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ORIGINAL PAPER

Crystal Structures of Cobalt Sandwich Complexes in the η^5-Cyclopentadienyl/η^4-Cyclobutadiene and η^5-Cyclopentadienyl/η^4-Cyclopentadienone Families

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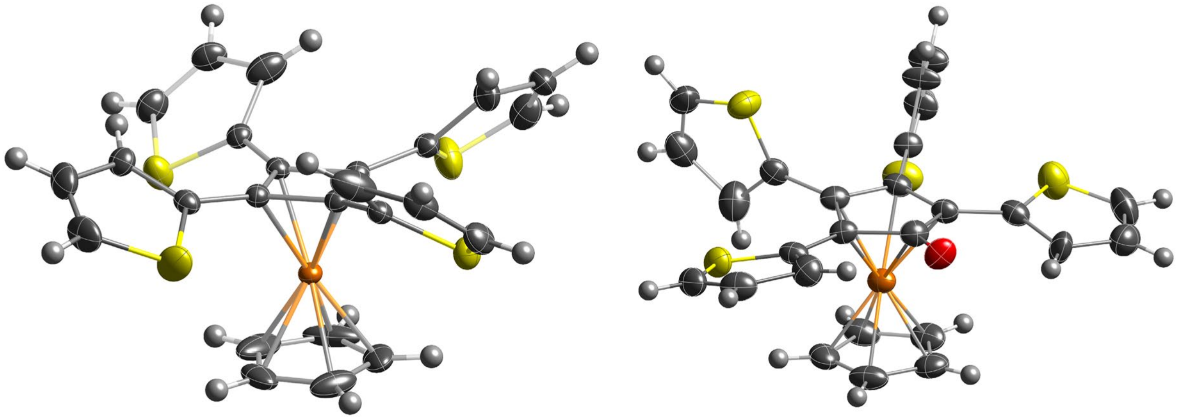
Abstract

The crystal structures of six cobalt sandwich complexes—four in the η^5-cyclopentadienyl/η^4-cyclobutadiene family, two from the related η^5-cyclopentadienyl/η^4-cyclopentadienone family—are presented and discussed alongside related structural precedents. In each of the complexes an undecorated cyclopentadienyl ligand is present whereas the partner cyclobutadiene or cyclopentadienone ligand bears four identical aromatic substituents (phenyl, *p*-tolyl, *p*-fluorophenyl, 2-thienyl or 2,2′-bithienyl). This range of substituents allows for detailed structural comparison between members of the families of sandwich complexes presented here, and with previously reported structures.

Graphic Abstract

Crystal structures of members of the η^5-cyclopentadienyl/η^4-tetraarylcyclobutadiene (left) and η^5-cyclopentadienyl/η^5-cyclopentadienone (right) families of sandwich complexes are presented.



Keywords Sandwich complex · π-Complex · Metallocene · Cyclopentadiene · Crystal structure

Introduction

The initial discovery of ferrocene [1, 2], the archetypal bis-η^5-cyclopentadienyl organometallic compound, was followed by structural proof that this material exists as a π-donor sandwich complex [3]. The formulation of this material as one which adheres to an 18-electron rule allowed for the proposition, and subsequent preparation, of a range

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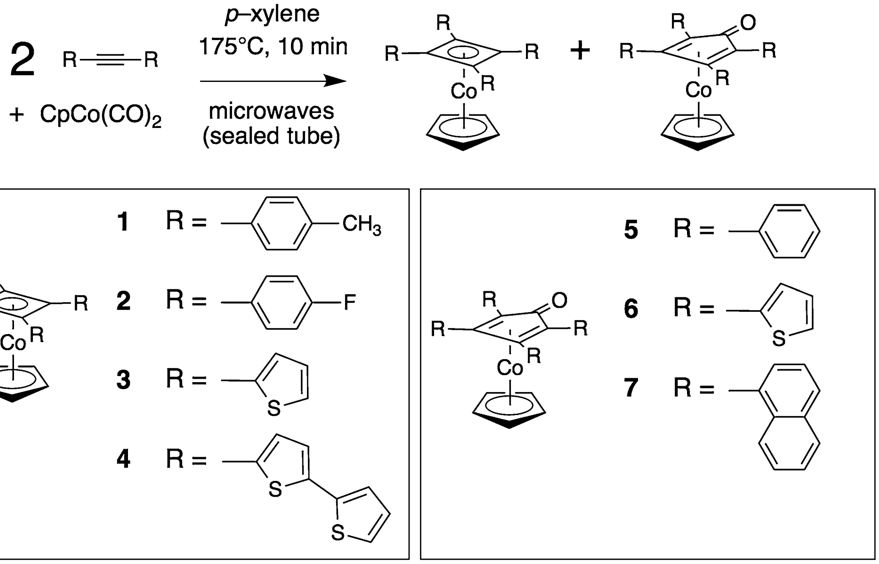
Scheme 1 Microwave-promoted synthesis of (η^5-Cp)Co(η^4-C_4R_4) and (η^5-Cp)Co(η^5-C_5R_4O) complexes and material key



of organometallic π-complexes assembled from rule-compliant combinations of π-donor ligand and transition metal. A prominent example concerns η^5-cyclopentadienyl/η^4-tetraphenylcyclobutadiene sandwich complexes of cobalt(I) in which the cyclobutadiene π-donor ring is prepared from cyclodimerization of an acetylene derivative [4]. The in situ preparation and capture on a metal center of the anti-aromatic cyclobutadiene system remains a compelling example of the predictive power of the 18-electron rule.

