Synthesis and Structural Characterisation of a Novel Chiral *ansa*-Cobaltocenium Hexafluorophosphate

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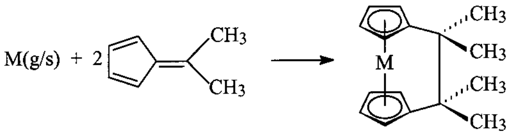
trans-[(1,2-Diphenyl-1,2-dicyclopentadienyl)ethanediyl]cobalt(III) hexafluorophosphate (**1**) was synthesised and its structure derived by X-ray crystallography and spectroscopic methods in conjunction with theoretical calculations. To gain an insight into the effect of these bridging atoms and the exocyclic substituents on the sandwich structure, a study was undertaken in which comparisons were drawn between this *ansa*-cobaltocenium ion and other previously reported structurally characterised metallocenes and *ansa*-metallocenes. DFT calculations were also performed to provide further data for this analysis, including reaction energies for the formation of, and breaking of, the bridging C–C bond to ascertain the extent to which this moiety imposes strain on the system.

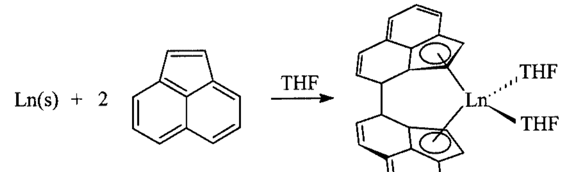
Introduction

The reductive dimerisation of either symmetrically or unsymmetrically substituted fulvenes leads to achiral or, in the latter case, chiral *ansa*-metallocenes. These direct syntheses can be carried out under cocondensation conditions using metal atoms like Sn, Pb[1] or Fe[2] or with electropositive metal powders like Ca,[3] Yb or Sm,[4] which reductively couple the fulvene in solution.



(M = Sn, Pb, Fe, Ca, Yb, Sm)

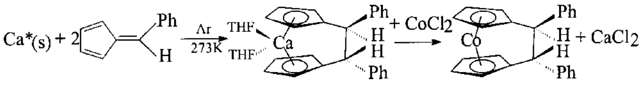
The activated metallic lanthanides Yb and Sm also form *ansa*-lanthanocenes in which the exocyclic moiety of the fulvene ligand is held in position due to its incorporation into an aromatic ring system.[5]



(Ln = Yb, Sm)

The metallocenes of the transition metals have been the subject of extensive research, especially in the area of catalysis.[6,7] Many of these compounds contain an *ansa*-bridge, which restricts the geometry of the rings and therefore changes the electronic properties of the metallocene.[8,9] The rings can be the same, as in bis-cyclopentadienyl,[10,11] bis-indenyl,[12] bis-fluorenyl[13] or bis-tetrahydroindenyl[14] systems, but they can also consist of different ligands as in the case of the fluorenyl-cyclopentadienyl metallocene.[15]

We wish to report the synthesis and structural characterisation of the *trans*-[1,2-$(Ph)_2C_2H_2(\eta^5\text{-}C_5H_4)_2$]$Co^+$ cation, which was isolated as its PF_6^- salt **1**. The synthesis first involves the production of an intermediate, [1,2-$(Ph)_2C_2H_2\{\eta^5\text{-}C_5H_4\}_2$]$Ca(THF)_2$ (**2**),[16] by reacting the ligand 6-phenylfulvene with Rieke calcium. From this point, it is possible to obtain a variety of *ansa*-metallocenes,[17] simply by carrying out a transmetallation using the appropriate anhydrous metal chloride, in this case $CoCl_2$.



The air-sensitive, paramagnetic [1,2-$(Ph)_2C_2H_2(\eta^5\text{-}C_5H_4)_2$]Co (**3**) is then oxidised to give the cation **1**. As this compound is isoelectronic with ferrocene and its analogues, a study can be undertaken, both theoretically and experimentally, to understand the effects of the two-atom bridge on the structure of the metallocene when compared with its unbridged counterpart.

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Results and Discussion

The synthesis of **1** was obtained by performing a transmetallation reaction between **2** and anhydrous $CoCl_2$ analogously to a method reported by Shapiro.[16] 6-Phenylfulvene[18] is the ligand of choice for this synthesis, undergoing reductive coupling to give solely the bridged metallocene. As reported earlier[19] this fulvene produces a radical anion that is readily formed and selective enough to give exclusive formation of the bridging moiety, thus eliminating the possibility of any unbridged metallocenes forming as an inseparable impurity.

The molecular structure of **1** (Figure 1) was determined by X-ray diffraction. Selected bond lengths can be found in Table 1, with diagrams depicting these values in Figure 2 and 3. Selected bond angles are presented in Table 2 and collection and refinement data in Table 3. From this, it can be seen that the cobalt is coordinated to the cyclopentadienyl rings in an η^5-fashion and the phenyl groups on the ethano bridge are in a *trans* position with respect to one another. Compound **1** is present only as the *S*,*S* stereoisomer, but there is no reason to believe that the *R*,*R* form is not also present as crystals and it is only the chance selection of the crystals that lead to the *S*,*S* form. The cation exhibits C_2 symmetry only, with a bridge length of 1.540 Å. In order to accommodate this bond, ring tilting from the parallel arrangement occurs, resulting in different Co^+-C bond lengths and hence a bent sandwich structure, with a ring centroid-Co^+-ring centroid angle of 163.1°. The unit cell is shown in Figure 4 where it can be seen that each PF_6^- anion is surrounded by four *ansa*-metallocene cations. The interaction between these oppositely charged ions occurs between both the cyclopentadienyl and phenyl hydrogens, and two of the fluorides.

