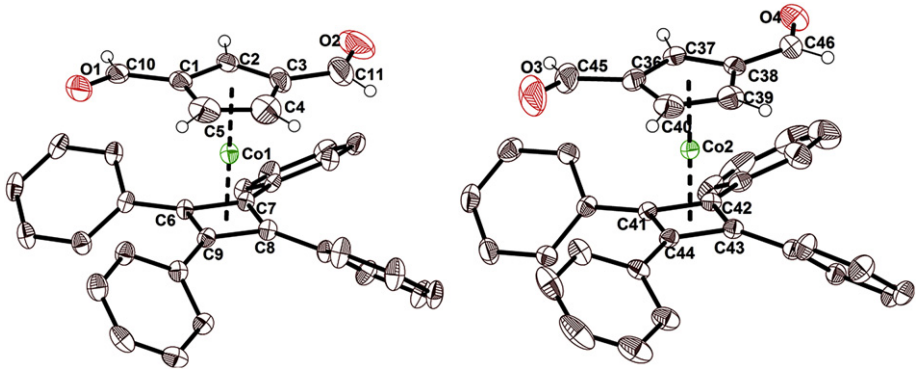


Fig. 3. ORTEP diagram of **3** with thermal ellipsoids at the 30% probability level (two molecules in asymmetric unit). Phenyl hydrogen atoms have been omitted for clarity. Selected bond lengths (Å), O(1)–C(10) 1.199(6), O(2)–C(11) 1.114 (10), C(1)–C(2) 1.418(6), C(2)–C(3) 1.396(7), C(1)–C(10) 1.465(7), C(3)–C(11) 1.465(8). Selected bond angles (°), O(1)–C(10)–C(1) 122.7(6), C(2)–C(1)–C(10) 124.7(5), C(2)–C(3)–C(4) 108.8(5), C(6)–C(7)–C(8) 89.8(3).

All the crystal structures were solved and refined using the SHELXTL (version 6.12) software [48–51]. The ORTEP diagrams for all the crystals **2**–**6**, **8** and **10** are shown in the Figs. 1–7 respectively. Data collection and structure refinement parameters of crystals **2**–**6**, **8** and **10** are given in Table 1. The relatively higher but acceptable R factors of compounds **4**, **5** and **10** which could not be improved after repeated attempts are possibly the consequence of room temperature data collection.

4.3. Preparation of $[\eta^5$-1,3-$(CH_2OH)_2C_5H_3]Co(\eta^4$-$C_4Ph_4)$ (**1**)

$\{\eta^5$-1,3-$[MeOC(O)]_2C_5H_3\}Co(\eta^4$-$C_4Ph_4)$ (2.39 g, 4.00 mmol) was dissolved in 60 mL of dry THF. To this solution, $LiAlH_4$ (0.34 g, 9.00 mmol) was added and the reaction mixture was stirred at room temperature for 15 h. The reaction was quenched and extracted with EtOAc (2 × 30 mL) using a separating funnel. The organic layer was dried over Na_2SO_4, filtered and evaporated to get a yellow powder which was recrystallised with dichloromethane/hexane mixture to get reddish yellow crystals of the pure compound **1**. Yield: 2.10 g, 3.88 mmol, 97%. Mp: 170–172 °C. Anal. Found: C, 77.89; H, 5.32. Calcd. for $C_{35}H_{29}O_2Co$: C, 77.77; H, 5.41. IR (ν, cm^{-1}): 3359 vs (–OH). ^{1}H NMR (δ, 300 MHz, $CDCl_3$): 0.93 (2H, brs, OH), 3.97–4.10 (4H, m, CH_2), 4.53 (2H, s, CpH), 4.69 (1H, s, CpH), 7.23–7.25 (12H, m, *m*/*p*-PhH), 7.41–7.45 (8H, m, *o*-PhH). ^{13}C NMR (δ, 75 MHz, $CDCl_3$): 59.20 (CH_2), 74.98 (C_4Ph_4), 79.39, 81.94, 98.66 (CpC), 126.76, 128.36, 128.47, 135.85 (PhC). HRMS: Calcd. for $C_{35}H_{29}O_2CoNa$: 563.1397, found 563.1395.

4.4. Preparation of $[\eta^5$-1,2-$(CH_2OH)_2C_5H_3]Co(\eta^4$-$C_4Ph_4)$ (**2**)

$\{\eta^5$-1,2-$[MeOC(O)]_2C_5H_3\}Co(\eta^4$-$C_4Ph_4)$ (2.39 g, 4.00 mmol) was taken in an identical reaction by which **1** was synthesized to prepare **2**. Yield: 2.08 g, 3.85 mmol, 96%. Mp: 201–203 °C. Anal. Found: C, 77.89; H, 5.32. Calcd. for $C_{35}H_{29}O_2Co$: C, 77.77; H, 5.41. IR (ν, cm^{-1}): 3359 vs (–OH). ^{1}H NMR (δ, 300 MHz, $CDCl_3$): 1.94 (2H, brs, OH), 4.03–4.13 (4H, m, CH_2) 4.52–4.54 (1H, t, ^3J = 2.7 Hz, CpH), 4.69 (2H, d, ^3J = 2.4 Hz CpH), 7.23–7.25 (12H, m, *m*/*p*-PhH),

