

Identification and characterization of intermediates in the formation of the cyclobutadiene linked dimeric cobalt sandwich compound $[(\eta^5\text{-RCp})\text{Co}(\eta^4\text{-C}_4\text{Ph}_3)]_2$ [R = H, CH₃C(O)O]

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Abstract. The synthesis of novel cyclobutadiene linked dimers of $[\eta^5\text{-RCp}]\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)$ was reported recently from a three-component reaction of 1,4-diphenylbutadiyne, diphenylacetylene and $[\eta^5\text{-RCp}]\text{Co}(\text{PPh}_3)_2$ [R = H or MeOC(O)]. The chiral *bis* oxazoline derivative of this dimer was found to form cobalt oxazolanyl palladacycles which were excellent chiral catalysts for the Overman–Claisen rearrangement of trichloroacetimidates, similar to the well-known COP catalysts. In this paper, we report reactions carried out for identifying the intermediates in the formation of the dimeric sandwich compound $\{[\eta^5\text{-MeOC(O)Cp}]\text{Co}(\eta^4\text{-C}_4\text{Ph}_3)\}_2$ (**1**). On varying the stoichiometric ratio of the reactants of the three component reaction, two new cobalt sandwich compounds $[\eta^5\text{-MeOC(O)Cp}]\text{Co}[\eta^4\text{-C}_4\text{Ph}_3(\text{C}\equiv\text{CPh})]$ (**2**) and $[\eta^5\text{-MeOC(O)Cp}]\text{Co}[\eta^4\text{-C}_4\text{Ph}_2(\text{C}\equiv\text{CPh})_2]$ (**3**) were found to form as viscous oily liquids. The identity of **2** was ascertained by oxidizing its alkyne moiety to yield crystalline $[\eta^5\text{-MeOC(O)Cp}]\text{Co}\{\eta^4\text{-C}_4\text{Ph}_3[\text{C(O)-C(O)Ph}]\}$ (**4**) which was structurally characterized. Further, the role of phenylethynyl derived monomeric sandwich compound **2** as a precursor to the dimeric compound **1** was established by reacting **2** with diphenylacetylene and CpCo(COD) which yielded the first example of an unsymmetrical cyclobutadiene linked dimeric cobalt sandwich compound $\{\eta^5\text{-[MeOC(O)Cp]Co}(\eta^4\text{-C}_4\text{Ph}_3)\}\{(\eta^5\text{-Cp})\text{Co}(\eta^4\text{-C}_4\text{Ph}_3)\}$ (**5**) which was also structurally characterized.

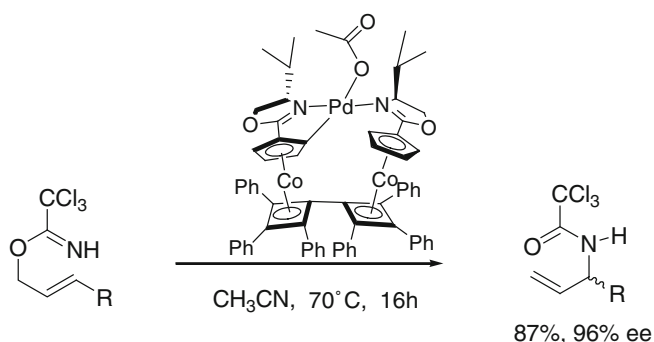
Keywords. Cyclobutadiene; cobalt sandwich; mechanism; dimer; unsymmetrical.

1. Introduction

Among metal sandwich compounds, the 18 electron cobalt complex $(\eta^5\text{-Cp})\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)$ has been found to be quite similar to ferrocene, especially in terms of air and moisture stability and ease of synthesis.^{1,2} We, as well as others have prepared a variety of compounds having different substituents on the cyclopentadienyl and cyclobutadiene rings of this compound.^{3–6} The most useful derivatives of $(\eta^5\text{-Cp})\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)$ are the chiral cobalt oxazoline palladacycles (COP catalysts) first reported by Overman, Richards and their coworkers.⁷ These palladacycles, which are commercially available are extremely efficient catalysts in promoting the Overman–Claisen rearrangement of trichloroacetimidates thereby providing a simple and elegant route

to chiral allylic amines which are not easily accessible otherwise.^{8,9} We have very recently reported the synthesis of the first examples of dimeric analogues of the COP catalysts derived from the cyclobutadiene linked dimer $\{[\eta^5\text{-MeOC(O)Cp}]\text{Co}(\eta^4\text{-C}_4\text{Ph}_3)\}_2$ and showed their efficiency in the Overman–Claisen rearrangement of selected trichloroacetimidates with high yield and good enantioselectivity (scheme 1).¹⁰ The preparation of these symmetrical dimers $[\eta^5\text{-RCpCo}(\eta^4\text{-C}_4\text{Ph}_3)]_2$ [R = H or MeOC(O)] in 40–50% yield was achieved by a three-component reaction involving 1,4-diphenylbutadiyne, diphenylacetylene and $[\eta^5\text{-RCp}]\text{Co}(\text{PPh}_3)_2$ [R = H or MeOC(O)] in the molar ratio 1:3:2. The mechanism of the formation of these novel dimers has not been studied so far and in this paper we have attempted to explore the same by identifying and characterizing a few vital intermediates formed during the reaction. We also illustrate how one of these intermediate can be utilized for preparing the hitherto unknown unsymmetrical dimers of $(\eta^5\text{-Cp})\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)$ as well.