Numerous X-ray crystal structures of members of this family of organometallic complexes—(η^5-Cp)Co(η^4-C_4R_4), where R is typically an aromatic group—are known. The overwhelming majority of these concern derivatives which bear a substituted cyclopentadienyl ring [5–13]. The structure of the fully unsubstituted parent complex, (η^5-Cp)Co(η^4-C_4H_4), was reported in 1979 [14, 15], fully 18 years after its initial, and challenging, preparation [4]. In contrast, syntheses of complexes derived from diarylacetylenes are straightforward. The seminal work of Rausch and Genetti established a simple synthetic route which continues to prove its usefulness and generality [16]. Their work also served as the basis for our development of a microwave-promoted approach which was used to prepare all of the materials whose structures are presented here [17]. Notably, both the original study and the microwave approach grant simultaneous access to sandwich complexes in both the η^5-cyclopentadienyl/η^4-cyclobutadiene, (η^5-Cp)Co(η^4-C_4R_4), and η^5-cyclopentadienyl/η^4-cyclopentadienone, (η^5-Cp)Co(η^4-C_5R_4O), families. The latter complexes result from CO insertion into the nascent four-membered cyclobutadiene ring. Avoidance of the use of CpCo(CO)$_2$ as the source of the CpCo fragment greatly reduces this possibility and represents a significant advance in the application of microwaves to the preparation of (η^5-Cp)Co(η^4-C_4R_4) complexes [18].

The microwave synthetic approach that was used to prepare a number of complexes in both the (η^5-Cp)Co(η^4-C_4R_4) and (η^5-Cp)Co(η^4-C_5R_4O) series is outlined in Scheme 1. Although these reactions typically produce isolable amounts of both cyclobutadiene and cyclopentadienone complexes, not all complexes provided crystals suitable for structure determination. Accordingly, those complexes presented here, **1–4** in the (η^5-Cp)Co(η^4-C_4R_4) series and **5** and **6** in the (η^5-Cp)Co(η^4-C_5R_4O) series, cover a range of aromatic substituents with complexes **3** and **6** representing the only matched pair of structures (one of each structural type). The crystal structure of the 1-naphthyl substituted cyclopentadienone complex **7** was reported in our original microwave paper [17]. A closer examination of this previously reported structure is included alongside the new structures presented here.

Experimental

All complexes were prepared according to the previously published procedure outlined in Scheme 1 and, with the exception of complex **4**, their complete analysis is reported therein [17]. A full description of the preparation and characterization of **4** will be published elsewhere. In each case single crystals suitable for X-ray crystallographic study were obtained by slow diffusion of water into a DMSO solution of the complex in a sealed vial.

Crystallographic data for **1**, **3**, **5**, and **6** and were collected on Bruker Nonius Kappa diffractometer with a CCD area detector using monochromatized Mo-Kα X-ray radiation (λ = 0.71073 Å) equipped with an Oxford Cryosystem low temperature device; for **2**, data was collected on a Bruker SMART APEX2 CCD diffractometer using synchrotron radiation (λ = 0.6848 Å); for **4**, data was collected using Mo-Kα X-ray radiation (λ = 0.71073 Å) on a Bruker APEX2 DUO CCD diffractometer equipped with Cu/Mo ImuS microfocus sources and an Oxford Cryosystem low temperature device. All structures were solved by direct methods SHELX97, and refined by full-matrix least-squares calculations. All hydrogen atoms were assigned riding isotropic displacement parameters and constrained to idealized geometries. Table 1 summarizes the X-ray crystal data and structure refinement details for complexes **1–6**.

Results and Discussion

(η^5-Cp)Co(η^4-C_4R_4) Structures

The structures of complexes **1–4** each contain discrete (η^5-Cp)Co(η^4-C_4R_4) units and all four structures crystallize in the $P2_1$/c space group. These four complexes form two distinct structural pairs. Complexes **1** and **2**, illustrated in Figs. 1 and 2, differ only in the nature of the *para*-substituent borne by the benzene rings (methyl and fluoro, respectively). Complexes **3** and **4**, illustrated in Figs. 3 and 4, present either four 2-thienyl or four 2,2′-bithienyl substituents. Table 2 lists the distances in each structure between the Co atom and the two ring centroids, together with comparative values from the structures of the unsubstituted parent complex (η^5-Cp)Co(η^4-C_4H_4) [19], and the phenyl substituted analogue (η^5-Cp)Co(η^4-C_4Ph_4) [14, 15]. Data from a number of other 4-substituted phenyl complexes are also included, and these may be identified by both their CCDC entry and the nature of the R group [13, 14, 20–22]. The entries in Table 2 are ordered by an approximation of steric bulk in both the R group and, in certain cases, in the nature of a cyclopentadienyl ring substituent.

Unsurprisingly, the shortest distance between the Co atom and the two ring centroids is found in the case of the unsubstituted (η^5-Cp)Co(η^4-C_4H_4) parent structure (CBCPCO). For complexes **1–4**, and for those previously reported complexes in which the R group is a relatively unencumbered aromatic ring (typically bearing only a 4-position substituent), the Co···Cp (centroid) distance is remarkably consistent at 1.670 ± 0.004 Å. A value in this range is also found for a complex in which a formyl group is present on the cyclopentadienyl ring (HIBMOV). The Co···Cp (centroid) distances for the remaining structures, all of which contain either a bulky cyclobutadiene aromatic substituent (mesityl-CPMSBC, 4-dodecaborylphenyl-NEVCUM, or 4-(dimethylamino)phenyl-HIBMIP), or an extended cyclopentadienyl system (2-tropyliumethenyl-KIMRAB), are consistently longer. The increase in Co···Cp (centroid) distance in the mesityl containing structure is likely the result of increased local steric hindrance; this complex is the sole example in which the aromatic groups possess more than one substituent and these groups are *ortho* to the point of attachment to the cyclobutadiene ring. In both the 4-dodecaborylphenyl (NEVCUM) and 4-(dimethylamino)phenyl (HIBMIP) cases the π-donating ability of the substituent group may play a role in increasing the Co···Cp (centroid) distance, an argument that is bolstered by noting that 4-pyridyl (NEVCIA) or 4-ethynylphenyl (TUSVOS) substituents, both of which are electron withdrawing, are present in structures with some of the shortest distances in this comparison group. Finally, a modest increase in Co···Cp (centroid) distance is observed when comparing three related complexes which are consistent in containing 4-tolyl groups on the cyclobutadiene ring while the nature of the Cp ring varies. Complex **1** contains an unsubstituted Cp ring whereas the additional members of this comparison subgroup possess either a formyl-substituted Cp ring (HIBMOV) or a far larger tropylium derived Cp ring (KIMRAB). The observed lengthening of the Co···Cp (centroid) distance with additional Cp ring adornment is consistent with a general increase in steric congestion.

