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An NMR study of the rotational barriers in cobalt-stabilized carbocations: X-ray crystal structures of (η^4-C$_4$Ph$_4$)Co-(η^5-C$_5$H$_4$R), where R is CH$_3$C=O, CH=O, CH(^{t}Bu)OH

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Abstract

Treatment of the aldehyde (η^4-C$_4$Ph$_4$)Co(η^5-C$_5$H$_4$-CH=O) (**4b**) with tert-butyllithium or phenyllithium yields the secondary alcohols (η^4-C$_4$Ph$_4$)Co(η^5-C$_5$H$_4$-CH(R)OH), where R = tert-butyl (**5**) or phenyl (**6**). Protonation of **5** and **6** at −80 °C furnishes the deep purple, cobalt-stabilized cations, **7** and **8**, respectively, both of which exhibit restricted rotation about the external C$_5$H$_4$–CHR$^+$ linkage on the NMR time-scale. These data indicate a *minimum* value for the barrier to rotation of 15 kcal mol^{-1}, but it is certainly much higher, indicating a considerable degree of C–C double bond character. X-ray crystal structures of **4b**, **5** and also of the ketone (η^4-C$_4$Ph$_4$)Co(η^5-C$_5$H$_4$-C(=O)CH$_3$ (**4a**) are reported. The secondary alcohol **5** exhibits disorder in the solid state because of the presence of diastereomers as a consequence of the stereogenic center at the α-carbon and the clockwise or anticlockwise propeller orientations of the tetraphenylcyclobutadiene ligand.
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1. Introduction

The stabilization of carbocationic sites by neighboring transition metal centers continues to attract widespread attention. Early reports on ferrocenylmethylium [1] or (chromium tricarbonyl)benzyl cations [2], and other related systems [3–6] were subsequently augmented by extensive studies on cluster-stabilized cations whose syntheses, structures and molecular dynamics have been comprehensively reviewed [7–9]. In favorable cases, the structures of M-CR$_2^+$ cations, where M is ferrocenyl or ruthenocenyl [10], or where M represents a tetrahedral metal cluster, have been established X-ray crystallographically [7–9,11], and the strength of the interaction between the carbocationic site and the relatively electron-rich metal has been gauged from NMR-derived barriers to migration or rotation.

Typically, in [Cp$_2$Mo$_2$(CO)$_4$(RC≡C-CR^{1}R^2)]$^+$ tetrahedral dimetallic clusters (**1**), the barrier toward migration of the (C-CR^{1}R^2)$^+$ moiety from one molybdenum vertex to the other ranges from 10 to 18 kcal mol^{-1} depending on the identity of the substituents R^1 and R^2. When R^1 = R^2 = H, the resulting primary cation must overcome a barrier of 17 kcal mol^{-1} during the fluxional process that interconverts **1a** and **1b** [12]. In contrast, for tertiary cations where R^1 and R^2 are both alkyl or aryl, the barrier falls to 10 kcal mol^{-1} [13]. These NMR-derived activation energies correlate very well with the M···C$^+$ distances observed crystallographically which range from 2.44 Å for M···CH$_2^+$ systems to 2.75 Å for M···CR$_2^+$ clusters [11]. These data indicate that relatively stable tertiary carbocations have little need for

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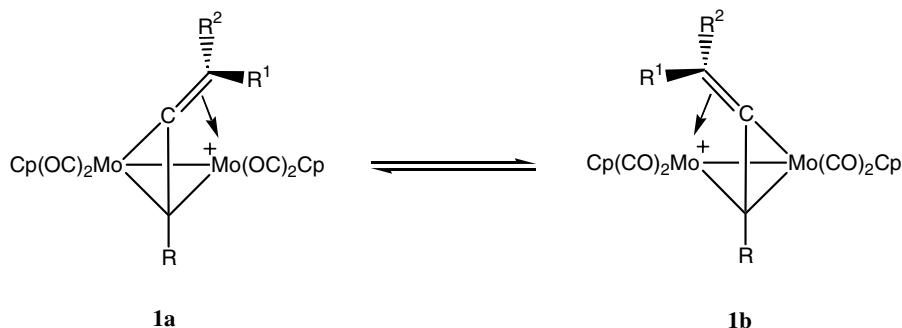
Scheme 1.

anchimeric assistance from a neighboring metal, whereas the positive charge formally associated with a primary cation is markedly delocalized via direct overlap of the vacant p-orbital on carbon with a filled d-orbital on the metal (see Scheme 1).