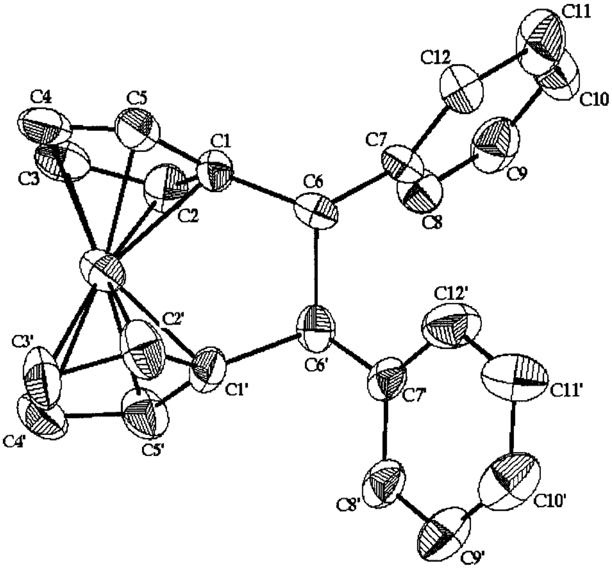


Figure 1. Molecular structure of *trans*-**1**, the PF_6^- counter anion is not shown

Table 1. Selected bond lengths in **1**

C1−C2	1.418	C1′−C2′	1.423
C2−C3	1.392	C2′−C3′	1.414
C3−C4	1.412	C3′−C4′	1.340
C4−C5	1.394	C4′−C5′	1.422
C5−C1	1.465	C5′−C1′	1.408
C1−C6	1.503	C1′−C6′	1.542
C6−R1	1.514	C6′−R1′	1.556
C6−C6′	1.540		
M−C1	1.978	M−C1′	1.963
M−C2	2.010	M−C2′	1.971
M−C3	2.054	M−C3′	2.059
M−C4	2.032	M−C4′	2.060
M−C5	1.997	M−C5′	2.004

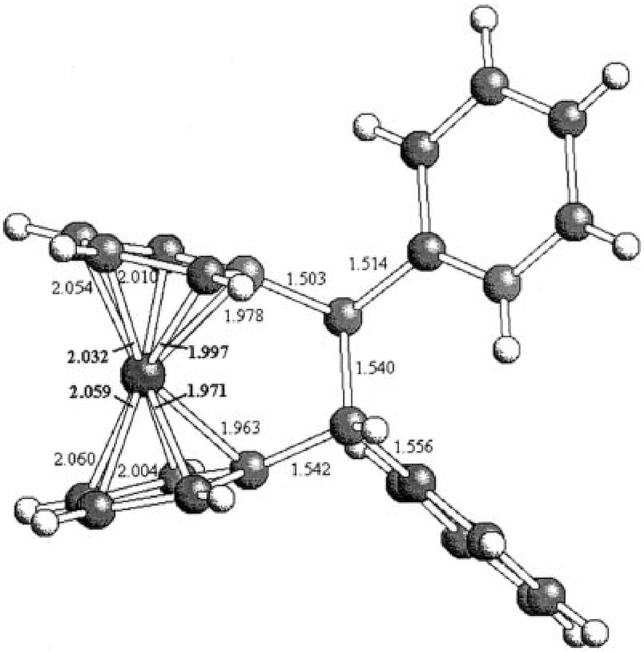


Figure 2. Side view of **1** showing the Co^+-C distances and bridging moiety bond

Structural Analysis

X-ray Crystallography

The inclusion of a two-carbon interannular bridge between the two cyclopentadienyl rings of a metallocene results in structural modification such as bending and lowering the symmetry of the metallocene. This can be demonstrated by comparing an unbridged and a bridged metallocene, namely ferrocene[20] and 1,1′-tetramethylethyleneferrocene (**4**).[21] In ferrocene, the metal is sandwiched equidistantly between the two parallel cyclopentadienyl rings, with the Fe−C distance being 2.045 Å. At room temperature, the rings adopt a staggered conformation, around 3.320 Å apart from each other with a C−C bond length of 1.403 Å. However, the presence of a two-carbon bridge in **4** introduces not only C_2 symmetry, but also a considerable amount of strain into the system, resulting in a C−C bond