In accordance with theoretical calculations for (η^5-Cp)Co(η^4-C_4Ph_4) structures [13, 22], the Co···C_4R_4 (centroid) distances listed in Table 2 are consistently longer than those for the Co···Cp (centroid) measurement.[1] An exception to this trend is found in the 4-dodecaborylphenyl substituted complex (NEVCUM) which presents a Co···C_4R_4 (centroid) distance that is shorter than the unsubstituted (η^5-Cp)Co(η^4-C_4H_4) structure (CBCPCO). Absent this outlier complex, the variability in Co···C_4R_4 (centroid) distances is around twice that found for the Co···Cp (centroid) distances which likely reflects the greater influence from the fully substituted cyclobutadienyl ring versus the typically unsubstituted cyclopentadienyl ring. There exists no obviously discernible correlation between the Co···C_4R_4 (centroid) distance and the nature of the substituent R group.

The dihedral angles between the planes of the cyclobutadiene and Cp rings are also included in Table 2. Nine of the thirteen complexes have dihedral angles of ≤ 3° while a

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[1] One previously reported structure which has been excluded from Table 2 is the (η^5–Cp)Co(η^4–C_4R_4) complex where R = 4–(ethoxycarbonyl)phenyl (this structure, CCDC entry NEVCOG, was published alongside NEVCIA and NEVCUM) [20]. The X-ray crystal structure of this material reveals a packing mode in which extended columns of stacked sandwich complexes exhibit fourfold symmetry about a central axis. Furthermore, these stacks contain partial occupancy Co atoms on either side of the rings with occupancies of 79% and 21%. In essence, the sandwich complexes are disordered over two sites within these columns. The measured Co···Cp (centroid) distance for the major fraction is 1.63 Å with a corresponding Co···C_4R_4 distance of 1.79 Å (with a dihedral angle of 2°). Both of these distances are clearly incomparable with the other structures in Table 2 and provide the reason for exclusion from comparison. It should be noted that it is possible that this type of disorder is also present in the structure of NEVCIA (Co occupancies of 97% and 3%).

Table 1 Crystal data and structure refinement details for **1–6**

	1	**2**	**3**
CCDC deposition no.	1898353	1898350	1898351
Empirical formula	$C_{37}H_{33}Co$	$C_{33}H_{21}CoF_4$	$C_{25}H_{17}CoS_4$
Formula weight	536.56	552.43	504.56
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
Temperature	120 K	120 K	120 K
Crystal form	Orange prism	Yellow plate	Orange plate
	0.24 × 0.10 × 0.07 mm	0.04 × 0.04 × 0.01 mm	0.24 × 0.22 × 0.04 mm
Unit cell dimensions	$a = 11.6308$ (2) Å	$a = 10.387$ (3) Å	$a = 9.8727$ (2) Å
	$b = 21.1946$ (4) Å	$b = 20.471$ (6) Å	$b = 18.9018$ (6) Å
	$c = 12.4325$ (2) Å	$c = 12.393$ (3) Å	$c = 12.5377$ (4) Å
	$\beta = 108.342$ (1)°	$\beta = 110.075$ (3)°	$\beta = 112.063$ (2)°
Volume	2909.03 (9) $Å^3$	2475.1 (12) $Å^3$	2168.35 (11) $Å^3$
Z	4	4	4
D_c	1.225 g cm^{-3}	1.483 g cm^{-3}	1.546 g cm^{-3}
Absorption coefficient	0.613 mm^{-1}	0.745 mm^{-1}	1.187 mm^{-1}
Radiation type, wavelength	Mo Kα, 0.71073 Å	Synchrotron, 0.69050 Å	Mo Kα, 0.71073 Å
$F_{(000)}$	1128	1128	1032
θ range	3.05°–26.00°	1.96°–25.58°	3.10°–27.48°
Limiting indices	$-14 \le h \le 14$ $-26 \le k \le 26$ $-15 \le l \le 15$	$-12 \le h \le 12$ $-25 \le k \le 25$ $-14 \le l \le 15$	$-12 \le h \le 12$ $-24 \le k \le 24$ $-16 \le l \le 16$
Reflections collected/unique	42103/5630	17855/4990	43633/4974
R_{int}	0.0804	0.0443	0.0914
Data/restraints/parameters	5630/348/0	4990/343/0	4974/271/415
Data with $I > 2\sigma(I)$	4624	4134	3448
Goodness of fit on F^2	1.121	1.021	1.022
R_1, wR_2 (data with $I > 2\sigma(I)$)	0.0652, 0.1034	0.0338, 0.0852	0.0446, 0.0920
R_1, wR_2 (all data)	0.0893, 0.1102	0.0450, 0.0852	0.0824, 0.1067
Largest diff. peak/hole (e·$Å^{-3}$)	0.462/− 0.399	0.372/− 0.360	0.570/− 0.524
	4	**5**	**6**
CCDC deposition no.	1898354	1898349	1898352
Empirical formula	$C_{41}H_{25}CoS_8$	$C_{34}H_{25}CoO$	$C_{26}H_{17}CoOS_4$
Formula weight	833.02	508.47	532.61
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/c$	Pbca	$P2_1/c$
Temperature	100 K	120 K	120 K
Crystal form	Pink prism	Red prism	Red prism
	0.55 × 0.32 × 0.16 mm	0.38 × 0.24 × 0.16 mm	0.32 × 0.24 × 0.06 mm
Unit cell dimensions	$a = 11.862$ (8) Å	$a = 12.7869$ (6) Å	$a = 20.1332$ (8) Å
	$b = 21.991$ (15) Å	$b = 15.0429$ (5) Å	$b = 12.4754$ (4) Å
	$c = 14.001$ (9) Å	$c = 25.5469$ (11) Å	$c = 18.5706$ (7) Å
	$\beta = 93.213$ (9)°		$\beta = 107.265$ (2)°
Volume	3647 (4) $Å^3$	4914.0 (4) $Å^3$	4454.2 (3) $Å^3$
Z	4	4	8
D_c	1.517 g cm^{-3}	1.375 g cm^{-3}	1.588 g cm^{-3}
Absorption coefficient	0.960 mm^{-1}	0.724 mm^{-1}	1.164 mm^{-1}
Radiation type, wavelength	Mo Kα, 0.71073 Å	Mo Kα, 0.71073 Å	Mo Kα, 0.71073 Å
$F_{(000)}$	1704	2112	2176

