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The new C–C bond formation in the reaction of *o*-amidophenolate indium(III) complex with alkyl iodides†

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The reaction of bis(4,6-di-*tert*-butyl-*N*-(2,6-di-iso-propylphenyl)-*o*-amidophenolato)indium(III) anion with alkyl iodides is reported. This process includes oxidative addition of two RI (R = Me, Et) molecules to the non-transition metal complex and results in an alkyl transfer to ring carbon atoms with the formation of two new C–C bonds. The interaction proceeds at mild conditions and gives new indium(III) derivatives containing iminocyclohexa-1,4-dienolate type ligands.

Introduction

The search for new highly selective reactions of C–C bond formation is one of the primary goals in organic chemistry. In the present time it is achieved quite effectively by using metal complex catalysis. The noble transition metal (Pd, Rh, Pt, *etc.*) derivatives play a dominant role in catalytic carbon–carbon (or carbon–heteroatom) bond formation.[1] This can be explained by the ability of such compounds to participate readily in one-step two-electron transfer processes, which are the elementary steps of numerous transition metal catalyzed transformations. The complexes of the first-row transition metals are mostly characterized by one-electron transformations and have less application in homogeneous catalysis. This is true for main group metal compounds, for which the processes of electron transfer are unusual at all. The problem of inactivity of these elements in multiple electron transformations may be solved by means of the insertion of redox active ligands in their coordination sphere.[2] Recently the excellent example of redox active ligand-mediated multielectron reactions for cross-coupling at square planar cobalt(III) complexes of the type $[\mathrm{Co(AP)_2}]^-$ (AP is *o*-amidophenolate dianion ligand) was demonstrated by J.D. Soper and coworkers.[3] These compounds are strong nucleophiles and able to interact with alkyl halides including CH_2Cl_2 under gentle conditions. The formal two-electron transition consists of two one-electron oxidations of each ligand and there is no change of metal oxidation state. Moreover the complexes obtained $\mathrm{(imSQ)_2CoAlk}$ (imSQ is *o*-iminosemiquinone radical-anion ligand) are able to react with organozinc halides. This leads to the regeneration of the square planar starting cobalt anions and elimination of C–C coupling products. These transformations result in a complete cycle for cobalt Negishi-like cross-coupling of alkyl halides with organozinc reagents. The involvement of redox active ligands into the non-transition metal complexes allows the last ones to participate in the oxidative addition and reductive elimination reactions. To date some examples of unusual reactivity of such types of complexes were found.[4] These include the transformations of tin(IV)[4a] and gallium(III)[4b] *o*-amidophenolate compounds in the reactions with dioxygen and sulfur and the unique ability of antimony(V) *o*-amidophenolate and catecholate complexes to reversibly bind the dioxygen.[4c,d] The latest works devoted to the gallium and aluminum compounds based on the redox active diiminoacenaphthene ligand (BIAN) have demonstrated their outstanding ability to activate the triple C≡C bond.[4e–g] A rare example of the interaction of main group metal complexes with alkyl halides is the reaction of $\mathrm{BIANMg(THF)_3}$ species with EtX (X = Cl, Br, I), which is accompanied by a one-electron transfer from the metal complex to the alkyl halide molecule.[5] The authors suggested the subsequent recombination of two radicals in the solvent cell and the new C–C bond formation between the ethyl group and the imine carbon atom of a diimine ligand. The present work is the investigation of potential participation of non-transition metal complexes containing redox active ligands in the cross-coupling reactions, in particular the possibility of alkyl halides activation by such types of compound.

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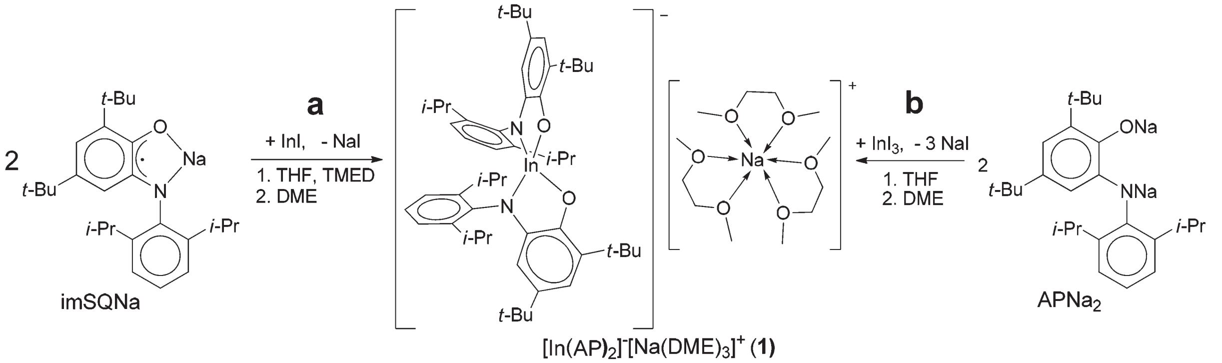


Scheme 1 The synthesis of the complex $[\mathrm{In(AP)_2}]^-[\mathrm{Na(DME)_3}]^+$ (**1**).