Similarly, the barrier to tripodal rotation in systems of the type [(benzyl)Cr(CO)$_3$]$^+$ has been found to be approximately 11–12 kcal mol^{-1}, and once again is a reflection of the strength of the interaction between the metal and the carbocationic site [2b,14]. Another approach is to probe the degree of double bond character developed between the complexed ring and the cationic carbon since this will result in an enhanced barrier to rotation about the C=CR^{1}R^2 linkage. This approach has recently been used to demonstrate the ability of a dicobalt–alkyne cluster, or of a ferrocenyl substituent, to stabilize antiaromatic fluorenyl, indenyl or cyclopentadienyl cations [15,16]. The particular focus of the current investigation is to explore the cation-stabilizing ability of systems of the type [(η^4-C$_4$Ph$_4$)Co(η^5-C$_5$H$_4$-CHR)]$^+$ and to compare the results with those for other sandwich compounds.

After much early controversy, there is compelling experimental and theoretical evidence that ferrocenyl cations of the type [(C$_5$H$_5$)Fe(C$_5$H$_4$-CHR)]$^+$ are stabilized by direct interaction of the iron atom with the carbocationic center. Thus, ^{57}Fe NMR data on the cations and their precursor alcohols exhibit marked differences in both ^{57}Fe chemical shifts and ^{13}C – ^{57}Fe coupling constants [17]. Even more convincingly, X-ray crystallographic results reveal that the exocyclic carbon can bend down by as much as 25° toward the metal such that the Fe···C$^+$ distance approaches 2.6 Å [10]. An extreme view would regard such complexes as being comprised of a neutral fulvene ligand coordinated in an η^6-fashion to a (C$_5$H$_5$)Fe$^+$ moiety, as in 2a. More recently, comparisons have been drawn between 2a and the analogous chromium, 2b, manganese, 2c, and cobalt, 2d, systems in terms of structural characteristics, NMR parameters and high level computational data [18].

2a   2b

2c   2d
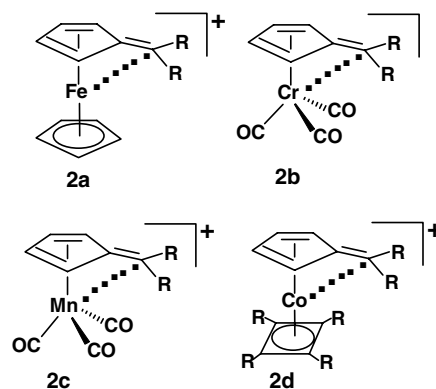
It is particularly relevant to cite a study by Gleiter et al. [19] aimed at probing the similarities and differences between the diarylferrocenylium ion (C$_5$H$_5$)Fe-(C$_5$H$_4$-CAr$_2$)]$^+$ and its isolobal cobalt analogue [(C$_4$R$_4$)Co(C$_5$H$_4$-CAr$_2$)]$^+$. It was concluded that there is a greater interaction of the 6,6-diphenylfulvene ligand with (C$_5$H$_5$)Fe$^+$ than with the corresponding (C$_4$H$_4$)Co$^+$ species, attributable to the enhanced ability of the latter moiety to distribute positive charge over the four-membered ring.

We here describe our efforts to provide an experimental value for the barrier to rotation about the exocyclic bond in [(C$_4$Ph$_4$)Co(C$_5$H$_4$-CHR)]$^+$, where R is phenyl or tert-butyl. Such data are, to the best of our knowledge, not available for cobalt cationic systems although corresponding values in ferrocenylium cations may be extracted from early work. Thus, it is reported that in Fc$_2$CH$^+$ (3), the ^{13}C NMR resonances of the C$_{2,5}$ environments in the C$_5$H$_4$ rings are clearly split at −70 °C, but have coalesced at +30 °C [17b]. These data were acquired on a 90 MHz spectrometer (^{13}C at 22.6 MHz), and the Gutowsky–Holm equation yields an activation energy of approximately 14 kcal mol^{-1}. Corresponding data on the Fc–CHMe$^+$ and Fc–CHPh$^+$ cations reveal that the C$_{2,5}$ and C$_{3,4}$ environments do not exhibit coalescence behavior, even at +15 °C, indicating a *minimum* barrier of 15 kcal mol^{-1}, and probably substantially higher. An

entirely different approach was adopted by Turbitt and Watts [20] who separated the enantiomers of Fc–CH(Me)OH, generated the chiral Fc–CHMe$^+$ cations, and measured the rate of racemization at several temperatures to obtain a rotational barrier of 20 kcal mol^{-1}.