Table 1 (continued)

	4	**5**	**6**
θ range	1.72°–25.34°	1.59°–26.00°	1.06°–26.00°
Limiting indices	$-14 \le h \le 14$ $-25 \le k \le 26$ $-16 \le l \le 16$	$-15 \le h \le 15$ $-18 \le k \le 17$ $-31 \le l \le 31$	$-24 \le h \le 24$ $-15 \le k \le 15$ $-22 \le l \le 22$
Reflections collected/unique	26444/6579	25325/4802	39938/8760
R_{int}	0.0629	0.0774	0.1279
Data/restraints/parameters	6579/463/14	4802/325/0	8760/577/950
Data with $I > 2\sigma(I)$	5281	3250	4537
Goodness of fit on F^2	1.870	1.094	0.992
R_1, wR_2 (data with $I > 2\sigma(I)$)	0.0883, 0.2646	0.0469, 0.1030	0.0630, 0.1455
R_1, wR_2 (all data)	0.1038, 0.2768	0.0921, 0.1274	0.1557, 0.1863
Largest diff. peak/hole (e Å^{-3})	4.059/− 1.225	0.487/− 0.585	0.575/− 0.565

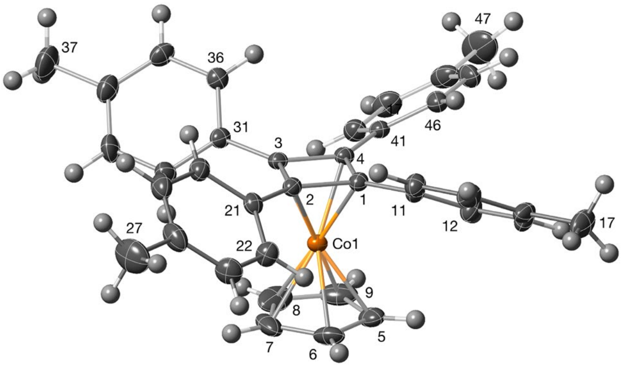

Fig. 1 Molecular structure and selected atom numbering scheme for **1** (displacement ellipsoids are drawn at the 50% probability level)

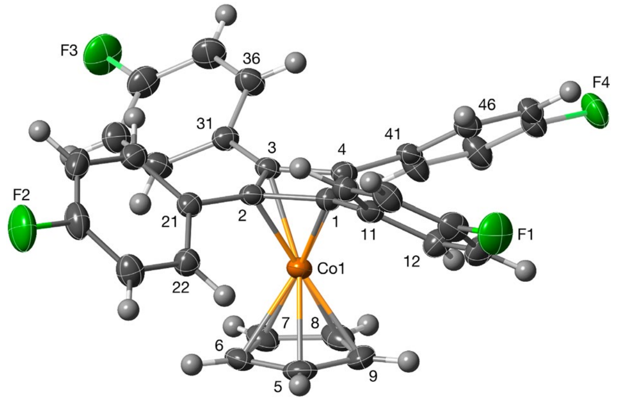

Fig. 2 Molecular structure and selected atom numbering scheme for **2** (displacement ellipsoids are drawn at the 50% probability level)

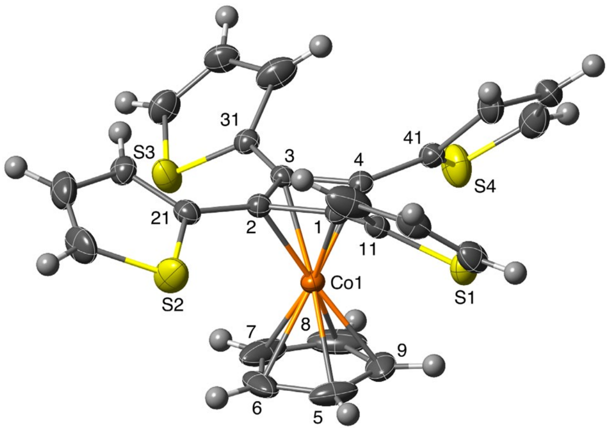

Fig. 3 Molecular structure and selected atom numbering scheme for **3** (displacement ellipsoids are drawn at the 50% probability level)