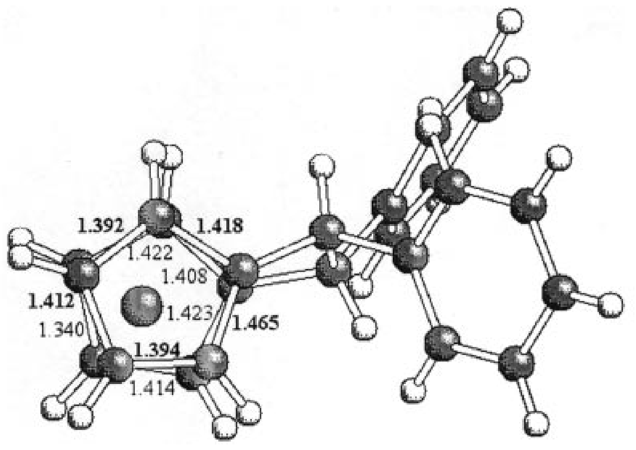


Figure 3. Top view of **1** showing the cyclopentadienyl C−C bond lengths (the C−C bond lengths of the upper ring are in bold)

Table 2. Structural comparisons of selected angles and distances of *ansa*-metallocenes **1**, **4**, **6**, and **7**

	1	4	6	7
α	22.9°	23.2°	4.2°	0.7°
β	12.4°	10.0°; 12.0°	10.8°	10.3°; 10.6°
δ	163.1°	156.8°	176.5°	179.4°
τ	9.0°	9.0°−10.0°	6.0°	2.9°
ε	37.2°; 37.4°	26.0°; 28.0°	7.9°; 8.4°	5.2°; 5.5°
D (C6−C6′)	1.540 Å	1.584 Å	2.354 Å	2.762 Å

Table 3. Summary of crystal data and intensity collection parameters

Compound	1
Molecular formula	$C_{24}H_{20}CoPF_6$
Mol. wt., g mol^{-1}	512.32
Crystal system	orthorhombic
Space group	$P2_1$
a, Å	12.363(3)
b, Å	12.615(2)
c, Å	13.321(4)
Radiation, Å	Mo-K_α (0.71073)
V, Å^3	2077.5(9)
Z	4
ρ, g·cm^{-3}	1.638
μ, mm^{-1}	0.966
F(000)	1040
Index Range	$0 \le h \le 17$, $-2 \le k \le 18$, $-6 \le l \le 18$
2θ, °	63.92
Temp, K	293(2)
Reflections Collected	3890
Reflections Unique	3572
*R*σ	0.179
*R*1 [$I > 4\sigma(I)$]	0.076
*wR*2	0.117
GOOF	0.952
Flack Parameter	−0.01(4)
Min., max. res.	−0.383, +0.418

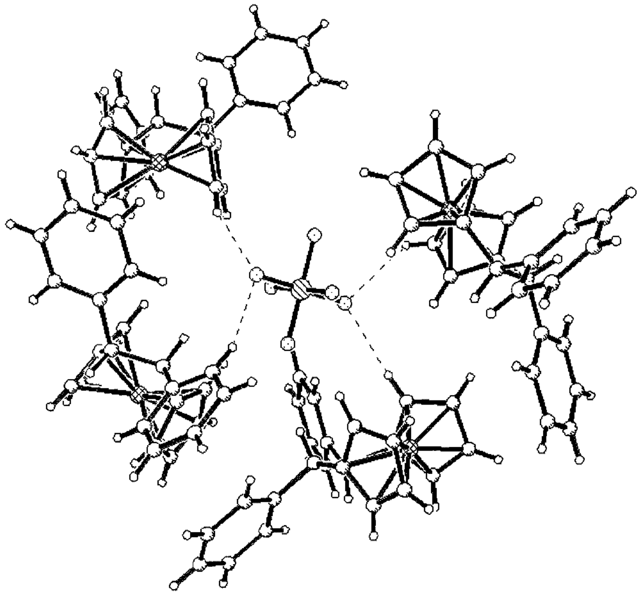


Figure 4. Crystal packing in the unit cell

of 1.584 Å. In order to accommodate this bond, the rings are forced to tilt by an angle (α) of 23.2° relative to one another (Table 2 and Figure 5). This, in turn, results in an angle between the metal and the ring centroids (δ) of 156.8°. The deviation from the fully eclipsed position (τ) of one ring with respect to the other is between 9.0° and 10.0°, so they are still very close to being eclipsed. As in ferrocene, the average Fe-ring C distance is 2.039 Å, but looking at each individual bond length reveals that this value actually varies from 1.965 Å to 2.099 Å. This is also the case with the inter-ring distance: the two carbons bonded to the bridge are pulled closer together (at 2.070 Å) than the carbons on the opposite side of the rings (3.600 Å and 3.650 Å). The C−C bond lengths of the rings themselves show a slight increase in going from 1.401 Å to 1.464 Å but this is still similar to ferrocene. Further evidence of strain is visible in the angles (β) occurring between the rings and the exocyclic bonds, 10.0° and 12.0°, which would not be present in an unstrained system. The two CMe_2 units of the bridge are displaced from the eclipsed arrangement by torsion angles (ε) of 26.0° and 28.0°.