Results and discussion

The object of the present investigation is the anionic indium(III) complex containing two 4,6-di-*tert*-butyl-*N*-(2,6-di-iso-propylphenyl)-*o*-amidophenolate dianion ligands $[\mathrm{In(AP)_2}]^-[\mathrm{Na(DME)_3}]^+$ (**1**), which is an analogue of the cobalt derivatives[3] mentioned above. Compound **1** forms as the result of the reaction between indium(I) iodide and sodium *o*-iminobenzosemiquinolate (imSQNa) (Scheme 1a). The interaction proceeds at −20 °C in the presence of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMED) which increases the solubility of InI.[6] During this reaction the mixture color changes from bright blue to pale yellow. This indicates the reduction of the *o*-iminosemiquinolate ligand to the *o*-amidophenolate one and the formation of indium(III) species. The related process was recently observed in the course of interaction of potassium 3,6-di-*tert*-butyl-*o*-semiquinolate with InI.[7]

The complex **1** can also be obtained by the exchange reaction between indium(III) iodide and disodium *o*-amidophenolate ($\mathrm{APNa_2}$) in the molar ratio 1 : 2 (Scheme 1b). This method seems to be more convenient for the preparation of **1**.

The structure of complex **1** was determined by X-ray diffraction analysis (Fig. 1).

The compound **1** is the ate-complex containing a bis-(*o*-amidophenolato)indium(III) anion and sodium cation coordinated with three dimethoxyethane molecules. The indium atom in the anion has a distorted tetrahedral ligand environment, the O and N atoms of both imQ ligands occupy the tetrahedron vertices. The dihedral angle between the $\mathrm{C_6H_2O(1)N(1)}$ and $\mathrm{C_6H_2O(2)N(2)}$ planes of the redox active ligands is 81.82°. On the contrary, the analogous cobalt(III) bis-*o*-amidophenolate anions have a square planar geometry of the coordination center.[3] The C–O (1.355(3)–1.364(3) Å) and C–N (1.394(3)–1.397(3) Å) distances lie in the range typical for the dianion form of the *o*-iminobenzoquinone ligand.[8] The values of In–O (2.0633(15)–2.0646(17) Å) and In–N (2.057(2)–2.070(2) Å) bond lengths are less than the sum of the covalent radii of the corresponding elements (2.16 Å for In–O[9] and 2.17 Å for In–N[9]) and are comparable with those values in known *o*-amidophenolate indium compounds.[10] The $\mathrm{C_6H_2}$ rings of AP ligands contain equalized C–C distances (1.384(3)–1.432(3) Å) and have an aromatic nature. All these facts point out the dianion nature of redox active ligands in **1**.

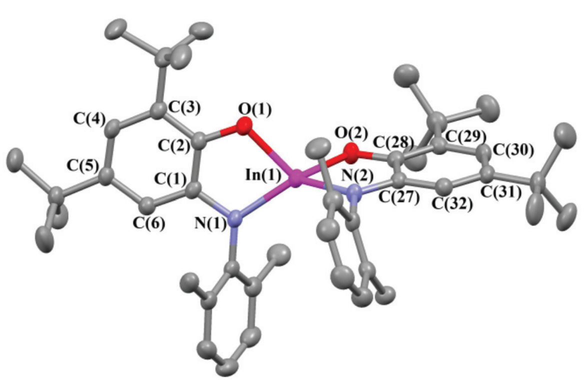
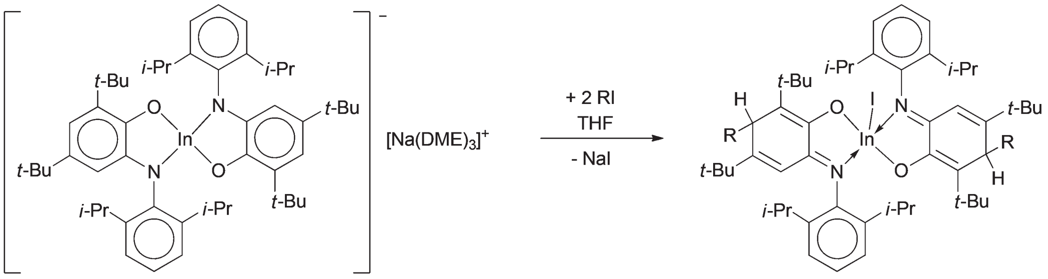


Fig. 1 The molecule structure of the $[\mathrm{In(AP)_2}]^-$ anion of **1** with 50% thermal probability ellipsoids. The H atoms and methyl groups of *i*-Pr substituents are omitted for clarity.

