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Thermolysis of $[(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{PPh}_3)(\eta^2\text{-DMAD})]$, revisited: a solid state analysis reveals the true structure of the triphenylphosphine–alkyne coupling product

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Abstract

Thermolysis of the η^2 -alkyne complex $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{PPh}_3)[\eta^2\text{-(MeO}_2\text{C)C=C(CO}_2\text{Me)}]$ (**1**-DMAD) leads to formation of an *ortho*-metalated vinyl-phosphonium derivative $(\eta^5\text{-C}_5\text{H}_5)\text{Co}[\eta^2\text{-(MeO}_2\text{C)HC=C(CO}_2\text{Me)PPh}_2(\eta^1\text{-}o\text{-C}_6\text{H}_4)]$ (**4**) as well as a small amount of the tricobalt bis(carbyne) cluster $[(\eta^5\text{-C}_5\text{H}_5)\text{Co}]_3[\mu^3, \eta^3\text{-C(CO}_2\text{Me)}_2]$ (**3**-CO₂Me). Thermolysis of **1**-DMAD in the presence of added triphenylphosphine gives **4** as the major product, with no evidence for formation of **3**-CO₂Me. Complexes **4** and **3**-CO₂Me were characterized by X-ray crystallographic analyses.

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Keywords: Cobalt–alkyne; Vinyl-phosphonium; Ortho-metalation; Carbon–hydrogen bond activation

1. Introduction

An important approach toward carbon–hydrogen bond activation and functionalization is the hydroarylation of triple bonds, wherein an alkyne inserts into a phenyl carbon–hydrogen bond. [1] One of the earliest examples of cobalt-mediated hydroarylation was a 1979 report on the thermal conversion of $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{PPh}_3)[\eta^2\text{-C(CO}_2\text{Me)=C(CO}_2\text{Me)}]$ (**1**-DMAD) to an alkyne insertion product which was proposed to have structure **2** (22% yield; Scheme 1) [2,3]. The structural assignment for **2** was consistent with the observation of resonances in the ¹H-NMR (CDCl₃) spectrum at δ 2.05 (d, J = 13 Hz, 1H), 3.45 (s, 3H), 3.68 (s, 3H), 4.60 (s, 5H), and 6.5–8.5 (phenyl hydrogens); and fragment ion peaks in the mass spectrum corresponding to C₂₃H₁₈O₃P and C₂₂H₁₈O₂P. In most cases, the thermal decomposition of $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{PPh}_3)[\eta^2\text{-(R}^1\text{C}\equiv\text{CR}^2)]$ (**1**) led to the formation of tricobalt bis(carbyne) clusters $[(\eta^6\text{-C}_5\text{H}_5)\text{Co}]_3[\mu^3, \eta^3\text{-CR}^1][\mu^3, \eta^3\text{-CR}^2]$ (**3**, R¹ or R² = TMS, Ph, CN, Me, C≡CTMS,

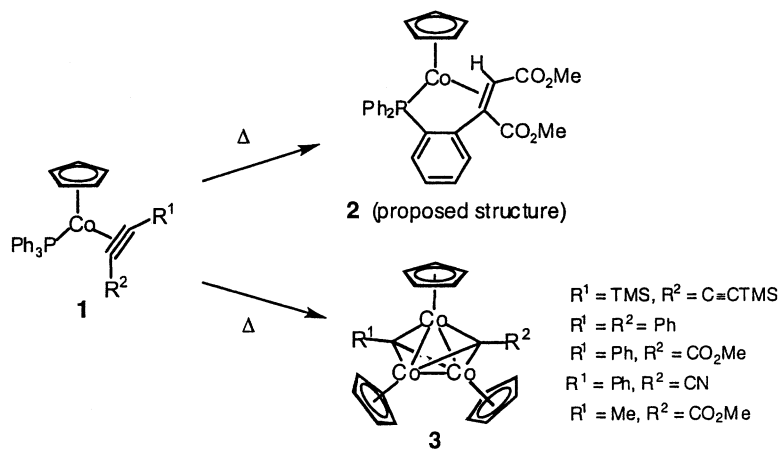
CO₂Me; Scheme 1), with no observable alkyne insertion products [2,4]. It was suggested that the unique reactivity observed for **1**-DMAD was due to the presence of two strong electron-withdrawing groups on the alkyne ligand.