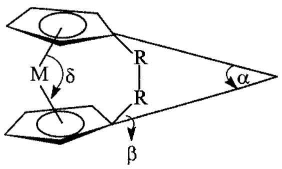


Figure 5. Selected angles from Table 2

A comparison of the structures of 1,1′-bis(benzhydryl)cobaltocenium (**5**)[22] and **1** further demonstrates the effect of the bridge. Again, the metal is sandwiched equidistantly between two parallel cyclopentadienyl rings in the unbridged metallocene, with Co-ring carbon lengths ranging from 2.016 Å to 2.068 Å. On insertion of the ethano bridge, this range increases to between 1.963 Å and 2.060 Å in order to accommodate this bond. The C−C bond lengths in the rings vary little, however, in going from the former (1.392 Å to 1.482 Å) to the latter (1.392 Å to 1.465 Å). As **1** is isoelectronic with **4**, comparisons can be made. The C−C bond length of the bridging moiety is 1.540 Å, indicating that the substituents present around this bond do not impose a strain on it, and therefore it maintains a normal C−C single bond length. This isn't the case for **4**, where a lengthening of the bridge occurred. In addition, a less-strained situation is seen for the rest of the structure due to the differing bridge substituents between this compound (**1**) and **4**. The tilt angle (α) is found to be 22.9° which is quite similar to the above-mentioned ferrocene derivative, while the ring centroid-metal-ring centroid angle (δ) increases to 163.1°, leading to a more parallel arrangement of the cyclopentadienyl groups. As before, the twist angle (τ) is 9.0° but a slight decrease occurs in the range of the metal to ring carbon distances (1.963 Å to 2.060 Å) as a result of the less-bent structure. No further change appears to have occurred in the ring C−C bond lengths (1.392 Å to 1.465 Å). Likewise the β angles of 12.3° and 12.6° remain relatively constant. The greatest structural change to occur is in the torsion angles, ε, which are 37.2° and 37.4°, but this is mainly due to the different bridging units $(CPhH)_2$.

The types of atoms present in the bridge also influence the degree to which structural changes occur. Five important angles from the structures of cyclic ferrocenyldisilane,[23] $[Fe(\eta\text{-}C_5H_4)_2(SiMe_2)_2]$ (**6**) and 1,2-distanna(2)ferrocenophane,[24] $[Fe(\eta\text{-}C_5H_4)_2(SnMe_2)_2]$ (**7**) were examined and in almost in all cases these vary greatly from those for 1,1′-tetramethylethyleneferrocene. The length increases in going from the disilanyl bridge (2.353 Å) to the distannyl bridge (2.762 Å), due to the increase in size of these atoms. The effect of this bridge lengthening can be seen from the ring-M-ring angle (δ). The angle for **6** is 176.4° and for **7** is 179.4°, with the cyclopentadienyl rings being almost parallel in both cases. The tilt angle (α) also decreases, going from 4.2° to 0.7°. The rings are also much closer to being fully eclipsed when the bridge length is increased. Evidence of this is found from the twist angle (τ), which is 6.0° for **6** and 2.9° for **7**. The bridging units themselves, adopt a more eclipsed arrangement, ε is 7.9° and 8.4° for the silane units and decreases to 5.2° and 5.5° for the stannyl units. However, there is one set of values that remains the same and this is the angle β between the exocyclic bond and the ring plane: in **6** it is 10.8° and in **7** it is 10.3° and 10.6°.

Finally, the bonds between the bridge and the cyclopentadienyl rings also increase with replacement of the bridging moieties by larger atoms. They are found to be 1.548 Å and 1.543 Å, 1.852 Å and 1.866 Å and 2.149 Å and 2.134 Å for the C_2 (**1**), Si_2 (**6**) and Sn_2 (**7**) bridges respectively.

Theoretical Calculations

In order to get a deeper understanding of the nature of metallocene formation, a series of density functional theory (DFT) calculations were performed in which iron atoms were reacted with selected fulvenes. These calculations provide structural data and enthalpies of formation and allow a discussion of the effect of varying the substituted fulvenes, namely 6,6-dimethylfulvene, 6-phenylfulvene and 6,6-diphenylfulvene. These calculations were extended to include the reaction of the *ansa*-metallocenes **9** and **11** and the bisfulvene complex **13** with hydrogen gas to form unbridged ferrocenes. Similar calculations were also carried out on **1**, the accuracy of which can be seen by comparing the calculated bond lengths (Table 4 and Figure 6) with the experimental values (Table 1), the difference between the two sets of results being only around 0.02 Å. Although the range of the cyclopentadienyl ring carbon bond lengths C1−C5 is shorter (1.423 Å to 1.439 Å) than the experimental values (1.392 Å to 1.465 Å) they mimic the results: bond elongation to the *ipso* carbon with shorter C−C bonds for the rest of the ring. The calculated M-ring carbon bonds also clearly show how the metallocene is bent due to the bridging moiety (1.584 Å), which is slightly longer than the actual length of 1.540 Å. As was found in the experimental values, the shortest Co^+-ring carbon bond is to the *ipso* carbon

