Communication

Ring expansion of a Cp moiety upon CO insertion: Synthesis and characterization of [(η^6-C$_6$H$_5$OCo)Co$_3$(CO)$_9$]

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A R T I C L E   I N F O

A B S T R A C T

Reaction of [(CpV)$_2$(B$_2$H$_6$)$_2$], **1** (Cp = η^5-C$_5$H$_5$) with four equivalents of [Co$_2$(CO)$_8$] or [Co$_4$(CO)$_{12}$] in hexane at 70 °C leads to the isolation of the tetranuclear carbonyl cluster, [(η^6-C$_6$H$_5$OCo)Co$_3$(CO)$_9$], **2** in modest yield. The geometry of **2** is similar to that of [Co$_4$(CO)$_{12}$] where all the four Co atoms are arranged in a tetrahedral geometry. The apical cobalt atom in **2** is coordinated to C$_6$H$_5$O ring in a η^6-fashion and the other three cobalt atoms are each coordinated to three carbonyl ligands. Compound **2** has been characterized in solution by IR, ^{1}H, ^{13}C NMR and mass spectrometry and the structural types were unequivocally established by crystallographic analysis.

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1. Introduction

In metallaborane chemistry, transition metal carbonyl compounds, for example, [Fe$_2$(CO)$_9$] or [Co$_2$(CO)$_8$], has received considerable attention in connection with their potential as versatile reagent in metal cluster building reactions [1–6]. For example, the reaction of [Fe$_2$(CO)$_9$] with [(Cp*Ru)$_2$B$_6$H$_{12}$] (Cp* = η^5-C$_5$Me$_5$) results in the formation of [Fe$_2$(CO)$_6$(Cp*RuCO)(Cp*Ru)B$_6$H$_{10}$] [4]. In a similar fashion, reaction of [Co$_2$(CO)$_8$] with [(Cp*ReH$_2$)$_2$B$_4$H$_4$] yielded [(Cp*Re)$_2$(μ−η^6:η^6-B$_4$H$_4$Co$_2$(CO)$_5$)] [7]. As a part of our interest in synthesizing metallaboranes containing a range of early transition metal atoms, we have recently synthesized a series of low boron content metallaboranes, [(CpM)$_2$(B$_2$H$_6$)$_2$] (Cp = η^5-C$_5$H$_5$; M = V, Nb) and [(Cp*Ta)$_2$(B$_2$H$_6$)$_2$], by the reaction of metal chlorides and monoborane reagent (LiBH$_4$·THF and BH$_3$·THF) [8]. Consequently, upon availability of [(CpV)$_2$(B$_2$H$_6$)$_2$] **1**, the chemistry is elaborated by the use of cluster expansion reaction with [Co$_2$(CO)$_8$], which led to the isolation of an unusual tetranuclear carbonyl cluster, [(η^6-C$_6$H$_5$OCo)Co$_3$(CO)$_9$], **2**. Reported here is the synthesis and structural characterization of the tetranuclear carbonyl cluster **2**.

2. Result and discussion

### 2.1. Isolation and characterization of [(η^6-C$_6$H$_5$OCo)Co$_3$(CO)$_9$], 2

Mild pyrolysis of **1** with four equivalents of [Co$_2$(CO)$_8$] yielded air-stable **2**, isolated by thin-layer chromatography (TLC) in 30% yield

(Scheme 1). Compound **2** can also be generated from [Co$_4$(CO)$_{12}$] under the same reaction conditions. Composition of **2** is defined by the mass, an isotopic distribution pattern characteristics of four cobalt atoms, and fragments corresponding to 9CO losses of the parent cation in the mass spectrum. The infrared spectrum in the ν(CO) region of **2** is particularly informative with four absorption bands, three corresponding to terminal carbonyl (2081s, 2013w, 2009vs cm^{-1}) and one corresponding to bridging carbonyl (1809s cm^{-1}), which are very similar to those (2074s, 2030vs, 2012w, 1821s cm^{-1}) of [(η^6-benzene)Co$_4$(CO)$_9$] in CH$_2$Cl$_2$ solution [9]. Furthermore, compound **2** exhibits absorption at 1729 cm^{-1}, characteristics of ketonic carbonyl group. In addition, the ^{13}C NMR of **2** shows the presence of ring carbon resonances at δ 94.6, 93.7 and 93.3 ppm and ketonic carbonyl carbon at δ 167.2 ppm similar to other oxocyclo cobalt complexes [10].

