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McMurry reactions of (η^5-acetylcyclopentadienyl) cobalt-(η^4-tetraphenylcyclobutadiene) with benzophenone: ketone couplings and a pinacol/pinacolone rearrangement

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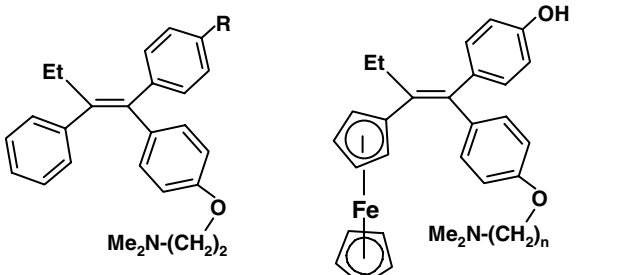
Abstract

The reaction of (η^4-C_4Ph_4) Co[η^5-C_5H_4–C(=O)Me], **5**, with benzophenone under McMurry conditions ($TiCl_4$/Zn/THF) gives the hetero-coupled product (η^4-C_4Ph_4)Co[η^5-C_5H_4–C(Me)=CPh_2], **7**, together with the dicobalt species: *trans*-(η^4-C_4Ph_4)Co[(η^5-C_5H_4–C(Me)=C(Me)-η^5-C_5H_4–] Co(η^4-C_4Ph_4), **9**, and the pinacolone Me[(η^4-C_4Ph_4)Co(η^5-C_5H_4)]$_2$C–C(=O)Me, **10**. The latter is apparently formed from the pinacol by migration of an (η^4-C_4Ph_4)Co[(η^5-C_5H_4)] group. Preferential migration of the cobalt sandwich moiety rather than a methyl group is rationalized in terms of a favored transition state involving a metal-stabilized cation. The products **7**, **9** and **10**, and also the ketone (η^4-C_4Ph_4)Co[η^5-C_5H_4–C(=O)Et], **6**, were all characterized by X-ray crystallography.

Keywords: Cyclobutadiene–cobalt complexes; McMurry couplings; X-ray crystallography; Pinacol rearrangement

1. Introduction

The emerging discipline of bio-organometallic chemistry has revealed its potential for applications in such varied areas as receptor assays [1], multi-immuno and anti-epileptic drug assays [2], agents for tumor imaging and therapy [3] and, more recently, organometallic sandwich compounds with significant anti-cancer activity [4]. Amongst the most promising of these are the ferrocifens, pioneered by Jaouen and his colleagues [5]. In these a phenyl substituent in tamoxifen, **1**, – the current first-line treatment for hormone-dependent breast cancer – has been replaced by a ferrocenyl moiety, as in **2**. While the mechanisms of cell death (apoptosis or necrosis) and of cell signaling mediated by the ferrocifens are yet to be unravelled, their efficacy against tamoxifen-resistant tumors has been clearly demonstrated [6]. We here report preliminary experiments directed towards the synthesis of an analogous series, the cobaltifens, **3**.



1a. R = H *(tamoxifen)*
1b. R = OH *(hydroxytamoxifen)*

2. *hydroxyferrocifens* (n = 2,3,4,5,8)

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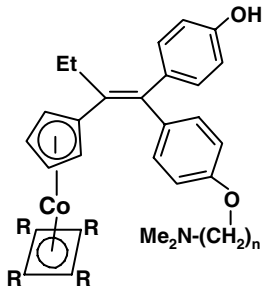