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Scheme 1. Overman–Claisen rearrangement of trichloroacetimidates using the palladacycle derived from $[\eta^5\text{-MeOC(O)CpCo}(\eta^4\text{-C}_4\text{Ph}_3)]_2$.

2. Experimental

2.1 General methods

All manipulations of the complexes were carried out using standard Schlenk techniques under nitrogen atmosphere. Tetrahydrofuran, xylene and toluene were freshly distilled from sodium benzophenone ketyl under nitrogen atmosphere and used. $\text{CpCo}(\text{COD})^{14}$ and 1,4-diphenylbutadiyne¹¹ were prepared according to literature procedures. Diphenylacetylene and dimethylcarbonate (Aldrich) were used as received.

2.2 Instrumentation

^1H and ^{13}C $\{^1\text{H}\}$ spectra were recorded on a Bruker Spectrospin DPX-300 NMR spectrometer at 300 and 75.47 MHz, respectively. IR spectra in the range of 4000–250 cm^{-1} were recorded on a Nicolet Protège

460 FT-IR spectrometer as KBr pellets. Mass spectra (HRMS) were recorded on Bruker Micro-TOF QII quadrupole time-of-flight (Q-TOF) mass spectrometer. Elemental analyses were carried out on a Carlo Erba CHNSO 1108 elemental analyzer.

2.3 X-ray crystallography

Suitable crystals of compounds **4** and **5** were obtained by slow evaporation of their saturated solutions in ethyl acetate/hexane solvent mixtures. Single-crystal diffraction studies were carried out on a Bruker SMART APEX CCD diffractometer with a Mo $\text{K}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) sealed tube. 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. The crystal structures were solved and refined using the *SHELXTL* (version 6.12) package.¹² All hydrogen atoms were included in idealized positions, and a riding model was used. Non-hydrogen atoms were refined with anisotropic displacement parameters. Selected bond distances and angles for compounds **4** and **5** are given in tables 1 and 2. Crystal data: Compound **4**: $\text{C}_{37}\text{H}_{27}\text{O}_4\text{Co}$, $M = 594.52$, Triclinic, space group: ‘P-1’, $a = 9.320(2)$, $b = 11.026(2)$, $c = 14.877(3) \text{ \AA}$, $\alpha = 99.915(3)$, $\beta = 103.676(4)$, $\gamma = 97.358(3)^\circ$, $V = 1440.4(5) \text{ \AA}^3$, $Z = 2$, $\rho = 1.371 \text{ g cm}^{-3}$, $T(\text{K}) = 293$, $\lambda(\text{Å}) = 0.71073$, $F(000) = 616$, $\mu = 0.636 \text{ mm}^{-1}$, θ range = 1.44–24.00, R indices ($I > 2\sigma(I)$): $R1 = 0.0944$, $wR2$ (all data) = 0.2099, CCDC No. 829105. Crystal data: Compound **5**: $\text{C}_{56}\text{H}_{42}\text{O}_2\text{Co}_2$, $M = 864.76$, Monoclinic, space group: ‘P2₁/n’, $a = 16.443(4)$, $b = 11.502(3)$, $c = 22.368(6) \text{ \AA}$, $\beta = 98.600(5)^\circ$, $V = 4182.8(19) \text{ \AA}^3$, $Z = 4$,

Table 1. Selected bond lengths and bond angles of compound **4**.

Bond lengths (Å)			
Co(1)–C(1)	2.064(7)	Co(1)–C(6)	1.968(6)
O(1)–C(10)	1.201(10)	O(2)–C(10)	1.315(12)
O(2)–C(11)	1.492(10)	O(3)–C(12)	1.229(7)
O(4)–C(13)	1.208(7)	C(1)–C(2)	1.389(12)
C(1)–C(10)	1.489(13)	C(6)–C(7)	1.471(9)
C(6)–C(12)	1.439(9)	C(12)–C(13)	1.537(9)
Bond angles (deg)			
C(1)–Co(1)–C(7)	116.7(3)	O(1)–C(10)–C(1)	121.8(11)
O(1)–C(10)–O(2)	126.4(10)	C(10)–O(2)–C(11)	114.7(9)
O(3)–C(12)–C(6)	125.3(6)	O(4)–C(13)–C(12)	116.0(6)
O(4)–C(13)–C(14)	124.6(6)	C(1)–C(2)–C(3)	107.7(9)
C(6)–C(7)–C(8)	88.8(5)	C(6)–C(12)–C(13)	119.3(6)

Table 2. Selected bond lengths and bond angles of compound **5**.