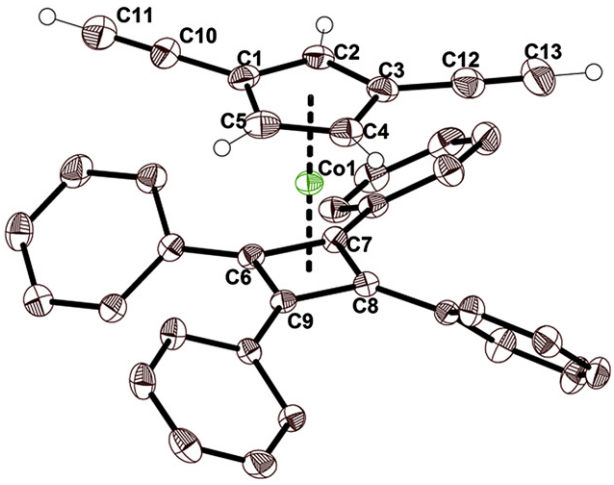


Fig. 4. ORTEP diagram of **5** with thermal ellipsoids at the 30% probability level. Phenyl hydrogen atoms have been omitted for clarity. Selected bond lengths (Å), C(10)–C(11) 1.183(9), C(3)–C(12) 1.427(9), C(12)–C(13) 1.176(9). Selected bond angles (°), C(1)–C(10)–C(11) 177.6(8), C(3)–C(12)–C(13) 179.1(7), C(2)–C(1)–C(10) 125.5(5), C(5)–C(1)–C(10) 126.9(6).

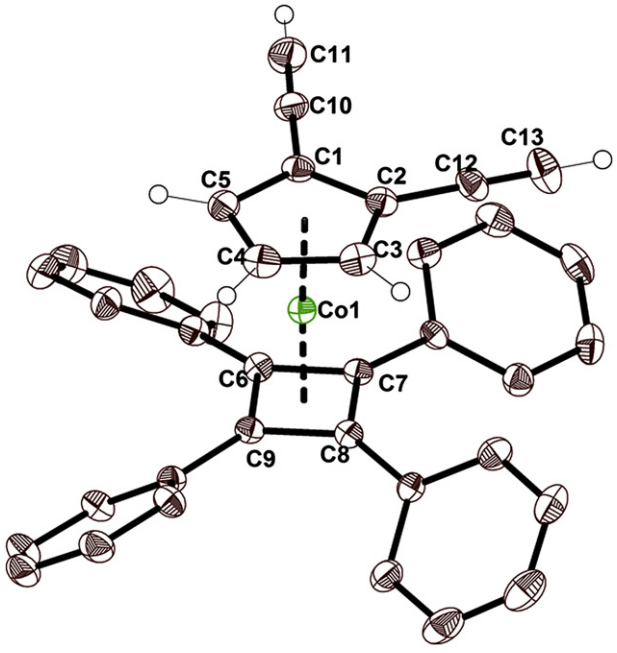


Fig. 5. ORTEP diagram of **6** with thermal ellipsoids at the 30% probability level. Phenyl hydrogen atoms have been omitted for clarity. Selected bond lengths (Å), Co(1)–C(1) 2.066(4), Co(1)–C(6) 1.980(3), C(1)–C(2) 1.427(5), C(2)–C(3) 1.418(5), C(1)–C(10) 1.441(5), C(10)–C(11) 1.163(5), C(2)–C(12) 1.427(6), C(12)–C(13) 1.156(6). Selected bond angles (°), C(1)–C(10)–C(11) 178.3(5), C(2)–C(12)–C(13) 177.5(5), C(2)–C(1)–C(10) 125.6(4), C(5)–C(1)–C(10) 126.0(4).