3. *hydroxycobaltifen*

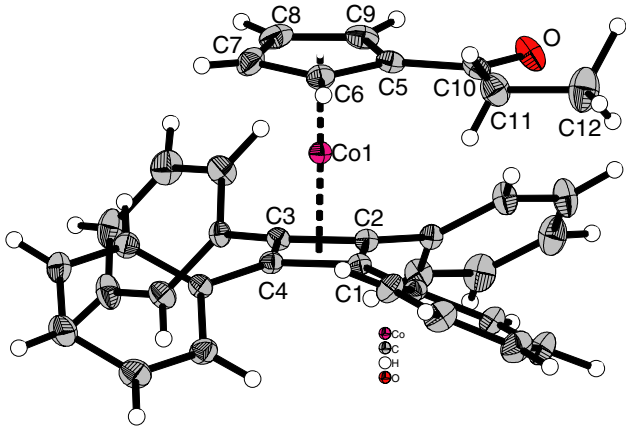


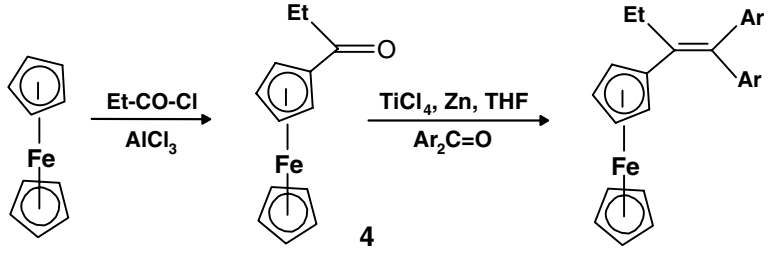
Fig. 1. X-ray crystal structure of (η^4-C_4Ph_4)Co[η^5-$C_5H_4C(=O)Et$], **6**. Selected bond lengths (Å) and angles (°): Co–Cp(ctrd), 1.681(1); Co–Cb(ctrd), 1.694(1); C_5–C_{10}, 1.475(3); C_{10}–C_{11}, 1.504(3); C_{10}–O, 1.224; Cp(ctrd)–Co–Cb(ctrd), 178.52(11); C_5–C_{10}–C_{11}, 117.94(16), C_5–C_{10}–O, 120.22(17); C_6–C_5–C_{10}–C_{11}, 2.0(3); C_9–C_5–C_{10}–O, 2.8(3).

2. Results and discussion

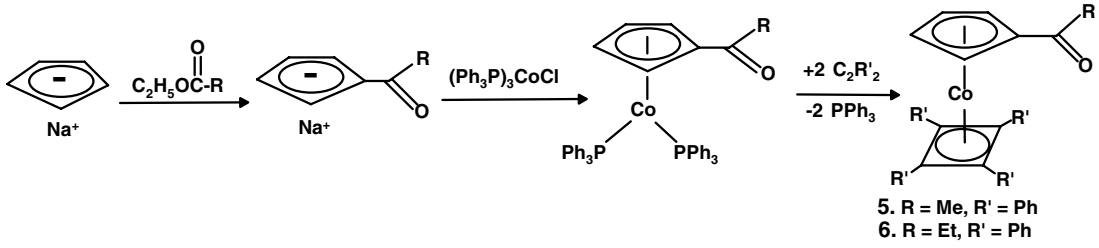
The most efficient route [5] to the ferrocifens involves a McMurry coupling between propionylferrocene, **4**, and an appropriately functionalized benzophenone, as depicted in Scheme 1. In the ferrocenyl system, Friedel-Crafts acylation provides a convenient, high-yield route to the ketone **4**. In contrast, for compounds of the type (η^5-C_5H_5)Co(η^4-C_4R_4), where R = H or Ph, it is the cyclobutadiene ring (or an attached phenyl substituent) that is the favored site for acylation [7].

Consequently, it is necessary to functionalize the five-membered ring before attachment of the organo–cobalt fragment. Early routes [8] to these cobalt sandwich complexes involved the reaction, and subsequent coupling, of two alkynes with $CpCo(CO)_2$; however, more recent work by Stevens and Richards [9] has demonstrated that higher yields are achievable by use of chlorotris(triphenylphosphine)cobalt(I), as shown in Scheme 2.

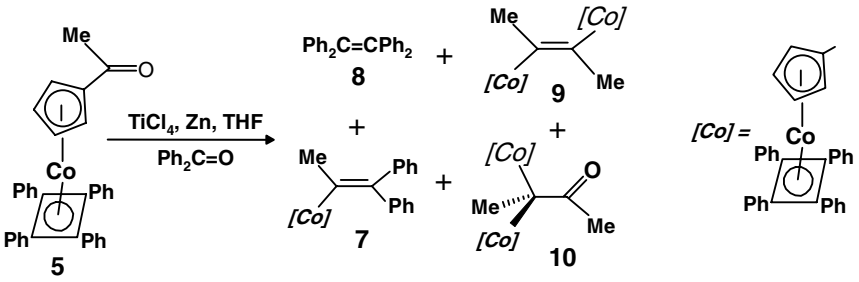
Typically, (η^5-acetylcyclopentadienyl)cobalt(η^4-tetraphenylcyclobutadiene), **5**, and its propionyl homologue, **6**, have been prepared in yields of 26% and 11%, respectively. The X-ray crystal structure of **6** appears as Fig. 1 and closely resembles that previously reported [10] for the acetyl complex **5**. The cobalt atom in **6** is almost equidistant from both rings (Co···Cp-centroid = 1.681(1) Å, Co···Cb-centroid = 1.694(1) Å), the propio-



Scheme 1. Synthetic route to the ferrocifens.



Scheme 2. Synthesis of cobalt sandwich complexes.



Scheme 3. McMurry coupled products from $(C_4Ph_4)Co[C_5H_4C(=O)Me]$ and $Ph_2C=O$.