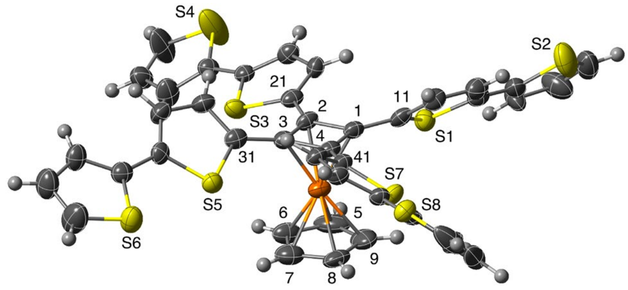

Fig. 4 Molecular structure and selected atom numbering scheme for **4** (displacement ellipsoids are drawn at the 50% probability level). (An unassigned residual electron density peak of > 4e·Å^{-3} is found 1.80 Å from C18. The source of this peak is unknown but may reside in the fact that the overall crystal quality for this compound was relatively poor, as evinced by a high R value.)

tenth, KIMRAB, presents disorder in the Cp ring but nonetheless has a similar, average, dihedral angle of 3.1°. The largest dihedral angle (7.5°) is found for the mesityl containing complex (CPMSBC) and, once again, is likely the result of steric effects introduced by the presence of the crowded mesityl substitution pattern. The rotational relationship of the essentially coplanar rings in complexes of this type has

Table 2 Distances from the Co atom to the two respective ring centroids for (η^5-Cp)Co(η^4-C_4R_4) structures

Complex or CCDC entry	Co···Cp (Å)	Co···C_4R_4 (Å)	Dihedral angle (°)	R group	References
CBCPCO	1.661	1.682	0.9	H	[19]
CPBUCO01	1.670	1.686	1.4	Phenyl	[15]
1	1.666 (3)	1.682 (2)	0.8 (1)	4-Tolyl	This work
2	1.669 (2)	1.683 (2)	3.2 (1)	4-Fluorophenyl	This work
3	1.670 (3)	1.687 (3)	2.7 (2)	2-Thienyl	This work
4	1.673 (7)	1.698 (6)	2.1 (6)	2,2′-Bisthienyl	This work
CPMSBC	1.691	1.703	7.5	Phenyl and mesityl (2 of each)	[14]
NEVCIA	1.669	1.698	4.0	4-Pyridyl	[20]
NEVCUM	1.677	1.668	3.0	4-Dodecaborylphenyl	[20]
TUSVOS	1.668	1.688	5.6	4-Ethynylphenyl	[21]
HIBMIP	1.683[a]	1.694	2.6	4-(Dimethylamino)phenyl	[22]
HIBMOV	1.673[a]	1.693	1.0	4-Tolyl	[22]
KIMRAB	1.683[b]	1.697	2.0/4.4[c]	4-Tolyl	[13]

Dihedral angles between the cyclobutadiene and Cp ring planes are also included

[a] Contains a formyl substituted cyclopentadienyl ring

[b] Contains a 2-(tropylium)ethenyl substituted cyclopentadienyl ring

[c] The Cp ring exhibits disorder over two positions

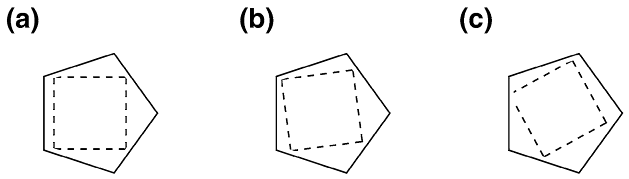

Fig. 5 The three possible mutual orientations of the cyclopentadienyl and cyclobutadiene rings in (η^5-Cp)Co(η^4-C_4Ph_4) sandwich complexes: **a** edge aligned; **b** corner aligned; **c** non-aligned

Table 3 Dihedral angles between the planes of each aryl R group and their parent cyclobutadiene ring, and out-of-plane deviations for the first atom of each attached ring, for complexes **1–4**

Complex	Dihedral angle (°) and out-of-plane distance (Å)			
	Ring 1	Ring 2	Ring 3	Ring 4
1	31.4 (1) 0.104 (2)	37.8 (1) 0.015 (2)	46.2 (1) 0.210 (2)	29.3 (1) 0.092 (2)
2	38.1 (9) 0.189 (2)	42.0 (1) 0.126 (2)	33.4 (1) 0.168 (2)	35.7 (1) 0.075 (2)
3	39.8 (2) 0.201 (3)	29.8 (2) 0.177 (3)	39.4 (1) 0.171 (3)	44.3 (1) 0.229 (3)
4	39.3 (4)[a] 5.6 (4)[b] 0.190 (7)[a]	22.0 (4)[a] 10.1 (3)[b] 0.175 (7)[a]	42.0 (4)[a] 12.7 (4)[b] 0.096 (7)[a]	33.2 (4)[a] 9.9 (4)[b] 0.266 (7)[a]

[a] For **4**, left to right, rings 1, 3, 5 and 7 respectively

[b] Dihedral angle (°) between connected thiophene rings (1–2, 3–4, 5–6, 7–8)

also been explored [8, 23]. For an unsubstituted cyclopentadiene ring there are three possible mutual orientations of the two rings (Fig. 5); (a) where the two rings are aligned along an edge, (b) where the two rings possess an aligned corner, or (c) where no alignment of either previous type exists. For the four new (η^5-Cp)Co(η^4-C_4R_4) complexes reported here **1** has an aligned edge, whereas **2**, **3** and **4** each present an aligned corner.