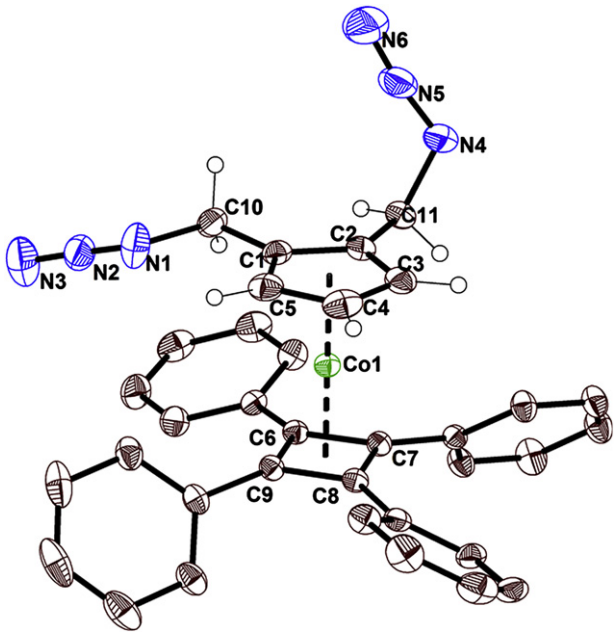


Fig. 6. ORTEP diagram of **8** with thermal ellipsoids at the 30% probability level. Phenyl hydrogen atoms have been omitted for clarity. Selected bond lengths (Å), Co(1)–C(1) 2.067(4), Co(1)–C(4) 2.076(4), N(1)–N(2) 1.207(6), N(5)–N(6) 1.118(7), N(4)–C(11) 1.466(6), C(3)–C(4) 1.413(6), C(2)–C(11) 1.483(6). Selected bond angles (°), N(1)–N(2)–N(3) 173.5(6), N(4)–N(5)–N(6) 171.8(6), N(2)–N(1)–C(10) 119.0(4), N(5)–N(4)–C(11) 116.1(4), N(1)–C(10)–C(1) 109.3(4), N(4)–C(11)–C(2) 114.3(4).

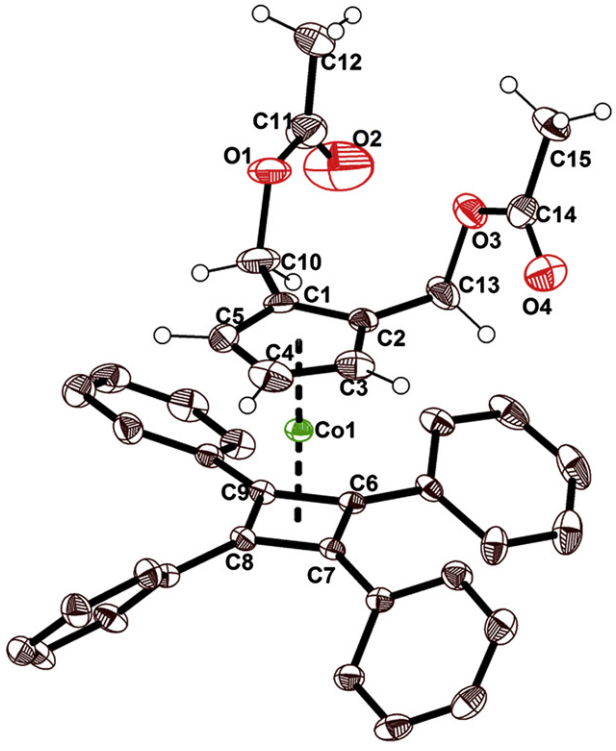


Fig. 7. ORTEP diagram of **10** with thermal ellipsoids at the 30% probability level. Phenyl hydrogen atoms have been omitted for clarity. Selected bond lengths (Å), O(1)–C(11) 1.303(9), O(2)–C(11) 1.170(10), O(4)–C(14) 1.196(7), C(1)–C(10) 1.488(10), C(1)–C(2) 1.437(8), C(2)–C(3) 1.393(8). Selected bond angles (°), O(1)–C(11)–O(2) 121.8(9), O(2)–C(11)–C(12) 124.9(9), O(4)–C(14)–O(3) 124.9(7), O(1)–C(10)–C(1) 110.7(6), C(2)–C(1)–C(10) 128.0(6).

7.41–7.45 (8H, m, *o*-PhH). ^{13}C NMR (δ, 75 MHz, $CDCl_3$): 57.93 (CH_2), 74.98 (C_4Ph_4), 83.73, 84.04, 95.14 (CpC), 126.64, 128.21, 128.62, 135.73 (PhC). HRMS: Calcd. for $C_{35}H_{29}O_2CoNa$: 563.1397, found: 563.1403.

4.5. Preparation of $[\eta^5$-1,3-$(CHO)_2C_5H_3]Co(\eta^4$-$C_4Ph_4)$ (**3**)

To a solution of compound **1** (0.65 g, 1.20 mmol) in 15 mL of CH_2Cl_2, molecular sieves 4 Å and N-methyl morpholine-N-oxide (0.48 g, 4.08 mmol) were added. To this, tetrapropylammonium perruthenate (0.04 g, 0.12 mmol) was added. The mixture was found to darken and it was stirred at room temperature for 2 h. The reaction mixture was then washed with saturated sodium sulphite (20 mL), brine (20 mL) and saturated $CuSO_4$ solution (20 mL). The organic layer was dried (Na_2SO_4), filtered and the solvent was evaporated off. The remaining residue was chromatographed on neutral alumina using 4:1 hexane/ethylacetate as eluent. The only yellow fraction was collected which on evaporation of solvent gave a reddish orange powder which was characterized as **7**. Yield: 0.59 g, 1.10 mmol, 92%. Mp: 185–187 °C. Anal. Found: C, 78.47; H, 4.59. Calcd. for $C_{35}H_{25}O_2Co$: C, 78.35; H, 4.70. IR (ν, cm^{-1}): 1676 vs (C=O). ^{1}H NMR (δ, 300 MHz, $CDCl_3$): 5.43 (2H, s, CpH), 5.83 (1H, s, CpH), 7.24–7.36 (12H, m, *m/p*-PhH), 7.43–7.45 (8H, m, *o*-PhH), 9.35 (2H, s, CHO). ^{13}C NMR (δ, 75 MHz, $CDCl_3$): 79.33 (C_4Ph_4), 82.91, 87.47, 96.17 (CpC), 127.85, 128.43, 128.78, 133.51 (PhC), 190.30 (CHO). HRMS: Calcd. for $C_{35}H_{25}O_2CoNa$: 559.1081, found: 559.1086.

