

The unusual reactions of indium(I) trifluoromethanesulfonate with some first row metallocenes and the structure of “indium(II) cyclopentadienide”

Christopher G. Andrews, Charles L.B. Macdonald *

Department of Chemistry and Biochemistry, University of Windsor, Windsor, Ont., Canada N9B 3P4

Received 3 February 2005; received in revised form 16 March 2005; accepted 16 March 2005

Available online 4 May 2005

Abstract

The soluble reagent indium(I) trifluoromethanesulfonate, InOTf, does not appear to react or interact with ferrocene (Cp_2Fe , $\text{Cp} = \text{C}_5\text{H}_5$) whereas cobaltocene reacts with InOTf to produce $[\text{Cp}_2\text{Co}]^+[\text{OTf}]^-$ and indium metal. Unexpectedly, the reaction of InOTf with manganocene results in the formation of the unprecedented salt $[\text{In}(\mu^2, \eta^5\text{-Cp})\text{In}]^+[\text{Cp}_3\text{In}(\mu^2, \eta^1\text{-Cp})\text{InCp}_3]^-$: a form of “ Cp_2In ” that is characterized by X-ray crystallography. Similarly, the reaction of InOTf with $[\text{Cp}_2\text{Fe}]^+[\text{PF}_6]^-$ produces Cp_2Fe and “ In_4OTf_6 ” in addition to other products. The unusual structural features and the formation of the new indium-containing products are rationalized.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Indium; Subvalent; Metallocenes; Main group; Redox chemistry

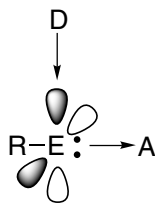
1. Introduction

The oxidation state of an element significantly affects the structural features and reactivity of the compound in which it is found. By definition, an element in a low oxidation state has a greater number of electrons associated with it than it would in a higher oxidation state; these additional electrons can completely alter the chemistry of compounds containing such centers. For example the +3 oxidation state is the most stable for most of the elements of group 13 (E) making neutral molecules containing such elements behave as Lewis acids. In contrast, the relatively rare compounds that contain group 13 elements in the +1 oxidation state can behave either as Lewis bases or Lewis acids, as illustrated in Scheme 1. The potential of using E^{I} compounds, especially cyclopentadienyl (C_5R_5 , Cp') compounds of the type

$\text{Cp}'\text{E}$ [1], as ligands for transition metal and main group acceptors has been exploited significantly since the late 1990s for the synthesis of new catalysts or materials precursors [2,3].

The full potential of the chemistry of compounds containing group 13 elements in the +1 oxidation state has not been realized, in part because of the lack of convenient starting materials other than certain organometallic E^{I} reagents [3,4]. Well-characterized oligomeric E^{I} halides for $\text{E} = \text{B}, \text{Al}$ and Ga are prepared by gas-phase reactions requiring a special apparatus and the materials are often only meta-stable [5,6]. The oft-used compound “ Ga^{I} ” [7] has been shown to have neither the structure nor the composition suggested by the indicated formula [8]. In contrast to the lighter congeners, thallium(I) salts are favored over their thallium(III) analogues because of relativistic effects. For indium, simple halide salts of both +1 and +3 oxidation states are available, however the In^{I} salts are insoluble in most common organic solvents [4]. As a necessary starting point for our

* Corresponding author. Tel.: +51925330003991; fax: +5199737098.
E-mail address: cmacd@uwindsor.ca (C.L.B. Macdonald).



Scheme 1.

investigation and exploitation of low oxidation state group 13 chemistry, we synthesized the unusually soluble indium(I) trifluoromethanesulfonate salt (indium(I) triflate, $\text{InOSO}_2\text{CF}_3$, InOTf , **1**) as an improved starting material for such studies [9]. Herein, we report some unique and unexpected reactivity that we have discovered using this new reagent.

In 2002, Wagner [10] reported the unexpected isolation of the coordination polymer **2** from the reaction of ferrocene ($(\text{C}_5\text{H}_5)_2\text{Fe}$, Cp_2Fe) with GaCl_3 . The coordination polymer almost certainly resulted from the reduction of GaCl_3 to Ga_2Cl_4 , which disproportionates to form $[\text{Ga}]^+[\text{GaCl}_4]^-$ in the presence of aromatic molecules (ferrocene, in this instance); each Ga^I center is coordinated by two arenes to produce **2**, as depicted in Scheme 2. The behavior and structure of arene complexes of Ga^I , In^I and Tl^I have been examined and reviewed by Schmidbaur [11] and Tuck [4], among others. In this context, we wished to investigate the possibility of using InOTf to obtain similar arene complexes.