Here we report the true structure of **2** to be the *ortho*-metalated vinyl-phosphonium derivative **4**, as revealed by an X-ray crystallographic analysis. Structural characterization of the bis(carbyne) cluster $[(\eta^5\text{-C}_5\text{H}_5)\text{Co}]_3[\mu^3, \eta^3\text{-C(CO}_2\text{Me)}_2]$ (**3**-CO₂Me) is also reported.

2. Results and discussion

Mononuclear cobalt–alkyne complexes of the general type $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{PPh}_3)(\eta^2\text{-alkyne})$ (**1**) are useful precursors for the synthesis of metallaiminocyclobutenes [5], metallacyclopentenenes [6], alkene complexes [7], diene complexes [8], cyclobutadiene complexes [9], metallacyclopentene complexes [10], metallacyclopentadiene complexes [11], and a variety of products stemming from [2+2+2] cyclization reactions [12]. During the course of studies on the use of cobalt–alkyne complexes, **1**, as precursors to metallacyclobutenes [13], we observed that

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Scheme 1.

$(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{PPh}_3)[\eta^2\text{-(CO}_2\text{Me)C}\equiv\text{C(CO}_2\text{Me)}]$ (**1**-DMAD) underwent a slow thermal decomposition to a new complex, **4**, which was confirmed by NMR spectroscopy to be identical to the compound previously assigned structure **2**. After heating a benzene- d_6 solution of **1**-DMAD, containing 0.5 equivalents of PPh_3 , at 60°C for 27 days, a ^1H -NMR spectrum of the sample indicated the presence of 34% **1**-DMAD, 43% of **4**, and 6.5% of bis(carbyne) **3**- CO_2Me . When a similar reaction

was carried out in the presence of a large excess of PPh_3 the formation of **3**- CO_2Me was not observed.

An X-ray crystallographic analysis (Fig. 1, Tables 1 and 2) of **4** revealed that *ortho*-metalation of the triphenylphosphine ligand had indeed occurred, but that a phosphorus and hydrogen had added across the alkyne triple bond to give a zwitterionic vinyl-phosphonium complex, rather than the originally proposed alkyne hydroarylation product. The five-membered