The framework geometry of **2** became clear when a solid state structure was determined. The X-ray structure of **2**, shown in Fig. 1, confirms the presence of terminal, bridging and ketonic carbonyl group. The molecule has four cobalt atoms approximately in regular tetrahedron geometry. The most likely arrangement of CO groups for the molecule is one in which a single cobalt atom is bound to (η^6-C$_6$H$_5$O) group while the other three Co atoms are each coordinated to two terminal CO groups with the three edges between them being spanned by bridging CO groups. Further, the existence of compound **2** permits a spectroscopic data comparison with other related complexes, which are shown in Table 1.

The geometry of **2** is comparable to [(η^6-arene)Co$_4$(CO)$_9$] compounds, where the arene is benzene, xylene or [2.2.2]para-cyclophane [9,13]. The Co–Co distances in the tetrahedral core of **2**

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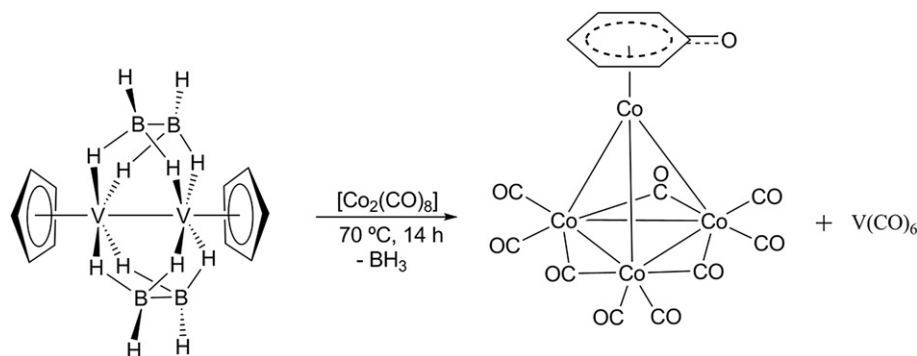
Scheme 1. Synthesis of [(η^6-C$_6$H$_5$OCo)Co$_3$(CO)$_9$] 2.

are all essentially the same (2.477 ± 0.0001 Å) except for Co1–Co3 and Co1–Co4 which have a somewhat shorter distance (2.4486 (5) Å), perhaps as a result of the asymmetric bonding of the η^6-C$_6$H$_5$O ligand. The average Co–C distance to the bridging CO groups in the basal plane is longer (1.93 Å) than that of the terminal CO groups (1.78 and 1.80 Å). The angle between the Co1–Co4–Co3 plane and the plane of the (η^6-C$_6$H$_5$O) ligand is 0° which suggests that the Co$_2$–C distances to the coordinated (η^6-C$_6$H$_5$O) ligand all are same. The average Co–Co bond distances in the base of the cluster **2** is short compared to the sides owing to the contracting action of the bridging CO groups (2.4486(5), 2.4773(5) Å). Both bridging and equatorial terminal carbonyl ligands point upwards toward the C$_6$H$_5$O ligand.

The cobalt nucleus (^{59}Co) provides an interesting probe to investigate tetrahedral clusters in order to get information about their structure [14–19]. The two cobalt environments (apical and basal) in the structure of **2** is similar to that of [Co$_4$(CO)$_{12}$], thus, two resonances are likely to be observed at room temperature ^{59}Co NMR [20]. Indeed, the ^{59}Co NMR spectra recorded at room temperature as well as at low temperature show two very broad resonances at δ −2023 and −2492 ppm, however signals sharpened on going to

Fig. 1. Molecular structure and labeling diagram for [(η^6-C$_6$H$_5$OCo)Co$_3$(CO)$_9$] **2**. The oxygen atom is disordered over three positions in C$_6$H$_5$O ring, each with 33.3% occupancy. Relevant bond lengths (Å) and angles (°): Co(1)–Co(2) 2.4773(5), Co(1)–Co(3) 2.4486(5), C(4)–O(4) 1.257(8); Co(3)–Co(1)–Co(2) 60.381(8), Co(4)–Co(1)–Co(3) 60.0, Co(1)–Co(2)–Co(4) 59.237(17).

the elevated temperature (70 °C). The apical:basal signal ratio (1:3) does not match with the observed peak intensities at any temperature. Discrepancies about the relative intensities are partly due to the loss of magnetisation under the effect of transverse relaxation during the receiver dead time [18,21–23].