Steric constraints prevent the four cyclobutadiene-appended aromatic groups in (η^5-Cp)Co(η^4-C_4Ph_4) complexes from achieving co-planarity. As a result these four rings adopt a propeller-like array with all four rings inclined in the same direction. This structural feature is conserved across all (η^5-Cp)Co(η^4-C_4Ph_4) complexes and the values for those reported here, **1–4**, are detailed in Table 3. The inclinations of the planes of the aromatic rings to their cyclobutadiene parent average around 35° and fall in the typical range for complexes of this type [5–13]. Another conserved structural feature for these complexes is that the directly appended aromatic ring carbons sit slightly out of the plane of the cyclobutadiene ring and away from the cobalt center. These modest out-of-plane deviations are included for complexes **1–4** in Table 2 and are, once again, commonly observed for (η^5-Cp)Co(η^4-C_4Ph_4) complexes.[2]

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[2] For **1–3** ring designations proceed in numerical order as indicated by the labelled carbon attachment points in Figs. 1, 2 and 3; for **4** the individual thiophene rings are paired, 1 with 2 and so forth, according to the labelled sulfur atoms in Fig. 4. The dihedral angles between connected thiophene rings in **4** are also listed.

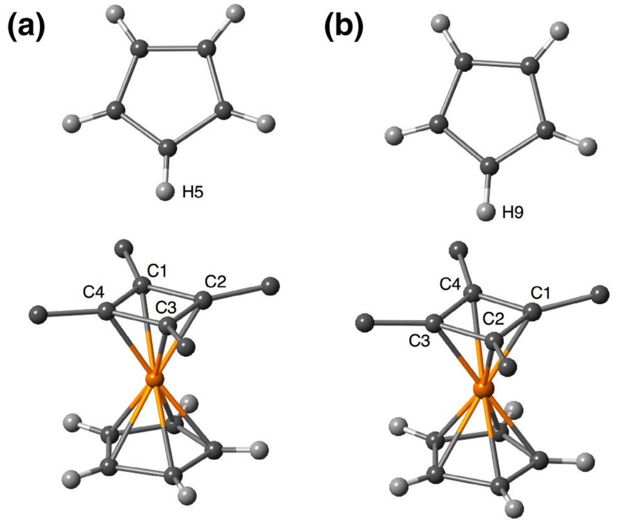

Fig. 6 C–H···π (cyclobutadiene) close contacts revealed in the structures of complexes **a** **2** and **b** **3**. For **2**: H5···C1 2.827(2) Å; H5···C2 2.736(2) Å; H5···C3 2.788(2) Å; H5···C4 2.888(2) Å. For **3**: H9···C1 2.749(3) Å; H5···C2 2.715(3) Å; H5···C3 2.794(3) Å; H5···C4 2.812(3) Å

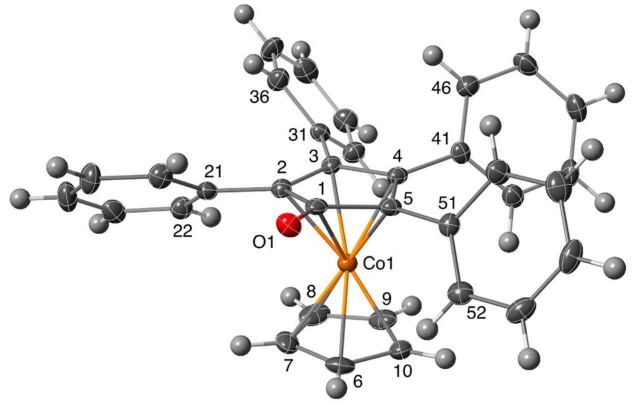

Fig. 7 Molecular structure and selected atom numbering scheme for **5** (displacement ellipsoids are drawn at the 50% probability level)

For tetrathienyl complex **3** there exists rotational disorder in rings 1, 3, and 4 that is typical of thienyl groups: the sulfur atom orientation is at 80/20 occupancy for Ring 1, 85/15 occupancy for ring 3, and 65/35 occupancy for ring 4. Similarly, rotational disorder is also found in the tetra-2,2′-bithienyl complex **4**: ring 4 (70/30 occupancy) and ring 6 (60/40 occupancy). Both Figs. 3 and 4 show only the major site. Finally, the structures of both **2** and **3** reveal a close contact between a cyclopentadienyl hydrogen atom, H5 for complex **2** and H9 for complex **3**, and the π-system of the cyclobutadiene ring of an adjacent molecule. The geometry and parameters of these contacts are illustrated in Fig. 6.

(η^5-Cp)Co(η^5-C_5R_4O) Structures

The structures of η^5-cyclopentadienyl/η^4-cyclopentadienone complexes **5** (R = phenyl) and **6** (R = 2-thienyl) are shown in Figs. 7 and 8 respectively. Complex **5** crystallizes in the *Pbca* space group, while complex **6**, like all four previously discussed cyclobutadiene complexes **1–4**, crystallizes in the $P2_1/c$ space group. Complex **7** (Fig. 9), whose structure we have previously published, also crystallizes in the latter space group [17].

In contrast to the essentially planar cyclobutadiene rings observed in the previously discussed (η^5-Cp)Co(η^4-C_4R_4) structures **1–4**, the cyclopentadieneone rings of complexes **5–7** are slightly puckered. Table 4 lists the deviation (in Å) of each of the five carbon atoms in each cyclopentadieneone ring from the Cremer and Pople mean ring plane [24]. A consistent pattern concerning the direction of deviation from the mean plane is readily apparent with C1, C3 and C4 all residing slightly above the plane whereas C2 and C5 sit slightly below it. For comparison, typical deviations for either the cyclopentadienyl or cyclobutadiene rings in the previous set of complexes (**1–4**) were < 0.010 Å. Table 4 also includes data for two previously reported structures (KEKBUY and KEKCAF [25]) that are similar to complexes **5**–**7** except that they possess phenyl substituents in only the C2 and C5 positions, while alkyl bridges of five carbons (KEKBUY) and seven carbons (KEKCAF) connect the C3 and C4 positions.[3] These two complexes provide the closest points of structural comparison outside of the current work: when compared with (η^5-Cp)Co(η^4-C_4R_4) complexes, known structures of (η^5-Cp)Co(η^4-C_5R_4O) complexes are far less numerous.