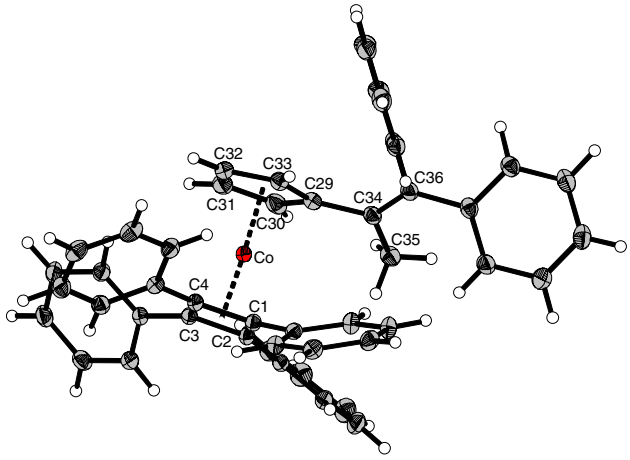


Fig. 2. X-ray crystal structure of $(\eta^4\text{-}C_4Ph_4)Co[\eta^5\text{-}C_5H_4\text{–}C(Me)=CPh_2]$, **7**. Selected bond lengths (Å) and angles (°): Co–Cp(ctrd), 1.678(1); Co–Cb(ctrd), 1.694(1); C_{29}–C_{34}, 1.4776(17); C_{34}–C_{36}, 1.3539(18); C_{34}–C_{35}, 1.5129(18); Cp(ctrd)–Co–Cb(ctrd), 177.40(1); C_{29}–C_{34}–C_{35}, 115.41(11), C_{29}–C_{34}–C_{36}, 122.05(12); C_{35}–C_{34}–C_{36}, 122.45(12).

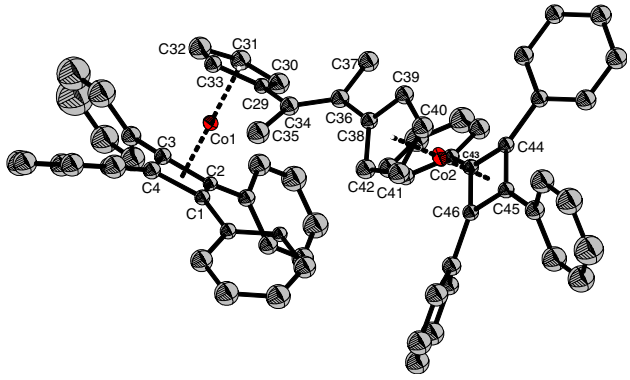


Fig. 3. X-ray crystal structure of *trans*-(Me)*[Co]*–C=C(Me)*[Co]*, **9**. Selected bond lengths (Å) and angles (°): Co(1)–Cp(ctrd), 1.671(6); Co(1)–Cb(ctrd), 1.688(6); Co(2)–Cp(ctrd), 1.678(5); Co(2)–Cb(ctrd), 1.676(5); C_{29}–C_{34}, 1.44(2); C_{34}–C_{36}, 1.37(2); C_{36}–C_{38}, 1.51(2); Cp(ctrd)–Co(1)–Cb(ctrd), 176.7(2); Cp(ctrd)–Co(2)–Cb(ctrd), 176.7(2); C_{29}–C_{34}–C_{35}, 116.3(16), C_{29}–C_{34}–C_{36}, 123.9(17); C_{35}–C_{34}–C_{36}, 119.5(18); C_{34}–C_{36}–C_{37}, 120.1(17), C_{34}–C_{36}–C_{38}, 123.8(17); C_{37}–C_{36}–C_{38}, 115.6(16); C_{35}–C_{34}–C_{36}–C_{37}, 163.9(16); C_{29}–C_{34}–C_{36}–C_{38}, 178.7(14).

nyl group lies almost perfectly coplanar with the cyclopentadienyl ring, and the phenyl substituents on the cyclobutadiene ring adopt a propeller arrangement with dihedral angles ranging from 25° to 60°.

When a 3:1 mixture of the acetyl derivative **5** and benzophenone was subjected to the McMurry procedure, chromatographic separation of the products furnished the desired hetero-coupled alkene **7** in 23% yield and three homo-coupled products **8**, **9** and **10** (Scheme 3). As anticipated, the McMurry coupling of benzophenone gave some tetraphenylethylene, **8**, but the other two products were evidently derived from the cobalt starting material, **5**. The unsymmetrical alkene **7** was identified spectroscopically, and by microanalysis, but was also characterized by X-ray crystallography (Fig. 2). The metric parameters within the cobalt sandwich are normal, the new carbon–carbon double bond length is 1.354 Å, and the two phenyl rings derived from benzophenone are oriented almost mutually orthogonally (interplanar angle 83°).

