Unusual reactivity and isomerisation in dicobalt *s*-indacene complexes

Paul Roussel, Mark J. Drewitt, Douglas R. Cary, Catherine G. Webster and Dermot O’Hare*

Inorganic Chemistry Laboratory, South Parks Road, Oxford, UK OX1 3QR. E-mail: dermot.ohare@chem.ox.ac.uk

Di-{Co(Cp)} derivatives of Bu$^t{}_4$-*s*-indacene (Ic′) have been prepared, they exist as both *cis* and *trans* isomers which can interconvert in solution; the solution electrochemistry of these complexes show that these bimetallic complexes can exhibit up to four redox events; unusually, attempted oxidation by a protic oxidising agent of $(CoCp)_2$Ic results in attack at the central carbons of the indacene rings.

Organometallic polymers are known to show interesting magnetic and electronic properties arising from the communication of adjacent metal centres. For example, polyferrocenophanes exhibit two oxidation waves for the alternate iron sites.[1] Manriquez *et al*. have reported substantial intramolecular metal–metal communication for bimetallic complexes containing bridging indacene and pentalene ligands,[2] however attempts at synthesis of oligo- and poly-meric transition metal complexes incorporating these ligands have met with limited success owing to their insolubility.

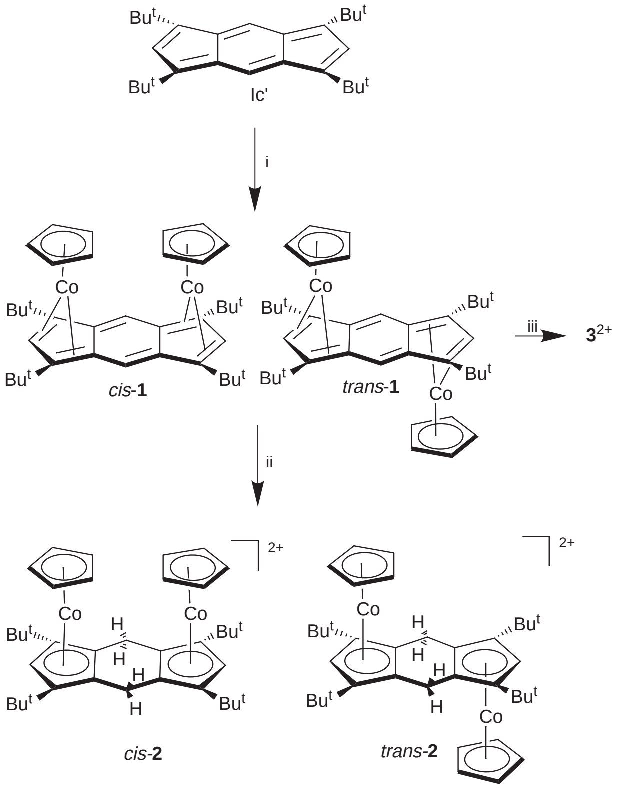
We have been investigating the organometallic chemistry of Ic′ (Ic′ = 1,3,5,7-tetra-*tert*-butyl-*s*-indacene)[3] with the view of making soluble oligomeric complexes with significant intramolecular electron–electron correlation.[4] So far, bimetallic transition metal complexes of Ic′ have only exhibited *cis* coordination of the two metal centres to the planar ligand, however, the transition metal starting materials were dimeric thus favouring this geometry. Thus, syntheses involving suitable monomeric transition metal starting materials should afford a mixture of both *cis* and *trans* bimetallic Ic′ complexes.