In the diferrocenyl case, **3**, the relatively low barrier can be readily accounted for by the fact that the cation is not strongly bonded to one iron center but instead is partially stabilized by each of two metal atoms. Such behavior is reminiscent of the X-ray crystal structures of {bis[(cyclobutadiene)Fe(CO)$_3$]CH}$^+$ [3], and {[Co$_2$(CO)$_6$(*tert*-Bu-C≡C)]$_2$*tert*-Bu-C}$^+$ [21], in which the cationic carbon is displaced only minimally toward both metals and is not firmly bonded to either.

In order to probe the rotational barriers in systems of the type [(C$_4$Ph$_4$)Co(C$_5$H$_4$-CHR)]$^+$ one must first develop synthetic routes to their precursor alcohols. Previous reports have focussed on the readily available ester, (C$_4$Ph$_4$)Co(C$_5$H$_4$-CO$_2$Me) [22], which, when treated with Grignard or organo-lithium reagents, yields the symmetrical alcohols (C$_4$Ph$_4$)Co(C$_5$H$_4$-CR$_2$OH), where R = H, Me or Ph [23]. Careful oxidation of the primary alcohol furnishes the aldehyde (C$_4$Ph$_4$)Co (C$_5$H$_4$-CH=O) [24]. The carbinol (C$_4$Ph$_4$)Co(C$_5$H$_4$-CPh$_2$OH) had been previously prepared by the reaction of (C$_4$Ph$_4$)Co(C$_5$H$_4$Li) with benzophenone [4].

Unlike ferrocene, which readily undergoes electrophilic attack (Friedel–Crafts, Vilsmeier–Haack, etc.) on the five-membered ring, the cobalt systems are preferentially substituted, where possible, on the four-membered ring and functionalization of the five-membered ring proceeds in very poor yields [25]. Consequently, analogously to the route originally described by Rausch and co-workers [26], one must functionalize the cyclopentadienyl ring prior to coordination by cobalt. The early syntheses of cobalt sandwiches of the type (C$_5$H$_4$R)Co(C$_4$Ph$_4$) proceeded

by treatment of (C$_5$H$_4$R)Co(CO)$_2$ with diphenylacetylene. However, much better yields can be realized by reaction of the sodium salt of the appropriately substituted cyclopentadienide anion, C$_5$H$_4$R$^-$, with chloro-tris(triphenylphosphine)cobalt(I), and then incorporating the four-membered ring by the coupling of two alkyne ligands [27] to yield the required complexes, as shown in Scheme 2.

2. Results and discussion

Initial synthetic studies focussed on attempts to generate unsymmetrical tertiary alcohols by treatment of (C$_4$Ph$_4$)Co(C$_5$H$_4$-COCH$_3$) (**4a**), with phenyllithium or a phenyl Grignard reagent. Somewhat surprisingly, this simple ketone has not, to our knowledge, been characterized X-ray crystallographically, and the structure appears as Fig. 1. Crystallographic data are collected in Table 1.

The cobalt to ring-carbon distances average 2.070(2) Å to the cyclopentadienyl ring and 1.982(2) Å to the cyclobutadiene ring; the net result is to place the cobalt almost equidistant from the two ring centers (Co-to-4-membered ring 1.682 Å; Co-to-5-membered ring 1.692 Å). The phenyls adopt a propeller conformation with dihedral angles ranging from 21° to 42°, and are bent in an *exo* fashion out of the plane of the cyclobutadiene ring by ca. 7.5°. These metric parameters are typical for sandwich complexes of this type [28].