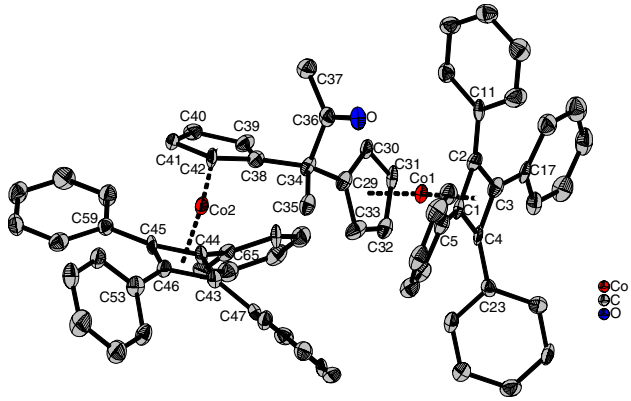


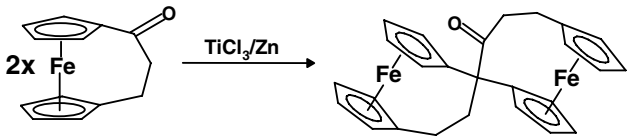
Fig. 4. X-ray crystal structure of $Me[(\eta^4\text{-}C_4Ph_4)Co(\eta^5\text{-}C_5H_4)]_2C\text{–}C(=O)Me$, **10**. Selected bond lengths (Å) and angles (°): Co(1)–Cp(ctrd), 1.683(2); Co(1)–Cb(ctrd), 1.700(2); Co(2)–Cp(ctrd), 1.700(3); Co(2)–Cb(ctrd), 1.708(3); C_{29}–C_{34}, 1.528(15); C_{34}–C_{35}, 1.528(14); C_{34}–C_{36}, 1.553(15); C_{34}–C_{38}, 1.531(14) Cp(ctrd)–Co(1)–Cb(ctrd), 174.2(1); Cp(ctrd)–Co(2)–Cb(ctrd), 173.6(1); C_{29}–C_{34}–C_{36}, 107.9(9), C_{35}–C_{34}–C_{36}, 107.1(8); C_{38}–C_{34}–C_{36}, 110.3(8).

The dicobalt complex **9** was identified as the *trans*-2,3-disubstituted 2-butene in which the methyl and organo–cobalt moieties have adopted the sterically least hindered orientation. The presence of the methyl groups prevents the two cyclopentadienyl rings from displaying a coplanar arrangement that would presumably have maximized conjugation between the organometallic units. As shown in Fig. 3, the molecule exhibits a conformation of almost ideal C_2 symmetry whereby the cyclopentadienyl rings are twisted through $42 \pm 2°$ out of the plane of the alkene (C=C bond length 1.37(2) Å), and the helicity of the two C_4Ph_4 propellers is the same in any given molecule.

Turning now to molecule **10**, one might have anticipated the formation of the *cis*-analogue of **9**, but such is not the case. The ^1H and ^{13}C NMR spectra of **10** exhibit two methyl environments, while its infrared spectrum has a peak at 1704 cm^{-1} indicating the presence of a ketone. These observations were confirmed by X-ray crystallography and the molecular structure of **10** is shown in Fig. 4. The product is clearly the result of a pinacol/pinacolone rearrangement whereby a cobalt sandwich substituent, rather than a methyl group, has migrated. This is perhaps most readily rationalized in terms of the enhanced migratory aptitude of the organometallic moiety such that the positive charge can be delocalized onto the metal centre in the transition state, as depicted in Scheme 4.

In seeking a precedent for such an observation, we note the recent report by Härter [11] in which a ferrocenyl group undergoes migration in preference to an alkyl chain during the rearrangement of a ferrocenophane, as depicted in Scheme 5.

The mechanism of the McMurry coupling has been extensively investigated, most notably by Bogdanovič [12], and by Geise [13]. It has been proposed that alkene formation proceeds via a dimetallic intermediate, **11**, as depicted in Scheme 6, that would lead to the *trans* isomer of $(\eta^4\text{-}C_4Ph_4)Co(\eta^5\text{-}C_5H_4)$–CMe=CMe-$(\eta^5\text{-}C_5H_4)Co(\eta^4\text{-}C_4Ph_4)$, **9**. However, the steric crowding required to form the *cis* isomer of **9** may be such as to favor migration of the organocobalt moiety, leading ultimately to the pinacolone rearranged product **10**.