Table 4. Calculated bond lengths (Å) for selected *ansa*-metallocenes

	8	9	10	11	**12**	**12**[a]	**13**[a]	**1**[b]
C1−C2	1.433	1.440	1.431	1.436	1.432	1.442	1.472	1.438
C2−C3	1.428	1.429	1.427	1.429	1.428	1.439	1.431	1.430
C3−C4	1.425	1.426	1.427	1.427	1.426	1.439	1.434	1.423
C4−C5	1.428	1.427	1.427	1.427	1.428	1.439	1.431	1.428
C5−C1	1.433	1.442	1.431	1.439	1.432	1.442	1.475	1.439
C1−C6	1.524	1.545	1.504	1.534	1.527	1.519	1.395	1.534
C6−R1	1.538	1.545	1.527	1.530	1.532	1.535	1.479	1.521
C6−C6′	N/A	1.631	N/A	1.570	N/A	N/A	N/A	1.584
C1′−C2′		1.440		1.436				1.438
C2′−C3′		1.429		1.429				1.430
C3′−C4′		1.426		1.427				1.423
C4′−C5′		1.427		1.427				1.428
C5′−C1′		1.442		1.439				1.439
C1′−C6′		1.545		1.534				1.534
C6′−R1′		1.545		1.530				1.521
M−C1	2.075	1.975	2.059	1.974	2.073	2.059	2.224	1.980
M−C2	2.051	2.025	2.052	2.026	2.051	2.038	2.036	2.017
M−C3	2.048	2.081	2.052	2.082	2.048	2.040	2.033	2.074
M−C4	2.048	2.087	2.052	2.089	2.048	2.040	2.039	2.080
M−C5	2.051	2.030	2.052	2.031	2.051	2.038	2.028	2.027
M−C1′		1.976		1.974				1.980
M−C2′		2.025		2.026				2.017
M−C3′		2.081		2.082				2.074
M−C4′		2.087		2.089				2.080
M−C5′		2.030		2.031				2.027

[a] Calculation performed at the B3LYP level using 3-21G as the basis set. [b] Calculation performed at the B3LYP level using 6-311G** as the basis set.

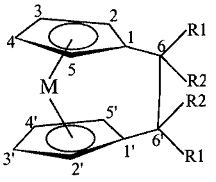


Figure 6. Numbering scheme for observed and calculated metallocene structures

(1.980 Å) and the longest to the two carbons furthest away from this (2.074 Å and 2.080 Å).

The bridged and unbridged ferrocenes that were measured were derived from 6,6-dimethylfulvene, 6-phenylfulvene and 6,6-diphenylfulvene (unbridged only). For the unbridged tetramethylferrocene (**8**), the C−C bonds in the cyclopentadienyl rings range from 1.425 Å to 1.433 Å, and are very similar to those of the bridged tetramethylferrocene **9** (1.426 Å to 1.442 Å). The difference between these two compounds is found in their Fe-ring carbon bonds (2.048 Å to 2.075 Å, compared to 1.975 Å to 2.087 Å for the bridged structure). This is a result of the C6−C6′ bridge of 1.631 Å distorting the sandwich structure of **9**. Again, these values show a slight elongation compared to the measured experimental bond lengths for 1,1′-tetramethylethyleneferrocene (**4**), whose bridge length is 1.584 Å.

In the case of the unbridged **10** and bridged diphenylferrocene **11**, the ring carbon bond lengths are very similar (1.427 Å to 1.431 Å and 1.427 Å to 1.439 Å respectively). As before, the longest bonds are to the *ipso* carbon, although the presence of a bridge (1.570 Å) causes the M-ring carbon distances to change from 2.052 Å to 2.059 Å — a parallel arrangement — to 1.974 Å to 2.089 Å — a bent structure.

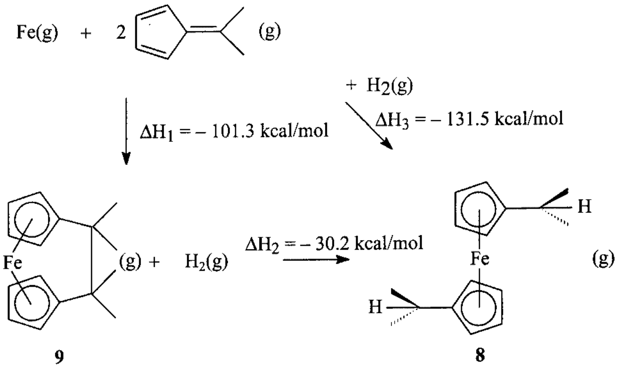
The third group of calculations involved 6,6-diphenylfulvene as the ligand. Only the unbridged tetraphenylferrocene **12** was studied, as bridge formation in this case is not possible due to the large steric overload that would result.[25] As for the previous two ferrocenes, the bond lengths lie within a very similar range: the cyclopentadienyl carbon-carbon bonds are between 1.426 Å and 1.432 Å and the metal-carbon distances are between 2.048 Å and 2.073 Å.