2.2. Reaction pathway

The migratory CO insertion reaction is well-known in organo-transition-metal chemistry and in organometallic applications in organic synthesis for carbon–carbon bond formation and ring expansion reaction [24–34]. Ring expansion of 2-cyclopropene-1-carbonyl intermediate to η^3-oxocyclobutenyl complex has been shown to occur intramolecularly involving iron-promoted expansion of a three to four-membered ring (Scheme 2a) [10,25]. As shown in Scheme 2b, a two step mechanism has been suggested to account for the formation of hexmethylbenzene by ring expansion of a Cp* ligand by incorporation of the 'CH$_3$C≡' fragment of the acetyl group of [Cp$^*_2$Ti(η^2-COCH$_3$)(OCMoCp(CO)$_2$)] [31]. Messerle and coworkers [32] have shown that a highly distorted η^2-acyl complex [(η^5-C$_5$Me$_4$R)Ta(C(O)CH$_2$CMe$_3$)Cl$_3$] (R = Me, Et) can be reduced by Mg, Na/Hg, K/Hg, Zn or sodium naphthalenide to arene C$_6$Me$_5$(CH$_2$CMe$_3$) (Scheme 2c). Further, surprising carbon–carbon bond activation during certain cobalt-mediated allyl/alkyne cyclo-additions reactions, leading to substituted η^5-cycloheptadienyl products and, in others, to the activation of ancillary cyclo-pentadienyl ligands have been reported (Scheme 2d) [29c].

As far as the synthetic pathway of this unforeseen reaction is concerned, the formation of **2** may have occurred from an electro-cyclic rearrangement, promoted by a metal centre. The substitution of three apical carbonyl ligands in [Co$_4$(CO)$_{12}$] by a η^6-arene is well precedented [9,13]. Thus, the replacement of two carbonyl ligands from the apical cobalt atom in [Co$_4$(CO)$_{12}$] by η^4-cyclopentadiene is probable. In the second step, the electrophilic carbonyl carbon atom may react with the electron-rich Cp ring, followed by the scission of Co–C bond, with concomitant formation of the (η^6-C$_6$H$_5$O) ring.

Further, to evaluate any significant role of the metal into this unprecedented CO insertion reaction, analogue reactions were carried out with [(CpNb)$_2$(B$_2$H$_6$)$_2$] and [(Cp*Ta)$_2$(B$_2$H$_6$)$_2$]. Unfortunately, in both the cases no product(s) could be identified except the decomposition of niobaborane or tantalaborane compounds. Attempts were also made to obtain products from the Cp ring exchange of [(CpV)$_2$(B$_2$H$_6$)$_2$] in the presence of the following metal carbonyls/derivatives: [Fe$_2$(CO)$_9$], [Cr(CO)$_6$], [η^6-C$_6$H$_6$Cr(CO)$_3$], [M(CO)$_5$·THF] (M = Mo and W) and [M(CO)$_3$(CH$_3$CN)$_3$] (M = Cr, Mo and W). None of these reactions provided a tractable product.
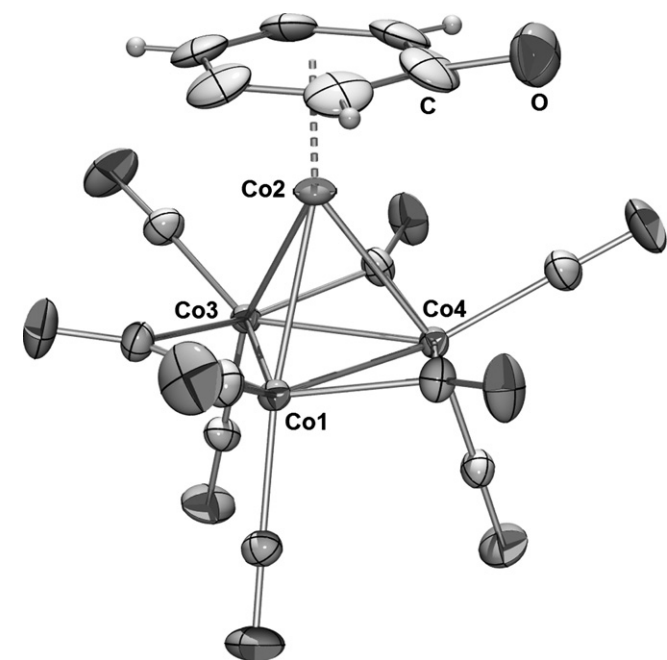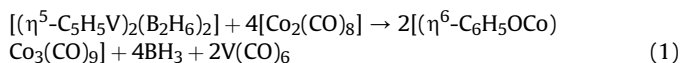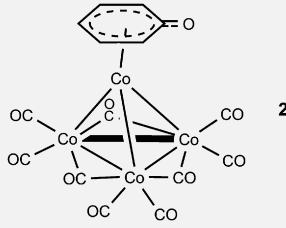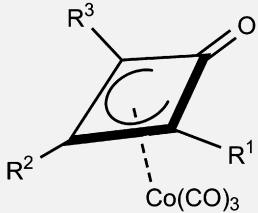
$$[(\eta^5\text{-C}_5\text{H}_5\text{V})_2(\text{B}_2\text{H}_6)_2] + 4[\text{Co}_2(\text{CO})_8] \rightarrow 2[(\eta^6\text{-C}_6\text{H}_5\text{OCo})\text{Co}_3(\text{CO})_9] + 4\text{BH}_3 + 2\text{V}(\text{CO})_6 \qquad (1)$$