Bond lengths (Å)			
O(1)-C(10)	1.209(9)	O(2)-C(11)	1.435(10)
O(2)-C(10)	1.339(9)	C(1)-C(10)	1.463(10)
C(1)-C(2)	1.427(9)	C(6)-C(17)	1.446(7)
C(17)-C(18)	1.471(7)	C(18)-C(21)	1.453(7)
C(1)-Co(1)	2.041(6)	C(6)-Co(1)	2.014(5)
Bond angles (deg)			
O(1)-C(10)-O(2)	122.4(9)	C(10)-O(2)-C(11)	118.6(8)
O(1)-C(10)-C(1)	125.9(9)	C(2)-C(1)-C(10)	126.2(7)
C(2)-C(1)-C(5)	106.2(6)	C(7)-C(6)-C(17)	136.1(5)

$\rho = 1.373 \text{ g cm}^{-3}$, $T(\text{K}) = 293$, $\lambda(\text{Å}) = 0.71073$, $F(000) = 1792$, $\mu = 0.837 \text{ mm}^{-1}$, θ range = 1.84–25.00, R indices ($I > 2\sigma(I)$): $R_1 = 0.0826$, wR_2 (all data) = 0.1663, CCDC No. 829104. $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$; $wR_2 = \sum (|F_o|^2 - |F_c|^2)^2 / \sum |F_o|^2$.

2.4 Reaction of 1,4-diphenylbutadiyne and diphenylacetylene with $[\eta^5\text{-MeO(O)C]CpCo(COD)}$

A solution containing MeO(O)C]CpCo(COD) (0.290 g, 1.00 mmol) and 1,4-diphenylbutadiyne (0.222 g, 1.10 mmol) in 50 mL of xylene was refluxed for 60 min. Diphenylacetylene (0.376 g, 2.10 mmol) in 30 mL of xylene was added to this and the mixture refluxed for 24 h. After completion of the reaction, the residue was chromatographed through a neutral alumina column using a hexane-ethylacetate mixture as the eluent. Using 4% ethylacetate/hexane mixture the first fraction came out which upon evaporation gave the monomeric sandwich compound $[\eta^5\text{-MeO(O)C]CpCo}(\eta^4\text{-C}_4\text{Ph}_4)]^7$ (Yield: 0.153 g, 0.28 mmol, 28%). The second fraction which came out at the same polarity upon evaporation gave a viscous liquid which was characterized as $[\eta^5\text{-MeO(O)C]CpCo}[\eta^4\text{-C}_4\text{Ph}_3(\text{C}\equiv\text{CPh})]$ (**2**) (Yield: 0.054 g, 0.10 mmol, 10%). IR (ν , cm^{-1}): 2186 (w, $\text{C}\equiv\text{CPh}$), 1714 (vs, $\text{C}=\text{O}$). HRMS: Calcd for $\text{C}_{37}\text{H}_{27}\text{CoO}_2\text{H}$. Exact mass: 583.1421 Measured mass: 583.1435. NMR (CDCl_3): ^1H , δ 3.31 (s, 3H, -CpH), 4.80 (s, 2H, -CpH), 5.20 (s, 2H, -CpH), 7.06–7.25 (m, 12H, $m + p\text{-PhH}$), 7.57–7.65 (m, 6H, $o\text{-PhH}$), 7.66–7.71 (m, 2H, $o\text{-PhH}$); $^{13}\text{C}\{^1\text{H}\}$, δ 51.29 (OCH_3) 76.40, 77.31, 78.44 (CbC), 84.51, 86.34, 86.73 (CpC), 94.34 (CbC $\equiv\text{CPh}$), 94.79 (CbC $\equiv\text{CPh}$), (PhC), 165.96 (Cp-C=O). On running the column at the same polarity a third fraction was obtained which upon evaporation gave a viscous liquid identified as $[\eta^5\text{-MeO(O)C]Cp}[\text{Co}[\eta^4\text{-C}_4\text{-Ph}_2(\text{C}\equiv\text{CPh})_2]$

(**3**) (Yield: 0.012 g, 0.02 mmol, 2%). IR (ν , cm^{-1}): 2190 (w, $\text{C}\equiv\text{CPh}$), 1712 (vs, $\text{C}=\text{O}$). HRMS: Calcd for $\text{C}_{39}\text{H}_{27}\text{CoO}_2$. Exact mass: 586.1346 Measured mass: 586.1343. NMR (CDCl_3): ^1H , δ 3.41 (s, 3H, -CpH), 4.83 (s, 2H, -CpH), 5.18 (s, 2H, -CpH), 7.33–7.35 (m, 6H, $m + p\text{-PhH}$), 7.41–7.42 (m, 6H, $m + p\text{-PhH}$), 7.62–7.64 (m, 4H, $o\text{-PhH}$), 7.88–7.89 (m, 4H, $o\text{-PhH}$). The fourth fraction which came out at 5% ethylacetate/hexane on evaporation gave a red crystalline compound which was characterized as the cyclobutadiene linked dimer $\{\eta^5\text{-[MeOC(O)Cp]Co}(\eta^4\text{-C}_4\text{Ph}_3)\}_2$ (**1**)¹⁰ (Yield: 0.085 g, 0.10 mmol, 18%).