4.6. Preparation of $[\eta^5$-1,2-$(CHO)_2C_5H_3]Co(\eta^4$-$C_4Ph_4)$ (**4**)

Compound **2** (0.65 g, 1.20 mmol) was taken in place of **1** in an identical reaction by which **3** was synthesized to prepare **4**. Yield: 0.59 g, 1.10 mmol, 91%. Mp: 220–222 °C. Found: C, 78.22; H, 4.76. Calcd. for $C_{35}H_{25}O_2Co$: C, 78.35; H, 4.70. IR (ν, cm^{-1}): 1674 vs (C=O). ^{1}H NMR (δ, 300 MHz, $CDCl_3$): 5.05 (1H, s, CpH), 5.50 (2H, s, CpH), 7.24–7.35 (12H, m, *m/p*-PhH), 7.40–7.43 (8H, m, *o*-PhH), 9.79 (2H, s, CHO). ^{13}C NMR (δ, 75 MHz, $CDCl_3$): 79.61 (C_4Ph_4), 89.42, 91.22, 92.04 (CpC), 127.84, 128.38, 128.70, 133.49 (PhC), 191.18 (CHO). HRMS: Calcd. for $C_{35}H_{25}O_2CoNa$: 559.1081, found: 559.1084.

4.7. Preparation of $[\eta^5$-1,3-$(CH{\equiv}C)_2C_5H_3]Co(\eta^4$-$C_4Ph_4)$ (**5**)

n-BuLi (2.40 mL, 1.6 M in hexanes, 3.84 mmol) was added to a solution of (chloromethyl) triphenylphosphonium chloride (0.82 g, 3.80 mmol) in 30 mL of THF at −78 °C. The solution was warmed to room temperature while stirring and then re-cooled to −78 °C. To the deep red-orange solution of the resulting ylide was added a solution of **3** (1.17 g, 2.05 mmol) in THF (20 mL) via cannula over a period of 5 min. The resulting reaction mixture was warmed to room temperature and stirred for 15 h. After evaporation of the solvent, the residue was extracted with 10% aqueous NH_4Cl (50 mL) and Et_2O (2 × 30 mL) The combined organic layers were dried (Na_2SO_4), filtered and evaporated to get a dark orange residue. This residue was washed with hexane, dried in vacuum and dissolved in 35 mL of THF. The solution was cooled to −40 °C and n-BuLi (4.00 mL, 1.6 M, 6.40 mmol) was added while stirring, The reaction mixture was found to darken slowly and after 15 min, the solution was cooled further to −80 °C. To the cooled solution, 20% H_2SO_4 (5 mL) was added upon which it turned yellow. The reaction mixture was warmed to room temperature and was extracted with diethyl ether (2 × 30 mL), washed with brine (30 mL) and dried over Na_2SO_4. The dried ether extract was filtered and the solvent was evaporated off to get a yellow residue which was chromatographed on alumina using ethyl acetate–hexane as eluent. The first band was collected at 2% ethyl acetate/hexane which upon evaporation of solvent gave a yellow crystalline

Table 1
X-ray crystal structure parameters of compounds **2**–**6**, **8** and **10**.

