On the behaviour of dimethyl acetylenedicarboxylate in carbonylation and Khand reactions

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Abstract

Dimethyl acetylenedicarboxylate (DMAD) has been used as the alkyne component in the Khand reaction with norbornene under both thermal and *N*-oxide promoted conditions. Its thermolysis under CO pressure has also been reinvestigated and the structure of one of the trinuclear rearrangement products, $MeO_2C \cdot CH_2CCo_3(CO)_9$, confirmed by X-ray crystallography; $(MeOOC)_2CHCH(COOMe)_2$ is the principal metal-free product from this reaction. Methyl but-2-ynoate undergoes similar rearrangement yielding $MeO_2C \cdot CHMe \cdot CCo_3(CO)_9$. © 1999 Elsevier Science S.A. All rights reserved.

*Keywords:* Khand reaction; Dimethyl acetylenedicarboxylate; Norbornene; Cobalt carbonyl; Carbonylation

1. Introduction

In the preceding paper [1] we reported the preparation of a series of (alkynylphosphonate)dicobalt hexacarbonyl complexes, $[RC\equiv CP(O)(OR')_2]Co_2(CO)_6$ and their failure to couple with alkynes (cyclotrimerisation) or to undergo Khand reactions or carbonylation. Since there is only limited information about the effect of other electron withdrawing groups on these processes, we were led to re-investigate aspects of the behaviour of alkynyl carboxylate complexes in each of the reactions. Our results on the formation of cobaltacyclopentadiene complexes $(RC\equiv CR')_2Co_2(CO)_5$, 'flyover' complexes $(RC\equiv CR')_3Co_2(CO)_4$ and arenes from their reactions with the same or different alkynes have been reported elsewhere [2,3]. Studies of the other two reactions are the subject of this paper.

2. Results and discussion

2.1. Khand reaction

Krafft et al. [4] have used the $Co_2(CO)_6$ complexes of ethyl propiolate and ethyl but-2-ynoate in Khand reactions [5] and concluded that the regiochemical outcome depends on a subtle balance of steric and electronic factors. No other intermolecular examples of the behaviour of alkynyl esters appear to be known. In view of our failure [1] with the bis-phosphonate $C_2[P(O)(OMe)_2]_2$ it was of interest to examine the use of the DMAD complex **1b**. When this was heated to 70°C with norbornene in toluene, the expected tricyclic product, **2**, was formed in 48% yield, but a Me_3NO promoted reaction at room temperature (r.t.) boosted this to 74% (Eq. (1)).
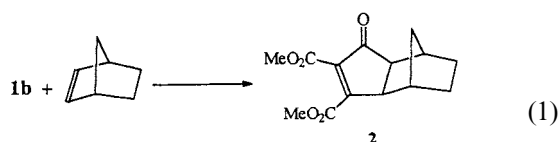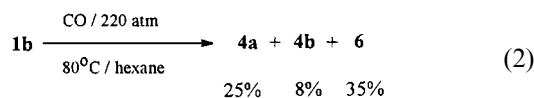
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$$1b + \quad \longrightarrow \quad 2 \tag{1}$$

2.2. Carbonylation reactions

Many alkynehexacarbonyldicobalt complexes react with carbon monoxide under pressure to yield lactone complexes of type **3** [6], but reaction of $Co_2(CO)_6$(DMAD) with CO at 220 atmospheres and 80°C for 40 h, attempted as a model for the reaction of $[(MeO)_2P(O)C\equiv CP(O)(OMe)_2]Co_2(CO)_6$, yielded a complex set of products (Eq. (2)).

	R	R'
a	H	Me
b	CO_2Me	Me
c	Me	Et
d	H	CD_3
e	CO_2CD_3	CD_3
f	Ph	Me
g	CO_2H	H

$(CH_3O_2C)_2CH\text{-}C\equiv C\text{-}CH(CO_2CH_3)_2$
5

$(RO_2C)_2CH\text{-}CH(CO_2R)_2$
6a R = CH_3
6b R = CD_3

$$1b \xrightarrow[80°C / hexane]{CO / 220 atm} 4a + 4b + 6 \qquad (2)$$
$$\phantom{1b \xrightarrow[80°C / hexane]{CO / 220 atm}} 25\% \quad 8\% \quad 35\%$$

