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Electron transfer activity of a cobalt crown carbene complex

Stuart R. Park, Neil J. Findlay, Jean Garnier, Shengze Zhou, Mark D. Spicer *, John A. Murphy *

WestCHEM, Department of Pure and Applied Chemistry, Thomas Graham Building, University of Strathclyde, 295 Cathedral Street, Glasgow G1 1XL, UK

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ABSTRACT

The novel cobalt(II) crown carbene complex **12(II)** has been prepared and characterised by X-ray crystallography. This complex is reduced in a one-electron process to a cobalt(I) complex that acts as a powerful single electron donor, reducing aryl halides, including aryl chlorides and demonstrating the strong electron-enriching effect on cobalt of the crown carbene ligand. The metal ion is tightly held in a tetrahedral conformation by its enveloping crown ligand—this prevents what would otherwise be expected to be an easy oxidation to cobalt(III) under standard electrochemical conditions. Complex **12** is shown to be an effective catalyst in mediated electrochemical reductions of aryl iodides at room temperature and aryl bromides at 90 °C. The electrochemically produced catalyst [from 10 mol % of added Co(II) complex] also triggers reduction of aryl chlorides, although this seems at the limit of its reactivity. However, when the cobalt(II) complex is reduced by sodium amalgam, this affords stoichiometric quantities of the active cobalt reducing agent, which affords reduction of aryl iodides and bromides as above, but also reduces aryl chlorides at elevated temperatures.

1. Introduction

The development of *N*-heterocyclic carbenes (NHCs) as ligands and reagents has expanded enormously during the last 20 years, since their initial isolation by Arduengo in 1991.[1] Since then, NHCs have seen widespread application as reagents in the benzoin condensation,[2] the Stetter reaction[3] and transesterification,[4] as well as in functional group transfer[5] and the *umpolung* behaviour of Michael acceptors.[6] However, NHCs are best known as ligands for metals, for example, providing powerful catalysts for coupling reactions.[7] This is attributed to the ability of the NHC to enhance both the oxidative addition step, due to its strong electron donor properties, and also, where steric bulk is associated with these systems, the reductive elimination step. The importance of carbenes as ligands is exemplified by their role in the development of olefin metathesis, celebrated in the award of the 2005 Nobel Prize in chemistry.[8] NHC ligands are strong σ-donors relative to phosphine ligands, and use of carbenes avoids the severe P–C bond degradation of phosphine ligands that is seen at high temperatures.[9]

In redox chemistry, ligands can greatly affect the behaviour of a metal. Flowers and Knettle[10] reported that the addition of a large excess of hexamethylphosphoramide (HMPA) to samarium dibromide enhanced the reduction potential notably from −2.07 V to −2.63 V (both vs Ag/AgNO$_3$). In view of the considerable σ-donating power of NHCs, our interest focussed on developing highly reducing, low-valent metal complexes for electron transfer chemistry.

In 2007, we reported the synthesis of a series of homoleptic crown *N*-heterocyclic carbene complexes of palladium(II), copper(I) and silver(I)[11] featuring the crown carbene ligand **2** (Fig. 1). It was found by X-ray crystallography that the copper and silver complexes contained *iso*-structural cations, in which two metal ions were bound by the macrocycle, in contrast to the monometallic square-planar complex of palladium. This paper now reports the preparation and properties of the first monometallic redox-active member of this family, containing a single cobalt ion bound within the ligand.

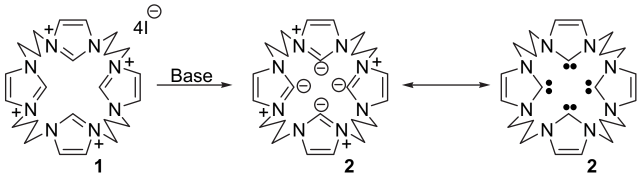

Figure 1. Macrocyclic ligand precursor **1** and ligand **2**.

The prominent role of cobalt in electron transfer chemistry partly derives from its biological importance in coenzyme B$_{12}$. A recent review documents the advances in our understanding of the chemistry of this cofactor and related compounds.[12]

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* Corresponding authors. Tel.: +44 141 548 2800 (M.D.S), +44 141 548 2389 (J.A.M).

E-mail addresses: mark.spicer@strath.ac.uk (M.D. Spicer), john.murphy@strath.ac.uk (J.A. Murphy).