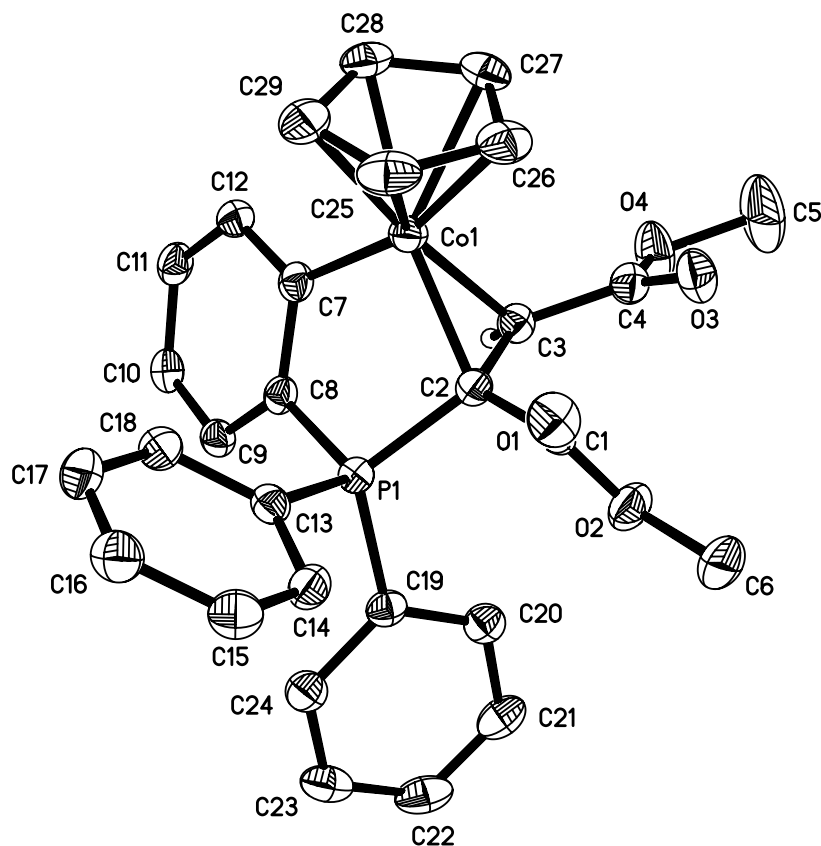


Fig. 1. An ORTEP view of vinyl-phosphonium complex (**4**) (50% probability thermal ellipsoids). Hydrogen atoms are omitted for clarity.

Table 1
Selected bond lengths and angles for (4)

Bond lengths (Å)							
A	B	Distance	A	B	Distance		
Co	C(7)	1.9318 (16)	C(2)	C(1)	1.510(2)		
Co	C(2)	1.9605 (16)	C(3)	C(4)	1.467(2)		
Co	C(3)	1.9984 (16)	C(1)	O(1)	1.199 (2)		
C(7)	C(8)	1.412 (2)	C(1)	O(2)	1.347 (2)		
C(8)	C(9)	1.397 (2)	C(4)	O(3)	1.214 (2)		
C(9)	C(10)	1.386 (2)	C(4)	O(4)	1.355 (2)		
C(10)	C(11)	1.392 (2)	C(8)	P(1)	1.7692 (16)		
C(11)	C(12)	1.389 (2)	C(13)	P(1)	1.8011 (16)		
C(12)	C(7)	1.414 (2)	C(19)	P(1)	1.8003 (16)		
C(2)	C(3)	1.461 (2)	C(2)	P(1)	1.7707 (16)		
Bond angles (°)							
A	B	C	Angle	A	B	C	Angle
C(7)	Co	C(2)	92.03(7)	C(3)	C(2)	Co	69.73 (9)
C(7)	Co	C(3)	88.01 (7)	C(2)	C(3)	Co	66.97 (9)
C(2)	Co	C(3)	43.30 (6)	C(8)	C(7)	Co	117.28 (11)
C(8)	P(1)	C(2)	102.94 (7)	C(7)	C(8)	P(1)	110.59 (11)
C(8)	P(1)	C(13)	110.50 (7)	C(2)	C(3)	C(4)	119.08 (14)
C(8)	P(1)	C(19)	110.74 (7)	C(2)	C(1)	O(1)	127.18 (16)
C(3)	C(2)	C(1)	120.98 (14)	C(3)	C(4)	O(3)	127.40 (16)
C(3)	C(2)	P(1)	117.76 (11)				

metallacycle ring consisting of Co–C(7)–C(8)–P–C(2) is puckered, with a pronounced fold angle of 36.6° between the Co–C(7)–C(8)–P, and Co–C(2)–P mean

Table 2
Crystal data and structure refinement for (4) and (3–CO₂Me)

Compound	(4)	(3–CO ₂ Me)
Molecular formula	C ₂₉ H ₂₆ CoO ₄ P	C ₂₁ H ₂₁ Co ₃ O ₄
Molecular weight	528.40	514.17
Color	red	purple
Crystal system	monoclinic	monoclinic
Space group	<i>P</i> 2(1)/ <i>n</i>	<i>C</i> 2/ <i>c</i>
Temperature (K)	150(2)	100(2)
<i>a</i> (Å)	9.5920(14)	15.440(2)
<i>b</i> (Å)	14.558(2)	9.2788(12)
<i>c</i> (Å)	17.362(3)	14.8018(19)
α (°)	90	90
β (°)	93.871(2)	115.818(2)
γ (°)	90	90
<i>V</i> (Å ³)	2419.0(6)	1908.9(4)
<i>Z</i>	4	4
<i>D</i> _{calc} (cm m ^{−3})	1.451	1.789
Absorption, coefficient, (mm ^{−1})	0.810	2.601
Crystal size (cm ³)	0.40 × 0.24 × 0.14	0.19 × 0.15 × 0.08
Wavelength (Å)	0.71073	0.71073
Reflections collected	20 683	7989
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data/parameters	5550/348	2184/179
Goodness-of-fit	1.057	1.087
Final <i>R</i> indices	<i>R</i> ₁ = 0.0319, <i>wR</i> ₂ = 0.0810	<i>R</i> ₁ = 0.0200, <i>wR</i> ₂ = 0.0511
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0382, <i>wR</i> ₂ = 0.0842	<i>R</i> ₁ = 0.0213, <i>wR</i> ₂ = 0.0518