The role of the substituents is evident from these results. In order to synthesise an *ansa*-metallocene, the groups present on the exocyclic carbon must not be so sterically demanding that they prevent dimerisation occurring, as in the case of 6,6-diphenylfulvene. Despite its suitability for radical anion stabilisation,[19] the steric hindrance between the four phenyl rings results in the sole production of the unbridged metallocene. Changing the phenyl groups for methyl groups reduces these clashes and bridge formation occurs. However, the structure still possesses substantial strain and so to compensate the C_2 bridge is elongated to 1.631 Å. Replacing the methyl groups for a phenyl and a hydrogen decreases the strain even further and this is reflected in the bridge length of 1.570 Å. This effect can also be seen in the formation energies of the respective molecules (Table 5). In both the bridged and unbridged cases, going from the tetramethylferrocene to the diphenylferrocene results in a lowering of the energy of these compounds. The energy of the unbridged tetraphenylferrocene is lower still, despite having large substituents, as these are responsible for producing the most stable radical anion. The enthaplies of bridge formation for **9** and **11** were also calculated (Scheme 1 and 2) and found to be −101.3 kcal/mol and −129.2 kcal/mol respectively. From this, it can be seen that the formation of **11** is energetically more favourable. Further ΔH values were calculated for the breaking of the bridging moiety, to give the unbridged metallocene, namely −30.2 kcal/mol (**8**) and −28.2 kcal/mol (**10**). These values show that not only does the bridge impose a strain on the metallocene, but the substituents do as well. The presence of four methyl groups on the bridge imposes greater stress on the structure than two phenyls and two hydrogens, occupying the *trans* position. Hence breaking this bond releases more energy (−30.2 kcal/mol) and thus removes the strain in the system. The ΔH value for the formation of **12** was also measured and found to be −124.3 kcal/mol (Scheme 3). This too shows that the synthesis of **12** is viable but is the lowest of the three values, for **8** the value is −131.5 kcal/mol and for **10** it is −157.4 kcal/mol.

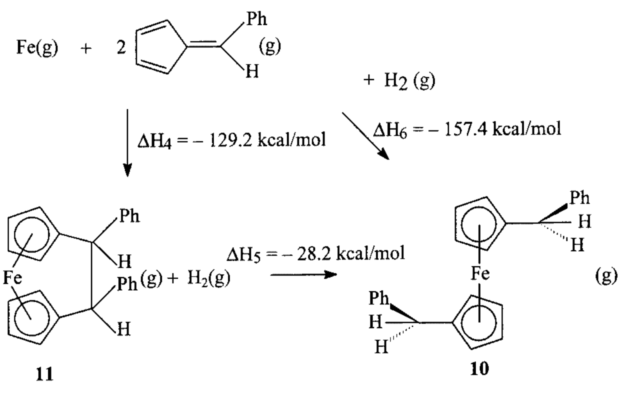
Table 5. Calculated energies (Hartrees) and reaction enthalpies (kcal/mol) for bridged and unbridged ferrocenes

	E	ZPE	E'	ΔH
8	−1886.619006	0.339256	−1886.27975	−131.5
9	−1885.382299	0.318964	−1885.063335	−101.3
10	−2191.469967	0.318964	−2191.081835	−157.4
11	−2190.236630	0.368083	−2189.868547	−129.2
12	−2653.570935	0.550408	−2653.020527	−124.3
12[a]	−2640.004865	0.553349	−2639.451516	−169.4
13[a]	−2638.748619	0.529476	−2639.451516	−124.2

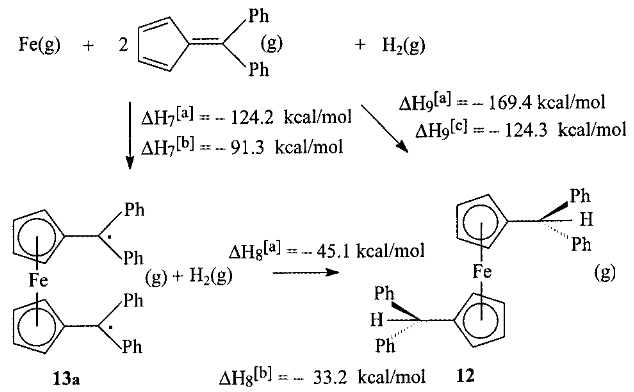
[a] Calculated with the 3-21G basis set.



Scheme 1. Calculated reaction enthalpies for the formation of **8** and **9**, using 6,6-dimethylfulvene as the starting ligand

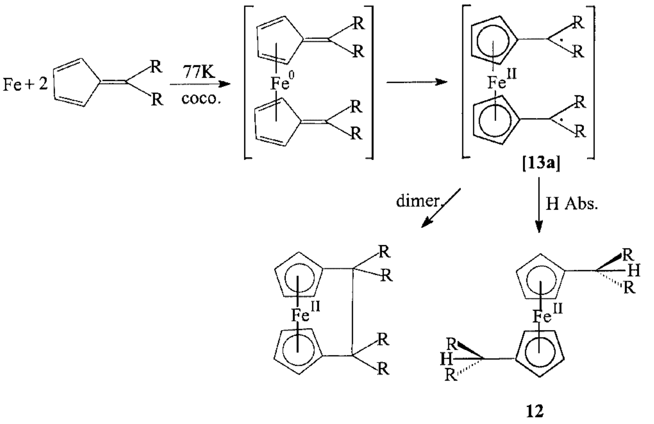


Scheme 2. Calculated reaction enthalpies for the formation of **10** and **11**, using 6-phenylfulvene as the starting ligand