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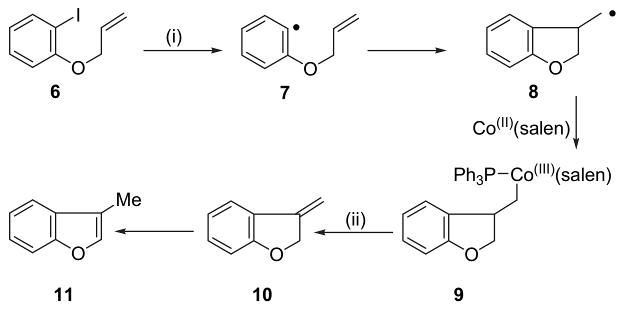
Whereas cobalt is routinely found as Co(II) and Co(III) salts, the interesting complexes, as reducing agents, are Co(I) complexes. They can be accessed by reducing complexes in the higher oxidation states, and their reactions have been well studied both in solution and using solid-supported chemistry. Using a modified cobalt corrinoid derived from coenzyme B_{12} linked through a polylysine chain to an oxidised carbon electrode, Rusling et al. saw a reversible electron transfer potential for the Co(II)/Co(I) redox couple of −0.7 V versus SCE,[13] and used the Co(I) complex in the catalytic reduction of aliphatic vicinal dihalides.

However, cobalt(I) complexes with ligands other than corrins have featured most prominently in synthetic studies.[14] The reducing power of the Co(I) complex is dependent upon the ligand[15] and when reacted with challenging substrates, such as aryl halides, the choice of ligand has proved important. Pattenden et al. showed that Co(I) cobaloximes derived from the Co(III) analogue **3** cannot reduce aryl iodides to aryl radicals, whereas the Co(I) complexes derived from the analogous salen **4** and salophen complexes **5** are effective.[16] The salen and salophen ligands are dianionic, whereas the dimethylglyoxime ligands are neutral, and this provides a simple rationalisation of the differences in reduction potential at cobalt. Our crown carbene ligand **2** is also neutral, and so we were keen to prepare and test a cobalt complex to assess the effect of this special ligand system on the reducing power of the metal ion.

The accepted mechanism for the reaction with aryl iodides is shown in Scheme 1. Electron transfer to the aryl iodide **6** leads to formation of a Co(II) salen complex[16] and an aryl radical **7** that undergoes rapid cyclisation in the case shown to afford alkyl radical **8**. The alkyl radical is then trapped by the Co(II) salen to afford the isolable Co(III) salen complex **9**. (When a tertiary alkyl radical is involved, C–Co bond formation may not occur, and instead, abstraction of an H-atom from the radical by the Co(II) complex can result to afford an alkene directly.) Irradiation or other activation leads to cleavage of the weak C–Co bond resulting in **10**, the product of dehydrocobaltation, which easily tautomerises to benzofuran **11**.



Scheme 1. Reagents and conditions: (i), BrCo(III)(salen)PPh_3, 1% Na/Hg, THF, dark; (ii), hν, N_2.

An extensive range of synthetic reactions, based on activation of aryl halides,[16,17,21] acyl halides[18–20] and alkyl halides[21] has been developed by the Pattenden team. Cobalt(I) salen (derived from **4**, Fig. 2) has also been used as an electrochemical catalyst. Peters and Alleman have reduced a variety of halogenated compounds by the electrochemical generation of cobalt(I) salen using carbon electrodes.[22] Peters et al. also showed that catalytic, cobalt-mediated reduction of environmentally important molecules could be achieved, as seen in the dehalogenation of CFC-113[23] and CFC-113a,[24] and the pesticides DDT[25] and hexachlorobenzene.[26] The hexachlorobenzene example provides a guide to the limit of reactivity of cobalt(I) salen, which can reduce this compound to pentachlorobenzene and tetrachlorobenzenes, but shows no catalytic activity towards tetrachlorobenzene or less chlorinated benzenes.

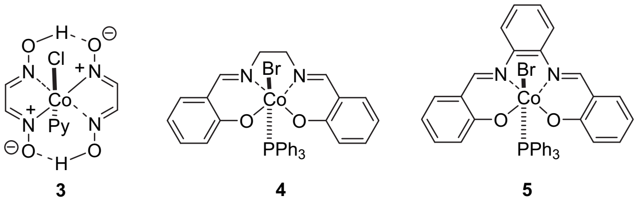
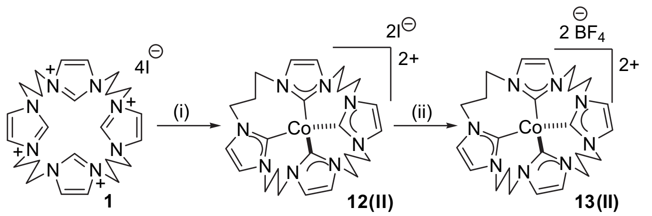


Figure 2. Cobalt(III) complexes: cobaloxime (**3**), salen (**4**), salophen (**5**).

2. Results and discussion

The cobalt(II) complex **12(II)**, with oxidation state indicated in parentheses, was initially prepared by deprotonation of the macrocyclic ligand precursor **1** using sodium hydride in DMF and addition of this solution to anhydrous $CoCl_2$ (Scheme 2). Removal of DMF by distillation and recrystallisation from methanol afforded **12(II)** (22%) as bright blue needles, from which a crystallographic characterisation was possible (Fig. 3). This showed that the four-coordinate cobalt atom was situated in a slightly compressed tetrahedral environment, fully encapsulated by the macrocyclic NHC ligand. The solution phase electronic spectrum and the solid state magnetic moment (4.9 BM) are also consistent with a tetrahedral Co^{2+} ion.