Parameters	**2**	**3**	**4**	**5**	**6**	**8**	**10**
Empirical formula	$C_{35}H_{29}CoO_2$	$C_{35}H_{25}CoO_2$	$C_{35}H_{25}CoO_2$	$C_{37}H_{25}Co$	$C_{37}H_{25}Co$	$C_{35}H_{27}CoN_6$	$C_{39}H_{32}CoO_4$
Formula weight	540.51	536.48	536.48	528.50	528.50	590.56	624.58
Crystal system	Monoclinic	Triclinic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*C2/c*	*P*	*Pbca*	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_1/n$
a (Å)	21.195(5)	9.683(4)	16.953(2)	9.537(2)	10.423(3)	17.524(3)	13.297(2)
b (Å)	16.947(4)	14.309(6)	15.521(2)	15.933(3)	15.407(4)	12.633(2)	17.806(3)
c (Å)	15.867(4)	20.351(9)	19.524(2)	17.997(4)	17.166(5)	13.439(3)	13.394(2)
α (deg)	90	101.771(8)	90	90	90	90	90
β (deg)	110.629(4)	94.356(9)	90	93.846(5)	105.669(6)	103.753(4)	98.018(3)
γ (deg)	90	104.851(8)	90	90	90	90	90
V (Å^3)	5334.0(2)	2643.5(2)	5137.6(10)	2728.6(10)	2654.3(12)	2889.9(9)	3140.2(9)
Z	8	4	8	4	4	4	4
T/K	298	298	150	298	298	298	298
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
ρ_{calcd} (g/cm3)	1.346	1.348	1.387	1.287	1.323	1.357	1.319
μ (mm-1)	0.674	0.680	0.700	0.653	0.671	0.629	0.587
Goodness of fit	1.039	1.057	1.406	1.065	1.016	1.014	1.266
θ range	1.58–25.00	1.51–25.00	2.08–25.0	1.71–25.00	1.81–25.00	1.2–25.00	1.20–25.00
Total reflections	25274	19171	46756	14140	13824	15651	14806
Unique reflections	4693	9253	4522	4800	4686	3522	5520
Ovserved data [$I > \sigma(I)$]	3730	6760	4429	3092	3123	5077	4631
R_{int}	0.051	0.046	0.068	0.076	0.069	0.050	0.048
R_1[a][$F2 > 2\sigma(F2)$], wR_2[b]($F2$)	0.0440, 0.1243	0.0647, 0.1469	0.0864, 0.1646	0.0712, 0.1898	0.0575, 0.1377	0.0539, 0.1792	0.0919, 0.1974
CCDC number	880636	880637	880638	880639	880640	880641	880642

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

powder characterized as **5**. Yield: 0.49 g, 0.93 mmol, 45%. Mp: 181–183 °C. Anal. Found: C, 84.23; H, 4.71. Calcd. for $C_{37}H_{25}Co$: C, 84.08; H, 4.77. IR (ν, cm^{-1}): 2109 m (C≡CH). ^{1}H NMR (δ, 300 MHz, $CDCl_3$): 2.44 (1H, s, C≡CH), 4.76 (2H, s, CpH), 4.93 (1H, s, CpH), 7.24–7.26 (12H, m, *m/p*-PhH), 7.46–7.49 (8H, m, *o*-PhH). ^{13}C NMR (δ, 75 MHz, $CDCl_3$): 77.19 (C_4Ph_4), 76.73 (C≡CH), 78.73(C≡CH), 87.28, 88.67 (CpC), 126.66, 127.95, 128.6, 134.46 (PhC). HRMS: Calcd. for $C_{37}H_{25}CoNa$: 551.5186, found: 551.5186.

4.8. Preparation of [η^5-1,2-(CH≡C)$_2$C$_5$H$_3$]Co(η^4-C$_4$Ph$_4$) (**6**)

Compound **4** (1.17 g, 2.05 mmol) was taken in place of **3** in an identical reaction by which **5** was synthesized to prepare compound **6**. Yield: 0.45 g, 0.86 mmol, 42%. Mp: 172–174 °C. Anal. Found: C, 84.30; H, 4.83. Calcd. for $C_{37}H_{25}Co$: C, 84.08; H, 4.77. IR (ν, cm^{-1}): 2113 m (C≡CH). ^{1}H NMR (δ, 300 MHz, $CDCl_3$): 2.64 (2H, s, C≡CH), 4.56–4.58 (1H, t, ^{3}J = 2.7 Hz, CpH), 4.78–5.79 (2H, d, ^{3}J = 2.7 Hz, CpH), 7.15–7.26 (12H, m, *m/p*-PhH), 7.40–7.55 (8H, m, *o*-PhH). ^{13}C NMR (δ, 75 MHz, $CDCl_3$): 77.20 (C_4Ph_4), 78.54 (C≡CH), 80.78(C≡CH), 85.24, 87.06 (CpC), 126.70, 127.99, 128.89, 134.56 (PhC). HRMS: Calcd. for $C_{37}H_{25}CoH$: 529.1366, found 529.1362.