Compound **1** was found to react readily with methyl and ethyl iodides. The interaction with an excess of RI (R = Me, Et) proceeds slowly at room temperature but completes in 4 hours in boiling THF. The reaction mixture color changes from pale yellow to bright orange-yellow and the precipitation of NaI is observed. This process involves two equivalents of RI per one equivalent of complex **1** and results in the formation of the diamagnetic products **2** and **3** (Scheme 2). On the contrary, related cobalt(III) derivatives react with alkyl halides in molar ratio 1 : 1 that leads to the oxidation of amidophenolate ligands to the *o*-iminosemiquinolate ones and the formation of a Co–alkyl bond.[3]

The structures of compounds **2** and **3** were confirmed by X-ray diffraction analysis (Fig. 2 and 3). Selected bond lengths and angles of the complexes are given in Table 1. The geometry of the coordination polyhedra in **2** and **3** can be described as distorted tetragonal pyramidal or a trigonal bipyramidal. The N(1), N(2), O(1) and O(2) atoms form the tetragonal pyramid base while the I(1) atom occupies the apical site. The N(1), N(2) and I(1) atoms lie in equatorial positions and O(1) and O(2) atoms are in apical sides in the case of the second polyhedron. The univocal choice of the coordination polyhedron type is unclear. The authors[11] propose to use the



$[In(AP)_2]^{-}[Na(DME)_3]^{+}$ (**1**)

R = Me (**2**), Et (**3**)

Scheme 2 The reaction of complex **1** with alkyl iodides.

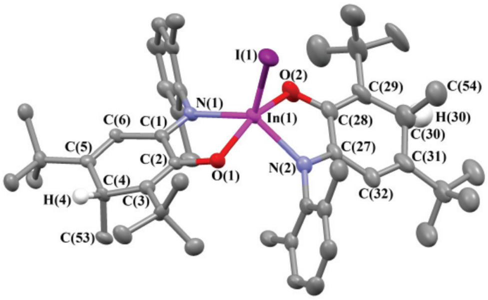


Fig. 2 The molecule structure of complex **2** with 50% thermal probability ellipsoids. The H atoms and methyl groups of *i*-Pr substituents are omitted for clarity.

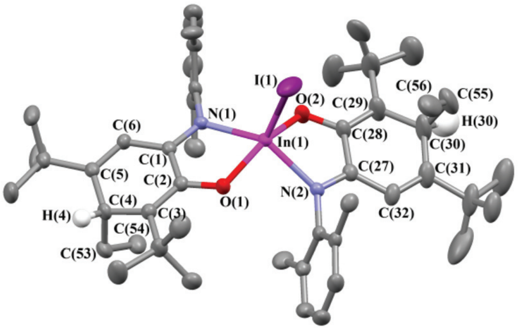
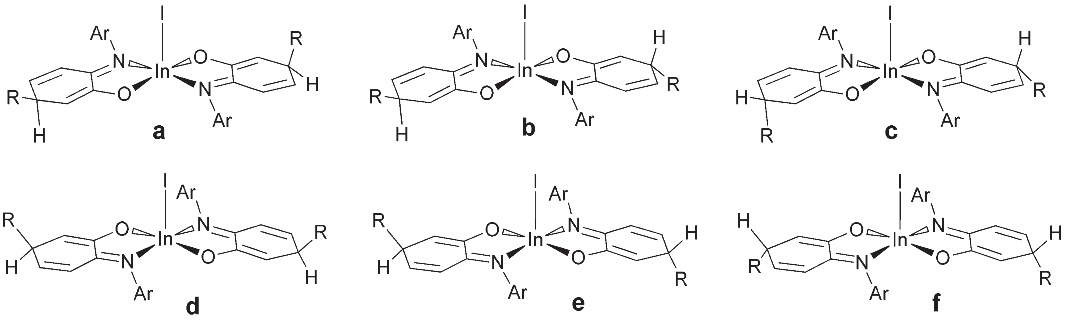


Fig. 3 The molecule structure of complex **3** with 50% thermal probability ellipsoids. The H atoms and methyl groups of *i*-Pr substituents are omitted for clarity.