Colourless crystals that had sublimed onto the lid of the autoclave were collected, while the reaction liquor was concentrated and purified by column chromatography. This yielded unreacted starting material (34%), two purple complexes (in 25 and 8% yields) and a yellow solid. The two purple complexes were apparently identical to the products previously reported by Váradi et al. [7] from a similar reaction. Indeed, their spectroscopic properties (IR, MS and ^{1}H-NMR) were also consistent with their formulation as tricobalt nonacarbonyl complexes with μ_3-CCH$_2$CO$_2$Me (**4a**) and μ_3-CCH(CO$_2$Me)$_2$ (**4b**) groups, respectively. Single crystals of the former were obtained by slow evaporation of a hexane solution at 0°C and the X-ray crystal structure was obtained. This unequivocally confirmed the assignment. The compound crystallises with two molecules in the asymmetric unit, which differ slightly in the orientation of the ester group of the organic function. This may be defined with respect to the two torsion angles C(10)–C(11)–C(12)–O(10) and C(23)–C(24)–C(25)–O(21), which have values of + 48(1)° and + 102.1(9)°, respectively. The remainder of the structure is in keeping with other crystallographically characterised Co$_3$(CO)$_9$(μ_3-CR) complexes [8]. It is notable that the μ_3-carbon is symmetrically disposed above the equilateral Co$_3$ triangle, and that the axial Co–C$_{CO}$ bond lengths are some 0.03 Å longer than the equatorial Co–C$_{CO}$ distances, indicative of a weaker π-back donation from the metal to the axial ligands. The equatorial carbonyl ligands are directly *trans* to the Co–Co bonds, while the axial carbonyls are approximately *trans* to the μ_3-carbon, and it would appear that the Co–Co interaction affects the orbitals required for back-bonding to the carbonyl less than the μ_3-C–Co interaction does. Selected bond lengths and angles are collected in Table 1 and thermal ellipsoid plots of the two unique molecules are shown in Fig. 1.
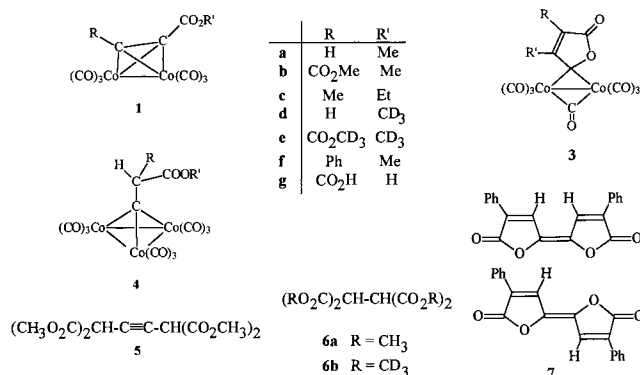
The yellow solid obtained from the reaction was found (after recrystallisation from dichloromethane) to be identical to the colourless crystals found on the autoclave lid. The ^{1}H-NMR spectrum showed two singlet resonances at $\delta = 3.78$ and 4.19 ppm in a 6:1 ratio. IR spectroscopy confirmed the presence of the ester group. These facts, and precedent [9] at first suggested structure **5**, but mass spectrometry, ^{13}C-NMR spec-