However, nucleophilic attack on the carbonyl moiety in **4a** with either PhLi or PhMgBr was in all cases less favorable than proton abstraction from the methyl ketone. The reverse process, i.e. addition of a methyl Grignard, was thwarted by our inability to prepare (C$_4$Ph$_4$)Co(C$_5$H$_4$-COPh) in synthetically useful yields, even though (C$_5$H$_4$-COPh)Co(CO)$_2$ has been previously reported [29]. However, the secondary alcohols (C$_4$Ph$_4$)Co(C$_5$H$_4$-CHR-OH), where R is *tert*-butyl (**5**),
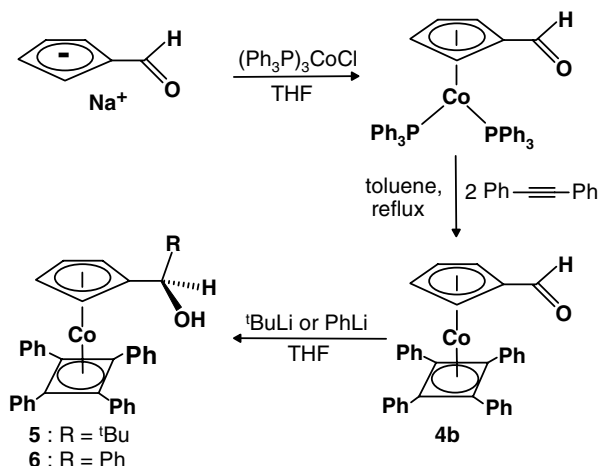
Scheme 2.
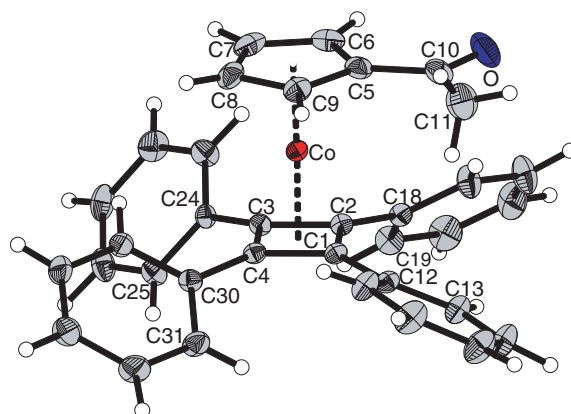
Fig. 1. X-ray crystal structure of (C$_4$Ph$_4$)Co(C$_5$H$_4$-CO-Me) (**4a**).

Table 1
Crystallographic collection and refinement parameters

Identification code	4a	4b	5
Empirical formula	$C_{35}H_{27}OCo$	$C_{35}H_{27}Cl_2OCo$	$C_{38}H_{35}OCo$
Formula weight	522.50	593.40	566.59
Temperature (K)	293(2)	298(2)	293(2)
Wavelength (Å)	0.71073	0.71069	0.71073
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_12_12_1$ (#19)	$P2_1/c$ (#14)	$P2_1/c$ (#14)
Unit cell dimensions			
a (Å)	9.0008 (13)	11.3769 (14)	11.6707 (8)
b (Å)	9.9706 (14)	15.022 (3)	9.6187 (7)
c (Å)	29.868 (4)	16.908 (5)	26.2564 (18)
α (°)	90	90	90
β (°)	90	81.210 (16)	92.4570 (10)
γ (°)	90	90	90
Volume (Å^3)	2680.5(7)	2855.7(10)	2944.8(4)
Z	4	4	4
D_{calc} (Mg/m^3)	1.295	1.380	1.278
Absorption coefficient (mm^{-1})	0.666	0.815	0.611
$F(000)$	1088	1224	1192
Crystal size (mm^3)	$2.00 \times 2.00 \times 1.00$	$0.48 \times 0.43 \times 0.39$	$0.70 \times 0.46 \times 0.30$
θ Range for data collection (°)	2.15–28.24	1.81–20.89	2.26–27.50
Index ranges	$-11 \leqslant h \leqslant 11, -13 \leqslant k \leqslant 13,$ $-39 \leqslant l \leqslant 39$	$-11 \leqslant h \leqslant 11, -14 \leqslant k \leqslant 14,$ $-16 \leqslant l \leqslant 16$	$-15 \leqslant h \leqslant 15, -12 \leqslant k \leqslant 12,$ $-34 \leqslant l \leqslant 34$
Reflections collected	44 796	11 788	49 162
Independent reflections	6404 [$R_{int} = 0.0320$]	2944 [$R_{int} = 0.0535$]	6772 [$R_{int} = 0.0221$]
Completeness for θ range	98.1%	97.3%	99.9%
Absorption correction	Numerical	None	Numerical
Max. and min. transmission	0.5557 and 0.3494	Not given	0.8378 and 0.6742
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	6404/0/443	2944/0/352	6772/0/505
Goodness-of-fit on F^2	1.088	1.006	1.053
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0294, wR_2 = 0.0704$	$R_1 = 0.0565, wR_2 = 0.1496$	$R_1 = 0.0407, wR_2 = 0.1076$
R indices (all data)	$R_1 = 0.0313, wR_2 = 0.0713$	$R_1 = 0.0649, wR_2 = 0.1627$	$R_1 = 0.0479, wR_2 = 0.1119$
Largest diff. peak and hole (e/Å^{-3})	0.34 and -0.26	0.74 and -0.42	0.89 and -0.22
Absolute structure parameter	0.010(9)	–	–