Table 1 Selected bond lengths [Å] and angles [°] of complexes **1**·0.5DME, **2** and **3**

Bond lengths (Å)	**1**·0.5DME	**2**	**3**
In(1)–O(1)	2.0651(15)	2.083(3)	2.0771(16)
In(1)–O(2)	2.0645(13)	2.077(3)	2.0869(18)
In(1)–N(1)	2.0565(17)	2.214(4)	2.2018(18)
In(1)–N(2)	2.0684(18)	2.224(3)	2.2222(19)
In(1)–I(1)	—	2.7106(6)	2.7001(3)
N(1)–C(1)	1.399(3)	1.308(5)	1.308(3)
N(2)–C(27)	1.392(2)	1.300(5)	1.300(3)
O(1)–C(2)	1.359(3)	1.354(6)	1.332(3)
O(2)–C(28)	1.358(3)	1.342(4)	1.329(3)
C(1)–C(2)	1.423(3)	1.474(7)	1.477(3)
C(2)–C(3)	1.404(3)	1.344(6)	1.357(4)
C(3)–C(4)	1.404(3)	1.526(8)	1.507(3)
C(4)–C(5)	1.387(3)	1.485(8)	1.500(3)
C(5)–C(6)	1.392(3)	1.317(6)	1.343(4)
C(1)–C(6)	1.394(3)	1.436(7)	1.433(3)
C(27)–C(28)	1.432(3)	1.472(5)	1.472(4)
C(28)–C(29)	1.398(3)	1.351(5)	1.349(4)
C(29)–C(30)	1.411(3)	1.517(5)	1.523(4)
C(30)–C(31)	1.390(3)	1.503(5)	1.475(5)
C(31)–C(32)	1.393(3)	1.337(5)	1.325(4)
C(27)–C(32)	1.400(3)	1.450(5)	1.451(4)
C(4)–C(53)	—	1.623(8)	1.584(4)
C(30)–C(54)	—	1.571(6)	—
C(30)–C(55)	—	—	1.598(6)
Angles (°)			
O(1)–In(1)–O(2)	111.07(6)	157.54(13)	151.94(8)
O(1)–In(1)–N(1)	82.00(6)	76.50(13)	77.14(7)
O(1)–In(1)–N(2)	129.09(6)	97.85(11)	91.96(7)
N(1)–In(1)–N(2)	131.30(7)	126.28(13)	135.37(7)
N(1)–In(1)–O(2)	125.41(6)	88.87(12)	94.18(7)
O(2)–In(1)–N(2)	81.99(6)	76.99(11)	75.42(7)
O(1)–In(1)–I(1)	—	100.90(10)	106.60(5)
N(1)–In(1)–I(1)	—	115.64(9)	114.35(5)
O(2)–In(1)–I(1)	—	100.78(8)	101.30(6)
N(2)–In(1)–I(1)	—	117.85(9)	110.25(5)

geometric parameter τ for the definition of coordination geometry in five-coordinate complexes. τ is equal to zero for a perfectly tetragonal geometry, while it becomes one for a perfectly trigonal-bipyramidal geometry. In the case of **3** (τ = 0.28) the coordination geometry is probably better described as a trigonally distorted tetragonal pyramid, while in the case of **2** the τ parameter has an intermediate value (0.52). The six-membered carbon C(1)–C(6) and C(27)–C(32) cycles of both ligands in **2** and **3** contain sp^3-hybridized C(4) and C(30) atoms bonded with methyl (ethyl) groups. The In–O bond lengths (2.077(3)–2.0869(18) Å) are comparable with those in complex **1** and typical for an In–O single bond in catecholate and *o*-amidophenolate indium complexes.[7,10] On the other hand, the values of the In–N distances (2.2018(18)–2.224(3) Å) are more than the sum of the covalent radii of the corresponding elements (2.17 Å)[9] and close to those in an indium(III) complex containing the neutral form of the imQ ligand.[12] These bonds have donor–acceptor nature. The C–O bond lengths (1.329(3)–1.354(6) Å) are comparable with these distances in complex **1** and are single while the C–N bonds (1.300(5)–1.308(5) Å) are shorter than the corresponding distances in **1** and are double. In the six-membered carbon cyclohexadiene rings the double C═C bonds alternate with two single C–C bonds. Thus, both



Scheme 3 The possible isomers of complexes **2** (R = Me) and **3** (R = Et).

ligands in the complexes obtained are iminocyclohexa-1,4-dienolates. Such a type of ligand was recently described for a tin(IV) compound.[4a] It should be noted that alkyl groups bonded with C(4) and C(30) atoms are located on the opposite sides of the basal plane of the complexes both in **2** and **3**. Moreover, the methyl groups of the ethyl substituents in complex **3** are turned towards the six-membered C(1)–C(6) and C(27)–C(32) rings. Such a configuration was found for a Sn(IV) derivative containing the same iminocyclohexa-1,4-dienolate ligand.[4a] The calculation of the energy barrier of the Et-groups rotation shows that this rotation is hindered and two different orientations of these fragments are possible for the Sn(IV) complex. Only one of them is realized in the crystal.[4a] In the case of complex **3** one probable orientation of the Et-groups is realized too. It is necessary to note that the new C–C bonds are much longer (1.571(6)–1.623(8) Å) than the typical bonds between sp^3 hybridized carbon atoms (1.54 Å). It may cause the lability of new C–C bonds and promote their chemical transformations.