Reaction of Ic′ and 2 equiv. of monomeric $[CoCp(C_2H_4)_2]$ gave a brown solution, from which analytically pure $[(CoCp)_2Ic']$ **1**† can be isolated (Scheme 1). The room temperature ^1H NMR spectrum of a solution of **1** in $[^2H_8]$toluene shows two sets of uncorrelated resonances in the ratio 8 : 1, upon cooling the solution to 233 K this ratio changes to 5 : 1. We believe the resonances attributable to the major species are due to the *cis* isomer of **1** (Scheme 1) *vide infra*. In fact, on warming a solution of **1** in $[^2H_8]$toluene we can observe exchange broadening and eventual coalescence of some of the proton resonances due to the *cis* and *trans* isomers for **1** indicating rapid interconversion on the NMR timescale. The mechanism for this interconversion is presently under investigation. The fact that compound **1** is diamagnetic suggests that we should consider the Ic ligand as an L_4 donor in this case coordinated to two monovalent CoCp moieties.[5]

The cyclic voltammetric response of a tetrahydrofuran solution of **1** and tetrabutylammonium hexafluorophosphate (0.1 M) gave four quasi reversible waves at −0.12, −0.75, −1.18 and −1.49 V *vs* $F_c–F_c{}^+$.[6] $[Fv(CoCp^*)_2]$[7] (Fv = fulvalene) is reported to give a cyclic voltammogram containing four waves, attributable to the mono- and di-anionic, neutral, mono- and di-cationic species. The fact that we observe stepwise redox events indicates significant intramolecular interaction between the cobalt centres. Astruc and coworkers have demonstrated that $[Fv(CoCp^*)_2]$ may be conveniently oxidised to the dication with HPF_6.[7] We therefore employed a similar approach to the synthesis of the dication of **1**.

Reaction of **1** with 2 equiv. of ammonium tetrafluoroborate at room temperature, after work up, afforded a yellow air stable crystalline powder characterised as $[(CoCp)_2(Ic'H_2)][BF_4]_2$ **2**. The ^1H and ^{13}C NMR spectra of **2** showed that the Ic′ ligand has been protonated at the 4,8 carbon positions (Scheme 1) giving a mixture of *cis* and *trans* isomers. However, in this case the ^1H NMR does allow us to assign the resonances due to the *cis* isomer, since the two protons on each of the 4,8 carbon atoms are now chemically inequivalent. We observe no evidence for any interconversion on the ^1H NMR timescale between the *cis* and *trans* isomers in the temperature range 223–322 K. When the reaction is carried out at room temperature the *cis* : *trans* ratio of **2** is 8 : 1, which reduces to 5 : 1 when the reaction temperature is lowered to 233 K. The reaction of **1** with ND_4BF_4 affords $[^2H_2]$**2**, the ^1H NMR spectrum of the *cis* isomer indicates exclusive deuteration at one site. Geiger has showed that the protonation of $[CoCp_2]^-$ proceeds exclusively at the *exo* position, implying that it does not occur *via* the metal centre.[8]

Suitable crystals for single crystal X-ray diffraction analysis of *trans*-**2** were grown from a concentrated mixture of dichloromethane and acetonitrile. The molecular structure of *trans*-**2** (Fig. 1)‡ contains a crystallographic inversion centre at the middle of the six membered ring of the $Ic'H_2$ ligand and cocrystallised with one molecule of each of acetonitrile, dichloromethane and tetrafluoroborate in the asymmetric unit. The Cp moiety is only slightly staggered with respect to the



Scheme 1. *Reagents and conditions*: i, $[CoCp(C_2H_4)_2]$ (2.2 mol. equiv.), THF, 24 h, room temp.; ii, NH_4BF_4 (2 mol. equiv.), THF, room temp.; iii, Ag(OTf) (2 mol. equiv.), THF, room temp.