4.9. Preparation of [η^5-1,3-(CH$_2$N$_3$)$_2$C$_5$H$_3$]Co(η^4-C$_4$Ph$_4$) (**7**)

Compound **1** (0.27 g, 0.50 mmol) was dissolved in 5 mL of glacial acetic acid. Sodium azide (0.26 g, 4.00 mmol) was added to the solution and stirred at 70 °C for 15 h. The reaction mixture was neutralized with aq. $NaHCO_3$, extracted with CH_2Cl_2 (3 × 25 mL) and combined organic layer was dried over Na_2SO_4. After evaporating the solvent, the residue was purified by column chromatography on silica gel using 10% ethyl acetate/hexane as eluent. Evaporation of the solvent gave yellow crystalline solid characterized as **7** Yield: 0.28 g, 0.48 mmol, 95%. Mp: 150–152 °C. Found: C, 71.39; H, 4.56; N, 14.40. Calcd. for $C_{35}H_{27}N_6Co$: C, 71.18; H, 4.61; N, 14.23. IR (ν, cm^{-1}): 2095 vs (N_3). ^{1}H NMR (δ, 300 MHz, $CDCl_3$): 3.44–3.48 (2H, d, ^{2}J = 13.5 Hz CHH), 3.64–3.70 (2H, d, ^{2}J = 13.5 Hz, CHH), 4.70 (2H, s, CpH), 4.79 (1H, s, CpH), 7.23–7.26 (12H, m, *m/p*-PhH), 7.40–7.42 (8H, m, *o*-PhH). ^{13}C NMR (δ, 75 MHz, $CDCl_3$): 48.40 (CH_2), 75.84 (C_4Ph_4), 82.22, 83.85, 92.35 (CpC), 126.85, 128.25, 128.58, 135.27 (PhC). HRMS: Calcd. for $C_{35}H_{27}CoN_6Na$ 613.1527, found 613.1538.

4.10. Preparation of [η^5-1,2-(CH$_2$N$_3$)$_2$C$_5$H$_3$]Co(η^4-C$_4$Ph$_4$) (**8**)

Compound **2** (0.27 g, 0.50 mmol) was used instead of **1** in an identical reaction by which **7** was synthesized. The reaction yielded **8** Yield: 0.28 g, 0.47 mmol, 94%. Mp: 158–161 °C. Found: C, 71.36; H, 4.50; N, 14.37. Calcd. for $C_{35}H_{27}N_6Co$: C, 71.18; H, 4.61; N, 14.23. IR (ν, cm^{-1}): 2102 vs (N_3). ^{1}H NMR (δ, 300 MHz, $CDCl_3$): 3.55–3.60 (2H, d, ^{2}J = 13.5 Hz CH_2), 3.66–3.70 (2H, d, ^{2}J = 13.5 Hz, CH_2), 4.65–4.67 (1H, t, ^{3}J = 2.7 Hz, CpH), 4.75–4.76 (2H, d, ^{3}J = 2.7 Hz, CpH), 7.23–7.25 (12H, m, *m/p*-PhH), 7.40–7.42 (8H, m, *o*-PhH). ^{13}C NMR (δ, 75 MHz, $CDCl_3$): 46.67 (CH_2), 75.65(C_4Ph_4), 84.41, 89.71 (CpC), 126.90, 128.34, 128.65, 135.23 (PhC). HRMS: Calcd. for $C_{35}H_{27}CoN_6Na$ 613.1527, found 613.1560.

4.11. Preparation of [η^5-1,3-(CH$_2$OAc)$_2$C$_5$H$_3$]Co(η^4-C$_4$Ph$_4$) (**9**)

Compound **1** (0.15 g, 0.27 mmol) was dissolved in 3 mL of glacial acetic acid and stirred at 80 °C for 1 h. The reaction mixture was neutralized with aq. $NaHCO_3$ and extracted with CH_2Cl_2 (3 × 25 mL). The combined organic layer was dried over Na_2SO_4 and after evaporating the solvent, the residue was purified by column chromatography on silica gel using 10% ethyl acetate/hexane as eluent. Evaporation of the solvent gave yellow crystalline solid characterized as **9** (Yield: 0.16 g, 0.26 mmol, 95%). Mp: 150–152 °C. Anal. Found: C, 74.95; H, 5.32; Calcd. for $C_{39}H_{33}CoO4$: C, 74.99; H, 5.33; IR (ν, cm^{-1}): 1739 vs (C=O). ^{1}H NMR (δ, 300 MHz, $CDCl_3$): 1.96(6H, s, CH_3), 4.37–4.41 (2H, d, ^{2}J = 12.0 Hz CH_2), 4.50–4.54 (2H, d, ^{2}J = 12.0 Hz, CH_2), 4.81 (2H, s, CpH), 4.96 (1H, s, CpH), 7.07–7.34 (12H, m, *m/p*-PhH), 7.53–7.55 (8H, m, *o*-PhH). ^{13}C NMR (δ, 75 MHz, $CDCl_3$): 20.75 (CH_3), 60.73 (CH_2), 75.59 (C_4Ph_4), 82.22, 83.95, 92.39 (CpC), 126.67, 128.13, 128.58, 135.43 (PhC), 170.52 (C=O). HRMS: Calcd. for $C_{35}H_{27}CoO_4Na$ 647.1608, found 647.1614.