Scheme 2. Initial synthesis of **12(II)** and ion exchange to **13(II)**: (i) **1**, NaH, DMF, 18 h, then added to $CoCl_2$, DMF, 2 h, rt, 22%; (ii) **12(II)**, $AgBF_4$, CH_3CN, rt, 18 h, 78%.

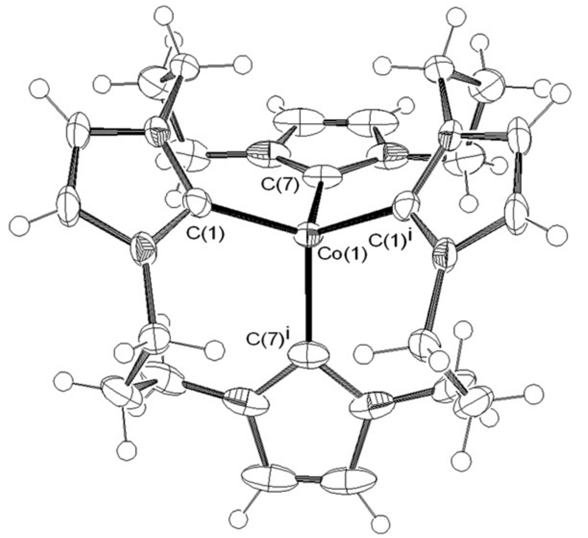


Figure 3. X-ray crystal structure of **12** indicating tetrahedral geometry at the central Co ion. Thermal ellipsoids are drawn at the 50% level. Selected bond distances (Å) and angles (°): Co(1)–C(1)=2.056(4), Co(1)–C(7)=2.057(4); C(1)–Co(1)–$C(1)^i$=113.6(2), C(1)–Co(1)–C(7)=107.99(6), C(1)–Co(1)–$C(7)^i$=107.99(6), $C(1)^i$–Co(1)–C(7)=107.99(6), $C(1)^i$–Co(1)–$C(7)^i$=107.99(6), C(7)–Co(1)–$C(7)^i$=111.3(2).

Since the iodide counterion is electrochemically active, an anion exchange reaction with silver tetrafluoroborate was carried out to yield the corresponding salt, **13(II)**. The redox chemistry of **13** was investigated by cyclic voltammetry, which showed (Fig. 4) a single reversible electron transfer with a potential of $E_{1/2}$=−1.15 V

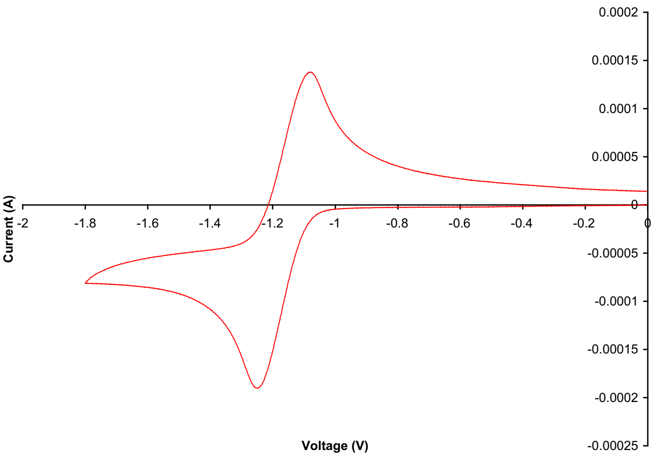


Figure 4. Cyclic voltammogram of **13** as a 0.01 M solution in 0.1 M tetrabutylammonium hexafluorophosphate/DMF, using a Pt counter and a glassy carbon working electrode (diameter 7 mm, area 38.38 mm^2) and a Ag/AgCl/KCl (satd) reference electrode, with sweep rate=50 mV/s.

[vs Ag/AgCl/KCl (satd) (equivalent to -1.19 V vs SCE)]. Calibration with Fc/Fc^+ as a standard indicated that this process is a one-electron transfer and this, coupled with the reversibility, suggests that the product is the tetrahedral Co(I) complex, **13(I)** analogous to **13(II)**.