Table 1
Selected bond lengths (Å) and angles (°) for **4a**

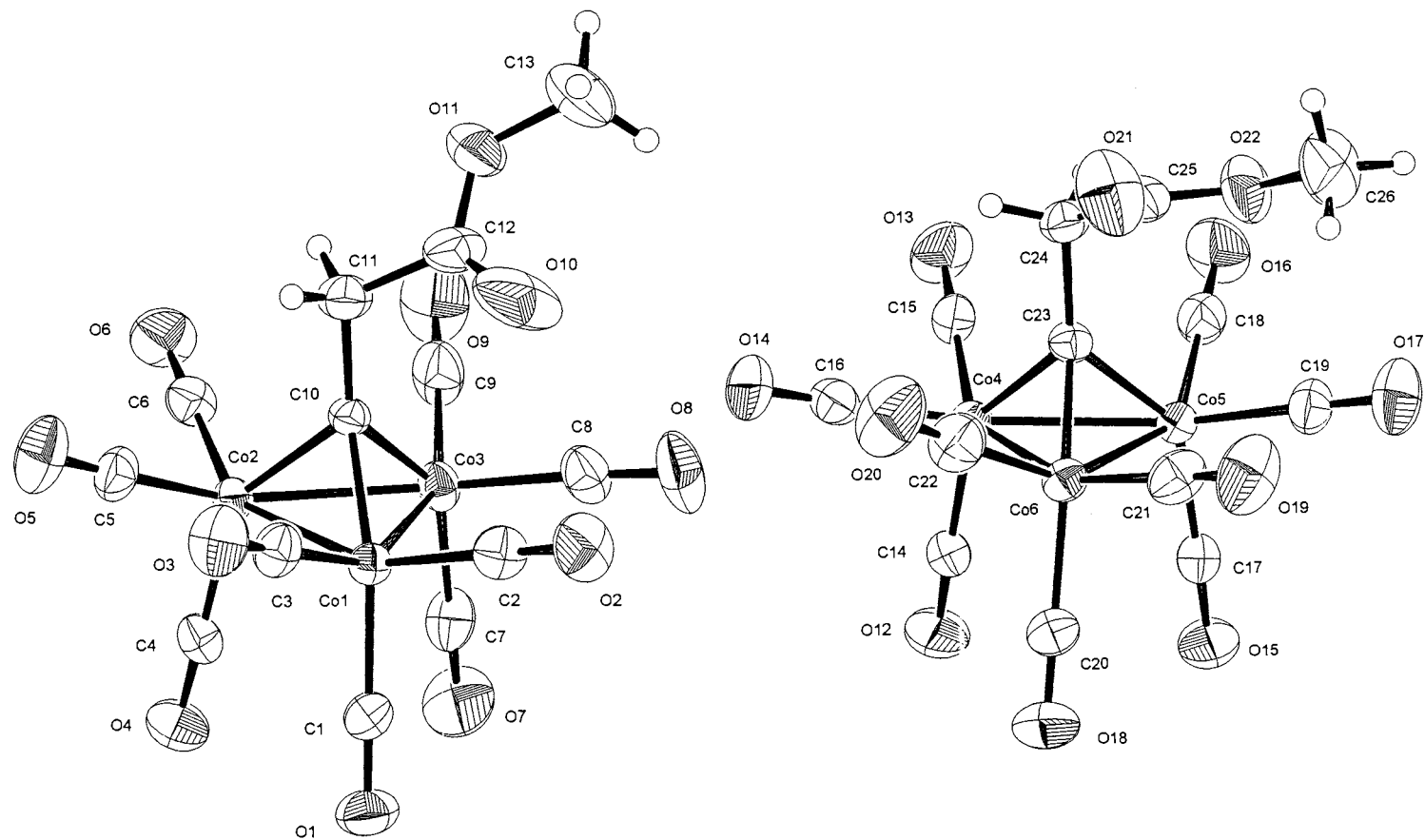| Molecule 1		Molecule 2	
Bond lengths			
Co(1)–Co(2)	2.470(1)	Co(4)–Co(5)	2.463(1)
Co(1)–Co(3)	2.466(1)	Co(4)–Co(6)	2.473(1)
Co(2)–Co(3)	2.470(1)	Co(5)–Co(6)	2.475(1)
Co(1)–C(1)	1.819(7)	Co(4)–C(14)	1.844(7)
Co(1)–C(2)	1.796(7)	Co(4)–C(15)	1.788(7)
Co(1)–C(3)	1.781(7)	Co(4)–C(16)	1.804(8)
Co(2)–C(4)	1.832(7)	Co(5)–C(17)	1.834(7)
Co(2)–C(5)	1.771(8)	Co(5)–C(18)	1.789(7)
Co(2)–C(6)	1.770(7)	Co(5)–C(19)	1.794(7)
Co(3)–C(7)	1.834(8)	Co(6)–C(20)	1.822(7)
Co(3)–C(8)	1.788(7)	Co(6)–C(21)	1.775(8)
Co(3)–C(9)	1.791(8)	Co(6)–C(22)	1.806(8)
Co(1)–C(10)	1.894(5)	Co(4)–C(23)	1.903(6)
Co(2)–C(10)	1.905(5)	Co(5)–C(23)	1.908(6)
Co(3)–C(10)	1.893(6)	Co(5)–C(23)	1.885(6)
C(10)–C(11)	1.504(8)	C(23)–C(24)	1.505(8)
C(11)–C(12)	1.491(9)	C(24)–C(25)	1.493(9)
C(12)–O(10)	1.179(8)	C(25)–O(21)	1.197(8)
C(12)–O(11)	1.278(8)	C(25)–O(22)	1.305(8)
O(11)–C(13)	1.429(9)	O(22)–C(26)	1.463(9)
Bond angles			
Co(1)–Co(2)–Co(3)	59.89(3)	Co(4)–Co(5)–Co(6)	60.11(3)
Co(2)–Co(3)–Co(1)	60.06(3)	Co(5)–Co(6)–Co(4)	59.70(3)
Co(3)–Co(1)–Co(2)	60.04(3)	Co(6)–Co(4)–Co(5)	60.19(3)
Co(1)–C(10)–C(11)	133.1(5)	Co(4)–C(23)–C(24)	128.9(4)
Co(2)–C(10)–C(11)	127.8(4)	Co(5)–C(23)–C(24)	132.7(4)
Co(3)–C(10)–C(11)	132.8(5)	Co(6)–C(23)–C(24)	132.2(4)
C(10)–C(11)–C(12)	115.7(6)	C(23)–C(24)–C(25)	112.4(5)
C(11)–C(12)–O(10)	125.2(7)	C(24)–C(25)–O(21)	122.8(8)
C(11)–C(12)–O(11)	112.6(6)	C(24)–C(25)–O(22)	112.7(6)
O(10)–C(12)–O(11)	122.2(8)	O(21)–C(25)–O(22)	124.5(7)
C(12)–O(11)–C(13)	118.0(7)	C(25)–O(22)–C(26)	117.4(7)