2. Results and discussion

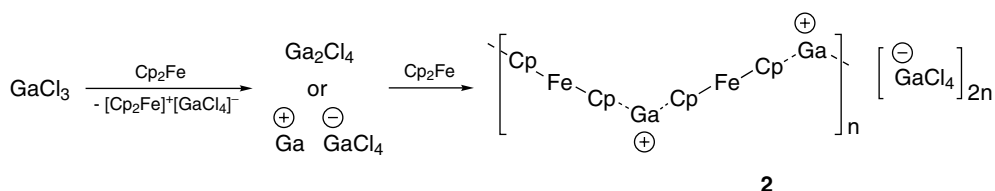
With the initial hope of obtaining a coordination polymer analogous to **2**, toluene solutions containing equimolar amounts of **1** and Cp_2Fe were mixed. The color of the solution remained orange and ^1H , ^{13}C and ^{19}F NMR spectra did not reveal any changes from the starting materials. Removal of all of the volatile substances under vacuum yielded a mixture of colorless and orange crystals which were identified as the starting materials. That the reaction did not form an arene-complex coordination polymer is likely a consequence of the stability of the InOTf structure, which contains numerous $\text{In}\cdots\text{O}$ contacts that fill the coordination sphere of

each In atom and thus render additional arene– In contacts unnecessary. Such an interpretation is consistent with the lack of arene complex formation or even arenes of recrystallization when **1** is crystallized from toluene [9].

The reaction of InOTf with cobaltocene also proceeds in a predictable fashion. When a solution of Cp_2Co in toluene is mixed with an equimolar solution of **1**, the deep purple color of the cobaltocene solution immediately changes to bright yellow and a fine grey precipitate is formed. Removal of the precipitate by filtration generates a clear yellow filtrate from which yellow crystalline material characterized as $[\text{Cp}_2\text{Co}]^+[\text{OTf}]^-$, **3**, is obtained upon concentration. The grey precipitate was identified as metallic In by its melting point thus the reaction is readily understood as being the one-electron reduction of In^I to In^0 with the concomitant oxidation of the Co^{II} center to Co^{III} . The high isolated yield of **3** suggests that this reaction is essentially quantitative and thus may be of preparative utility.

In contrast to the reactions with Cp_2Fe and Cp_2Co , the reaction of manganocene and InOTf resulted in the production of completely unexpected products. Stirring an equimolar toluene solution of **1** with Cp_2Mn rapidly formed a bright yellow solution that fades with time and a colorless precipitate. While the composition of the extremely air-sensitive precipitate has yet to be confirmed, concentration of the yellow solution results in the formation of air-sensitive yellow crystals suitable for analysis by X-ray diffraction. The crystals were identified as $[\text{In}(\mu^2, \eta^5\text{-Cp})\text{In}]^+[\text{Cp}_3\text{In}(\mu^2, \eta^1\text{-Cp})\text{InCp}_3]^-$, **4**, and the structure obtained from the crystallographic experiment is shown in Fig. 1; pertinent metrical parameters are collected in Table 1.

The structure of **4** consists of inverse sandwich cations of the type $[\text{In}(\mu^2, \eta^5\text{-Cp})\text{In}]^+$ and complex mono-anions of the form $[\text{Cp}_3\text{In}(\mu^2, \eta^1\text{-Cp})\text{InCp}_3]^-$. The cyclopentadienyl ring in the cation (labeled with C(51)) sits on an inversion center (X(1)) at the fractional coordinates (0.25, 0.75, 0.5) and is extremely disordered. The indium atoms in the cation are found at a distance of 2.659(3) Å from the inversion center and have significantly longer contacts with the π -systems of the Cp rings on adjacent anions; the closest $\text{In}(1)$ to centroid distances are 3.050, 3.178 and 3.669 Å and the centroids of the four closest Cp rings are arranged in a roughly tetrahedral manner about the $\text{In}(1)$ atom. While the $[\text{In}(\mu^2, \eta^5\text{-Cp})\text{In}]^+$ cation



Scheme 2.

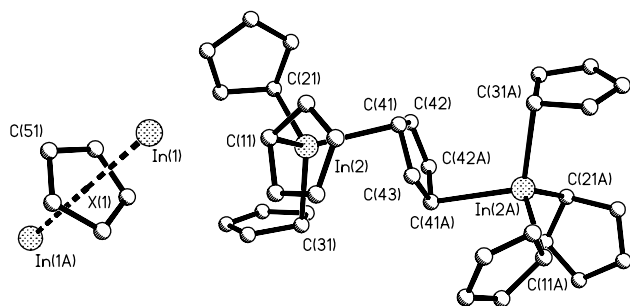


Fig. 1. Ball and stick representation of $[\text{In}(\mu^2, \eta^5\text{-Cp})\text{In}]^+[\text{Cp}_3\text{In}(\mu^2, \eta^1\text{-Cp})\text{InCp}_3]^-$, **4**.