The presence of two bidentate ligands containing sp^3-hybridized carbon atoms in the five-coordinated complexes **2** and **3** should lead to the formation of isomeric molecules that vary in the position of the Me(Et) groups relative to the basal plane. Another type of isomerism was shown to be characteristic for related five-coordinated *o*-iminoquinolate metal derivatives.[4a,b,12] This was due to the different location of two *o*-iminoquinone ligands about the metal–X bond (X is any substituent). These types of isomerism can lead to the formation of six probable isomers **a–f** (Scheme 3). Moreover, the possibility of formation of conformers with a different orientation of Et substitutes relatively to the cyclohexadiene rings should not be excluded in the case of complex **3**.

In accordance with X-ray diffraction analysis data, isomer **b** is present in the crystal unit of both complexes **2** and **3** only. However, the ^{1}H and ^{13}C NMR spectra of solutions prepared using microcrystalline samples of **2** and **3** are typical for systems containing several isomers/diastereomers mixtures. Almost any signals observed in the ^{1}H or ^{13}C NMR spectra are represented by groups of signals belonging to different isomers. These signals are either separated or overlapping. The ratio of isomers may be approximately determined by comparing the intensities of resolved signals in the ^{13}C NMR spectra. This ratio depends on the recrystallization conditions and doesn't depend on NMR sample temperature. The sample of complex **3** prepared from the solution of single crystals suitable for X-ray diffraction shows the presence of predominantly one isomer according to the NMR spectroscopy. ge-HSQC, ge-HMBC, and ge-COSY were used for attributing the groups of signals to the structure fragments and assignments of ^{1}H and ^{13}C NMR spectra.

The authors[3] proposed a nucleophilic substitution S$_N$2 nature of the interaction between square-planar Co(III) bis-*o*-amidophenolate and alkyl halides. It is likely that the reaction of the related tetrahedral indium anion proceeds by an another mechanism. This is indicated by the basically different reaction products and stoichiometry. The univocal choice of the mechanism of the reaction requires additional research and will be the subject of subsequent studies.

Experimental

Experimental details

All reactants were purchased from Aldrich. Solvents were purified by standard methods.[13] The following reactants sodium *o*-iminosemiquinolate (imSQNa),[12] disodium *o*-amidophenolate (APNa$_2$),[12] indium(III) iodide (InI$_3$)[14] and indium(I) iodide (InI)[14] were prepared according to known procedures. All manipulations on complexes were performed in vacuum under conditions in which oxygen and moisture were excluded.

The infrared spectra of complexes in the 4000–400 cm^{-1} range were recorded on a FSM 1201 Fourier-IR spectrometer in nujol. NMR spectra were recorded in CDCl$_3$ solution by using a Bruker Avance III 400 MHz instrument with TMS as an internal standard. The elemental analysis was performed on an Elemental Analyzer Euro EA 3000 instrument.

Synthesis of $[In(AP)_2]^-[Na(DME)_3]^+$ (1)

Method 1. The solution of imSQNa (0.48 g, 1.19 mmol) in THF (25 mL) was added to an InI dispersion (0.1438 g, 0.595 mmol) in the same solvent (5 mL). The TMED (0.5 mL) was added to this solution. The reaction mixture was stirred for 1 h at −20 °C till the complete disappearance of the InI precipitate. During this the reaction mixture color changed from bright blue to pale yellow. THF was removed under reduced pressure and the residue was dissolved in hexane (25 mL). The

NaI precipitate was removed by filtration. The DME (5 mL) was added to the hexane solution. The dimethoxyethane solvated complex **1** was obtained as fine crystalline nearly colorless product after cooling. Yield for **1**·0.5DME: 0.587 g (81.4%). $C_{66}H_{109}InN_2NaO_9$: calcd C 65.38, H 9.06, In 9.47, Na 1.90; found C 65.44, H 9.11, In 9.39, Na 1.85.