Fig. 1. Thermal ellipsoid plot of **4a** showing the two crystallographically unique molecules in the unit cell and the atom numbering scheme. The thermal ellipsoids are at the 35% level.

troscopy and microanalysis were consistent with the tetraester **6a**. The melting point was subsequently found to agree with the literature value [10]. This product was apparently not observed by Váradi et al. [7].

The identity of the products obtained raises a number of points regarding the mechanism of the reactions taking place. Firstly, the formation of $Co_3(CO)_9$ clusters is unexpected, since they are normally formed either under acidic conditions and/or when a terminal alkyne is used. In addition, the formation of **4a** and **4b** requires ester cleavage and 1,2-migration[1] of an ester group, respectively. The source of the CH and CH_2 hydrogen atoms is not clear. The formation of **6a** is also unexpected and seems most likely to result from C–C bond fission in **4b** to give $[Co_3(CO)_9(\mu_3-C)]^\bullet$ and $[(MeO_2C)_2CH]^\bullet$, although we have found no evidence for the formation of the dimer, $Co_3(CO)_9C–CCo_3(CO)_9$ [11], which might also be expected to result from such a bond fission.

In order to assess the generality of this reaction other $Co_2(CO)_6$(alkyne) complexes were reacted under the previously described conditions. The complex of methyl propiolate, $HC\equiv CCO_2Me$, **1a**, was known to rearrange to **4a** [7] and we have now shown that the complex of ethyl but-2-ynoate, $MeC\equiv CCO_2Et$, **1c**, is similarly converted to $Co_3(CO)_9[\mu_3-CCH(Me)(CO_2Et)]$ **4c**, but it is not possible to deduce which of the substituents (H, Me, CO_2R) undergoes 1,2-migration. By contrast, $PhC\equiv CCO_2Me$ and $HO_2CC\equiv CCO_2H$ complexes **1f,g**, like that of the diphosphonate $(MeO)_2P(O)C\equiv CP(O)(OMe)_2$ [1] do not react to any extent as evidenced by the near quantitative recovery of starting complex. We also confirmed that the $PhC\equiv CH$ complex only yields the known lactone complex **3** (R = Ph, R′ = H) and an organic residue, believed to be the bifurandiones **7** [12], with no sign of tricobaltnonacarbonyl cluster formation. It is interesting to note that the formation of the organic product **6** seems to be unique to the reaction with $Co_2(CO)_6$(DMAD) and its deuteriated analogue.