Table 1
Comparison of the IR ($\nu C=O$) frequency and ^{13}C NMR of oxocyclo cobalt complexes with **2**.

Compound		ν_{CO} [cm^{-1}]	δ ^{13}C NMR[a] [ppm]	Ref.
2		2081, 2020, 2009, 1809, 1729	167.2, 94.6, 93.7, 93.3	This work
	$R^1 = Ph; R^2 = Ph; R^3 = H$	2088, 2038, 2027, 1734	164.8, 93.8, 90.2, 70.8	[10]
	$R^1 = Ph; R^2 = Me; R^3 = H$	2085, 2035, 2021, 1737	164.7, 95.6, 88.9	[10]
	$R^1 = tBu; R^2 = H; R^3 = H$	2089, 2029, 2016, 1736	166.5, 113.7, 71.1, 69.0	[10]
	$R^1 = iPr; R^2 = H; R^3 = H$	2085, 2031, 2019, 1735	167.4, 107.3, 72.1, 69.2	[10]
		2032, 1984, 1741	172.6, 110.1, 97.9, 64.1	[11]
		1992, 1940, 1618	157.6, 97.9, 87.2	[12]

[a] First values for ketonic carbonyl carbon and the other values for ring carbon.

The mechanism for the formation of **2** is not fully implicit; however a plausible reaction stoichiometry is shown in equation (1). Hexacarbonylvanadium, [V(CO)$_6$], is known to disproportionate with aromatic hydrocarbons to give ionic [V(CO)$_4$(arene)][V(CO)$_6$] [35]. In addition, it is very volatile and known to decompose at elevated temperature [36]. Therefore, it was not viable to detect neutral [V(CO)$_6$] spectroscopically from the above-mentioned reactions. As a result, the reaction was carried out with toluene in the absence of light at 50 °C and ionic [V(CO)$_4$C$_6$H$_5$CH$_3$][V(CO)$_6$] complex was detected spectroscopically in the solutions [37]. In order to validate the production of BH$_3$, the above reaction was performed at 70 °C in the presence of Lewis base, PMe$_2$Ph. The reaction was monitored by ^{11}B NMR spectroscopy, which revealed the formation of borane base adduct (BH$_3$·PMe$_2$Ph), as indicated by the presence of a singlet resonance in the ^{11}B{^{1}H} NMR spectrum at δ −36.4 ppm [38].

3. Conclusions

One of the appealing aspects of metallaborane chemistry is its parallel to organometallic chemistry [39]. An example from the present chemistry reinforces this association. In this present study we have elucidated a new mode of reactivity for metallaboranes with transition metal carbonyl fragments, which demonstrates the Cp ring exchange from [(CpV)$_2$(B$_2$H$_6$)$_2$] **1**, to [Co$_4$(CO)$_{12}$], followed by ring expansion by CO insertion. Nevertheless, the argument over the complete understanding of the reaction pathway still remains.