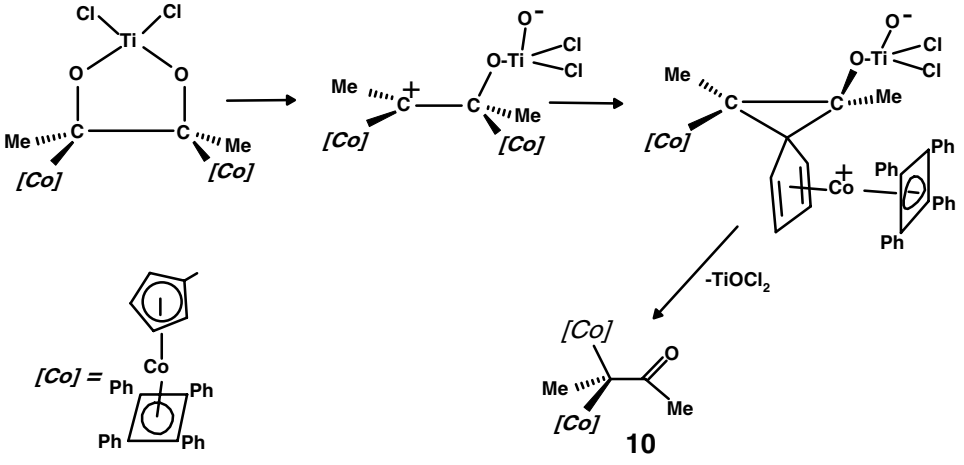


Scheme 5. Pinacol/pinacolone rearrangement of [3]-ferrocenophan-1-one.

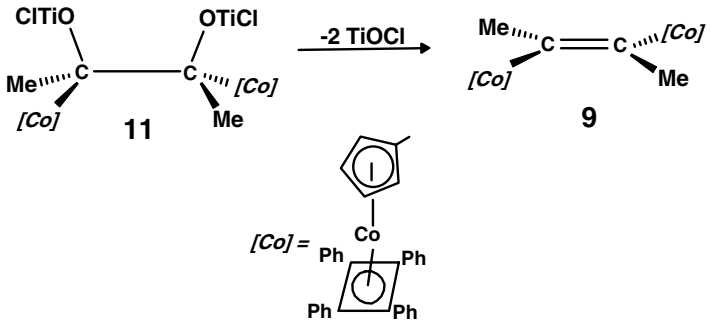
Interestingly, although the *cis* analogue of **9** was not isolable from the McMurry reaction, an molecular model of this isomer generated by rotating about the central double bond of the *trans* compound, **9** (see Fig. 5) reveals no particular steric problems. This reinforces the idea that crowding in the intermediate depicted in Scheme 4, whereby two bulky $(\eta^4\text{-}C_4Ph_4)Co(\eta^5\text{-}C_5H_4)$ groups are eclipsed when bonded to adjacent tetrahedral carbons, leads to ring-opening and migration.

When the McMurry reaction was carried out with a 5:1 ratio of benzophenone to the cobalt ketone, **5**, the unsymmetrical alkene **7** was obtained in 71% yield and only traces of the dicobalt complexes **9** and **10** were observed.

To conclude, the McMurry reaction of $(\eta^4\text{-}C_4Ph_4)Co[\eta^5\text{-}C_5H_4\text{–}C(=O)Me]$, **5**, with benzophenone yields not only the desired hetero-coupled alkene $(\eta^4\text{-}C_4Ph_4)Co(\eta^5\text{-}C_5H_4)\text{–}C(Me)=CPh_2$, **7**, but also tetraphenylethylene, **8**, and two products, **9** and **10**, derived from the homo-coupling of the ketonic cobalt sandwich **5**. Our continuing efforts to synthesize cobaltifens and to gauge their biological activity will be the subject of future reports.



Scheme 4. Proposed transition state for migration of an $(\eta^4\text{-}C_4Ph_4)Co(\eta^5\text{-}C_5H_4)$ group.



Scheme 6. Proposed mechanism of alkene formation in a McMurry coupling reaction.

Fig. 5. Molecular model of *cis*-(Me)*[Co]*–C=C(Me)*[Co]*.

3. Experimental

3.1. General methods

All reactions were carried out under an atmosphere of dry nitrogen. Alumina 90 standardized (Merck) was used for flash chromatography. NMR spectra were recorded on Varian Inova 300 or 500 MHz spectrometers. Electrospray mass spectrometry was performed on a Micromass Quattro micro instrument. Infrared spectra were recorded on a Perkin–Elmer paragon 1000 FT-IR instrument and were calibrated with polystyrene. Melting points were determined on an Electrothermal ENG. instrument and are uncorrected. Elemental analyses were carried out by the Microanalytical Laboratory at University College Dublin.