^{1}H NMR (CDCl$_3$, J^1_{HH}/Hz, 20 °C): δ = 6.95–7.06 (m, 6H, H$_{\mathrm{anyl}}$); 6.48 (d, J = 2.4, 2H, C–H$_{\mathrm{arom}}$); 5.93 (d, J = 2.4, 2H, C–H$_{\mathrm{arom}}$); 3.54 (s, 14H, CH$_2$ (DME)), 3.31 (s, 21H, CH$_3$ (DME)); 2.7 (broad m, 4H, C–H (*i*-Pr)); 1.46, 1.06 (s, 36H, CH$_3$ (*t*-Bu)); 1.10, 0.10 (broad, CH$_3$ (*i*-Pr)) ppm.

^{13}C NMR (CDCl$_3$, 20 °C): δ = 146.6, 146.5, 144.0, 143.6, 137.9, 132.6 (C$_{\mathrm{anyl}}$); 124.9, 123.4 (broad, CH$_{\mathrm{anyl}}$); 109.2, 107.1 (CH$_{\mathrm{arom}}$); 71.5, 59.0 (DME); 34.7, 34.2 (C (*t*-Bu)); 31.7, 30.6 (CH$_3$ (*t*-Bu)); 31.6 (CH (*i*-Pr)); 23.7 (broad, CH$_3$ (*i*-Pr)) ppm.

IR (Nujol): ν = 1582 w, 1551 m, 1445 s, 1415 s, 1359 m, 1332 s, 1282 s, 1258 m, 1235 s, 1218 m, 1204 m, 1191 m, 1167 w, 1159 w, 1122 s, 1115 m, 1084 s, 1042 w, 1030 w, 986 m, 936 w, 920 w, 899 w, 882 w, 857 w, 840 w, 829 w, 817 w, 799 m, 765 w, 743 w, 714 w, 674 w, 654 w, 609 w, 579 w, 545 w, 530 w, 510 w, 499 w cm^{-1}.

Method 2. The solution of APNa$_2$ (0.485 g, 1.14 mmol) in THF (25 mL) was added to the solution of InI$_3$ (0.282 g, 0.57 mmol) in the same solvent (5 mL). The reaction mixture became pale yellow in a few minutes. The forming complex **1**·0.5DME was isolated according to the method 1. Yield: 0.625 g (86.7%).

The reaction of complex 1 with methyl and ethyl iodides

An excess of RI (1.65 mmol) was added to the solution of complex **1** (0.4 g, 0.33 mmol) in THF (30 mL). The reaction mixture was heated at the temperature of boiling solvent for 4 h. The reaction was accompanied by the color change from pale yellow to bright orange-yellow and precipitation of NaI. The THF was removed under reduced pressure and the residue was dissolved in hexane (25 mL). The NaI was removed by filtration. The hexane was replaced by acetonitrile (30 mL). The complexes **2** and **3** were isolated as finely crystalline products.

Complex **2**. Yield: 0.277 g (81.4%). $C_{54}H_{80}IInN_2O_2$: calcd C 62.91, H 7.82, In 11.14, I 12.31; found C 62.99, H 7.89, In 11.08, I 12.28.

^{1}H NMR (CDCl$_3$, 20 °C): δ = 7.14–7.26 (m, 4H, H$_{\mathrm{anyl}}$); 7.04–7.11 (m, 2H, H$_{\mathrm{anyl}}$); 5.86–5.92 (s, 2H, H (C–H)); 3.35–3.51 (q, 2H, H(H–C$_{\mathrm{sp3}}$)); 3.10–3.35, 2.52–2.76 (sept, 4H, CH (*i*-Pr)); 1.27–1.40 (d, 6H, CH$_3$ (*i*-Pr)); 1.11–1.25 (d, 6H, CH$_3$ (Me–C$_{\mathrm{sp3}}$)); 0.93–1.11 (18H + 36H, CH$_3$ (*i*-Pr), CH$_3$ (*t*-Bu)) ppm.

^{13}C NMR (CDCl$_3$, 20 °C): δ = 175.8–176.1 (=C-(*t*-Bu)); 165.7–166.5 (C=N); 146.3–147.2 (C–O); 140.9–142.4 (=C-(*i*-Pr)); 140.9–141.5 (N–C$_{\mathrm{anyl}}$); 140.1–140.7 (=C-(*t*-Bu)); 125.9–126.2, 123.2–123.9 (CH$_{\mathrm{anyl}}$); 114.4–115.2 (=CH); 38.1–38.4 (C$_{\mathrm{sp3}}$); 36.8–37.0 (C (*t*-Bu)); 35.6–35.9 (CH$_3$ (Me–C$_{\mathrm{sp3}}$)); 30.1–30.3 (CH$_3$ (*t*-Bu)); 28.3–28.7 (CH$_3$ (*t*-Bu)); 28.0–28.6 (CH (*i*-Pr)); 23.5–27.1 (CH$_3$ (*i*-Pr)) ppm.