2.5 Synthesis of $[(\eta^5\text{-MeOC(O)Cp)Co}[\eta^4\text{-C}_4\text{Ph}_3\{\text{C(O)-C(O)Ph}\}]]$ (**4**)

A mixture of **2** (0.080 g 0.14 mmol), I_2 (0.040 g, 0.15 mmol) and DMSO 8 mL was heated at 155°C for 24 h. The solution was thereafter poured into 1% aqueous $\text{Na}_2\text{S}_2\text{O}_3$ (20 mL), extracted with CH_2Cl_2 (50 mL) and extracts dried over Na_2SO_4 . Solvents were removed under vacuum and the residue was chromatographed on silicagel using 5% ethyl acetate-hexane as eluent to get a single fraction which upon evaporation gave a red crystalline solid which was characterized as $[\eta^5\text{-MeOC(O)Cp]Co}\{\eta^4\text{-C}_4\text{Ph}_3\{\text{C(O)-C(O)Ph}\}\}$ (**4**) (Yield: 0.070 g, 0.12 mmol, 83%). Mp: 126–128°C. IR (ν , cm^{-1}): 1254.90 s, 1280.64 s ($\text{C}=\text{C}$) 1624.57 vs, 1676.44 s, 1714.93 vs ($\text{C}=\text{O}$). NMR(CDCl_3). ^1H , δ 3.33 (s, 3H, - COOCH_3), 5.17 (s, 2H, -CpH), 5.36 (s, 2H, -CpH), 7.18–7.48 (m, 13H, -PhH), 7.56–7.59 (m, 5H, -PhH), 7.87–7.90 (m, 2H, -PhH). $^{13}\text{C}\{^1\text{H}\}$, δ 51.51 (OCH_3) 84.91, 86.44, 87.27, (CpC), 127.68, 127.73, 127.91, 128.19, 128.65, 128.93, 129.74, 129.97, 132.28, 132.74, 134.19 (PhC), 165.41(Cp-C=O), 192.86, 202.52 (Cb-C=O). Anal. Found: C, 74.72; H, 4.50 Calcd for $\text{C}_{37}\text{H}_{27}\text{O}_4\text{Co}$: C, 74.75; H, 4.58.

2.6 Synthesis of the dimer $[(\eta^5\text{-MeOC(O)Cp})\text{Co}(\eta^4\text{-C}_4\text{Ph}_3)] [(\eta^5\text{-Cp})\text{Co}(\eta^4\text{-C}_4\text{Ph}_3)]$ (**5**)