4.12. Preparation of [η^5-1,2-$(CH_2OAc)_2C_5H_3$]Co(η^4-C_4Ph_4) (**10**)

Compound **2** (0.15 g, 0.27 mmol) was used instead of **1** in an identical reaction by which **9** was synthesized. The reaction yielded **10** Yield: 0.16 g, 0.26 mmol, 96%. Mp: 158–161 °C. Found: C, 74.93; H, 5.30; Calcd. for $C_{39}H_{33}CoO_4$: C, 74.99; H, 5.33. IR (ν, cm^{-1}): 1740 vs (C=O). ^{1}H NMR (δ, 300 MHz, $CDCl_3$): 1.88 (6H, s, CH_3), 4.45–4.50 (4H, m, CH_2), 4.62 (1H, s, CpH), 4.77–4.78 (2H, s, CpH), 7.23–7.25 (12H, m, *m/p*-PhH), 7.40–7.42 (8H, m, *o*-PhH). ^{13}C NMR (δ, 75 MHz, $CDCl_3$): 20.80 (CH_3), 59.18 (CH_2), 75.50 (C_4Ph_4), 84.71, 85.02, 90.32 (CpC), 126.75, 128.21, 128.67, 135.42 (PhC), 170.53 (C=O). HRMS: Calcd. for $C_{39}H_{33}CoO_4Na$ 647.1608, found 647.1616.

4.13. Preparation of [η^5-1,3-$(CH_2SPh)_2C_5H_3$]Co(η^4-C_4Ph_4) (**11**)

To the solution of **1** (0.27 g, 0.50 mmol) in 5 mL of dry dichloromethane was added phenyl mercaptan (0.06 g, 0.50 mmol). Trifluoroacetic acid (0.12 g, 1.05 mmol) was added drop wise to the solution and stirred for 2 min. The solvent was evaporated and residue was chromatographed on an alumina column using 1:3 ethylacetate–hexane mixture as eluent. The yellow fraction on evaporation of solvent gave **11** Yield: 0.34 g, 0.46 mmol, 92%. Mp: 200–204 °C (decom). Anal. Found: C, 77.69; H, 5.19. Calcd. for $C_{47}H_{37}S_2Co$: C, 77.88; H, 5.14. IR (ν, cm^{-1}): 1566 vs (CH_2SPh) ^{1}H NMR (δ, 300 MHz, $CDCl_3$): 3.10–3.15 (2H, d, ^2J = 13.3 Hz CH_2), 3.26–3.30 (2H, d, ^2J = 13.3 Hz, CH_2), 4.4–4.44 (2H, s, CpH), 4.51 (1H, s, CpH), 7.04–7.07 (4H, m, *o*-SPhH), 7.13–7.23 (18H, m, *m/p*-PhH, *m/p*-SPhH), 7.38–7.41 (8H, m, *o*-PhH). ^{13}C NMR (δ, 75 MHz, $CDCl_3$): 31.75 (CH_2), 75.20 (C_4Ph_4), 83.06, 83.47, 94.04 (CpC), 126.12, 126.40, 128.15, 128.60, 128.69, 129.81 (PhC), 135.75 (ipso-Ph), 136.30 (ipso-SPh) HRMS: Calcd. for $C_{47}H_{37}S_2Co$ 724.1669, found 724.1695.

4.14. Preparation of [η^5-1,2-$(CH_2SPh)_2C_5H_3$]Co(η^4-C_4Ph_4) (**12**)

Compound **2** (0.27 g, 0.50 mmol) was used instead of **1** in an identical reaction to synthesize **12** Yield: 0.34 g, 0.47 mmol, 94%. Mp: 155–157 °C. Anal. Found: C, 77.96; H, 5.05. Calcd. for $C_{47}H_{37}S_2Co$: C, 77.88; H, 5.14. IR (ν, cm^{-1}): 1564 vs (CH_2SPh). ^{1}H NMR (δ, 300 MHz, $CDCl_3$): 3.27–3.32 (2H, d, ^2J = 13.5 Hz CH_2), 3.33–3.37 (2H, d, ^2J = 13.5 Hz, CH_2), 4.43–4.44 (1H, t, ^3J = 2.7 Hz, CpH), 4.49–4.50 (2H, d, ^3J = 2.7 Hz, CpH), 7.10–7.28 (22H, m, *m/p*-PhH, -SPhH), 7.39–7.42 (8H, m, *o*-PhH). ^{13}C NMR (δ, 75 MHz, $CDCl_3$): 29.70 (CH_2), 74.93 (C_4Ph_4), 83.05, 83.83, 91.85 (CpC), 126.03,126.35, 127.47, 128.12, 128.67, 129.63, (PhC), 135.62 (ipso-Ph), 136.61 (ipso-SPh) HRMS: Calcd. for $C_{47}H_{37}S_2Co$ 724.1669, found 724.1682.