planes. The deviations of C(2) and C(3) from the mean plane defined by Co–C(7)–C(8)–P are −0.68 and −1.80 Å, respectively. The alkene bonding to cobalt in 4 is unsymmetrical with cobalt–carbon distances of 1.9605(16) Å and 1.9984(16) Å for Co–C(2) and Co–C(3), respectively.

A related aryl–alkene complex, (η⁵-C₅H₅)Co(η²-CH₂CH₂)[C₆H₅MgBr (tmeda)] (5), was previously char-

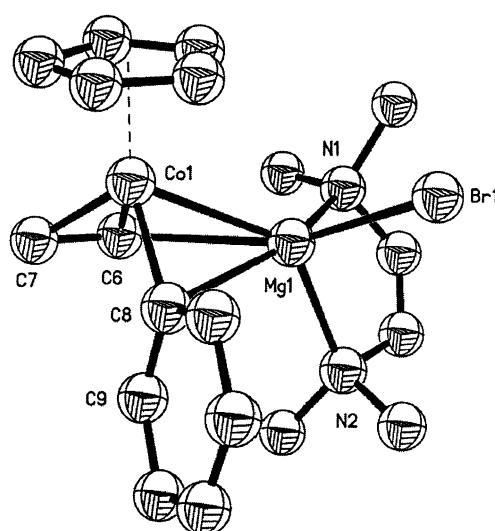


Fig. 2. Solid state structure of (5) with the atom numbering scheme from Ref. [14]. Selected bond lengths (Å) and angles (°): Co–C(6) 2.01, Co–C(7) 1.981, Co–C(8) 1.977, Co–Mg 2.565, Mg–C(8) 2.572; C(6)–C(7) 1.434, C(6)–Co–C(8) 95.21, C(7)–Co–C(8) 93.58, Mg–Co–C(8) 67.41, C(6)–C(7)–Co 70.03; C(7)–C(6)–Co 67.85.

acterized by X-ray crystallography (Fig. 2) [14]. In the case of **5**, the magnesium atom is within bonding distance to both cobalt and C(8) of the phenyl ligand. By comparison the cobalt–phosphorus non-bonded distance in **4** is 2.930(3) Å. The cobalt–aryl bond distance, Co–C(7), in **4** is 0.04 Å shorter than the corresponding distance, Co–C(8), in **5**. The C(2)–C(3) alkene distance of 1.461(2) Å in **4** is significantly longer than the C(6)–C(7) double bond distance in **5**, as expected for a greater degree of π -backbonding.

Vinyl–phosphonium complexes have been previously prepared from *ortho*-metalation reactions of allyl–phosphonium salts. For example, reaction of $\text{PtCl}_2(\text{NPh})_2$ and $[\text{Ph}_3\text{PCH}_2\text{CH}=\text{CH}_2]\text{Cl}$ in 2-methoxyethanol at reflux (22 h) leads to a 61% yield of the vinyl–phosphonium complex **6** (Scheme 3) [15]. In the ^1H -NMR spectrum of **6** (CD_2Cl_2) the vinyl hydrogen resonance at δ 4.56 exhibits a coupling constant $^3J_{\text{P-H}} = 17.1$ Hz. For **4** the related *cis* phosphorus–hydrogen coupling constant is $^3J_{\text{P-H}} = 13$ Hz [2]. The platinum–alkene bond lengths in **6** are similar within experimental error.