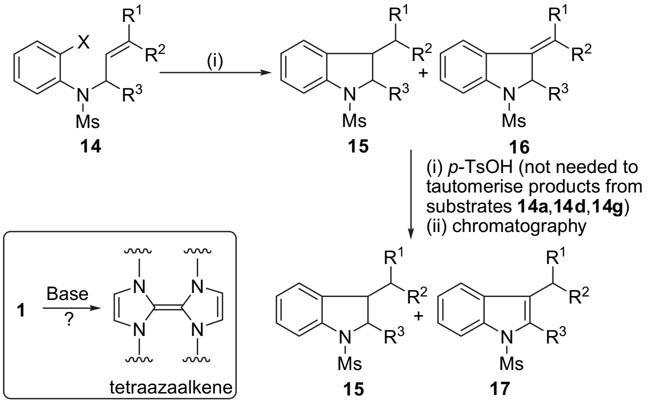
The measured potential reveals a more powerful Co(I) reducing agent than previously observed using neutral ligands, and is comparable with Co(I) complexed by anionic ligands.[15] Intriguingly, no oxidative process corresponding to a Co(II)/Co(III) couple is observed up to $+2$ V. This is unexpected, as the strong electron donor ability of the NHC ligands should favour oxidation of the Co(II). Cobalt(III) complexes highly favour octahedral geometry, and we believe that the ligand conformation is such that no facile ligand dissociation and rearrangement to such a geometry are possible. Oxidation within a tetrahedral geometry is not tenable.

The redox potential of **13(II)** is close to the imidazole-derived electron donor developed by Murphy et al. in 2007,[27] which reduced iodobenzenes; accordingly the cobalt (I) complexes, **12**(**I**) and **13(I)**, should be able to reduce aryl iodides. To this end, a series of aryl halides (**14a**–**i**) were synthesised. In our initial experiments, chemical reduction to the cobalt(I) complex **12(I)** was achieved by reaction of a DMF solution of **12(II)**, prepared in situ, with sodium amalgam and was evidenced by the formation of a deep green solution. This solution was removed from the amalgam by cannula and added to the haloaryl substrates **14**. The products isolated following chromatography were indolines **15** and indoles **17**, with the indoles arising from the tautomerism of indolenines **16** cf. Scheme 1. [A blank reaction involving reduction of $CoCl_2$ with sodium amalgam and then heating with the substrate **14a** gave no reaction.]

The reactions of aryl iodides shown in this table afforded more **15** and less **17** than expected, suggesting that efficient interception of alkyl radicals by Co(II) was not occurring (cf. Scheme 1). This might be accounted for by the steric hindrance to reaction at cobalt posed by complex **2**, and by ready abstraction of hydrogen atoms by these radicals either from DMF or from benzylic positions on the macrocyclic ligand.

However, we also considered another possibility. Since the preparation of **12(II)** mentioned above had led to a low 22% yield of isolated product, the in situ process used here on substrates **14** had deliberately used excess quantities of **1** and $CoCl_2$ in order to achieve sufficient amounts of **12(II)**. Incomplete formation of **12(II)** could have been accompanied by formation of tetraazaalkenes from **1**, which can be powerful electron donors that can reduce iodoarenes[27,28] (see scheme accompanying Table 1). To avoid this possible complication, a new and high yielding preparation of **12(II)** was undertaken so that pure crystalline **12(II)** could be used in the reduction of haloarenes.

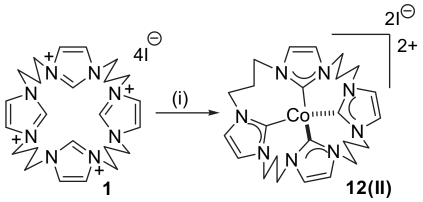
Table 1
Reaction of aryl halides **14** using complex **12** generated in situ



14	X	R^1	R^2	R^3	15	17
a	I	Me	H	H	81%	—
b	I	Me	Me	H	56%	7%
c	I	Me	$(CH_2)_3$		80%	—
d	Br	Me	H	H	64%	—
e	Br	Me	Me	H	28%	56%
f	Br	H	$(CH_2)_3$		76%	9%
g	Cl	Me	H	H	73%	Trace
h	Cl	Me	Me	H	24%	45%
i	Cl	H	$(CH_2)_3$		73%	6%

Reaction conditions: (i) **12** (2.5 equiv), NaH, 12 h, then added to $CoCl_2$, DMF, Na/Hg, 6 h, then added to **14**, 18 h, 90 °C.

An improved synthesis of the cobalt(II) complex **12** was achieved by refluxing a methanolic solution of sodium hydroxide, **1** and cobalt dichloride hexahydrate for 18 h (Scheme 3). Concentration of the resulting blue solution gave a crude residue that was recrystallised by slow cooling of a saturated aqueous solution to afford the same bright blue needles (60%) as reported above.



1 **12(II)**

Scheme 3. New improved method for synthesis of **12(II)**; (a) **1**, $CoCl_2 \cdot 6H_2O$, NaOH, CH_3OH, reflux, 18 h, 60%.