Scheme 3. Calculated reaction enthalpies for the formation of **12** and **13a**, using 6,6′-tetraphenylferrocene as the starting ligand [a] Calculations performed using the 3-21G basis set. [b] Correction factor applied to the results from the 3−21G basis set to give corresponding values from the 6-31G** basis set. [c] Calculations performed using the 6-31G** basis set

It was previously proposed[26] that a further intermediate is involved in the synthesis of these metallocenes, namely a bis-fulvene complex. This intermediate was thought to form initially from the reaction of metal atoms with fulvenes to give a complex whose metal centre has an oxidation state of zero. The next step is an electron transfer — one electron goes to each ring — resulting in an M^{2+} ion centred between two radical anions, which can then dimerise to give the *ansa*-metallocene or undergo hydrogen abstraction yielding the unbridged compound (Scheme 4). Proof of this postulate was obtained from the X-ray structure of a bis(6,6-diphenylfulvenyl)iron intermediate **13**.[26] A theoretical examination of this complex can give a further insight into its role in the reaction mechanism. The structure was calculated to obtain a minimum in the singlet state, **13a**, but this had to be performed using 3-21g* as the basis set to save calculation time. This revealed C−C ring lengths of 1.431 Å to 1.475 Å and M−C distances of 2.028 Å to 2.224 Å. These are similar to the experimentally found values of 1.406 Å to 1.452 Å for the cyclopentadienyl C−C bonds and 2.035 Å to 2.209 Å for the M−C lengths. Using these values, it can be determined whether or not **13** is really a bis-fulvene complex or a ferrocene derivative. To be the former of the two, the cyclopentadienyl rings should consist of alternating single and double bonds, with the two phenyl substituents located at the exocyclic double bond. These bond lengths should mirror the values determined both theoretically[19] and experimentally[26] for the 6,6-diphenylfulvene. Alternatively, to be the ferrocene derivative, the cyclopentadienyl rings should be more aromatic in character due to their reduction by the iron centre. The structure of the 6,6-diphenylfulvene radical anion has previously been calculated, using the 6-31G** basis set.[19] It can clearly be seen that the C−C bonds in the cyclopentadienyl ring are no longer comprised of distinct single and double bonds and lie in the range of 1.387 Å to 1.446 Å. The exocyclic bond has elongated to 1.434 Å, showing increased single bond character. A study of the crystal structure of **13** reveals that the equivalent bond in this complex is 1.408 Å and there is no clear distinction between what were formally single and double bonds in the ring. Therefore, structurally, **13** is a complex in which an Fe^{II} centre is coordinated to two fulvene radical anions with the two formally unpaired electrons in the C6 and C6′ positions. The crystal geometry also shows that the phenyl substituents are eclipsed with respect to one another, despite the steric crowding. As stated earlier, theoretical calculations found the optimised structure in the singlet state. This indicates that there is coupling occurring between the two electrons, hence allowing such an arrangement to occur, satisfying the 18 VE rule. The ΔH values for the formation of complex **13a** and the ultimate formation of **12** were also calculated at this lower level (Scheme 3). Formation of the singlet was exothermally favourable at −124.2 kcal/mol and the overall enthalpy of formation of the unbridged ferrocene was −169.4 kcal/mol. There is a considerable difference between this latter value and the original one calculated using the higher basis set (−124.3 kcal/mol). The ratio difference between these two is 1.36 and this can be used as a correction factor to get a more accurate value for the formation of the singlet. This was calculated to be −91.3 kcal/mol, and since this is too low to result in the formation of a C−C bond (−100 kcal/mol is necessary), only the unbridged metallocene is seen.



Scheme 4. Reaction mechanism for the synthesis of metallocenes, showing the role of the bis-fulvene complex **13a**

Conclusion

The formation of **1** was achieved and it was isolated as a PF_6^- salt. Theoretical calculations were also carried out in order to obtain a geometry optimised structure, and from this it was seen that these results mirror the experimental values very closely. The main difference was found in the length of the bridging moiety, which the calculations had over-estimated by about 0.04 Å. This too was also the case for the other *ansa*-metallocene calculations. Despite this, the effect of the bridge on the structure and the effect of the substituents on the bridge can be seen. From both experimental and theoretical data, it is apparent that the presence of four methyl groups on the bridge of **9** imposes strain on the bond, elongating it. This then has a knock-on effect on the structure, causing the rings to tilt more away from the parallel and a smaller δ angle. Replacing the groups with ones that produce less steric hindrance as in **1**, results in a bridge with a normal C−C bond length. This less-strained structure is also reflected in the more parallel arrangement of the rings and the larger ring centroid-M-ring centroid angle, with respect to **9**. Finally, the structure of **13** has been proposed to be that of a ferrocene derivative, with the iron centre donating two electrons to the cyclopentadienyl rings, where they occupy the C6 and C6′ positions. Here they experience a degree of coupling which results in an eclipsed arrangement of the phenyl substituents.

Experimental Section

Synthetic Work. General: The preparation of **2** was carried out according to a literature procedure.[16] THF was dried over and distilled from Na/benzophenone prior to use. Air- and moisture-sensitive compounds were stored and handled in an argon glove box and manipulations of these substances were carried out with standard Schlenk techniques using argon to avoid calcium nitride formation.