The source of the CH or CH_2 hydrogen atoms was also investigated. Four potential sources were considered: abstraction from solvent, residual water (largely ruled out by Váradi et al. [7]), the ester methyl groups and traces of H_2 in the CO. In order to eliminate solvent as a source, the reaction was initially performed in benzene, which is less prone to proton abstraction, but since the three products were still obtained, an aprotic solvent, namely hexafluorobenzene, was used. The three major products were obtained in similar yields and proportions as in benzene, but in lower yield

than in hexane. Thus, it seems unlikely that the solvent is the chief proton source. Reaction in rigorously dried apparatus and solvents yielded all of the main products, but in diminished yield, while addition of water (1% in hexane) resulted in considerable decomposition together with a fair yield of $Co_3(CO)_9[\mu_3-CCH_2CO_2Me]$ **4a** alone. Reaction of the $CD_3O_2CC\equiv CCO_2CD_3$ complex in hexafluorobenzene proceeds to yield $(CD_3O_2C)_2$-$CHCH(CO_2CD_3)_2$ **(6b)**, $Co_3(CO)_9[\mu_3-CCH_2CO_2CD_3]$ **(4d)** and $Co_3(CO)_9[\mu_3-CCH(CO_2CD_3)_2]$ **(4e)**. In each case there is no incorporation of deuterium into the CH or CH_2 sites, nor is there isotopic scrambling at the methyl groups, confirming that the ester methyl groups remain intact and are not the source of hydrogen. This leaves the presence of H_2 impurity in the CO as the only likely remaining possibility. The purity of the CO used was ca. 99.8% with sufficient H_2 impurity (according to the suppliers' analysis) to account for the formation of the observed products in the quantities obtained. We conclude, therefore, that this is the most plausible source of the extra hydrogen atoms, but some may also be derived from hexane when used as solvent. These reactions and their product distributions are summarised in Table 2.

The mechanism of the reaction is not immediately clear. The formation of the trinuclear clusters is unusual under the reaction conditions, since normally an acidic medium is required for such transformations. In this case it seems likely that since a small amount of H_2 impurity is present, a catalytic amount of $HCo(CO)_4$ is formed, which in turn reacts with the parent cobalt alkyne complex. In the absence of more definitive evidence we are unwilling to speculate further on the detailed mechanism of the reaction.

3. Experimental

For general directions see [1]. d_6-Dimethyl acetylenedicarboxylate, prepared according to a literature method [13], was complexed with $Co_2(CO)_8$ in THF using standard procedures:

1e: $Co_2(CO)_6(CD_3O_2CC\equiv CCO_2CD_3)$. Yield, 87%. Analysis. Found: C, 33.25%. Calc. for $C_{12}Co_2D_6O_{10}$: C, 33.18%. MS. Found: $m/z = 405.9031$. $[M^+–CO]$, $M_r = 405.9052$. IR (hexane): ν(CO) 2110, 2078, 2053, 2015, 1998, 1721 cm^{-1}. ^{1}H-NMR $(CDCl_3)$: no signals observed. ^{13}C-NMR $(CDCl_3)$ δ 52.59 (sept, $^1J\{^2H–^{13}C\} = 22.4$ Hz), 78.15, 169.36, 196.77 ppm.

3.1. Khand reactions

3.1.1. Thermal reaction

$Co_2(CO)_6$(DMAD) **(1b)** (29 mg, 0.067 mmol), norbornene (7 mg, 0.074 mmol) and toluene (20 ml) were

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[1] Metal-assisted 1,2-shifts are relatively common for terminal alkynes, but unusual for internal alkynes see e.g. [22]; Lewis acids catalyse the 1,2-migration of -I, -OMe and -SMe in Pd-promoted reactions of alkynes [23].

Table 2
Carbonylation reactions of $Co_2(CO)_6(RC\equiv CR')$

Starting material		Solvent	T (°C)	Pressure (atm)	Products								
					Complex **1** (recovered)			Complexes **4**			Organic product		
Alkyne	mg				No.	mg	%	No.	mg	%	No.	mg	%
DMAD	2080	*n*-hexane	80	220	**1b**	707	34	**4a**	424	25	**6a**	241	38
								4b	139	8			
	1220	dry *n*-hexane	80	220	**1b**	383	31	**4a**	190	19	**6a**	37	10
								4b	114	10			
	1940	benzene	80	110	**1b**	930	48	**4a**	116	7	**6a**	24	4
								4b	52	3			
	1000	C_6F_6	80	110	**1b**	540	54	**4a**	48	6	**6a**	25	8
								4b	27	3			
	380	*n*-hexane/H_2O	80	100	**1b**	19	5	**4a**	68	22	**6a**	–	–
								4b	Trace				
d_6-DMAD	1720	C_6F_6	80	100	**1e**	740	43	**4d**	246	12	**6b**	97	9
								4e	92	4			
$MeC\equiv CCO_2Et$	2700	*n*-hexane	100	120	**1c**	1160	43	**4c**	117	3			
$PhC\equiv CCO_2Me$	2080	*n*-hexane	80	220	**1f**	1720	83						

combined and heated at 70°C for 48 h. After cooling and filtering through kieselguhr, the solvent was removed under reduced pressure to yield a brown oil. Chromatography on silica gel [9:1 light petroleum:diethyl ether] yielded unchanged starting complex, followed [3:1 diethyl ether:light petroleum] by a pale yellow band, which after the removal of solvent yielded the ketodiester **2** as a yellow oil (8.5 mg, 48%).