3.2. Preparation of (η^5-propionylcyclopentadienyl) (η^4-tetraphenylcyclobutadiene)cobalt (**6**)

In a 3-necked flask equipped with a condenser, sodium metal in excess was added to a solution of freshly distilled cyclopentadiene (0.50 mL, 7.6 mmol) in dry THF (25 mL) and the mixture stirred until all the reaction had ceased (ca. 30 min). After removal of the excess sodium metal, methyl propionate (0.75 mL, 7.8 mmol) was added to the reaction mixture and the whole was stirred at reflux for 4 h. During this time a dark red colour developed. After cooling the solution to room temperature, dry toluene (100 mL) was added, followed by chlorotris(triphenylphosphine)cobalt (I) (5.0 g, 5.7 mmol). The solution was stirred at room temperature for 30 min after which time diphenylacetylene (2.0 g, 11.2 mmol) was added, and the mixture was heated at reflux overnight. The mixture was cooled, filtered through celite, concentrated in vacuo and chromatographed on an alumina column. Four bands were eluted using hexane/toluene; the product was collected in the third band as a dark red fraction, which was concentrated to yield an orange solid (0.46 g, 0.86 mmol, 11%), m.p. 241 °C. X-ray quality crystals were grown from toluene/hexane. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.52–7.27 (m, Ph); 5.31 and 4.85 (m, Cp); 2.09 (q, CH_2); 0.78 (t, CH_3). ^{13}C–{^{1}H} NMR (75.4 MHz, $CDCl_3$): δ 199.9 (CO); 135.2 (C_{ipso}, Ph); 128.8 and 128.2 (C_{ortho} and C_{meta}, Ph); 126.9 (C_{para}, Ph); 94.0, 87.2, 83.1 (Cp); 32.8 (CH_2); 7.5 (CH_3). IR (THF, ν_{CO}): 1672 cm^{-1}. MS (ES+) *m/z* 537.1 $[(M + H)]^+$, 559.1 $[(M + Na)]^+$. Calc. for $C_{36}H_{29}OCo$: C, 80.59; H, 5.45; Co, 10.98. Found: C, 79.14; H, 5.46; Co, 11.23%.

3.3. McMurry reaction of (C_4Ph_4)Co(C_5H_4COMe) (**5**) and benzophenone in a 3:1 ratio

Zn (0.6 g, 15.3 mmol), which had been previously activated with dilute HCl (5.0 mL), washed several times with distilled water and dried, was added to dry THF (30 mL) and the mixture was cooled to 0 °C. $TiCl_4$ (9.0 mL, 1M solution in CH_2Cl_2) was added, the solution was stirred for 10 min during which time the colour changed from clear to yellow to light green. The solution was allowed to warm to room temperature and was then heated at reflux for 2 h to yield a dark blue/black solution. (C_4Ph_4)Co(C_5H_4COMe) (1.5 g, 2.9 mmol), prepared as previously described [10], and benzophenone (0.17 g, 0.9 mmol) were added together and the mixture heated at reflux for a further 12 h, resulting in the formation of a dark blue precipitate. The reaction was

quenched with of saturated sodium carbonate solution (80 mL), transferred to a separatory funnel and the product extracted with ether until the organic layer was no longer yellow. After removal of solvent and dissolution in a minimum quantity of ether, the product was chromatographed on alumina. Initially, the eluent was pentane, but this was gradually changed in 1% increments to ether/pentane 25/75, and yielded five fractions.

Fraction 1: Tetraphenylethene (**8**) (0.10 g, 33%), m.p. 210–222 °C (dec.) was eluted by using a mixture of ether/pentane (6/94), and was isolated as a white solid that was characterized by comparison of its melting point, NMR and mass spectra with literature data [14]. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.09 (m, CH *ortho* and *meta*, Ph), 7.03 (m, CH *para*, Ph). ^{13}C–{^{1}H} NMR (125.7 MHz, $CDCl_3$): δ 143.8 (Cq, Ph), 141.0 (=*C*Ph$_2$), 131.4, 127.7(CH *ortho* and *meta*, Ph), 126.5 (CH *para*, Ph).