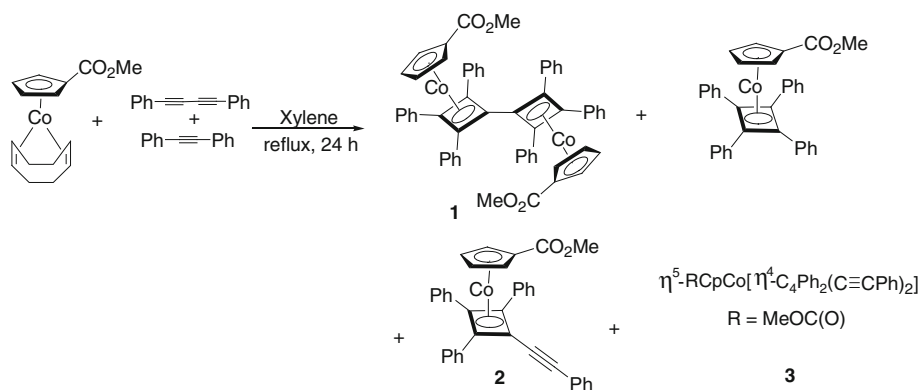
A solution containing $(\eta^5\text{-Cp})\text{Co}(\text{COD})$ (0.105 g, 0.40 mmol), $[\eta^5\text{-MeOC(O)Cp}]\text{Co}[\eta^4\text{-C}_4\text{Ph}_3(\text{C}\equiv\text{CPh})]$ (0.112 g, 0.20 mmol) and diphenylacetylene (0.107 g, 0.60 mmol) in 50 mL of xylene was refluxed for 48 h. The reaction was monitored by thin-layer chromatography and after complete consumption of $(\eta^5\text{-Cp})\text{Co}(\text{COD})$, the solvent was evaporated off and the remaining residue was chromatographed through a neutral alumina column using ethylacetate-hexane mixture as the eluent. While using a 2% ethylacetate/hexane mixture, the first fraction came out which upon evaporation gave a compound identified as $[(\eta^5\text{-Cp})\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)]^{1a}$ [yield: 0.038 g, 0.08 mmol, 20%]. On increasing the polarity up to 4% the second fraction came out which upon evaporation yielded a red crystalline solid which was identified as $[\eta^5\text{-MeOC(O)Cp}]\text{Co}(\eta^4\text{-C}_4\text{Ph}_3)[\eta^5\text{-Cp}]\text{Co}(\eta^4\text{-C}_4\text{Ph}_3)$ (**5**) (Yield: 0.095 g, 0.11 mmol, 55%). Mp: 190–192°C. Found: C, 77.56; H, 4.81. Calc. for $\text{C}_{56}\text{H}_{42}\text{O}_2\text{Co}_2$: C, 77.78; H, 4.90. IR (ν , cm^{-1}): 1709 vs (C=O), 1598 m, 1495 v, NMR(CDCl_3): ^1H , δ 3.28 (s, 3H, $-\text{COOCH}_3$), 4.58 (s, 2H, $-\text{CpH}$), 4.62 (s, 5H, $-\text{CpH}$), 5.20 (s, 2H, $-\text{CpH}$), 7.10–7.22 (m, 18H, $-\text{PhH}$), 7.28–7.34 (m, 4H, $-\text{PhH}$), 7.41–7.43 (m, 4H, $-\text{PhH}$); 7.47–7.50 (m, 4H, $-\text{PhH}$). $^{13}\text{C}\{^1\text{H}\}$, δ 51.17 (OCH_3) 70.40, 73.83, 76.88, 77.64, 78.06, 79.32 (CpC), 82.77, 84.38, 85.15, 86.94 (CpC), 126.08, 126.44, 126.51, 126.84, 127.58, 127.64, 127.87, 128.00, 130.21, 130.25, 134.52, 135.33, 136.67 (PhC), 166.56 (Cp-C=O).

An identical reaction were carried out with $[\eta^5\text{-MeOC(O)Cp}]\text{Co}(\text{COD})$ (0.117 g, 0.40 mmol), $[\eta^5\text{-MeOC(O)Cp}]\text{Co}[\eta^4\text{-C}_4\text{Ph}_3(\text{C}\equiv\text{CPh})]$ (0.112 g,

0.20 mmol) and diphenylacetylene (0.107 g, 0.60 mmol). After completion of reaction the solvent was evaporated off and the remaining residue was chromatographed through a neutral alumina column using ethylacetate-hexane mixture as the eluent. While using a 4% ethylacetate/hexane mixture, the first fraction came out which upon evaporation gave a compound identified as $[\eta^5\text{-MeOC(O)Cp}]\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)]^{7j}$ [(yield: 0.050 g, 0.09 mmol, 23% (based on COD)]. On increasing the polarity up to 5% the second fraction came out which upon evaporation yielded a red crystalline solid which was identified as $\{\eta^5\text{-[MeOC(O)Cp]Co}(\eta^4\text{-C}_4\text{Ph}_3)\}_2$ (**1**)¹⁰ (Yield: 0.085 g, 0.10 mmol, 50%).

3. Results and discussion

While both $\text{RCpCo}(\text{COD})$ and $\text{RCpCo}(\text{PPh}_3)_2$ can yield monomeric and dimeric cobalt sandwich compounds, the present study has been carried out using the former due to ease of purification of products as well as relatively better yields of the intermediates as observed from preliminary studies. The reactions of 1,4-diphenylbutadiyne, diphenylacetylene in different stoichiometries were carried out with $(\eta^5\text{-RCp})\text{Co}(\text{COD})$ [$\text{R} = \text{MeOC(O)}$]. The reactions yielded the monomer $(\eta^5\text{-RCp})\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)$ as the major product along with the dimer $[\eta^5\text{-MeOC(O)Cp}]\text{Co}(\eta^4\text{-C}_4\text{Ph}_3)]_2$ (**1**), a monoalkyne $[\eta^5\text{-MeOC(O)Cp}]\text{Co}[\eta^4\text{-C}_4\text{Ph}_3(\text{C}\equiv\text{CPh})]$ (**2**) and a dialkyne $[\eta^5\text{-MeOC(O)Cp}]\text{Co}[\eta^4\text{-C}_4\text{Ph}_2(\text{C}\equiv\text{CPh})_2]$ (**3**) (scheme 2). The reaction parameters and isolated yield of compounds are given in table 3. As the table indicates, the monoalkyne compound **2** was found to form in almost all reactions with yields varying from 8 to 22% and it was also evident that



Scheme 2. Synthesis of compound 1.

Table 3.