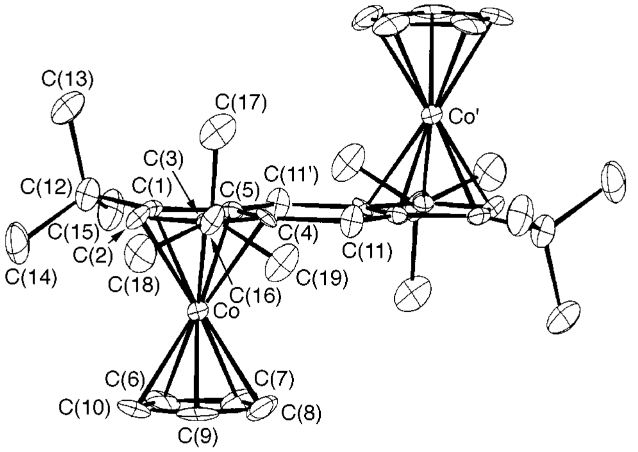


Fig. 1. Molecular structure of the *trans* isomer of **2** (CH_2Cl_2, MeCN, BF_4^- and H atoms have been omitted for clarity). Selected bond lengths (Å): Co–Ic′(centroid) 1.647(1), Co–Cp(centroid) 1.633(1), Co–C(1) 2.055(7), Co–C(2) 2.018(8), Co–C(3) 2.035(8), Co–C(4) 2.028(7), Co–C(5) 2.035(7), Co–C(6) 2.034(9), Co–C(7) 2.028(8), Co–C(8) 2.022(8), Co–C(9) 2.025(8), Co–C(10) 2.022(9).

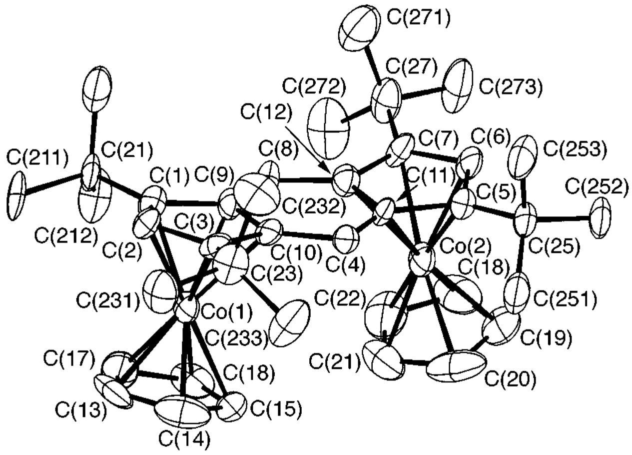


Fig. 2. Molecular structure of the *cis*-isomer of **3** (CH_2Cl_2, $CF_3SO_3^-$ and H atoms have been omitted for clarity). Selected bond lengths (Å): Co(2)–Cp(centroid) 1.66(1), Co(1)–C(1) 2.05(1), Co(1)–C(2) 2.03(1), Co(1)–C(3) 2.04(1), Co(1)–C(9) 2.15(1), Co(1)–C(10) 2.11(1), Co(1)–C(13) 2.04(1), Co(2)–C(5) 2.05(1), Co(2)–C(6) 2.01(1), Co(2)–C(7) 2.06(1), Co(2)–C(11) 2.18(1), Co(2)–C(12) 2.14(1), C(4)–C(10) 2.03(1).

IcH_2 ligand being out of phase by 7.8°, compared to cobaltocene and cobaltocenium cation which are staggered by 30°.[9] Thus **2** can be considered as two doubly bridged cobaltocenium cations. In contrast to the reported dimethyl silyl doubly bridged cyclopentadienyl complexes which are bent, the $Ic'H_2$ fragment is planar.[10] The cyclic voltammetric response of a tetrahydrofuran solution of **2** and tetrabutylammonium hexafluorophosphate (0.1 M) gave an irreversible oxidation wave at 0.65 V and an irreversible reduction wave at −1.31 V *vs* F_c–Fc^+.

Typically, electrophilic addition of a proton to cobaltocene occurs with a one electron reduction to afford the monovalent complex $[Co(\eta^5\text{-}Cp)(\eta^4\text{-}C_5H_6)]$.[11] However the synthesis of **2** proceeds with a two electron oxidation at the cobalt atom. This is possible as the Ic′ undergoes electrophilic addition at the 4,8 carbon positions, which appear to be more reactive than the carbon atoms in the five membered rings.