The formation of **4** from **1**-DMAD involves the breaking of carbon–hydrogen and cobalt–phosphorus bonds, and the formation of cobalt–carbon, carbon–phosphorus and carbon–hydrogen bonds; making the mechanism of formation a complex process. Triphenylphosphine is known to react with DMAD to give the reactive zwitterion, $[\text{Ph}_3\text{P}^+\text{C}(\text{CO}_2\text{Me})=\text{C}=\text{C}(\text{O}^-)(\text{OMe})]$ (**7**, Fig. 3) [16]. Thus, alkyne dissociation followed by reaction with PPh_3 could generate **7**, followed by reaction at cobalt to give intermediate **8**. At least two reasonable mechanisms with no alkyne dissociation are also possible. Intermediate **8** could form by either an intramolecular migration of PPh_3 from cobalt to the coordinated alkyne, or via an intermolecular attack of PPh_3 at the alkyne ligand. *Ortho*-metalation [17] from **8** to give a cobalt(III) hydride complex and reductive elimination would then generate **4**. Alternatively, a mechanism involving cyclopentadienyl ring-slippage followed by *ortho*-metalation of the PPh_3 ligand to give intermediate **9** is a possibility. Migration of phosphorus from cobalt to the alkyne ligand in **9** would lead to a vinyl hydride complex from

which a reductive elimination of the hydride and vinyl ligands would give **4**.

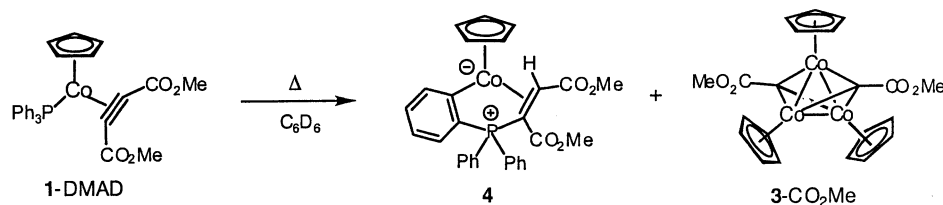
A vinyligous analogue of **4** is the dienyl–phosphonium complex **10**, formed from reaction of ruthenium cation **11** and two equivalents of alkyne (Scheme 4). The proposed mechanism for the formation of **10** involves an intramolecular migration of PPh_3 from ruthenium to the alkyne-derived metallacyclopentatriene α -carbon, followed by *ortho*-metalation of the PPh_3 substituent and hydride migration to the carbene ligand [18].

Finally, in addition to vinyl–phosphonium complex **4**, thermolysis of **1**-DMAD led to the isolation of a small amount of crystalline $[(\eta^5\text{-C}_5\text{H}_5)\text{Co}]_3[\mu^3, \eta^3\text{-C}(\text{CO}_2\text{Me})]_2$ (**3**- CO_2Me ; Scheme 2). Complex **3**- CO_2Me was previously prepared in 16% yield from the high temperature reaction of $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$ and DMAD [4b]. Trinuclear bis(carbyne) clusters are of interest as substrates for the study of surface-homogeneous cluster analogies [4b] and as building blocks for new materials [19]. We therefore determined the solid state structure of **3**- CO_2Me (Fig. 4, Table 2) and provide bond length and angle data in the caption for Fig. 4 and in the supplementary material.