Ratio of RCpCo(COD): PhC≡CPh: PhC≡C–C≡CPh (mol %)	Isolated yield of products (%) [#]			
	1	2	3	monomer
1:4:2	10	22	3	25
2: 2:1	16	9	2	32
2 :3:1	14	8	2	35
1:2:1	18	10	2	28
2:3:1*	41	45

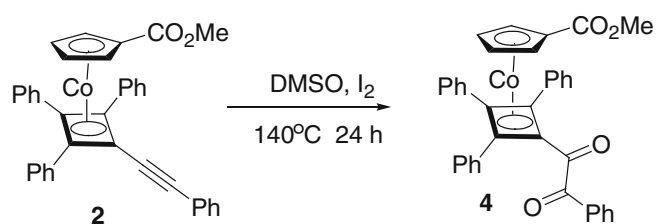
[#]In refluxing xylene for 24 h; Yields based on MeOC(O)-CpCoCOD;

*MeOC(O)CpCo(PPh₃)₂ was used and addition of reagents were carried out in 2 steps.¹⁰

wherever the dimer **1** has formed in better yields, it has been at the expense of **2**. This observation suggests that compound **2** is possibly an intermediate in the formation of **1**. The formation of the dialkyne **3** was found to be only in traces in spite of varying the reaction parameters. A reported reaction carried out using [η^5 -RCp]Co(PPh₃)₂ in 2:3:1 molar ratio in two stages did not yield compounds **2** and **3** and gave the monomer and dimer **1** as the only isolable products.¹⁰

The identity of compound **2** was ascertained by oxidation of its alkyne moiety with DMSO and iodine¹³ which gave the alkyne oxidized product **4** in 83% yield (scheme 3). Unlike **2**, compound **4** was found to be a solid whose crystal structure was also determined. Compound **3** was found to form only in trace amounts as a viscous liquid and was also found to be contaminated with **2** which came in the way of its further derivatization.

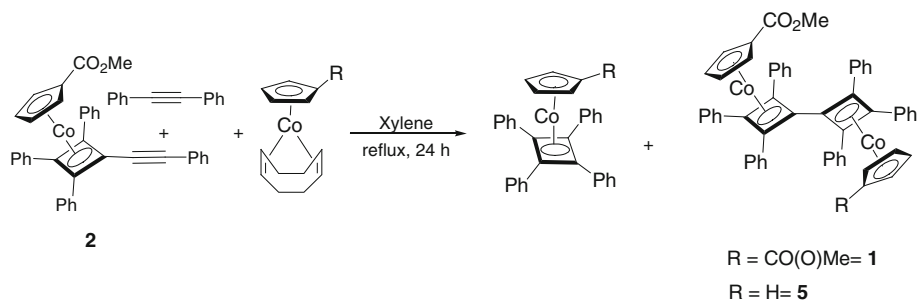
A reaction of **2** with (η^5 -Cp)Co(COD) and diphenylacetylene in the molar ratio 1:2:3 was found to proceed readily in refluxing xylene and yielded the first example of an unsymmetrical cyclobutadiene linked dimer { η^5 -[MeOC(O)Cp]Co(η^4 -C₄Ph₃)}[(η^5 -Cp)Co(η^4 -C₄Ph₃)] (**5**) in 55% yield along with the monomer [η^5 -Cp]Co(η^4 -C₄Ph₄) (scheme 4). An identical reaction of **2** using [η^5 -MeOC(O)Cp]Co(COD) instead of (η^5 -Cp)Co(COD) gave the symmetrical

**Scheme 3.** Oxidation of **2** to **4**.

dimer **1** in 50% yield. These reactions conclusively prove that compound **2** is an intermediate in the formation of cyclobutadiene linked dimers of [η^5 -Cp]Co(η^4 -C₄R₄) and also provide a simple route to prepare unsymmetrical examples of such dimeric compounds.

Consolidating the information obtained from these specific reactions, we propose a scheme showing the possible pathways and intermediates involved in the formation of cyclobutadiene linked dimer **1** and related compounds (scheme 5).