The successful synthesis of the dication of **1** was achieved by employing aprotic oxidising reagents. Reaction of **1** with 2 equiv. of silver triflate afforded dark red crystalline $[(CoCp)_2\text{-}Ic']^{2+}[OTf]_2$ **3**. We presume that compound exists as both *cis* and *trans* isomers. Compound **3** is paramagnetic, solutions in CD_3CN give a magnetic moment of 2.1 μ_B per cobalt atom. The molecular structure of *cis*-**3** (Fig. 2) shows the Ic′ ligand is slightly distorted to a convex structure with respect to the two CoCp fragments, thus reducing their steric interaction. The Co–C(Cp) bond lengths are all essentially equivalent [2.02(1)–2.05(1) Å], however, the Co–Ic′ bond lengths vary slightly, shifting the cobalt atoms towards the outside carbon atoms [*cf.* Co(1)–C(1–3) 2.03–2.05 Å, Co(1)–C(9,10) 2.11–2.15 Å]. This is similar to that found in *trans*-$[(CoCp^*)_2(s\text{-indacene})]$. The Cp(centroid)–Co–Ic′ bond angle of 175° further reducing the steric interaction between the CoCp moieties.

The *cis* isomer of **1** displays greater thermodynamic stability in solution over the *trans* isomer as indicated by the NMR experiments. The prevalence of the *cis* isomer seems somewhat strange from the distortion observed of the Ic ligand in the molecular structure of **3** and that only *trans* isomers are observed in unsubstituted *s*-indacene bimetallic transition metal complexes. We are presently undertaking density functional theory calculations on **1** in an effort to explain this unusual phenomenon.

We thank the EPSRC for financial support and a studentship (M. J. D.).

Notes and References

† *Characterisation data*: **1**: Anal. Calc. for $C_{38}H_{50}Co_2$: C, 73.06; H, 8.07. Found C, 72.19; H, 8.21%. ^1H NMR (293 K, C_6D_6) *cis*-**1**, δ 5.14 (s, 2H, CH), 4.95 (s, 2H, CH), 4.47 (s, 10H, Cp), 1.33 (s, 36H, Bu^t). *trans*-**2**, δ 6.36 (s, 2H, CH), 5.18 (s, 2H, CH), 4.47 (s, 10H, Cp), 1.33 (s, 36H, Bu^t). For **2**: Anal. Calc. for $C_{38}H_{40}B_2F_8Co_2$: C, 57.03; H, 6.55. Found C, 57.45; H, 6.44%. ^1H NMR (293 K, CD_3CN) *cis*-**2**, δ 5.81 (s, 10H, Cp), 5.49 (s, 2H, CH), 4.11 (d, *J* 20.5 Hz, 2H), 3.65 (d, *J* 20.5 Hz, 2H), 1.41 (s, 36H, Bu^t). *trans*-**2**, δ 5.55 (s, 10H, Cp), 5.34 (s, 2H, CH), 3.95 (s, 2H, CH), 1.47 (s, 36H, Bu^t). For **3**: Anal. Calc. for $C_{40}H_{50}O_6F_6S_2Co_2$: C, 52.06; H, 5.46%. Found: C, 52.29; H, 5.42.

‡ *X-Ray crystal structure analysis*: **2** monoclinic, space group $P2_1/c$, a = 10.564(7), b = 12.721(9), c = 18.019(6) Å, β = 90.578(4)°, U = 2421.35(5) Å^3, Z = 4, D_c = 1.44 g cm^{-3}, μ = 0.97 mm^{-1}, crystal size 0.3 × 0.25 × 0.05 mm, T = 150 K, 90 frames, 31 054 total (5256 independent) reflections, R = 0.08 and R_w = 0.095 for 4749 reflections with $I > 5\sigma(I)$; **3**: monoclinic, space group $P2_1/n$, a = 11.166(1), b = 14.461(1), c = 27.361(2) Å, β = 86.167(4)°, U = 4408.14(5) Å^3, Z = 4, D_c = 1.52 g cm^{-3}, μ = 1.03 mm^{-1}, crystal size 0.3 × 0.2 × 0.05 mm, T = 150 K, 90 frames, 30 179 total (5533 independent) reflections, R = 0.068 and R_w = 0.073 for 3257 reflections with $I > 5\sigma(I)$. CCDC 182/1013.

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Received in Cambridge, UK, 13th August 1998; 8/06391E