In light of the results in Table 1, we wondered whether it would be possible to afford indolines **15** as the sole products of the reaction with a pure Co(I) complex. This would mean that intermediate radicals should not react with Co(II) and should instead abstract an H-atom. To enhance the possibility of such a reductive termination, 1,4-cyclohexadiene (CHD), a useful hydrogen atom donor to radicals, was added to the reactions of substrates that had afforded indoles in Table 1. Pure complex **12** was reduced using sodium amalgam to cobalt(I) and then added as a solution to each substrate **14**. The results are shown in Table 2.

It is seen that complex **12** reduces aryl iodides and bromides, resulting in high yields of the cyclised products. Surprisingly, even aryl chlorides are also reduced, giving moderate yields of the cyclised products. Previous examples of cobalt(I) complexes donating an electron to aryl chlorides are rare (see above[26]), and require assistance by appropriately placed activating groups.[29]

Table 2
Reduction and cyclisation of aryl halides **14** using pure **12**

14	X	R^1	R^2	R^3	CHD	**15**
a	I	Me	H	H	—	81%
b	I	Me	Me	H	5 equiv	70%
c	I	H	$(CH_2)_3$		5 equiv	77%
d	Br	Me	H	H	—	74%
e	Br	Me	Me	H	5 equiv	89%
f	Br	H	$(CH_2)_3$		5 equiv	80%
g	Cl	Me	H	H	—	23%[a]
h	Cl	Me	Me	H	5 equiv	37%[a]
i	Cl	H	$(CH_2)_3$		5 equiv	55%[a]

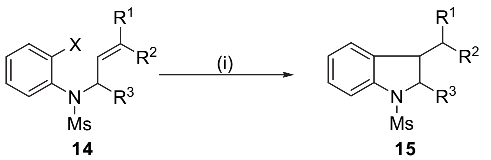
Reaction conditions: (a) **12(II)** (1.2 equiv), Na/Hg, DMF, 4 h, rt, then added to **14** (with or without 1,4-cyclohexadiene (CHD) as shown above (5.0 equiv)), 18 h, 90 °C.

[a] The remainder was starting material.

Due to the chemically reversible nature of the Co(II) to Co(I) redox couple (Fig. 4), it was proposed that **12** could be converted to its cobalt(I) active species by electrochemical reduction and used catalytically with continuous application of a negative potential. Using just 10 mol % of complex **12** and an applied potential of −1.5 V, a series of aryl iodides (**14a**–**c**) were converted to their corresponding cyclised products in excellent yields (Table 3). Addition of 1,4-cyclohexadiene to the reactions of **14b** avoided any unwanted by-products and, surprisingly, also seemed to improve the yield of products from **14a**. Attempts to reduce aryl bromide **14e** at room temperature using the catalytic method were unsuccessful. This was not too surprising, as reduction of the analogous iodides had proceeded smoothly under non-electrochemical conditions at room temperature but reduction of aryl bromides had required heating when using greater than stoichiometric amounts of **12** (Table 2, substrates **14d**, **14e** and **14f**). However, when an electrochemical experiment was conducted on bromide **14d** at 90 °C, but for 24 h, 70% of **15a** was formed. A similar experiment with chloride **14g** led to traces of **15a**, the product of reductive cyclisation, together with unreacted substrate and some *N*-(2-chlorophenyl)methanesulfonamide. This indicates that the reactivity observed in the electrochemical and sodium amalgam activations is the same, but mass action dictates that the sodium amalgam activation is more efficient at reducing the difficult chloride substrates. The effective concentration of cobalt(I) complex in the sodium amalgam experiments is stoichiometric, while with the catalytic experiments, only a small fraction of the 10 mol % of the cobalt complex is present as Co(I) at any time.

In conclusion, we have revealed the first tetrahedral complex of crown carbene (**2**) incorporating a cobalt(II) ion and, following reductive activation, this has been applied to the reduction of aryl halides, including challenging aryl chlorides. Thus, the unique ligand in **12** has significant impact on the reducing power of its Co(I) form—the effect of the crown carbene ligand system in inhibiting oxidation to Co(III) was more surprising, but reinforces its special nature as a ligand. The reversible nature of the Co(II)/Co(I) redox couple has allowed a catalytic methodology to be developed with electrochemical cycling, which has proven successful for the reduction of aryl iodides at room temperature and aryl bromides at 90 °C.

Table 3
Reduction of aryl halides **14** using **12**—catalytic, electrochemical method



14	X	R^1	R^2	R^3	CHD	**15**
a	I	Me	H	H	—	43%
a	I	Me	H	H	10 equiv	95%
b	I	Me	Me	H	10 equiv	77%[a]
c	I	H	$(CH_2)_3$		10 equiv	90%
d[b]	Br	Me	H	H	—	77%
e	Br	Me	Me	H	10 equiv	0%[a]
g[b]	Cl	Me	H	H	—	Trace[c]

Reaction conditions: (a) **12** (0.1 equiv), TBAHFP/DMF (0.05 M), rt, 18 h, −1.5 V.

[a] Remainder isolated as starting material.

[b] 24 h, 90 °C.