IR (Nujol): ν = 1633 s, 1623 s, 1565 s, 1535 s, 1528 s, 1508 s, 1503 s, 1447 s, 1397 s, 1365 s, 1357 s, 1323 m, 1314 m, 1260 m, 1254 m, 1247 m, 1236 s, 1223 s, 1212 s, 1185 m, 1149 m, 1102 m, 1081 w, 1056 w, 1036 m, 1013 w, 1000 m, 980 m, 937 w, 888 m, 877 m, 820 w, 800 m, 786 m, 764 m, 702 w, 688 w, 673 w, 643 w, 627 w, 615 w, 578 m, 537 w, 524 w, 508 w, 497 w cm^{-1}.

Complex **3**. Yield: 0.272 g (77.8%). $C_{56}H_{84}IInN_2O_2$: calcd C 63.51, H 7.99, In 10.84, I 11.98; found C 63.56, H 8.05, In 10.78, I 11.91.

^{1}H NMR (CDCl$_3$, J^1_{HH}/Hz, 20 °C): δ = 7.16–7.25 (m, 4H, H$_{\mathrm{anyl}}$); 7.06–7.11 (m, 2H, H$_{\mathrm{anyl}}$); 6.05–6.12 (s, 2H, H (C–H)); 3.68–3.77 (t, 2H, H(H–C$_{\mathrm{sp3}}$)); 3.06–3.30, 2.58–2.74 (sept, 4H, CH (*i*-Pr)); 1.76–1.97 (m, 4H, CH$_2$(Et–C$_{\mathrm{sp3}}$)); 1.28–1.35 (d, 6H, CH$_3$ (*i*-Pr)); 0.96–1.10, 0.93–1.11 (18H + 36H, CH$_3$ (*i*-Pr), CH$_3$ (*t*-Bu)) ppm.

^{13}C NMR (CDCl$_3$, 20 °C): δ = 171.5–171.8 (=C-(*t*-Bu)); 166.4–166.9 (C=N); 148.3–148.8 (C–O); 139.7–142.5 (=C-(*i*-Pr)); 135.6–136.4 (=C-(*t*-Bu)); 125.9–126.2, 122.7–123.9 (CH$_{\mathrm{anyl}}$); 117.2–117.9 (=CH); 42.6–43.6 (*C*H$_2$CH$_3$); 35.5–37.2 (C (*t*-Bu)); 30.2–30.5, 28.3–28.5 (CH$_3$ (*t*-Bu)); 27.9–28.2 (CH (*i*-Pr)); 23.5–26.2 (CH$_3$ (*i*-Pr)); 5.3–5.5 (CH$_2$*C*H$_3$) ppm.

For the single crystal sample of complex **3** ^{1}H NMR (CDCl$_3$, J^1_{HH}/Hz, 20 °C): δ = 7.20 (m, 4H, H$_{\mathrm{anyl}}$), 7.09 (m, 2H, H$_{\mathrm{anyl}}$), 6.08 (s, 2H, H (C–H)), 3.72 (t, 2H, H (H–C$_{\mathrm{sp3}}$)), 3.16 (sept, J = 6.64, 2H, CH (*i*-Pr)), 2.68 (sept, J = 6.64, 2H, CH (*i*-Pr)), 1.85 (m, 4H, CH$_2$ (Et–C$_{\mathrm{sp3}}$)), 1.31 (d, J = 6.64, 6H, CH$_3$ (*i*-Pr)), 1.08 (d, J = 6.64, 6H, CH$_3$ (*i*-Pr)), 1.05 (s, 18H, CH$_3$ (*t*-Bu)), 1.04 (d, J = 6.64, 6H, CH$_3$ (*i*-Pr)), 1.02 (d, J = 6.64, 6H, CH$_3$ (*i*-Pr)), 0.99 (s, 18H, CH$_3$ (*t*-Bu)), 0.46 (t, J = 7.16, CH$_3$ (Et–C$_{\mathrm{sp3}}$)) ppm.

IR (Nujol): ν = 1626 s, 1592 m, 1567 s, 1533 s, 1450 s, 1399 s, 1395 s, 1355 s, 1350 s, 1332 m, 1311 s, 1257 s, 1235 s, 1223 s, 1187 s, 1164 m, 1148 m, 1094 m, 1039 w, 1027 w, 1018 w, 988 w, 970 w, 922 w, 891 m, 885 m, 879 m, 868 m, 838 w, 821 w, 808 w, 792 w, 767 s, 744 w, 705 w, 682 w, 668 m, 635 w, 621 w, 568 w, 550 m, 539 m, 533 w, 494 w cm^{-1}.