Distances from the Co atom to the two respective ring centroids for (η^5-Cp)Co(η^4-C_5R_4O) complexes **5**, **6** and **7** are collected in Table 5. For **5** and **6** the shorter Co-ring centroid distances are observed to the Cp ring and the dihedral angles between the sandwich complex ring planes are < 3°. In contrast, the corresponding dihedral angle in 1-naphthyl complex **7** is, at 5.5°, substantially higher, and the longer Co-ring centroid distance is to the cyclopentadienone ring. The substantial steric interactions introduced by the bulky naphthyl groups likely play a role in this instance. Examination of the packing in complex **7** reveals the presence of two C–H···O close contacts as illustrated in Fig. 10 (from H41 and H8 to O1, symmetry relation: *x*, ½ − *y*, − ½ + *z*). A similar three-centre C–H···O close contact motif occurs in the phenyl analogue **1** but in this case the similarities in

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[3] There exists one other structure worthy of note (DAKJAA) that features a mixed superphane structure of CpCo-capped cyclobutadiene and cyclopentadienone rings [26]. However, the lack of any aryl substituents in this case limits useful comparison with either of the sets of structures in this work.

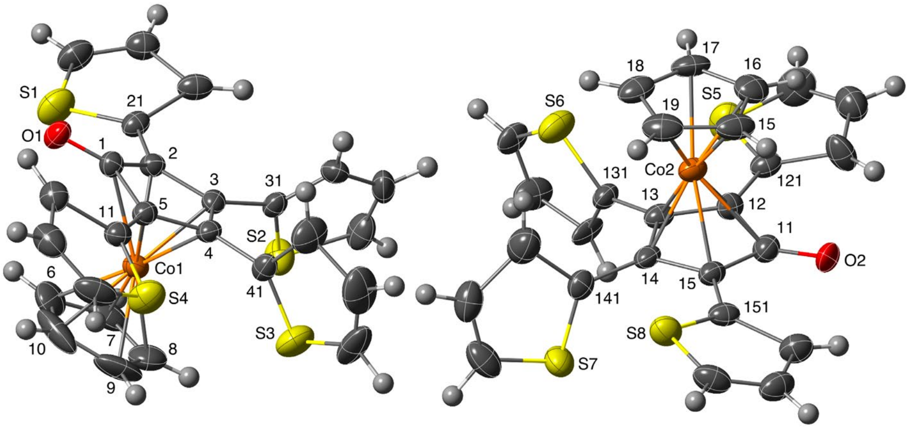

Fig. 8 Molecular structure and selected atom numbering scheme for **6** (displacement ellipsoids are drawn at the 50% probability level). Two crystallographically unique molecules are present in the asymmetric unit

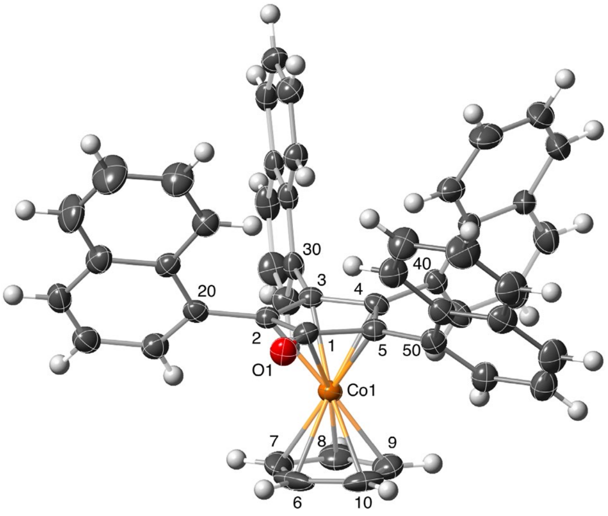

Fig. 9 Molecular structure and selected atom numbering scheme for **7** (displacement ellipsoids are drawn at the 50% probability level)

Table 4 Deviation (Å) of each of the five carbon atoms of the cyclopentadieneone rings in complexes **5**, **6** and **7**, and complexes KEKBUY and KEKCAF, from the Cremer and Pople ring plane [24]

Complex or CCDC entry	C1	C2	C3	C4	C5	References
5	0.078 (3)	−0.060 (3)	0.020 (3)	0.029 (3)	−0.066 (3)	This work
6	0.069 (6) 0.070 (6)	−0.056 (6) −0.060 (6)	0.022 (6) 0.027 (6)	0.021 (6) 0.016 (6)	−0.056 (6) −0.053 (6)	This work
7	0.044 (4)	−0.032 (4)	0.007 (4)	0.020 (4)	−0.040 (4)	[13]
KEKBUY	0.074	−0.067	0.035	0.010	−0.052	[25]
KEKCAF	0.080	−0.063	0.022	0.028	−0.066	[25]

both ring tilt and Co···Cp (centroid) distance with thienyl complex **6** provides further support for steric effects being the primary source of the deviations observed in naphthyl complex **7**.

The dihedral angles between the ring planes of the pendant aryl groups and the parent cyclopentadienone are collected in Table 6. For complexes **5** and **7** the attached aryl rings are inclined with a consistent directionality as observed in (η^5-Cp)Co(η^4-C_4R_4) complexes **1–4**. However, in contrast to **1–4** the angles of inclination are consistently and substantially higher as a direct result of their closer proximity to each other as adjacent substituents on a cyclopentadienone ring. For thienyl complex **6** the rings are not all inclined in the same direction and the rings attached to either side of the carbonyl group are inclined (on average) far less than expected, while the two remaining (non-C=O adjacent) rings are inclined (on average) at steeper angles than typically observed. A possible explanation for this result is the close packing of two unique molecules of complex **6** in the asymmetric unit (Fig. 8). The out-of-plane deviations for the first atom of each attached ring, and for the carbonyl oxygen atom, for complexes **5–7** are also given in Table 6. For complexes **5** and **6** the previously noted puckering of the parent five-membered cyclopentadienone ring, wherein some ring atoms sit above the mean plane and some below, tracks outward to the attached aryl group ring atoms. For naphthyl complex **7**, all atoms attached to the cyclopentadienone ring lie essentially in the same plane (for ring 4) or sit above it. Once again, this specific outcome is likely the result of the presence of bulky 1-naphthyl substituent groups.