[c] As seen in NMR and confirmed by GC–MS.

3. Experimental section

3.1. General experimental

^1H NMR spectra were recorded at 400.13 MHz on a Bruker DPX400 or AV400 spectrometer, or at 500.13 MHz on a Bruker DRX500 spectrometer. ^{13}C NMR spectra were recorded at 100.6 MHz or 125.6 MHz on the same spectrometers using a broadband decoupled mode. JMOD spectra were used to determine the multiplicities of the carbon resonances. Experiments were carried out using deuterochloroform ($CDCl_3$) unless otherwise stated and chemical shifts are reported in parts per million (ppm). Coupling constants *J* are reported in hertz (Hz). The following abbreviations are used for the multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad.

Infrared spectra were recorded on a Perkin Elmer 'spectrum One FTIR' spectrometer. Melting points were recorded using a Gallenkamp 2C 7065 melting point apparatus.

Column chromatography was performed using Prolabo 35–75 μm particle sized silica gel 60 (200–400 mesh). Reactions were followed using thin layer chromatography (TLC) carried out on Merck silica gel 60 F_{254} precoated aluminium plates. Visualisation was achieved under UVP mineralight UVG-11 lamp or by developing plates with methanolic vanillin or potassium permanganate.

All reagents were obtained from commercial suppliers. Tetrahydrofuran, dichloromethane, hexane, diethyl ether and toluene were dried and deoxygenated with a Pure-Solv 400 solvent purification system (Innovative Technology Inc., USA). The sodium amalgam was prepared freshly for each reaction, with sodium and mercury obtained from commercial suppliers. Dimethylformamide was obtained from commercial suppliers as anhydrous (99.8%) and used directly.

Cyclic voltammetry was performed in a nitrogen filled glovebox. A glassy carbon working electrode with a diameter of 7 mm was used (surface area of 38.38 mm^2). Prior to use, the electrode was cleaned using 1 μm alumina polish and distilled water on a Bueller polishing cloth and dried under compressed air. The counter electrode consisted of a fine Pt wire, which was cleaned thoroughly before use by heating in a flame for 5 min and allowing to cool. Potentials are quoted with respect to the Ag/AgCl/KCl (satd) reference electrode, in contact with 0.1 M tetrabutylammonium hexafluorophosphate in DMF. This electrode has a potential of 0.199 V versus the standard hydrogen electrode (SHE) at 25 °C. The electrolyte used was 0.1 M tetrabutylammonium hexafluorophosphate in DMF and the concentration of all solutions was 0.01 M. Ferrocene of equal concentration was used as a reference. Under these conditions, ferrocene has a reversible peak at +0.55 V. Cyclic voltammograms were obtained using an Eco Chemie B. V. Autolab type III potentiostat/galvenstat system, with General Purpose Electrochemical System (GPES) software for data interpretation. Electrochemically mediated cyclisations were performed using the same apparatus, with the exception of the working electrode. A Pt gauze working electrode was used, which was cleaned thoroughly prior to use by heating in a flame for 5 min and allowing to cool.

3.1.1. Cobalt(II) (1,5,8,12,15,19,22,26-octaazapentacyclo[24.2.1.15,8.112,15.119,22] dotriacinta-6,13,20,27-tetraene-29,30,31,32-tetraylidene)-iodide ***12(II)****—method A.* 1,1′,1″,1‴:3,3′,3″,3‴-Tetrakistrimethylene tetraimidazolium tetraiodide (**1**) (0.999 g, 1.059 mmol)[27] and sodium hydride (2.541 g, 0.106 mol) were washed with hexane (20 ml) and dried under an argon stream. DMF (50 ml) was added and the reaction mixture stirred for 18 h. Cobalt(II) chloride hexahydrate (252 mg, 1.059 mmol) was dried by heating to 90 °C while under vacuum for 1 h. The solution of NHC ligand was added to $CoCl_2 \cdot 6H_2O$ via cannula and stirred at room temperature for 2 h, then filtered and the DMF removed by distillation. The residue was dissolved in hot methanol and filtered, then the solvent reduced in volume and the resultant blue precipitate collected. Recrystallisation by slow cooling of a saturated methanol solution afforded **12** as blue needles (174 mg, 22%); mp (>300 °C, dec); [found: $[M-I]^+$ (ESI) 618.1121, $C_{24}H_{32}N_8I_2Co$ requires $[M-I]^+$ 618.1121]; ν_{max} (KBr disc/cm^{-1}) 3078, 2954, 2917, 1561, 1407, 1235, 755; *m*/*z* (ESI) 618 ($[M-I]^+$, 45%), 246 (100). μ_{eff}(293 K)=4.9 B.M. electronic spectrum (1×10^{-3} M in MeOH, λ_{max} nm(ϵ dm^3 mol^{-1} cm^{-1})): 323 (3481), 590sh, 624 (1933).