NMR investigation for 2 and 3

Almost all signals observed in ^{1}H or ^{13}C NMR spectra are represented by groups of signals belonging to different isomers. Some signals are separated and most are overlapped. Up to four lines with an intensities ratio of 1 : 1.2 : 1.2 : 1.8 are observed in the ^{13}C NMR spectrum for the signals of C–O, C–(*i*-Pr) and some others. According to this ratio there are three isomers/diastereomers in a ratio of approximately 1 : 1.8 : 2.4 or four isomers/diastereomers in a ratio of 1 : 1.2 : 1.2 : 1.8 in the mixture. This uncertainty is due to the presence of signals with equal intensity, which may be caused by two isomers with an equal ratio or one isomer with unsymmetrical fragments.

X-Ray crystallographic study of 1·0.5DME, 2 and 3

The single crystals suitable for X-ray diffraction analysis were obtained from DME (for **1**·0.5DME), hexane (for **2**) and acetonitrile (for **3**). Intensity data were collected at 150 K (for **1**·0.5DME) and 100 K (for **2** and **3**) on a Smart Apex diffractometer with graphite monochromated Mo-K$_\alpha$ radiation (λ = 0.71073 Å) in the φ–ω scan mode (ω = 0.3°, 10 s on each frame). The intensity data were integrated by the SAINT program.[15] SADABS[16] was used to perform area-detector scaling and absorption corrections. The structures **1**·0.5DME,

Table 2 Summary of crystal and refinement data for complexes **1**·0.5DME, **2** and **3**

Complex	**1**·0.5DME	**2**	**3**
Empirical formula	$C_{66}H_{109}InN_2NaO_9$	$C_{54}H_{80}IInN_2O_2$	$C_{56}H_{84}IInN_2O_2$
Formula weight	1212.36	1030.92	1058.97
Temperature (K)	150(2)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions	a = 13.1453(5) Å	a = 10.4639(19) Å	a = 11.1943(6) Å
	b = 16.6419(6) Å	b = 12.638(2) Å	b = 13.2672(7) Å
	c = 17.5596(6) Å	c = 22.385(4) Å	c = 20.1217(11) Å
	α = 65.2340(10)°	α = 74.287(3)°	α = 81.4470(10)°
	β = 85.4070(10)°	β = 78.611(2)°	β = 77.8950(10)°
	γ = 87.6900(10)°	γ = 72.322(2)°	γ = 71.0840(10)°
Volume (Å^3)	3476.8(2)	2693.6(8)	2753.6(3)
Z	2	2	2
Density (calculated) (g cm^{-3})	1.158	1.271	1.277
Absorption coefficient (mm^{-1})	0.397	1.050	1.029
Crystal size (mm^3)	0.40 × 0.38 × 0.15	0.46 × 0.16 × 0.07	0.26 × 0.13 × 0.12
Theta range for data collection, grad.	2.05 to 25.00	1.91 to 25.00	2.08 to 26.00
Reflections collected	19 479	20 315	23 822
Independent reflections (R_{int})	12 168 (0.0199)	9401 (0.0693)	10 757 (0.0229)
Completeness to theta max (%)	99.4	99.1	99.3
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.9428 and 0.8573	0.9302 and 0.6439	0.8865 and 0.7758
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	12 168/98/745	9401/10/569	10 757/13/605
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0481	R_1 = 0.0600	R_1 = 0.0398
	wR_2 = 0.1248	wR_2 = 0.1338	wR_2 = 0.0975
R indices (all data)	R_1 = 0.0557	R_1 = 0.1098	R_1 = 0.0530
	wR_2 = 0.1301	wR_2 = 0.1471	wR_2 = 0.1027
Goodness-of-fit on F^2	1.072	0.943	1.053
Largest diff. peak and hole (e Å^{-3})	1.232 and −0.841	1.906 and −0.957	1.524 and −1.167

2 and **3** were solved by direct methods and were refined on F^2 using all reflections with SHELXTL package.[17] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions and refined in the "riding-model". Selected bond lengths and angles of complexes obtained are given in Table 1. Table 2 summarises the crystal data and some details of the data collection and refinement.

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 928221–928223 for compounds **1**–**3**.

Conclusions

In summary, new C–C bond formation was observed in the course of the redox active ligand mediated reaction between alkyl iodides and an indium(III) bis-*o*-amidophenolate anion. The reaction proceeds at mild conditions and leads to new indium(III) derivatives containing iminocyclohexa-1,4-dienolate ligands.

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