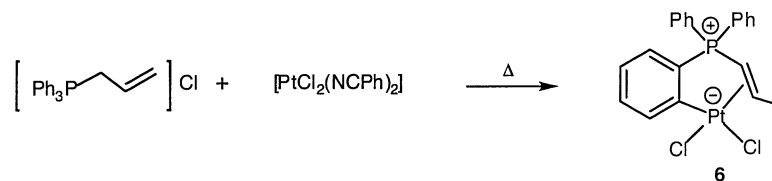
3. Experimental

3.1. Conversion of (**1**-DMAD) to (**3**- CO_2Me) and (**4**)

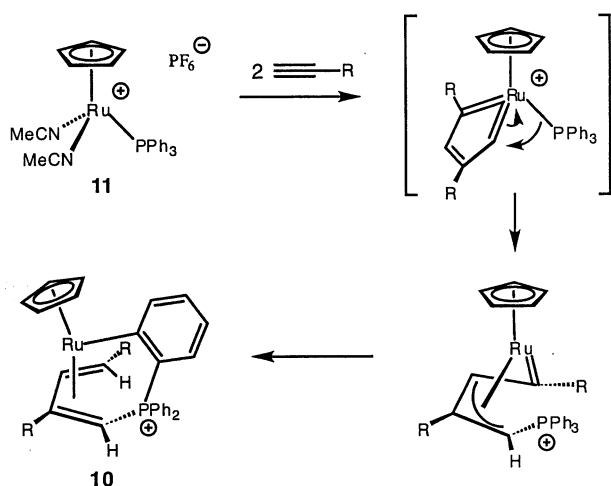
In a sealed NMR tube under a nitrogen atmosphere, a benzene- d_6 solution (0.51 ml) of (**1**-DMAD) (12.2 mg, 0.023 mmol, 0.046 M), PPh_3 (30.3 mg, 0.116 mmol, 0.226 M) and toluene (as internal standard) was heated at 60 °C. After 53 d, analysis of the sample by ^1H -NMR spectroscopy indicated a 70% yield of vinyl–phosphonium complex (**4**) and the presence of 16% starting material (**1**-DMAD). There was no evidence of bis(carbyne) cluster (**3**- CO_2Me). In a separate experiment, an NMR tube containing **1**-DMAD and 0.53 equivalents of PPh_3 was heated for 27 d at 60 °C. A ^1H -NMR spectrum of the sample indicated 39.5% starting material along with 30% of (**4**) and 6.1% of bis(carbyne) cluster (**3**- CO_2Me). The reaction temperature was then maintained at 100 °C for 7 d resulting in 28% **1**-DMAD, 50% **4**, and



Scheme 2.



Scheme 3.



Scheme 4.

4% 3- CO_2Me . Further heating of the sample led to slow decomposition of the identified products.

In a preparative scale experiment **1**-DMAD (0.153 g, 0.290 mmol) and PPh_3 (0.758 g, 2.89 mmol) were heated in dry benzene (ca. 5 ml) at 60°C . After 40 d the volatiles were removed in vacuo and the crude mixture subjected to chromatography (silica gel, 10–30% ethyl acetate/hexanes) in the air to give **4** (0.069 g, 45% yield) as air-stable dark orange crystals. X-ray quality crystals were grown by slow evaporation of the benzene solvent. ^1H -NMR (C_6D_6): δ 2.55 (d, 1H, $J_{\text{P-H}} = 13.8$ Hz), 3.32 (s, 3H), 3.56 (s, 3H), 4.89 (s, 5H), 6.64 (m, 3H), 6.83–7.13 (m, 6H), 7.64 (m, 4H), 8.10 (m, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 36.6, 50.8, 51.7, 85.6, 122.0 (d, $J_{\text{P-C}} = 13.5$ Hz), 124.9, 125.3 (d, $J_{\text{P-C}} = 4.3$ Hz), 126.0, 127.9, 128.3 (d, $J_{\text{P-C}} = 14.7$ Hz), 128.8 (d, $J_{\text{P-C}} = 10.9$ Hz), 130.9 (d, $J_{\text{P-C}} = 19.5$ Hz), 131.5, 132.2 (d, $J_{\text{P-C}} = 3.0$ Hz), 132.5, 132.7 (d, $J_{\text{P-C}} = 2.5$ Hz), 133.6 (d, $J_{\text{P-C}} = 9.2$ Hz), 134.5 (d, $J_{\text{P-C}} = 9.2$ Hz), 144.2 (d, $J_{\text{P-C}} = 17.6$ Hz), 172.6 (d,

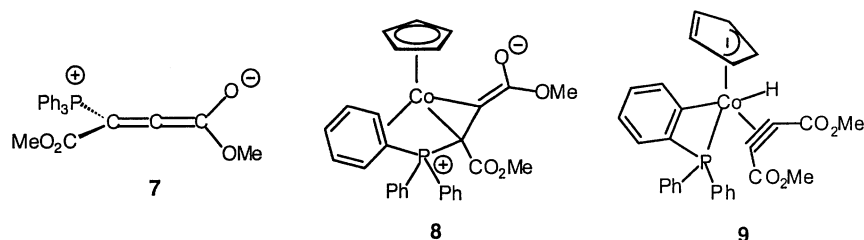
$J_{\text{P-C}} = 9.1$ Hz), 178.0 (d, $J_{\text{P-C}} = 10.9$ Hz), 186.7 (d, $J_{\text{P-C}} = 25.0$ Hz).