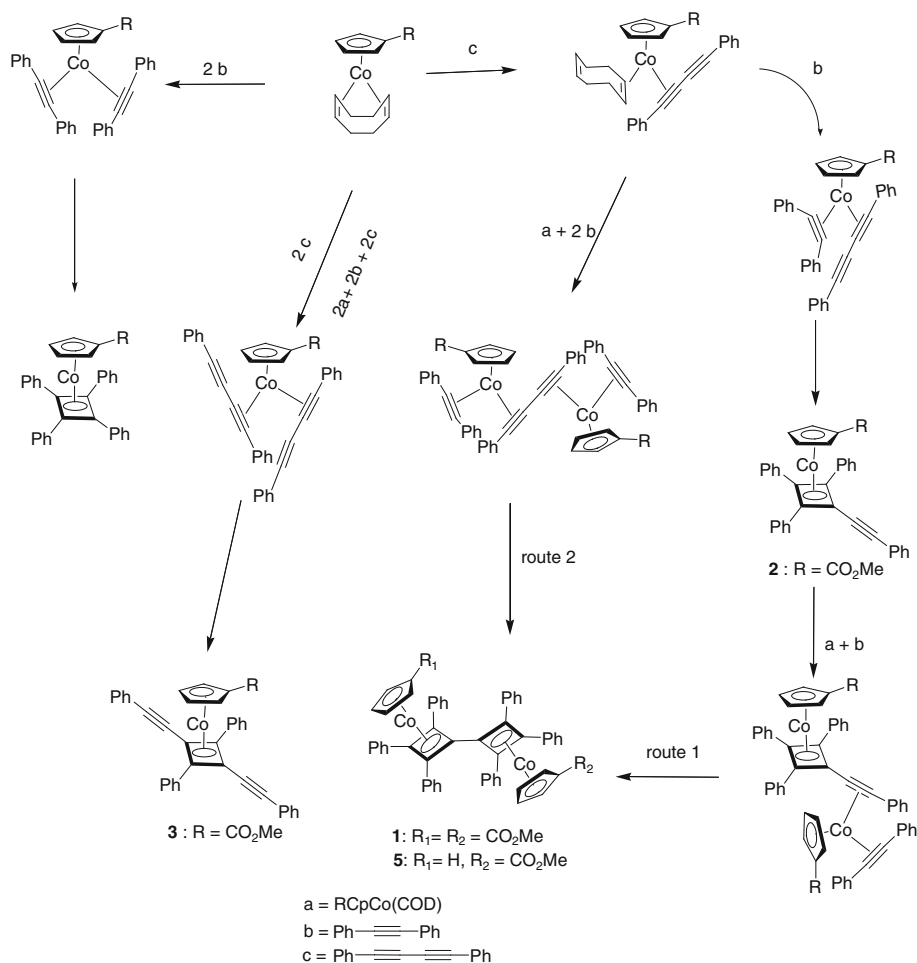
The first step of all these reactions involves the displacement of COD or PPh₃ with alkynes or butadiyne, a step which has been well-documented.^{4e,15} As scheme 5 shows there exists the possibility of two alkynes, two butadiynes or a combination of one an alkyne and a butadiyne being bound to the the RCpCo unit. Since the least sterically hindered is the first among these, it does happen in all three component reactions leading to the formation of the monomer [η^5 -RCp]Co(η^4 -C₄Ph₄). The coordination of two dialkynes to RCpCo unit is least likely and the fact that compound **3** is obtained only in trace amounts confirms this statement. Compound **2** is formed when both alkyne and butadiyne are bound to the same RCpCO unit. It needs to be mentioned that the formation of the sandwich compounds is preceded in all cases by an oxidative coupling of the alkyne moieties leading to the formation of an unstable cobaltacyclopentadiene which rearranges to the stable 18 electron metal sandwich compound. As shown in the present study (scheme 5) compound **2** gets converted to the cyclobutadiene linked dimer **1** (route 1, scheme 5). A similar reaction on compound **3** having two alkyne groups should lead to a cyclobutadiene linked trimer. Such a trimer has indeed been found to form in trace amounts when reactions involving CpCo(COD) with 1,4-diphenylbutadiyne and diphenylacetylene has been carried out.¹⁰ It is of importance to mention that an



Scheme 4. Synthesis of compounds **1** and **5**.

alternate route also exists for the formation of the cyclobutadiene lined dimer (route 2, scheme 5) which can result from the partial opening of the COD unit accommodating a butadiyne which further is the focal point of reactions with another CpCoCOD unit and fur-

ther displacement of the COD units by alkynes. Verifying this route by isolation of intermediates was found to be tedious and has not been possible so far. However, the existence of route 1 has been conclusively proved in the present work.



Scheme 5. Possible routes suggested for the synthesis of compounds **1–3** and **5**.

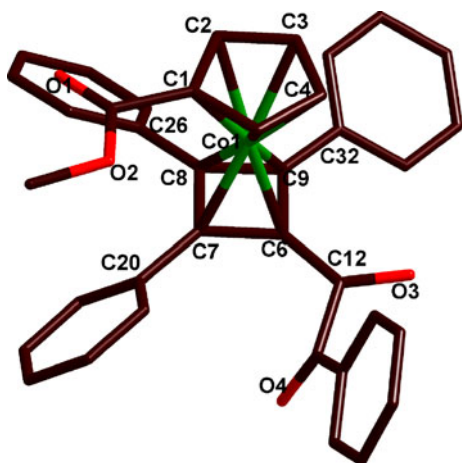


Figure 1. Crystal structure of compound **4** (hydrogen atoms have been omitted for clarity).