The presence of the carbonyl group in (η^5-Cp)Co(η^4-C_5R_4O) complexes **5–7** provides an orientational handle to

Table 5 Distances from the Co atom to the two respective ring centroids for (η^5-Cp)Co(η^4-C$_5$R$_4$O) complexes

Complex or CCDC entry	Co···Cp (Å)	Co···C$_5$R$_4$O (Å)	Dihedral angle (°)	R group	References
5	1.667 (1)	1.673 (1)	2.9 (2)	Phenyl	This work
6[a]	1.670 (3) 1.667 (3)	1.675 (2) 1.685 (2)	1.6 (3) 2.8 (3)	2-Thienyl	This work
7	1.684(2)	1.677(1)	5.5(2)	1-Naphthyl	This work
KEKBUY	1.660	1.673	2.9	Phenyl[b]	[25]
KEKCAF	1.670	1.678	1.5	Phenyl[b]	[25]

Dihedral angles between the cyclopentadienone and Cp ring planes are also included

[a] Two crystallographically unique molecules are present in the asymmetric unit and data is presented for both

[b] Substituents are present at only the C2 and C5 positions

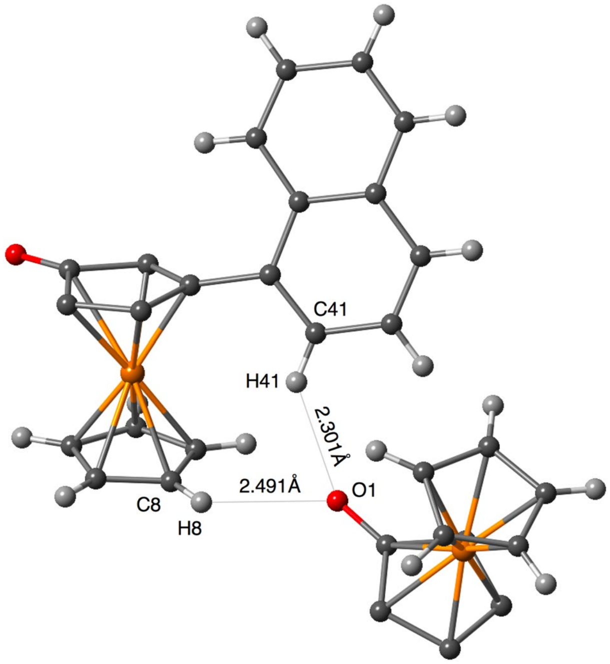

Fig. 10 C–H···O close contacts observed in the structure of 1-naphthyl complex **7**

facilitate estimation of the twist angle between the cyclopentadienyl and cyclopentadienone rings. This can be achieved through the use of the O1–C1–Co1–C6 torsion angle. For complex **5** this angle is − 9.2(3)°, for complex **6** (two values) 15.2(6)° and 19.9(7)°, and for complex **7** − 9.2(4)°. The values for phenyl complex **5** and 1-naphthyl complex **7** are strikingly consistent while the two values for thienyl complex **6** (one for each unique molecule present in the asymmetric unit) are larger, a result generally in line with the more varied structural parameters observed for this material.[4]

Table 6 Dihedral angles between the planes of each aryl R group and their parent cyclobutadiene ring, and out-of-plane deviations for the first atom of each attached ring, for complexes **5–7**

Complex	Dihedral angle (°)/out-of-plane distance (Å)				
	C=O	Ring 1	Ring 2	Ring 3	Ring 4
5	0.162 (2)	37.4 (2) − 0.171 (3)	48.8 (2) 0.180 (3)	59.9 (2) 0.239 (3)	59.7 (2) − 0.047 (3)
6	0.115 (4) 0.143 (4)	29.8 (3) − 0.008 (5) 9.3 (3) − 0.165 (5)	77.1 (3) 0.209 (5) 80.4 (3) 0.254 (5)	68.7 (3) 0.218 (5) 79.3 (3) 0.260 (5)	14.7 (3) − 0.130 (5) 15.6 (3) − 0.062 (5)
7	0.057(2)	62.7 (2) 0.117 (3)	89.4 (2) 0.199 (3)	69.5 (2) 0.215 (3)	50.8 (2) − 0.006 (3)

Conclusion

The six structures of discrete sandwich complexes presented here significantly extend both the number of complexes of this class for which X-ray structural analyses exist, and the range of substitution of the cyclobutadiene or cyclopentadienone ring, leading to the ability to compare and contrast structural features in a broader manner. The increased ease of access to complexes in both the Cp-cyclobutadiene and Cp-cyclopentadienone series afforded by the development of rapid and straightforward microwave-promoted syntheses has aided in this endeavor [17, 18, 25].

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[4] In addition to variation in thienyl ring orientation with respect to the central cyclopentadienone ring, complex **6** (while presenting two unique molecules in the asymmetric unit) also displays the

Footnote 4 (continued)

orientational disorder typical of thiophene rings: Ring 1, 55/45 (%) occupancy, ring 3, 70/30 occupancy, ring 4, 55/45 occupancy, ring 5, 85/15 occupancy, ring 7, 55/45 occupancy, and ring 8, 60/40 occupancy. The possibility exists that ring 6 (associated with S6) also possesses some minor disorder. The orientation of each disordered 2-thienyl ring in Fig. 6 is shown in the majority occupancy.

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