4. Experimental

4.1. General procedures and instrumentation

All the operations were conducted under an Ar/N$_2$ atmosphere using standard Schlenk techniques and glove box. Solvent was distilled prior to use under Argon. [Cp$_2$VCl$_2$], Co$_2$(CO)$_8$, Fe$_2$(CO)$_9$, Mo(CO)$_6$, Cr(CO)$_6$, W(CO)$_6$, [LiBH$_4$·THF] and [BH$_3$·THF] (Aldrich) were purchased and used as received. The compounds [η^6-C$_6$H$_6$Cr(CO)$_3$] [40], [M(CO)$_5$·THF] (M = Mo and W) [41] and [M(CO)$_3$(CH$_3$CN)$_3$] (M = Cr, Mo and W) [42] were prepared as described in literature. [(CpV)$_2$(B$_2$H$_6$)$_2$] was prepared as reported
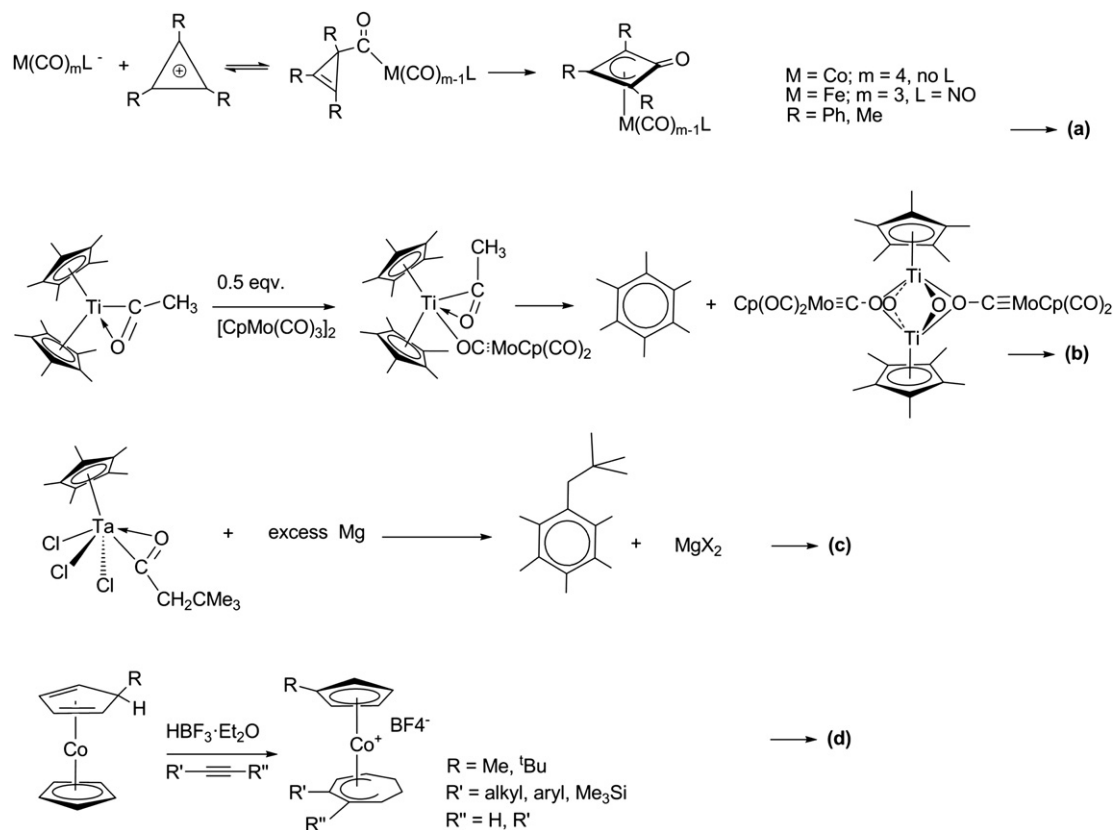
Scheme 2. (a–c) One carbon atom ring expansion reaction; (d) two carbon atom ring expansion reactions.

earlier [8]. Thin-layer chromatography was carried on 250 mm *via* aluminum supported silica gel TLC plates (MERCK TLC Plates). NMR spectra were recorded on a 400 and 500 MHz Bruker FT-NMR spectrometer. Residual solvent protons were used as reference (δ, ppm, CDCl$_3$, 7.26). The ^{59}Co NMR chemical shifts were referenced by setting the NMR peak from 1.0 M K$_3$Co(CN)$_6$ to 0.0 ppm. Infrared spectra were obtained on a Nicolet 6700 FT-IR spectrometer. Microanalyses for C, H and N were performed on Perkin Elmer Instruments series II model 2400. Mass spectra

were obtained on a Jeol SX 102/Da-600 mass spectrometer/Data System using Argon/Xenon (6 kV, 10 mA) as the FAB gas.

