New strongly coupled dinuclear metal centres in organometallic *s*-indacene complexes

Douglas R. Cary, Catherine G. Webster, Mark J. Drewitt, Stephen Barlow, Jennifer C. Green and Dermot O'Hare*†

Inorganic Chemistry Laboratory, South Parks Road, Oxford, UK OX1 3QR

The complexes *cis*-[{Fe(CO)$_3$}$_2$L] and *cis*-[{Co(CO)$_2$}$_2$L] are prepared from 1,3,5,7-tetra-*tert*-butyl-*s*-indacene; in solution, the diiron complexes exhibit very strong electron–electron coupling between iron centres as evidenced by a 810 mV separation between the 0/+ and +/2+ redox waves.

Oligomers or polymers based on metallocenes bridged by fused-ring ligands such as pentalene or *s*-indacene are anticipated to show interesting delocalised properties.[1,2] Indeed, EPR, Mössbauer, electrochemical and magnetic data show very strong metal–metal interactions in the bimetallic species $\{L^1[M(C_5Me_5)]_2\}^{n+}$ (L^1 = pentalene, *s*-indacene; M = Fe, Co, Ni; n = 0, 1 2).[3] However, the stepwise construction of higher oligomers has been hampered by escalating insolubility with increasing oligomerisation.[4] Here we report the use of the stable 1,3,5,7-tetra-*tert*-butyl-*s*-indacene L in the synthesis of new binuclear organometallic derivatives.

According to Hückel's rule, fully conjugated planar polycyclic alkenes with $4n + 2$ π-electrons should display benzenoid properties; those with $4n$ π-electrons are termed antiaromatic.[5] However, it has been shown that some $4n$ π-systems display 'aromatic character'.[6] *s*-Indacene has an antiaromatic 12 π-electron system and the relationship between its reactivity, aromaticity and stability has been the subject of many studies by theoretical organic chemists. According to LCAO calculations, *s*-indacene should have an electron delocalisation energy similar to that of the tropylium cation, yet the system can be expected to exhibit high reactivity due to the low energy difference of its ground and excited state.[7]

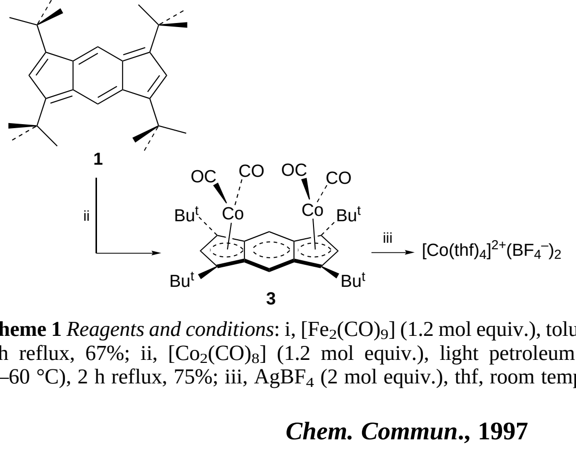
Due to the thermal instability of *s*-indacene, it has been necessary to synthesise more stable substituted derivatives. 1,3,5,7-Tetra-*tert*-butyl-*s*-indacene **1** is kinetically stabilised by the bulky alkyl groups, and has been studied intensively in this respect; its synthesis was briefly outlined by Hafner *et al.*[8]

Refluxing **1** with an excess of [Fe$_2$(CO)$_9$] for 2 h gave an emerald green solution from which dark-green crystals could be obtained by recrystallisation from toluene. Elemental microanalysis and mass spectral data were consistent with the formulation [{Fe(CO)$_3$}$_2$L] **2** (Scheme 1). The room temperature ^{1}H and ^{13}C NMR data indicated that the indacene ligand was complexed to two iron centres in such a way as to produce no change in the local symmetry of the ligand environment. However, the spectroscopic data did not allow us to determine unambiguously the bonding mode of the Fe centres.

The single-crystal X-ray structure determination of **2**‡ revealed that two iron tricarbonyl moieties have been coordinated to the indacene ligand (Fig. 1). This is a rare example of an indacene complex with two metal fragments coordinated to the same face of an indacene ligand. The distances Fe(1) to C(1), C(2), C(3), C(9) and C(10) and the distances Fe(2) to C(5), C(6), C(7), C(11) and C(12) suggest that each iron atom is coordinated to **1** in a very distorted manner. For example, the Fe(1)–C(10) and Fe(2)–C(12) bond lengths are *ca.* 0.11 Å longer than the Fe(1)–C(9) and Fe(2)–C(11) distances, respectively. The average Fe–CO distance is 1.793 Å and is very typical for iron carbonyl complexes. The indacene framework has been distorted in the following manner: the C(1), C(2) and C(3) plane twists [relative to the long C_2 axis that is present in the free ligand] so that C(3) becomes closer in space to C(9) than in the free indacene. The distortion also occurs for C(5), C(6) and C(7) plane with C(7) being closer to C(11).