3.1.2. Me_3NO promoted reaction

$Co_2(CO)_6$(DMAD) (**1b**) (565 mg, 1.32 mmol), norbornene (249 mg, 2.64 mmol), Me_3NO (1.47 g, 13.2 mmol) and CH_2Cl_2 (30 ml) were stirred together at r.t. After 16 h, the starting complex was completely consumed (TLC). Work up as in the previous example yielded **2** as a yellow oil (258 mg, 74%).

2c: MS. Found: $m/z = 264$, [M^+], $M_r = 264$. IR (CH_2Cl_2): ν(C=O) 1782, 1743, 1712, ν(C=C) 1636 cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ 1.18 (m, 2H), 1.53 (m, 2H), 1.82 (m, 2H), 2.53 (d, 1H), 2.64 (s, 2H), 3.12 (d, 1H), 3.99 (d, 6H) ppm. ^{13}C-NMR (CDCl$_3$) δ 28.17, 29.04, 31.59, 38.37, 40.01, 48.88, 52.58, 52.87, 54.76, 142.63, 163.11, 163.48, 164.22, 204.59 ppm.

3.2. Carbonylation reactions, general procedure

$Co_2(CO)_6$(DMAD) (**1b**) (2.08 g, 4.86 mmol) and *n*-hexane (200 ml) were placed in a 50 ml capacity stainless steel autoclave, pressurised to 220 atm with CO and heated at 80°C for 40 h. After cooling, colourless crystals from the inner surface of the autoclave were collected and washed with light petroleum. The reaction liquor and washings were combined, and after evapora-

tion to dryness, purified by chromatography on silica gel (9:1 light petroleum:diethylether).

The other carbonylation reactions were performed in a similar manner. The reagents, conditions and product distributions from each of the reactions are summarised in Table 2. The spectroscopic data for each of the complexes obtained follows here:

4a: $Co_3(CO)_9[\mu_3$-CCH$_2$CO$_2$Me]. Analysis. Found: C, 31.72; H, 1.32%. Calc. for $C_{13}H_5Co_3O_{11}$; C, 30.38; H, 0.98%. MS. Found: $m/z = 514.7819$. [$M^+ + H$], $M_r = 514.7906$. IR (hexane): ν(CO) 2104, 2057, 2042, 2022, 1983, 1749 cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ 3.77 (s, 3H), 4.64 (s, 2H) ppm. ^{13}C-NMR (CDCl$_3$) δ 52.28, 65.14, 164.74, 171.90, 192.13 ppm.

4b: $Co_3(CO)_9[\mu_3$-CCH(CO$_2$Me)$_2$]. MS. Found: $m/z = 544$. [$M^+ - CO$], $M_r = 544$. IR (hexane): ν(CO) 2106, 2061, 2042, 2030, 1743 cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ 3.87 (s, 6H), 5.06 (s, 1H) ppm.

4c: $Co_3(CO)_9[\mu_3$-CC(H)Me(CO$_2$Et)]. Analysis. Found: C, 38.31; H, 1.71%. Calc. for $C_{15}H_9Co_3O_{11}$: C, 38.24; H, 1.67%. MS. Found: $m/z = 513.8167$. [$M^+ - CO$], $M_r = 513.8191$. IR (hexane): ν(CO) 2104, 2060, 2042, 2028, 1744 cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ 1.30 (t, 3H), 1.75 (d, 3H), 4.19 (q, 2H), 4.57 (q, 1H) ppm.

4d: $Co_3(CO)_9[\mu_3$-CCH$_2$CO$_2$CD$_3$]. MS. Found: $m/z = 515$. [$M^+ - H$], $M_r = 515$. IR (hexane): ν(CO) 2106, 2054, 2040, 2022, 1981, 1749 cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ 4.62 (s) ppm.