4.2. Synthesis of **2** using [Co$_2$(CO)$_8$]

In a 100 mL Schlenk tube, containing 0.04 g (0.14 mmol) of **1** in 12 mL of hexane was added four equivalents of [Co$_2$(CO)$_8$] (0.19 g, 0.56 mmol). Reaction mixture was thermolysed at 70 °C for 14 h and cooled to room temperature. Volatiles were removed in vacuo, and the residue was extracted into hexane and filter through Celite. After removal of solvent from the filtrate, the residue was subjected to chromatographic workup using silica gel TLC plates. Elution with a hexane yielded brown [(η^6-C$_6$H$_5$OCo)Co$_3$(CO)$_9$], **2** (0.025 g, 30%). MS (FAB) P$^+$ (max) 580. ^{59}Co NMR (94 MHz, CDCl$_3$, 22 °C): δ −2023 (s, br), −2492 (s, br); ^{1}H NMR (400 MHz, CDCl$_3$, 22 °C): δ 5.23 (s, 3H), 4.28 (s, 2 H); ^{13}C NMR (100 MHz, CDCl$_3$, 22 °C): δ 206.6 (s, Co−CO), 167.2 (s, (CH)(CH)$_2$(CH)$_2$CO), 94.6 (s, (CH)(CH)$_2$(CH)$_2$CO), 93.7 (s, (CH)(CH)$_2$(CH)$_2$CO), 93.3 (s, (CH)(CH)$_2$(CH)$_2$CO); IR (hexane cm^{-1}): 2081 (s), 2013 (w), 2009 (vs) (C≡O), 1809 (s) (μ-C=O), 1729 (C$_5$H$_5$−C=O); Anal. Calc. for C$_{15}$H$_5$Co$_4$O$_{10}$: C, 31.01; H, 0.87. Found: C, 31.63; H, 1.01%.

4.3. Synthesis of **2** using [Co$_4$(CO)$_{12}$]

A mixture of **1** (0.06 g, 0.21 mmol) and [Co$_4$(CO)$_{12}$] (0.48 g, 0.84 mmol) in 15 mL of hexane was thermolysed at 70 °C with stirring for 14 h and cooled to room temperature. Volatiles were removed in vacuo, and the residue was extracted into hexane and filter through Celite. After removal of solvent from the filtrate, the residue was subjected to chromatographic workup using silica gel TLC plates. Elution with a hexane yielded brown [(η^6-C$_6$H$_5$OCo)Co$_3$(CO)$_9$], **2** (0.039 g, 32%).

Table 2
Crystallographic data for compound **2**.

	2
Formula	C$_{15}$H$_5$Co$_4$O$_{10}$
Formula weight	580.91
Crystal system	Trigonal
Space group	R−3
a (Å)	13.2567(2)
b (Å)	13.2567(2)
c (Å)	18.5849(3)
α (°)	90
β (°)	90
γ (°)	120
V (Å^3)	2828.53(8)
Z	6
D_{calc} (g/cm^3)	2.046
F (000)	1698
μ (mm^{-1})	3.509
Crystal size (mm)	0.18 × 0.16 × 0.15
θ Range (°)	2.09−29.90
Goodness-of-fit (GOF)	1.020
R indices [$I > 2\sigma(I)$]	R1 = 0.0312; wR2 = 0.0684
R indices (all data)	R1 = 0.0482; wR2 = 0.0741
Largest difference in peak and hole (e/Å^3)	0.582 and −0.510

4.4. X-ray structure determination

Suitable X-ray quality crystals of **2** were grown by slow diffusion of a hexane: CH_2Cl_2 (9.5:0.5 v/v) solution and single crystal X-ray diffraction studies were undertaken. Crystal data were collected and integrated using Bruker Apex II CCD diffractometer equipped with graphite monochromated Mo-Kα ($\lambda = 0.71073$ Å) radiation at 173 K. The structure was solved by heavy atom methods using SHELXS-97 [43] and refined using SHELXL-97 (Sheldrick, G.M., University of Göttingen) [44]. The structure solution and refinement showed electron density peaks (heavier than those expected from hydrogen atoms) connected to three alternate carbons of the C_6H_5O ligand. The peaks were assigned as oxygen and their site-occupancies were refined as free variables. The refinement converged the three occupancies to nearly equal with value of 1/3. During the final stages of refinement, these values were fixed at 1/3. The disorder can be interpreted as follows: in a given unit cell the oxygen can take only one of these positions, while different unit cells can take any one of these positions with an average occupancy of 1/3 in each position (Table 2).

Acknowledgements

Appendix A. Supplementary material

CCDC 754878 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2010.08.004.

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