or phenyl (**6**), were readily preparable from the aldehyde **4b**, whose structure appears as Fig. 2. As with the methyl ketone **4a**, the metric parameters for the aldehyde **4b** are normal. The cobalt is sited almost equidistant
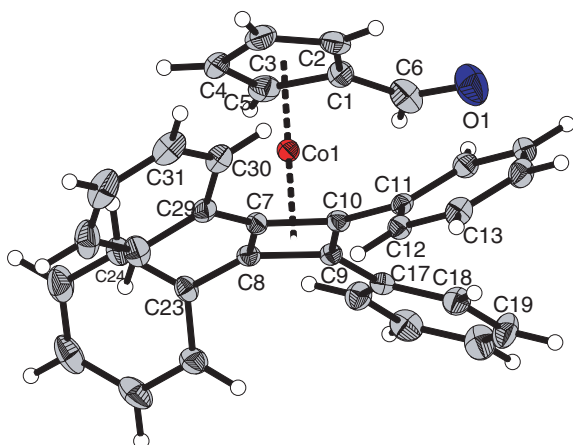

Fig. 2. X-ray crystal structure of (C$_4$Ph$_4$)Co(C$_5$H$_4$-CHO) (**4b**).

from the two rings, the average twist angle of the phenyl propeller blades is $40° \pm 14°$, and the aldehyde functionality is coplanar with the five-membered ring (see Fig. 2).

The secondary alcohols **5** and **6** were characterized spectroscopically and by microanalysis, and the former also yielded crystals suitable for an X-ray diffraction study. The molecular structure of **5** is shown as Fig. 3 and reveals several interesting features. As with the previously mentioned ketone, **4a**, and aldehyde, **4b**, the tetraphenylcyclobutadiene ligand in **5** adopts a propeller conformation such that each phenyl makes a dihedral angle of approximately $39° \pm 17°$ relative to the four-membered ring, thus rendering the molecule chiral. However, the compound already possesses a stereogenic center since the α-carbon bears four different substituents. The net result is, of course, to generate diastereomers in which the clockwise or counterclockwise pitch of the four phenyls could correlate with either the R or S configuration at Cα. Each unit cell possesses a crystallographic inversion
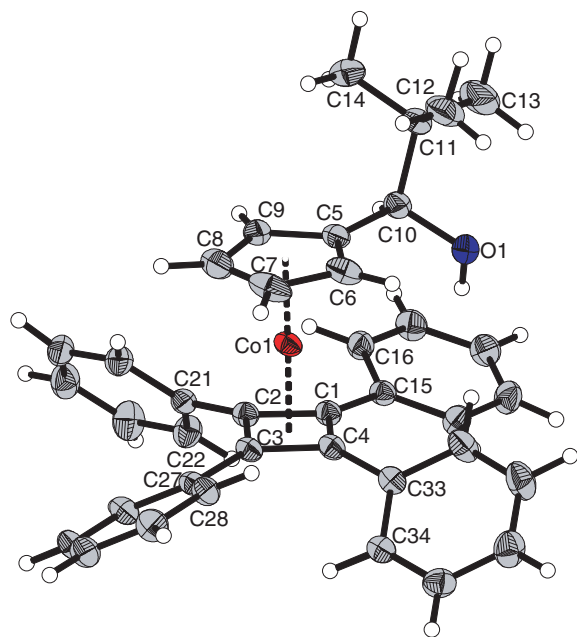
Fig. 3. X-ray crystal structure of $(C_4Ph_4)Co(C_5H_4-CHOH-{}^tBu)$ (5).

ring indicating that rotation of the C=CHR linkage was slow on the NMR time-scale. Upon protonation of the tert-butyl system, **5**, the α-carbon is deshielded by 107 ppm (**7**–**5**); the corresponding value for the phenyl complex, **6**, is 82 ppm (**8**–**6**). The ^{13}C assignments were established via HSQC and HMBC ^1H–^{13}C two-dimensional correlations.

It is now well established that in $M-CR_2^+$ systems where the R groups can help to stabilize the electronic deficiency, the ^{13}C NMR shift of the cationic carbon is very markedly deshielded. Typically, when going from $(C_6H_5–CPh_2OH)Cr(CO)_3$ to $[(C_6H_5–CPh_2)Cr(CO)_3]^+$, the α-carbon resonances are found at 79.7 δ and 185.8, respectively, a $\Delta\delta$ value of 106.1 ppm [31]. On the other hand, when the majority of the positive charge are ever more delocalized onto the organometallic moiety, the ^{13}C resonance of the cationic carbon is gradually less deshielded. Thus, for the alcohol–cation pairs $(C_6H_5–CHPhOH)Cr(CO)_3$/ $[(C_6H_5–CHPhCr(CO)_3]^+$ and $(C_6H_5–CH_2OH)Cr(CO)_3$/ $[(C_6H_5–CH_2)Cr(CO)_3]^+$, the $\Delta\delta$ values are 65 ppm [2b,2c] and ca. 27 ppm [14b], respectively. Similarly, the $\Delta\delta$ values for the alcohol–cation pairs $FcCPh_2OH$/ $FcCPh_2^+$ and $FcCHPhOH/FcCHPh^+$ are 71 and 49 ppm, respectively [19,32].