4e: $Co_3(CO)_9[\mu_3$-CCH(CO$_2$CD$_3$)$_2$]. MS. Found: $m/z = 578.0021$. [M^+], $M_r = 577.8259$. IR (hexane): ν(CO) 2064, 2040, 2032, 1745 cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ 5.05 (s) ppm.

Table 3
Crystallographic data for **4a**

Molecular formula	$C_{13}H_5Co_3O_{11}$
Molecular weight	513.98
Crystal color, habit	Black, needle
Crystal size (mm³)	$0.8 \times 0.15 \times 0.1$
Space group	$P\bar{1}$ (#2)
a (Å)	15.311(3)
b (Å)	15.348(2)
c (Å)	8.0118(8)
α (°)	84.55(1)
β (°)	79.12(1)
γ (°)	80.07(1)
V (Å³)	1817.3(9)
Z	4
$\rho_{calc.}$ (g cm⁻³)	1.878
μ (Mo–K_α) (cm⁻¹)	27.61
$F(000)$	1008.00
Diffractometer	Rigaku AFC7S
Radiation	Mo–K_α
Wavelength (Å)	0.71069
T (K)	293
Scan type	ω–2θ
Scan rate (° min⁻¹)	16 (in ω)
Scan width	$1.31 + 0.35 \tan \theta$
θ Range	2.5–30
Index ranges	h, 0–19; k, −21–21; l, −11–11
Reflcns measured	9764
Unique reflcns	9074 ($R_{int} = 0.093$)
Observed reflections ($I > 2.00\sigma(I)$)	4174
No. of variables	488
GOF	1.33
R	0.042
R_w	0.041
Residual electron density (eÅ³)	0.42 to −0.43

6b: $C_2H_2(CO_2Me)_4$. Analysis. Found: C, 45.66; H, 5.51%. Calc. for $C_{10}H_{14}O_8$: C, 45.81; H, 5.38%. MS. Found: $m/z = 262$. [M⁺], $M_r = 262$. IR. (CH_2Cl_2): 3059, 2986, 1746, 1604, 1006 cm⁻¹. ¹H-NMR ($CDCl_3$) δ 3.78 (s,12H), 4.19 (s, 2H) ppm. ¹³C-NMR ($CDCl_3$) δ 51.38, 53.40, 164.37 ppm.

6e: $C_2H_2(CO_2CD_3)_4$. Found: $m/z = 272$. [M⁺ − D], $M_r = 274$ [M⁺]. IR. (CH_2Cl_2): 3058, 2984, 1746, 1602 cm⁻¹. ¹H-NMR ($CDCl_3$) δ 4.18 (s) ppm.

3.3. X-ray crystal structure determination

Dark red–black needles of **4a** suitable for X-ray diffraction were grown by slow evaporation of an *n*-hexane solution at 0°C. The complex crystallises in the triclinic space group $P\bar{1}$. A crystal having dimensions 0.8 mm × 0.15 mm × 0.1 mm was glued to a glass fibre, mounted on a Rigaku AFC7S diffractometer [14] and accurate cell dimensions were obtained from 20 precisely centred reflections in the range $23.5 \leq 2\theta \leq 31.5$. A total of 9764 reflections ($2\theta_{max} = 60°$) were collected

at 20°C using graphite monochromated Mo–K_α radiation, of which 9074 were unique ($R_{int} = 0.093$). Standard reflections showed a decay in intensity of 9.5% over the duration of the data collection and a linear correction factor was applied to account for this. An empirical absorption correction (ψ-scans, $T_{min} = 0.86$, $T_{max} = 0.99$) was applied. The structure was solved by Patterson methods [15] and expanded using Fourier techniques [16]. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were included at calculated positions but not refined. Full-matrix least-squares refinement based on 4174 observed reflections ($F > 2\sigma(F)$) and 488 variables converged with $R = 0.042$, $R_w = 0.041$ and GOF = 1.33. Residual electron density was in the range $−0.43$–0.42 e Å⁻³.

The crystallographic details are collected in Table 3. In each case, the neutral atom scattering factors [17], $\Delta f'$ and $\Delta f''$ [18] and mass attenuation coefficients [19] were taken from the International Tables for Crystallography. Anomalous dispersion effects were included in F_{calc} [20]. All calculations were performed using the TeXsan crystallographic package [21].

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 111843 for compound **4a**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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