3.1.2. Method B. Cobalt(II) chloride hexahydrate (626 mg, 2.68 mmol) and 1,1′,1″,1‴:3,3′,3″,3‴-tetrakistrimethylene tetraimidazolium tetraiodide (**1**) (2.504 g, 2.65 mmol) were dissolved in methanol (200 ml) and sodium hydroxide (1.059 g, 26.5 mmol) added. The solution was heated to reflux for 18 h. The reaction mixture was cooled and the solvent removed in vacuo. The crude mixture was recrystallised from water to afford the title compound **12(II)** as blue needles (1.185 g, 60%); mp (>300 °C, dec); [found: $[M-I]^+$ (ESI) 618.1121, $C_{24}H_{32}N_8I_2Co$ requires $[M-I]^+$ 618.1121]; ν_{max} (KBr disc/cm^{-1}) 3078, 2954, 2917, 1561, 1407, 1235, 755; *m*/*z* (ESI) 618 ($[M-I]^+$, 45%), 246 (100).

3.2. Example of reduction using cobalt complex 2—Table 2, entry 14a, 3-ethyl-1-(methylsulfonyl)indoline (15a)

Cobalt complex **12(II)** (0.258 g, 3.47×10^{-4} mol) was dissolved in DMF (25 ml) and added to a freshly prepared sodium amalgam (1%, 10 g). The reaction mixture was stirred for 4 h. The solution of cobalt(I) complex was added to *N*-(but-2-enyl)-*N*-(2-iodophenyl)-methanesulfonamide (**8a**) (0.108 g, 3.07×10^{-4} mol) and 1,4-cyclohexadiene (0.137 g, 1.71×10^{-3} mol) after centrifuging. This mixture was then stirred at 65 °C for 18 h. The reaction mixture was then added to water (50 ml) and diethyl ether (50 ml) and then extracted with diethyl ether (3×50 ml). The organic layer was then washed with water (100 ml) and dried over $MgSO_4$. The solvent was removed under reduced pressure. The crude product was purified by column chromatography (10% ethyl acetate/petroleum ether) to give the title product (**15a**)[30] as a colourless oil (0.056 g, 81%). [Found: $[MNH_4]^+$ (ESI) 243.1169, $C_{11}H_{15}NO_2S$ requires $[MNH_4]^+$ 243.3503.] ν_{max} (KBr disc)/cm^{-1} 3016, 2963, 2932, 2876, 1601, 1480, 1462; δ_H (400 MHz, $CDCl_3$) 1.08 (3H, t, *J* 7, CH_3), 1.61–1.72 (1H, m, H–CH), 1.89–1.99 (1H, m, H–CH), 2.98 (3H, s, CH_3), 3.35–3.42 (1H, m, H–CH), 3.69–3.74 (1H, m, H–CH), 4.13–4.17 (1H, m, CH), 7.10–7.14 (1H, m, ArH), 7.27–7.31 (2H, m, ArH), 7.46–7.49 (1H, m, ArH); δ_C (100 MHz, $CDCl_3$) 11.8 (CH_3), 28.1 (CH_2), 34.9 (CH), 42.1 (CH_3), 56.5 (CH_2), 114.0 (CH), 124.1 (CH), 125.2 (CH), 128.8 (CH), 135.5 (C), 142.3 (C); *m*/*z* (EI) 225 (M^+, 45%), 196 (50), 146 (78), 130 (79), 118 (100), 91 (35).

3.3. Example of catalytic reactivity of 2—Table 3, entry 14c, 9-methanesulfonyl-2,3,4,4a,9,9a-hexahydro-1*H*-carbazole (15c)

Cobalt complex **12(II)** (0.018 g, 2.43×10^{-5} mol), *N*-cyclohex-2-enyl-*N*-(2-iodophenyl)methanesulfonamide (**14c**) (0.103 g, 2.77×10^{-4} mol) and 1,4-cyclohexadiene (0.213 g, 2.66×10^{-3} mol) were dissolved in DMF (10 ml containing 50 mM tetrabutylammonium hexafluorophosphate—TBAHFP). The solution was put in a two-compartment cell with the second compartment being filled with a 50 mM solution of TBAHFP in DMF (10 ml). The mixture was stirred at −1.5 V for 18 h. The solution was then added to water (50 ml) and diethyl ether (50 ml) and then extracted with diethyl ether (3×50 ml). The organic layer was washed with brine (50 ml) and dried over sodium sulfate. The solvent was removed under reduced pressure. The crude product was purified by flash chromatography (10% ethyl acetate/petroleum ether) to give the title compound (**15c**) as a colourless oil[31,32] (0.062 g, 90%); ν_{max} (neat)/cm^{-1} 2933, 2859, 1602, 1473, 1459, 1345, 1159; δ_H (400 MHz $CDCl_3$) 1.29–1.37 (2H, m, CH_2), 1.52–1.73 (3H, m, 3H–CH), 1.90–1.93 (1H, m, H–CH), 2.13–2.17 (1H, m, H–CH), 2.26–2.30 (1H, m, H–CH), 3.02 (3H, s, CH_3), 3.61 (1H, m, CH), 4.44–4.50 (1H, m, CH), 7.15–7.19 (1H, m, ArH), 7.25–7.31 (2H, m, ArH), 7.45 (1H, d, *J* 7.9, ArH); δ_C (100 MHz, $CDCl_3$) 20.9 (CH_2), 22.2 (CH_2), 24.7 (CH_2), 28.6 (CH_2), 38.6 (CH), 40.5 (CH), 64.1 (CH_3), 115.6 (CH), 123.6 (CH), 124.2 (CH), 128.0 (CH), 134.8 (C), 141.5 (C); *m*/*z* (ESI) 252 (MH^+, 100%), 250 (45%), 186 (15%).