The observed deshielding of 82 ppm upon protonating $(C_4Ph_4)Co(C_5H_4-CHPh-OH)$ (**6**), to yield the corresponding cation **8**, contrasts with the surprisingly large $\Delta\delta$ value of 107 ppm found for the tert-butyl analogue **7**, which implies a greater interaction of the metal with the α-$PhCH^+$ unit in **8** than with the t-$BuCH^+$ moiety in **7**. One might have anticipated that the phenyl group's ability to help delocalize the charge deficiency might have been more efficient than the hyperconjugative stabilization provided by the tert-butyl substituent; evidently, more examples are needed to clarify this point. ^{13}C NMR data for a series of related cobalt complexes are collected in Table 2.

When the temperature was gradually raised to −10 °C, the cyclopentadienyl ^{13}C NMR resonances showed no evidence of coalescence, but signs of decomposition be-

center in that the C_4Ph_4 propellers are enantiomeric. However, there is an 85:15 disorder of the hydroxyl and hydrogen substituents such that the *R* configuration at Cα primarily corresponds to the Δ propeller (while, of course, the *S* configuration favors the Λ propeller). Evidently, the crystal packing is dominated by the chirality of the propellers, and the substituents buried inside the molecule play only a secondary role. A similar phenomenon has been previously observed in $(C_5Ph_5)Fe(CO)(CH=O)PR_3$ where again an intrinsically chiral molecule gives rise to diastereomers when the propeller orientations are fixed [30].

Having prepared the alcohols $(C_4Ph_4)Co(C_5H_4-CHR-OH)$ (**5**) and (**6**), each was treated with $HBF_4 \cdot Et_2O$ at dry ice temperature and the yellow-orange precursors instantly turned deep purple. The ^{13}C NMR spectra of both **7** and **8** exhibited five resonances for the cyclopentadienyl

Table 2
^{13}C NMR data on selected cobalt sandwich complexes

^{13}C						
α	74.6	70.8	48.6	181.8	153.0	184.0
1	102.0	103.7	106.2	111.2	108.2	107.7
2	84.0, 83.0	84.0, 82.9	83.8	114.0, 111.3	108.9, 107.2	105.1
3	82.0, 81.0	81.0, 80.2	83.0	92.3, 86.1	91.4, 84	90.8
4	76.4	75.1	74.8	86.0	90.5	88.1

came evident for the tert-butyl derivative, **7**; the phenyl cation, **8**, survived until +15 °C but still did not exhibit peak coalescence. These data clearly indicate a "fulvene-type" structure with a relatively high activation energy toward rotation of the exocyclic double bond. Although one cannot directly calculate a barrier, the data yield a *minimum* value of ca. 15 kcal mol^{-1} indicating that the (C$_4$Ph$_4$)Co moiety provides substantial stabilization of a cationic charge at the α-carbon position. Current studies are aimed at generating a cation adjacent to both cobalt- and iron-containing fragments such that a direct competition can be allowed to develop.

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. Solvents were dried by standard techniques [33].

3.2. (η^5-Acetylcyclopentadienyl)(η^4-tetraphenylcyclobutadiene)cobalt (4a)

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 acetate (0.61 ml, 7.7 mmol) was added to the reaction mixture and the whole was stirred at reflux for 4 h. During this time a dark red color 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 a red-brown solid (0.76 g, 1.45 mmol,

26%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.51–7.13 (m, Ph), 5.20 and 4.77 (m, Cp), 1.65 (s, CH$_3$). ^{13}C NMR (75.4 MHz, CDCl$_3$): δ 197.27 (CO), 135.0 (C$_{ipso}$, Ph), 128.7 and 128.2 (C$_{ortho}$ and C$_{meta}$, Ph), 126.9 (C$_{para}$, Ph), 93.8, 87.6, 83.2 (Cp), 76.6 (*C*$_4$Ph$_4$), 27.1 (CH$_3$). IR (THF, ν$_{CO}$): 1672 cm^{-1}.