3.1 Spectral and crystal structure studies of compounds **4** and **5**

The crystal structures of the compounds **4** and **5** are given in figures **1** and **2**, respectively. The structure of **4** shows the oxidized acetylene unit with the two C=O units at an angle of $60.5(3)^\circ$ with each other. The three phenyl units are found to be at angles of $44.5(3)^\circ$, $36.8(3)^\circ$ and $29.6(3)^\circ$ with the Cb unit which is almost planar. The CpCoCb units of this molecule are found to be in almost *anti* orientation to each other with an angle of $7.0(2)^\circ$ between the two Cb units. This is slightly different from analogous structurally characterized symmetrical dimers where these units are perfectly *anti* to each other.¹⁰ The bond connecting the two Cb rings are of the distance $1.446(6)\text{\AA}$ indicating partial double bond character. The phenyl groups on the Cb rings are at angles in the range of $1.9(2)^\circ$

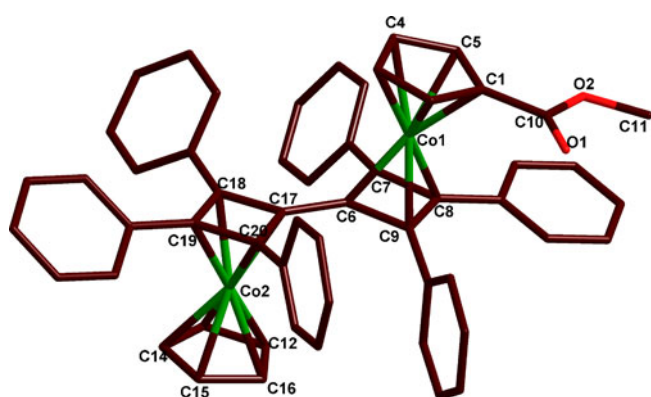


Figure 2. Crystal structure of the monoester **5** (hydrogen atoms have been omitted for clarity).

to $89.8(2)^\circ$ with the Cb unit. In the ^1H NMR, twenty protons of the four phenyl rings of compound **2** gave three peaks in the ratio 2:6:12 and compound **3** shows four peaks in the ratio 4:4:6:6 whereas the monomer $[\eta^5\text{-RCp}]\text{Co}(\eta^4\text{-C}_6\text{H}_5)_4$ shows only two peaks in the ratio 8:12 for the same number of phenyl hydrogens. This variation clearly supports the identities of compounds **2** and **3**. The ^{13}C NMR data of symmetrical dimers shows only three peaks whereas ^{13}C NMR of the unsymmetrical compound **5** gives six peaks as expected in the Cb region. For the Cp protons, ^1H NMR gave three peaks in ratio 2:5:2 at 4.58, 5.20 and 4.62 ppm, respectively. For the analogous symmetrical diester, two peaks in the ratio 1:1 at 4.63 and 5.23 ppm has been reported.¹⁰

4. Conclusion

The mechanism of the formation of cyclobutadiene linked dimers of the cobalt sandwich compound $(\eta^5\text{-Cp})\text{Co}(\eta^4\text{-C}_6\text{H}_5)_4$ has been studied. By varying the reaction parameters, two intermediate compounds having a monoalkyne derived cyclobutadiene ring $[\eta^5\text{-MeOC(O)Cp}]\text{Co}[\eta^4\text{-C}_6\text{H}_5(\text{C}\equiv\text{CPh})]$ **2** and a dialkyne derived cyclobutadiene ring $[\eta^5\text{-MeOC(O)Cp}]\text{Co}[\eta^4\text{-C}_6\text{H}_5(\text{C}\equiv\text{CPh})_2]$ **3** were isolated as viscous liquids. The identity of **2** was conclusively proved by oxidizing the alkyne moiety in the molecule to yield the solid $[\text{MeOC(O)Cp}]\text{Co}\{\eta^4\text{-C}_6\text{H}_5[\text{C(O)-C(O)Ph}]\}$ whose crystal structure was determined. Further, the role of **2** as an intermediate was ascertained by reacting it with CpCo(COD) and diphenylacetylene to yield the first example of an unsymmetrical cyclobutadiene linked dimer $\{\eta^5\text{-[MeOC(O)Cp]Co}(\eta^4\text{-C}_6\text{H}_5)\}\{[\eta^5\text{-Cp}]\text{Co}(\eta^4\text{-C}_6\text{H}_5)\}$ **5** which was also structurally characterized. The dialkyne substituted cyclobutadiene compound **3** was obtained only in traces which possibly is an intermediate for the small amounts of cyclobutadiene linked trimer observed to form in the three component reactions involving 1,4-diphenylbutadiyne, diphenylacetylene and $[\eta^5\text{-RCp}]\text{Co}(\text{COD})$ [R = H].¹⁰ The unsymmetrical dimer **5** prepared and structurally characterized in this study and the methodology used for its synthesis provides scope for developing a wide range of unsymmetrical chiral and non-chiral palladacycles similar to COP catalysts.

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