Refluxing **1** with an excess of [Co$_2$(CO)$_8$] in light petroleum (bp 40–60 °C) for 2 h gave a dark-red powder from an orange solution. Dark-red crystals of [{Co(CO)$_2$}$_2$L] **3** could be obtained by recrystallisation of the powder from toluene–pentanes. The single-crystal X-ray structure determination of **3**‡ revealed that two cobalt dicarbonyl units have been coordinated to the same face of **1** (Fig. 2). The distances Co(1)–C(1), Co(1)–C(2), Co(1)–C(3), Co(2)–C(5), Co(2)–C(6) and Co(2)–C(7) are very similar with a mean value of 2.077(2) Å. The two cobalt centres also have longer contacts to the central carbons C(9), C(10), C(11) and C(12) with a mean value of 2.229(2) Å. The average Co–CO distance is 1.738(3) Å.

The solution electrochemistry of **2** and **3** has been investigated in order to gauge the degree of interaction between the two metal centres in these compounds. The cyclic voltammogram (CV) of **2** in dichloromethane clearly shows two reversible waves at $E_{1/2}$ = 0.26 and −0.55 V (*vs.* [Fe(η-C$_5$H$_5$)$_2$]–[Fe(η-C$_5$H$_5$)$_2$]$^+$, in CH$_2$Cl$_2$) corresponding to two successive one-electron transfers *i.e.* oxidation to the mono- and di-cations respectively. The redox waves are separated by 0.81 V, which indicates that the second electron is more difficult to remove than the first. The extremely large value for ΔE is characteristic of strong electronic interactions between the metal centres and extensive delocalisation in the mixed-valence form of the complex. The CV of **3** in CH$_2$Cl$_2$ is much more complex and at moderate scan rates no reversible electrochemical events can be measured.



Scheme 1 *Reagents and conditions*: i, [Fe$_2$(CO)$_9$] (1.2 mol equiv.), toluene, 2 h reflux, 67%; ii, [Co$_2$(CO)$_8$] (1.2 mol equiv.), light petroleum (bp 40–60 °C), 2 h reflux, 75%; iii, AgBF$_4$ (2 mol equiv.), thf, room temp.

Density functional theory (DFT) has been used to try and rationalise the bonding of the indacene moiety to the $Fe(CO)_3$ and $Co(CO)_2$ metal fragments. Indacene has six occupied π orbitals which bear a close resemblance to linear combinations of the occupied orbitals of two cyclopentadienyl anions, though they include contributions from the π-orbitals of the two central carbons where symmetry allows, *i.e.* for the b_{1u} and b_{2g} combinations. Normal electron counting procedures for **2** and **3**, including all π electrons of the indacene ligand, result in an electron count of 40 for **2** and 38 for **3** for these binuclear systems, four and two electrons in excess of that required for two 18 electron metal centres.

Density functional calculations, including geometry optimisations, have been carried out for both $[Fe_2(CO)_6(C_{12}H_8)]$ **4** and $[Co_2(CO)_4(C_{12}H_8)]$ **5** using a generalised gradient approximation as implemented in the Amsterdam density functional code.[9] Initially the symmetries of **4** and **5** were constrained to C_{2v} symmetry, but subsequently the optimisation was carried out in each case with a constraint of C_2 symmetry. In the case of **4** relaxation of the symmetry constraint to C_2 led to an optimised geometry with a bond length pattern and buckling of the ring close to that found for **2**. For **5** there was little departure from C_{2v} symmetry for the optimised structure as was found experimentally for **3**.

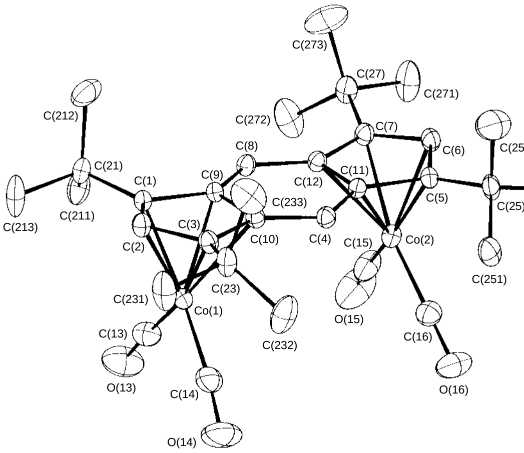


Fig. 1 Molecular structure of **2**. Selected interatomic distances (Å): Fe(1)–Fe(2) 5.414(5), Fe(1)–C(1) 2.131(5), Fe(1)–C(2) 2.065(6), Fe(1)–C(3) 2.166(5), Fe(1)–C(9) 2.325(5), Fe(1)–C(10) 2.436(5), Fe(2)–C(5) 2.143(5), Fe(2)–C(6) 2.069(5), Fe(2)–C(7) 2.165(5), Fe(2)–C(1) 2.350(5), Fe(2)–C(12) 2.446(5), C(1)–C(2) 1.420(7), C(1)–C(9) 1.452(6), C(2)–C(3) 1.427(6), C(3)–C(10) 1.467(6), C(4)–C(10) 1.384(6), C(4)–C(11) 1.416(7), C(5)–C(11) 1.449(6), C(5)–C(6) 1.418(6), C(6)–C(7) 1.428(6), C(7)–C(12) 1.456(7), C(8)–C(12) 1.383(6), C(8)–C(9) 1.413(6), C(9)–C(10) 1.459(6), C(11)–C(12) 1.462(6).