Fraction 2: 1,1-Diphenyl-2-[(η^5-cyclopentadienyl)(η^4-tetraphenylcyclobutadiene)cobalt]propene (**7**) (0.14 g, 23%) was eluted by using a mixture of ether/pentane (8/92), and was isolated as an yellow-orange solid, m.p. 207 °C. X-ray quality crystals were grown from ether/pentane. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.80–6.80 (m, C_4Ph_4); 4.37, 4.32 (CH, Cp); 1.50 (s, CH_3). ^{13}C–{^{1}H} NMR (125.7 MHz, $CDCl_3$): δ 144.8, 144.4 (C_{para}, CPh_2); 139.6 (=*C*Ph$_2$); 136.7 (C_{ipso}, C_4Ph_4); 132.7, 130.3 (C_{ipso}, CPh_2); 130.4, 129.9, 128.5, 128.1 (C_{ortho} and C_{meta} CPh_2); 129.1, 128.3 (C_{ortho} and C_{meta}, C_4Ph_4); 128.6 (C_{ipso}, =*C*CH$_3$); 126.5 (C_{para}, C_4Ph_4); 100.3 (C_q, Cp); 84.1, 82.7 (CH, Cp); 75.3 (*C*$_4$Ph$_4$); 20.5 (CH_3). Calc. for $C_{48}H_{37}Co$: C, 85.70; H, 5.54; Co, 8.76. Found: C, 84.84; H, 5.67; Co, 8.37%.

Table 1
Crystallographic collection and refinement parameters for **6**, **7**, **9** and **10**

Identification code	**6**	**7**	**9**	**10**
Empirical formula	$C_{36}H_{29}Co\ O$	$C_{48}H_{37}Co$	$C_{70}\ H_{54}Co_2$	$(C_{70}\ H_{54}Co_2O)_2{\cdot}CH_2Cl_2$
Formula weight	536.52	672.71	1012.99	2142.9
Temperature (K)	293(2)	100(2)	293(2)	100(2)
Wavelength (Å)			0.71073	
Crystal system	Orthorhombic	Triclinic	Monoclinic	Triclinic
Space group	$P2_12_12_1$	$P\bar{1}$	$P2_1$	$P\bar{1}$
Unit cell dimensions				
a (Å)	9.0263(10)	10.6350(6)	12.229(4)	10.845(3)
b (Å)	10.0028(11)	10.8827(6)	15.238(5)	16.201(4)
c (Å)	29.782(3)	15.1610(8)	14.638(5)	16.409(4)
α (°)	90	91.5590(10)	90	104.517(4)
β (°)	90	96.5830(10)	101.703(6)	108.514(4)
γ (°)	90	102.9290(10)	90	98.377(4)
Volume (Å^3)	2689.0(5)	1696.40(16)	2671.0(16)	2565.7(11)
Z	4	2	2	1
Density (calculated) (Mg/m^3)	1.325	1.317	1.260	1.387
Absorption coefficient (mm^{-1})	0.666	0.541	0.663	0.746
F(000)	1120	704	1056	1114
Crystal size (mm^3)	$0.80\times0.59\times0.58$	$0.50\times0.20\times0.20$	$0.20\times0.05\times0.05$	$0.20\times0.20\times0.10$
Theta range for data collection (°)	2.15–28.27	2.26–29.46	1.70–19.00	1.59–23.37
Index ranges	$-11\leqslant h\leqslant11$; $-13\leqslant k\leqslant13$; $-37\leqslant l\leqslant38$;	$-14\leqslant h\leqslant14$; $-14\leqslant k\leqslant14$; $-20\leqslant l\leqslant20$	$-11\leqslant h\leqslant11$; $-13\leqslant k\leqslant13$; $-13\leqslant l\leqslant13$	$-12\leqslant h\leqslant12$; $-18\leqslant k\leqslant17$; $-18\leqslant l\leqslant18$
Reflections collected	23 017	27 299	10 201	12 625
Independent reflections	6266 [R(int) = 0.0167]	8656 [R(int) = 0.0156]	4281 [R(int) = 0.0883]	6996 [R(int) = 0.0433]
Completeness to theta (%)	96.8	91.9	99.9	93.8
Absorption correction	Semi-empirical from equivalents			
Max. and min. transmission	0.6988 and 0.6180	0.8996 and 0.7738	0.9676 and 0.8788	0.9291 and 0.8651
Refinement method	Full-matrix least-squares on F^2			
Data/restraints/parameters	6266/0/459	8656/0/590	4281/1/197	6996/0/682
Goodness-of-fit on F^2	1.065	1.054	0.976	1.093
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0288, wR_2 = 0.0714	R_1 = 0.0349, wR_2 = 0.0894	R_1 = 0.1153, wR_2 = 0.2653	R_1 = 0.0879, wR_2 = 0.2931
R indices (all data)	R_1 = 0.0300, wR_2 = 0.0719	R_1 = 0.0373, wR_2 = 0.0913	R_1 = 0.1544, wR_2 = 0.2864	R_1 = 0.1218, wR_2 = 0.3150
Absolute structure parameter	0.000(8)		0.02(6)	
Largest diff. peak and hole (e Å^{-3})	0.353 and −0.208	0.514 and −0.241	3.034 and −0.374	1.165 and −1.233