NMR spectra were recorded on a VARIAN 300 MHz spectrometer. Chemical shifts are reported in ppm and are referenced to TMS, except for the ^{31}P NMR spectra, which are referenced to external triphenylphosphate.

The mass spectra were measured on a Finnigan MAT Incos 50 B mass spectrometer in EI mode.

Computational Study: DFT calculations were performed using the GAUSSIAN 98[27] programme implemented on an Origin 200 eight-processor cluster (SGI 180 MHz CPU/2 GB RAM). These were carried out at the B3LYP level, using either the 6-31G** or the 3-21G basis sets. The calculated electronic energies (E) of the complexes studied are presented in Table 5 in Hartrees. A correction value, namely the zero-point energy (ZPE), must be added to these values to give the overall energies (E') of the molecules. Finally, the reaction enthalpies in Table 5 have been calculated from the energy differences between the reactants and the products. For the formation of the *ansa*-metallocenes, this was found to be the difference between the bridged ferrocene and the combined energy of the iron atom with the desired fulvene. Two pathways were studied for the unbridged metallocene: direct reaction between the iron, selected fulvene and hydrogen gas and the breaking of the bridging moiety of the *ansa*-ferrocene with subsequent reaction with the hydrogen.

Synthesis of *ansa*-Cobaltocenium Hexafluorophosphate (1): A freshly made solution of **2** was prepared according to literature methods[16] and an equimolar amount of $CoCl_2$ (0.422 g, 3.25×10^{-3} mol) was added to it under argon. This was refluxed for eight hours, producing a dark green solution of **3**. After filtration, the solution was cooled to −30 °C to produce **3** as a lime green powder, which was then dried under vacuum. Principle IR absorptions (nujol): $\tilde{\nu}$ = 2950 cm^{-1} (m), 2865 (m), 1580 (w), 1304 (w), 1260 (s), 1092 (s), 1021 (s), 867 (w), 798 (s), 722 (m). MS (EI): m/z = 367.1 (54) [M$^+$], 308.1 (8.2) [M$^+$ − Co$^+$], 306.1 (51.3) [M$^+$ − Co$^+$ − 2H$^+$], 212.9 (8.2) [M$^+$ − $C_{12}H_{10}$], 154.1 (57) [$C_{12}H_{10}$], 153.1 (100) [$C_{12}H_{10}$ − H$^+$], 58.9 (2.3) [Co$^+$]. UV/Vis (CH_3CN): λ_{max} = 364 nm. The powder was redissolved in 6 M HCl (65 mL), while exposing the solution to air. This was stirred until the olive green colour changed to yellow-green. The mixture was then filtered and the filtrate was washed with diethyl ether. The aqueous layer was separated and a saturated aqueous solution of NH_4PF_6 was added dropwise. An orange precipitate was seen to slowly drop out of the solution and upon filtration gave 0.72 g of an orange/yellow powder (yield: 43%). ^{1}H NMR (CD_3CN, 25 °C): δ = 5.20 (s, 2 H, PHC*H*Cp), 5.33, 5.71, 6.43, 6.71 (m, 8 H, C_5H_4), 7.23−7.41 (m, 10 H, C_6H_5) ppm. ^{13}C NMR (CD_3CN, 25 °C): δ = 57.1 (Ph*C*HCp), 84.1, 84.9, 89.1, 90.0, 130.9 (C_5H_4), 128.1, 128.7, 129.5, 140.3 (C_6H_5) ppm. Principle IR absorptions (KBr): $\tilde{\nu}$ = 3117 cm^{-1} (m), 3063 (m), 3015 (m), 1548 (w), 1496 (s), 1398 (s), 1032 (s), 927 (m), 836 (s), 820 (m), 777 (m), 726 (s), 704 (m). $C_{24}H_{20}CoF_6P$ (512.3): calcd. C 56.26, H 3.93, Co 11.50, F 22.25, P 6.04; found C 55.95, H 4.03, Co 11.21, F 19.91, P 5.21. MS (EI): m/z = 367.1 (54) [M$^+$ − PF_6], 213.02 (8.8) [M$^+$ − $C_{12}H_{10}$], 154.1 (48) [$C_{12}H_{10}$], 153.1 (100) [$C_{12}H_{10}$ − H$^+$], 58.9 (20) [Co$^+$]. UV/Vis (CH_3CN): λ_{max} = 422.0 nm. Crystals were grown by the slow evaporation of acetonitrile at room temperature.

X-ray Crystallography: The crystals grown were found to be suitable for X-ray diffraction. The orange cross-shaped crystals that were obtained belong to the $P2_1$ space group and the crystallographic parameters are presented in Table 3. Data were collected on an Enraf−Nonius CAD4 four-circle diffractometer with monochromatized Mo-K_α radiation. An absorption correction turned out to be unnecessary. The crystal structure was solved by direct methods[28] and refined using a least-squares method.[29] All non-hydrogen atoms were refined with anisotropic displacement parameters. The H atoms were placed at idealised positions and refined with coupled, isotropic displacement parameters. The absolute structure could be determined because of a definite Flack parameter.

CCDC-190062 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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