3.3. (η^5-Formylcyclopentadienyl)(η^4-tetraphenylcyclobutadiene)cobalt (4b)

Using the procedure described in Section 3.2, the aldehyde **4b** was prepared from sodium cyclopentadienide, ethyl formate, ClCo(PPh$_3$)$_3$ and diphenylacetylene to yield **4b** as a red-brown solid (0.25 g, 0.5 mmol, 9%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 9.31 (s, CHO), 7.44–7.21 (m, Ph), 5.23 and 4.90 (m, Cp). ^{13}C NMR (75.4 MHz, CDCl$_3$): δ 191.0 (CO), 135.1 (C$_{ipso}$, Ph), 129.1 and 128.5 (C$_{ortho}$ and C$_{meta}$, Ph), 127.4 (C$_{para}$, Ph), 108.9, 89.0, 83.4 (Cp), 76.9 (*C*$_4$Ph$_4$). MS (ES+) *m/z* 531 [M + Na]$^+$, 509 [M + H]$^+$, 415 [M-(HCOC$_5$H$_4$)]$^+$. IR (THF, ν$_{CO}$): 1684 cm^{-1}.

3.4. [α-(η^4-Tetraphenylcyclobutadiene)cobalt(η^5-cyclopentadienyl)]benzyl alcohol (6)

A solution of **4b** (0.50 g, 1.0 mmol) in dry THF (15 ml) was cooled to −60 °C. Phenyllithium (0.53 ml, 1.8M, 0.95 mmol) was slowly added, the temperature of the mixture rose gradually to 20 °C and it was stirred overnight. The solution was quenched with water (0.1 ml), the mixture washed with water and dried. The organic layer was concentrated in vacuo, and chromatographed on an alumina column. Three bands were eluted using toluene/hexane mixture; the product was collected in the second band as a yellow-orange fraction, which upon concentration yielded an orange solid (0.21 g, 0.36 mmol, 36%). ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.60–7.11 (m, Ph), 5.16 (d, $^3J_{H,OH}$ = 3 Hz, CH), 4.98, 4.63, 4.57 and 4.55 (m, Cp), 1.64 (d, $^3J_{OH,H}$ = 3 Hz, OH). ^{13}C NMR (125.7 MHz, CDCl$_3$): δ 143.5 (C$_{ipso}$, Ph), 136.2 (C$_{ipso}$, C$_4$Ph$_4$), 128.3, 128.3 (C$_{ortho}$ and C$_{meta}$, C$_4$Ph$_4$), 128.3, 126.3 (C$_{ortho}$ and C$_{meta}$, Ph), 127.4 (C$_{para}$, Ph), 126.6 (C$_{para}$, C$_4$Ph$_4$), 103.7 (C$_{ipso}$, Cp), 84.0, 82.9, 81.0 and 80.2 (CH, Cp), 75.1 (*C*$_4$Ph$_4$), 70.8 (*C*HOH). MS (ES+) *m/z* 569 [M − OH]$^+$. Calc. for C$_{40}$H$_{31}$OCo: C, 81.90; H, 5.32; Co, 10.20. Found: C, 81.58; H, 5.40; Co, 9.61%.

3.5. [1-(η^4-Tetraphenylcyclobutadiene)cobalt(η^5-cyclopentadienyl)]-2,2-dimethyl-propanol (5)

In an analogous fashion to the synthesis of the phenyl alcohol, **6**, the tert-butyl alcohol was prepared by using *t*-BuLi rather than PhLi to yield **5** as a yellow solid (0.13 g, 0.23 mmol, 79%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.48, 7.46 (m, Ph), 4.83, 4.57, 4.51 (m, Cp), 3.68 (d, $^3J_{H-H}$ = 3 Hz, CH), 1.08 (d, $^3J_{H-H}$ = 3 Hz, OH), 0.74

(s, CH$_3$). ^{13}C NMR (75.4 MHz, CDCl$_3$): δ 136.3 (C$_{ipso}$, Ph), 128.7 and 128.3 (C$_{ortho}$ and C$_{meta}$, Ph), 126.5 (C$_{para}$, Ph), 102.0 (C$_{ipso}$, Cp), 84.0, 83.0, 82.0 and 81.0 (CH, Cp), 76.4 (*C*$_4$Ph$_4$), 74.6 (*C*HOH);,35.4 (*C*Me$_3$), 26.0 (C*Me*$_3$). Calc. for C$_{38}$H$_{35}$OCo: C, 80.55; H, 6.22; Co, 10.56. Found: C, 77.42; H, 6.22; Co, 10.00%.