3.3.1. 3-Isopropyl-1-methanesulfonyl-2,3-dihydro-1H-indole ***15b****.* [Found: $[MNH_4]^+$ (ES^+) 257.1320, $C_{12}H_{17}NO_2S$ requires $[MNH_4]^+$ 257.1318.] ν_{max} (neat)/cm^{-1} 2961, 2932, 2874, 1481, 1459, 1348, 1160; δ_H (400 MHz, $CDCl_3$) 0.86 (3H, d, *J* 6.8, CH_3), 1.01 (3H, d, *J* 6.9, CH_3), 2.04–2.12 (1H, m, CH), 2.87 (3H, s, CH_3) 3.31–3.36 (1H, m, CH), 3.80–3.84 (1H, m, *H*–CH), 3.89–3.94 (1H, m, *H*–CH), 7.02–7.06 (1H, m, ArH), 7.19–7.23 (2H, m, ArH), 7.40 (1H, d, *J* 7.9, ArH); δ_C (100 MHz, $CDCl_3$) 17.9 (CH_3), 20.3 (CH_3), 31.7 (CH), 34.6 (CH), 46.2 (CH_3), 52.7 (CH_2), 113.3 (CH), 123.5 (CH), 125.6 (CH), 128.5 (CH), 133.8 (C), 142.5 (C); *m*/*z* (CI^+) 257 (MNH_4^+, 100%), 239 (5%).

3.3.2. 3-Isopropyl-1-methanesulfonyl-1H-indole ***17b****.* [Found: $[M]^+$ (ES^+) 237.0819, $C_{12}H_{15}NO_2S$ requires $[M]^+$ 237.0818.] ν_{max} (neat)/cm^{-1} 3054, 2965, 2932, 2873, 1450, 1362, 1265, 1168; δ_H (400 MHz, $CDCl_3$) 1.37 (6H, d, *J* 6.8, 2×CH_3), 3.05 (3H, s, CH_3), 3.12–3.19 (1H, m, CH), 7.19 (1H, s, ArH), 7.30–7.39 (2H, m, ArH), 7.64 (1H, d, *J* 7.2, ArH), 7.91 (1H, d, *J* 8.0, ArH); δ_C (100 MHz, $CDCl_3$) 22.8 (CH_3), 25.6 (CH), 40.46 (CH_3), 113.5 (CH), 120.4 (CH), 121.1 (CH), 123.3 (CH), 125.0 (CH), 130.3 (C), 130.7 (C), 135.9 (C); *m*/*z* (EI^+) 237 (M^+, 45%), 222 (100%), 158 (50%).

3.3.3. X-ray crystallography. Crystals suitable for X-ray diffraction were obtained by slow cooling of a methanolic solution of **12**. Data were measured on a Nonius kappa CCD diffractometer equipped graphite monochromated with Mo Kα radiation. The structure was solved by direct methods using SHELXS-86[33] in the WinGX suite of programs.[34] $C_{24}H_{32}Co_1I_2N_8 \cdot 0.5CH_3OH$, M_r=759.32, deep blue needle, 0.40×0.20×0.15 mm, a=6.7987(1), b=11.0938(3), c=19.2961(5) Å, V=1455.38(6) Å^3, orthorhombic, *Pnmm*, Z=2, ρ_{calcd}=1.733 g cm^{-3}, μ=2.741 mm^{-1}, Mo Kα radiation (λ=0.71069 Å), T=123(2) K, $2\theta_{max}$=27.48°, 9778 reflections measured, 1790 independent reflections (R_{int}=0.0292), of which 1551 had $I>2\sigma(I)$. R(all)=0.0323, wR(all)=0.0642, gof=0.986, residual electron density in the range 1.720 to −0.506 e Å^{-3}. Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 741335. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44 01223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

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Supplementary data

Spectroscopic data for the products together with detailed experimental protocols for preparation of substrates **14** and reactions of Table 1 are provided. Supplementary data associated with this article can be found in online version, at doi:10.1016/j.tet.2009.10.090.

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