4.15. η^5-{1,2-[$PhCH_2(C_2HN_3)$]$_2C_5H_3$}Co(η^4-C_4Ph_4) (**13**)

1,2-dialkyne **6** (0.26 g, 0.50 mmol) was dissolved in 10 mL ^{t}BuOH; benzyl azide (0.13 g, 1.00 mmol) was added to this solution and stirred for 5 min. $CuSO_4.5H_2O$ (0.02 g, 0.10 mmol in 7 mL water) followed by sodium ascorbate (0.04 g, 0.2 mmol in 3 mL water) was added and the reaction mixture was stirred for 15 h at room temperature. CH_2Cl_2 (50 mL) was added to the reaction mixture, washed with brine (15 mL) and the organic layer was dried over sodium sulfate. After evaporating the solvent, the residue was purified by column chromatography on silica gel using 20% ethyl acetate/hexane as eluent. Evaporation of the solvent gave yellow crystalline solid characterized as **13** (Yield: 0.31 g, 0.39 mmol, 78%). Mp: 174–176 °C. Found: C, 77.16; H, 4.90; N, 10.48. Calcd. for $C_{51}H_{39}N_6Co$: C, 77.07; H, 4.95; N, 10.57. IR (ν, cm^{-1}): 1232 vs (triazole). NMR: ^{1}H, δ 4.75–4.77 (1H, t, ^3J = 2.7 Hz, CpH), 5.21–5.22 (2H, d, ^3J = 2.4 Hz, CpH), 5.30 (4H, s, CH_2Ph), 6.99–7.36 (32H, m, PhH + C=CH); $^{13}C\{^1H\}$, δ 53.64 (CH_2Ph), 75.58 (C_4Ph_4), 84.16, 84.88, 85.51 (CpC), 122.18, 126.14, 127.73, 128.39, 128.63, 128.87, 135.01 (PhC), 135.16 (C=CH), 142.20 (C=CH). HRMS: Calcd. for $C_{51}H_{39}CoN_6Na$: 817.2466, found: 817.2458.

4.16. Preparation of [η^5-1,3-$(CH_2NH_2)_2C_5H_3$]Co(η^4-C_4Ph_4) (**14**)

To the solution of **7** (0.30 g, 0.51 mmol) in 30 mL of THF, $LiAlH_4$ (0.06 g, 1.58 mmol) was added and the reaction mixture was refluxed for 3 h. The reaction was quenched and extracted with EtOAc (2 × 30 mL). The organic layer was dried over Na_2SO_4, filtered and solvent was evaporated to get a yellow powder which was recrystallised to get pure fine crystals of **14** Yield: 0.25 g, 0.46 mmol, 91%. Mp: 150–152 °C. Anal. Found: C, 77.97; H, 5.77; N, 5.26. Calcd. for $C_{35}H_{31}N_2Co$: C, 78.05; H, 5.80; N, 5.20. IR (ν, cm^{-1}): 2095 vs (N_3). ^{1}H NMR (δ, 300 MHz, $CDCl_3$): 3.11–3.15 (2H, d, ^2J = 14.4 Hz CH_2), 3.18–3.23 (2H, d, ^2J = 14.4 Hz, CH_2), 4.58 (2H, s, CpH), 4.70 (1H, s, CpH), 7.15–7.30 (12H, m, *m/p*-PhH), 7.44–7.45 (8H, m, *o*-PhH). ^{13}C NMR (δ, 75 MHz, $CDCl_3$): 39.16 (CH_2), 74.60 (C_4Ph_4), 79.07, 81.12, 100.47 (CpC), 126.40, 128.18, 128.56, 136.25(PhC). HRMS: Calcd. for $C_{35}H_{31}CoN_2$ 538.1819, found 538.1823.

4.17. Preparation of η^5-1,3-[$(PhN=CH)_2C_5H_3$]Co(η^4-C_4Ph_4) (**15**)

To the solution of **3** (0.28 g, 0.50 mmol) in 10 mL of toluene, molecular sieves 4 Å and aniline (0.50 mL) were added and the reaction mixture was refluxed for 1 h. After cooling, the solvent was evaporated and the residue was purified by column chromatography on silica gel using 15% ethyl acetate/hexane as eluent. Evaporation of the solvent gave red crystalline solid characterized as **15** Yield: 0.34 g, 0.49 mmol, 98%. Mp: 161–163 °C. Anal. Found: C, 82.26; H, 5.18; N, 4.12. Calcd. for $C_{47}H_{35}CoN_2$: C, 82.20; H, 5.14; N, 4.08. IR (ν, cm^{-1}): 1620, 1589 vs (C=N). ^{1}H NMR (δ, 300 MHz, $CDCl_3$): 5.39 (2H, s, CpH), 5.79 (1H, s, CpH), 6.60–6.71 (4H, m, PhH), 7.08–7.29 (18H, m, PhH), 7.44–7.47 (8H, m, PhH), 7.75 (2H, s, CH=N). ^{13}C NMR (δ, 75 MHz, $CDCl_3$): 77.74 (C_4Ph_4), 81.59, 86.11, 95.52 (CpC), 120.78, 125.51, 127.00, 128.16, 128.79, 128.83, 134.67(PhC) 151.86 (*ipso*ph), 157.10 (C=N). HRMS: Calcd. for $C_{47}H_{35}CoN_2Na$ 709.2030, found 709.2034.

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Appendix A. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 880636 to 880642 for compounds **2**–**6**, **8** and **10** respectively. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK (fax (int code): +44 1223 336 033 or e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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