3.2. X-ray structure determination of $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\eta^2\text{-(MeO}_2\text{C)HC=C(CO}_2\text{Me)PPh}_2)(\eta^1\text{-o-C}_6\text{H}_4)]$ (**4**)

A single crystal with dimensions $0.40 \times 0.24 \times 0.14$ mm³ was immersed in paratone and placed on a glass fiber. Data was collected on a Bruker SMART (APEX) CCD diffractometer by using graphite monochromator with Mo- K_α radiation ($\lambda = 0.71073$ Å) at 150 K. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 . Atom H3 (the hydrogen atom on C3) was refined, but all other hydrogen atoms were geometrically fixed on their attached atoms [20]. Table 2 summarizes the crystal data collection and refinement parameters.

3.3. X-ray structure determination of bis(carbyne) cluster $[(\eta^5\text{-C}_5\text{H}_5)\text{Co}]_3[\mu^3, \eta^3\text{-C(CO}_2\text{Me)}_2]_2$ (3- CO_2Me)

A single crystal with dimensions $0.19 \times 0.15 \times 0.08$ mm³ was immersed in paratone and placed on a glass fiber. Data was collected on a Bruker SMART (APEX) CCD diffractometer by using graphite monochromator with Mo- K_α radiation ($\lambda = 0.71073$ Å) at 100 K. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 . All hydrogen atoms were geometrically fixed on their attached atoms during the refinement. Equivalent atoms were generated by the symmetry transformation $-x+2, y, -z+1/2$ [20]. Table 2 summarizes the crystal data collection and refinement parameters.

Fig. 3. Mechanistic considerations for the formation of **4** from **1**-DMAD.

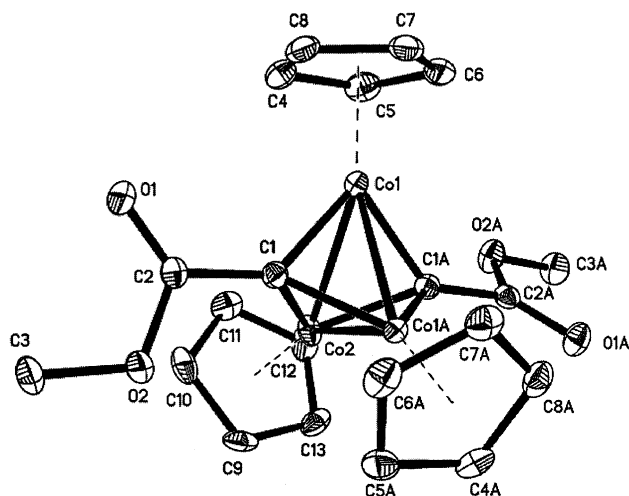


Fig. 4. An ORTEP view of bis(carbyne) cluster ($3\text{-CO}_2\text{Me}$) (50% probability thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): Co(1)–Co(2) 2.3785(4), Co(1)–Co(1A) 2.4027(4), Co(1)–C(1) 1.8628(14), Co(1)–C(1A) 1.8558(14), Co(2)–C(1) 1.8652(14), Co(2)–C(1A) 1.8652(14); C(1A)–Co(1)–C(1) 84.59(7), C(1A)–Co(2)–C(1) 84.26(9), Co(1A)–Co(1)–Co(2) 59.664(7), C(1A)–Co(1)–Co(2) 50.44(4), C(1)–Co(1)–Co(2) 50.40(4), C(1A)–Co(1)–Co(1A) 49.88(4), C(1)–Co(1)–Co(1A) 49.62(4), Co(1A)–C(1)–Co(1) 80.50(6), Co(1A)–C(1)–Co(2) 79.47(6), Co(1)–C(1)–Co(2) 79.29(6).

4. Supplementary material

Crystallographic data for $3\text{-CO}_2\text{Me}$ and **4** have been deposited with the Cambridge Crystallographic Data Center, CCDC nos. 192649 and 192312, respectively. Copies may be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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