3.6. Protonation of [(C$_4$Ph$_4$)Co(C$_5$H$_4$-CH(t-Bu)-OH)]

A solution of **5** (0.15 g, 0.03 mmol) in CD$_2$Cl$_2$ (0.75 ml) was placed in an NMR tube, under a argon atmosphere, and cooled to −80 °C. A drop of HBF$_4$·OEt$_2$ was then added. The yellow solution immediately turned purple.
^{1}H NMR (500 MHz, −25 °C, CD$_2$Cl$_2$): δ 11.48 (HBF$_4$), 7.62 (CH), 7.52, 7.48 (m, Ph), 6.04, 5.97, 5.84, 5.58 (m, Cp), 4.74 (q, CH$_2$, HBF$_4$.OEt$_2$), 3.78 (q, CH$_2$, OEt$_2$), 1.59 (t, CH$_3$, HBF$_4$·OEt$_2$), 1.28 (t, CH$_3$, OEt$_2$), 0.90 (CH$_3$, *t*-Bu). ^{13}C NMR (125.7 MHz, −25 °C, CD$_2$Cl$_2$): 181.8 (Cα), 132.6 (C$_{para}$, Ph), 132.4 (C$_{ipso}$, Ph), 131.5, 131.3 (C$_{ortho}$ and C$_{meta}$, Ph), 111.2 (C$_{ipso}$, Cp);,114.0, 111.3, 92.3, 86.1 (CH, Cp), 86.0 (*C*$_4$Ph$_4$), 70.1 (CH$_2$, OEt$_2$); 45.2 (*C* Me$_3$); 30.0 (C*Me*$_3$); 16.0 (CH$_3$, OEt$_2$).

3.7. Protonation of [(C$_4$Ph$_4$)Co(C$_5$H$_4$-CHPh-OH)]

A solution of **6** (0.30 g, 0.05 mmol) in CD$_2$Cl$_2$ (0.75 ml) was placed in an NMR tube, under a argon atmosphere, and cooled to −80 °C. A drop of HBF$_4$·OEt$_2$ was then added. The yellow solution immediately turned purple. ^{1}H NMR (500 MHz, −25 °C, CD$_2$Cl$_2$): δ 11.32 (HBF$_4$); 7.83, 7.45, 7.30, 7.29 (m, Ph), 7.60 (CH), 6.02, 5.87, 5.82, 5.76 (m, Cp), 4.72 (m, CH$_2$, HBF$_4$.OEt$_2$); 3.71 (m, CH$_2$, OEt$_2$), 1.58 (m, CH$_3$, HBF$_4$·OEt$_2$); 1.26 (m, CH$_3$, OEt$_2$). ^{13}C NMR (125.7 MHz, −25 °C, CD$_2$Cl$_2$): δ 153.0 (Cα), 135.5 (C$_{para}$, Ph), 133.7 (C$_{ipso}$, Ph), 132.7 (C$_{ortho}$, Ph), 130.8 (C$_{meta}$, Ph), 130.3 (C$_{ipso}$, C$_4$Ph$_4$), 129.8 (C$_{para}$, C$_4$Ph$_4$), 129.1 and 128.8 (C$_{ortho}$ and C$_{meta}$, C$_4$Ph$_4$), 108.2 (C$_{ipso}$, Cp), 108.9, 107.2, 91.4, 84.2 (CH, Cp), 90.5 (*C*$_4$Ph$_4$), 84.1 (CH$_2$, HBF$_4$·OEt$_2$); 67.0 (CH$_2$, OEt$_2$); 14.1 (CH$_3$, OEt$_2$); 12.4 (CH$_3$, HBF$_4$·OEt$_2$).

3.8. Crystallographic data for 4a, 4b and 5

X-ray crystallographic data for **4a** and **5** were 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) [34] and an X-ray tube utilizing graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Data processing was carried out by use of the program SAINT [35], while the program SADABS [36] 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 [37] program library and refined by full-matrix least-squares methods on F^2. All non-hydrogen atoms were refined using anisotropic thermal parameters. Disordered hydrogen atoms were added as fixed contributors at calculated positions, with isotropic thermal parameters based on the carbon/oxygen 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. Data for **4b** were collected on an Enraf Nonius CAD4 diffractometer as described in earlier papers [38].

4. Supplementary material

Crystallographic data for the structural analyses have been deposited at the Cambridge Crystallographic Data Center, CCDC nos. 229487 (**4a**), 229489 (**4b**) and 229488 (**5**). 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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