Fraction 3: *Trans*-2,3-bis[(η^5-cyclopentadienyl)(η^4-tetraphenylcyclobutadiene)cobalt]-2-butene (**9**) (0.24 g, 21%) was eluted by using a mixture of ether/pentane (8/92), and was isolated as a yellow solid, m.p. 135 °C. X-ray quality crystals were grown from ether/pentane. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.90–6.80 (m, C_4Ph_4); 4.48, 4.47 (m, Cp); 1.26 (s, CH_3). ^{13}C–{^{1}H} NMR (125.7 MHz, $CDCl_3$): δ 136.8 (C_{ipso}, C_4Ph_4); 129.1, 128.1 (C_{ortho} and C_{meta}, C_4Ph_4); 127.4 (=CCH$_3$); 126.25 (C_{para}, C_4Ph_4); 103.5 (C_q, Cp); 83.3, 82.8 (CH, Cp); 75.2 (C_4Ph$_4$); 20.8 (CH_3). Calc. for $C_{70}H_{54}Co_2$: C, 82.99; H, 5.38; Co, 11.63. Found: C, 82.36; H, 5.51; Co, 10.20%.

Fraction 4: 3,3-Bis[(η^5-cyclopentadienyl)(η^4-tetraphenylcyclobutadiene)cobalt]butan-2-one (**10**) (0.18 g, 15%) was eluted by using a mixture of ether/pentane (15/85), and was isolated as a yellow solid. X-ray quality crystals were grown from ether/pentane. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.5–7.18 (m, C_4Ph_4); 5.04 (1H), 4.44 (1H), 4.19 (2H) (m, Cp); 1.51 (s, COCH_3); 1.11 (s, CCH_3). ^{13}C–{^{1}H} NMR (125.7 MHz, $CDCl_3$): δ 206.7 (CO); 136.7 (C_{ipso}, C_4Ph_4); 129.3, 128.2 (C_{ortho} and C_{meta}, C_4Ph_4); 126.5 (C_{para}, C_4Ph_4); 105.7 (C_q, Cp); 83.5, 83.1, 82.9, 81.9 (CH, Cp); 75.1 (C_4Ph$_4$); 51.5 (CCH$_3$); 26.6 (COCH$_3$); 15.5 (CCH$_3$). IR ($CDCl_3$, νCO): 1704 cm^{-1}. Calc. for $C_{70}H_{54}Co_2O$: C, 81.73; H, 5.25; Co, 11.46. Found: C, 81.71; H, 5.74; Co, 9.79%.

Fraction 5: Starting material (**5**) (0.32 g, 21% recovered) was eluted by using a mixture of ether/pentane (25/75), and was isolated as an orange solid.

*3.4. McMurry reaction of (C_4Ph_4)Co(C_5H_4COMe) (**5**) and benzophenone in a 1:5 ratio*

Following the procedure described above, the hetero-coupled product (**7**) was isolated in 71% yield, and only traces of the cobalt complexes **9** and **10** were detected.

3.5. X-ray crystal structure determinations

X-ray crystallographic data (see Table 1) for **6**, **7**, **9** and **10** were each collected from a suitable sample mounted with grease on the end of a thin glass fiber. Data were collected on a D8 Bruker diffractometer equipped with a Bruker SMART APEX CCD area detector (employing the program SMART) [15] and an X-ray tube utilizing graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Data processing was carried out by use of the program SAINT [16], while the program SADABS [17] was utilized for the scaling of diffraction data and an empirical absorption correction based on redundant reflections. Structures were solved by using the direct-methods procedure in the Bruker SHELXL [18] program library and refined by full-matrix least-squares methods on F^2. As a result of the relatively poor quality of the available crystals of **9**, the *R*-factors are higher than we would normally report. Thus, in **9** all five- and 6-membered rings were constrained to be regular and all carbon atoms could only be refined with isotropic temperature factors. All other non-hydrogen atoms were refined using anisotropic thermal parameters. Hydrogen atoms in **9** and **10** were added as fixed contributors at calculated positions, with isotropic thermal parameters based on the carbon atom to which they are bonded. All other hydrogen atoms were located in the difference Fourier map and allowed to refine freely with isotropic temperature factors.

4. Supplementary material

Crystallographic data for the structural analyses have been deposited at the Cambridge Crystallographic Data Centre, CCDC Nos. 231150 (**6**), 231151 (**9**), 231152 (**7**) and 231153 (**10**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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