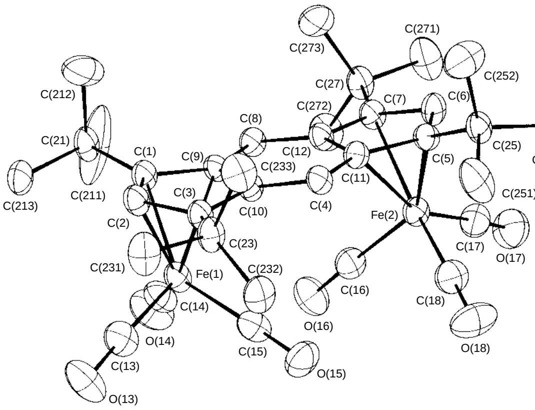


Fig. 2 Molecular structure of **3**. Selected interatomic distances (Å): Co(1)–Co(2) 4.931(3), Co(1)–C(1) 2.087(2), Co(1)–C(2) 2.073(2), Co(1)–C(3) 2.079(2), Co(1)–C(9) 2.234(2), Co(1)–C(10) 2.227(2), Co(2)–C(5) 2.080(2), Co(2)–C(6) 2.070(2), Co(2)–C(7) 2.075(2), Co(2)–C(11) 2.233(2), Co(2)–C(12) 2.224(2), C(1)–C(2) 1.416(3), C(1)–C(9) 1.470(3), C(2)–C(3) 1.422(3), C(3)–C(10) 1.468(3), C(4)–C(10) 1.393(3), C(4)–C(11) 1.393(3), C(5)–C(11) 1.472(3), C(5)–C(6) 1.417(3), C(6)–C(7) 1.421(3), C(7)–C(12) 1.466(3), C(8)–C(12) 1.400(3), C(8)–C(9) 1.395(3), C(9)–C(10) 1.447(3), C(11)–C(12) 1.446(3).

In the case of **4** both the HOMO (a_1 in C_{2v}) and the SOMO (b_1 in C_{2v}) are mainly localised on the metals and the two indacene central carbons, C(4) and C(8). The interaction between the metals and these carbons is antibonding. We suggest that it is the occupancy of these two orbitals by the four excess electrons that leads the metals to be closer to the outer carbons and drives the structural distortion with the consequent relief of the antibonding character of these interactions. Both the HOMO and SOMO are stabilised on distortion, the SOMO more than the HOMO. Lower energy orbitals conform to the expectations for three legged piano stools. In the case of **5** the HOMO is of b_2 symmetry, with a node at the central indacene carbons, and metal indacene antibonding though metal CO bonding. The antibonding interaction is evenly distributed along the indacene and leads to less displacement towards the outer carbons than found in **4** and no obvious distortion.

We believe that the indacene ligand will be able to form π complexes with a wide range of metal fragments. The extensive π-electron delocalisation of the ligand orbitals means that the metal centres will be able to interact strongly with each other.

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Footnotes

* E-mail: dermot.ohare@icl.ox.ac.uk

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‡ X-Ray crystal structure analyses: **2**: monoclinic, space group $P2_1/n$, a = 10.4730(9), b = 18.147(1), c = 17.366(1) Å, β = 95.397(5), U = 3285.8 Å^3, Z = 4, D_c = 1.23 g cm^{-3}, μ = 9.2 cm^{-1}, crystal size *ca.* 0.16 × 0.22 × 0.27 mm, T = 170 K, 70 frames, 39 683 total (7195 independent) reflections, R = 0.055 and R_w = 0.058 for 4352 reflections with $I > 4\sigma(I)$, max., min. peak in final Fourier difference synthesis 0.45, -0.62 e Å^{-3}, respectively. **3**: triclinic, space group $P\bar{1}$, a = 10.588(1), b = 12.509(1), c = 14.103(1) Å, α = 70.090(2), β = 80.401(2), γ = 67.942(2)°, U = 1604.9 Å^3, Z = 2, D_c = 1.33 g cm^{-3}, μ = 10.5 cm^{-1}, crystal size *ca.* 0.50 × 0.60 × 0.70 mm, T = 150 K, 90 frames, 22358 total (6967 independent) reflections, R = 0.039 and R_w = 0.044 for 5796 reflections with $I > 3\sigma(I)$, max., min. peak in final Fourier difference synthesis 0.68, -0.54 e Å^{-3}, respectively. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/418.

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