Table 1
Selected metrical parameters for **4**

Parameter	Parameter	Parameter	Parameter
C(11)–In(2)	2.253(3)	C(31)–In(2)	2.280(3)
C(11)–C(15)	1.424(5)	C(31)–C(32)	1.420(5)
C(11)–C(12)	1.447(5)	C(31)–C(35)	1.429(5)
C(12)–C(13)	1.349(6)	C(32)–C(33)	1.348(6)
C(13)–C(14)	1.390(6)	C(33)–C(34)	1.380(7)
C(14)–C(15)	1.344(5)	C(34)–C(35)	1.357(6)
C(21)–In(2)	2.276(3)	C(41)–In(2)	2.431(3)
C(21)–C(22)	1.416(5)	C(41)–C(43)	1.399(4)
C(21)–C(25)	1.436(5)	C(41)–C(42)	1.423(5)
C(22)–C(23)	1.358(6)	C(42)–C(42)#1	1.343(7)
C(23)–C(24)	1.391(6)	C(43)–C(41)#1	1.399(4)
In(1)–C(5n)cent	2.659(3)		
In(2)–C(11)–H(11)	94(3)	In(2)–C(31)–H(31)	97(3)
In(2)–C(21)–H(21)	100(2)	In(2)–C(41)–H(41)	92(2)

Bond distances are reported in (Å) and angles are reported in (°).

has not been reported previously, the metrical parameters in the ion are consistent with those expected on the basis of those observed in the related In^{I} -containing species. In particular, the In^{I} -centroid distance in **4** lies almost exactly halfway between the short In^{I} -centroid contacts (2.609 and 2.629 Å, respectively) and long contacts (2.771 and 2.667 Å, respectively) in the two structures reported previously for the neutral coordination polymer CpIn [12,13]. Furthermore, the In^{I} -centroid distance in **4** is significantly longer than those (2.435–2.528 Å) reported for the cations $[\text{In}(\mu^2, \eta^5\text{-C}_5\text{Me}_5)\text{In}]^+$ that bear the more electron donating pentamethylcyclopentadienyl substituent [14,15].

The structure of the anion in **4** is unique and is depicted in Fig. 2. The anion consists of two indium atoms that are each coordinated by three σ -bonded Cp rings and that are linked to each other by a bridging bis- η^1 -Cp ring situated on a crystallographic 2 axis. The locations of the hydrogen atoms on the *ipso*-carbon atoms of the σ -bonded groups, as well as each of the hydrogen atoms on the bridging ring, were used in conjunction with the metrical parameters of the carbon skeletons to assign the hapticities of the rings. While the anion is without precedent, the structural features are similar

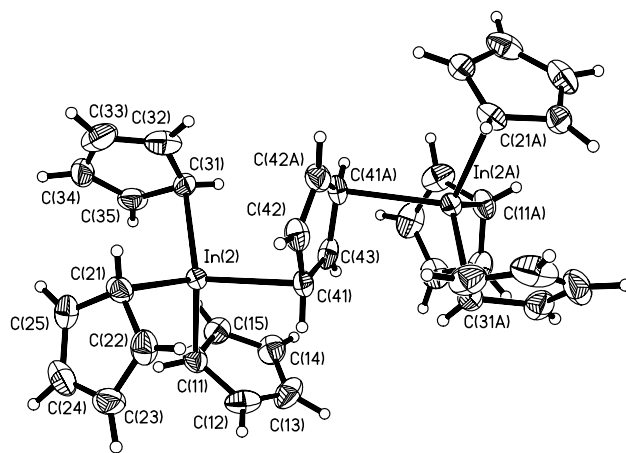


Fig. 2. Thermal ellipsoid plot (30% probability surface) of the anion in **4**.

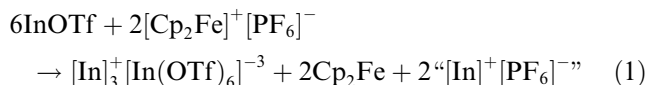
to those reported for the coordination polymeric neutral In^{III} compound InCp_3 , **5** [16]. In particular, the In – C distances to the σ -bonded Cp ligands of 2.253(3)–2.280(3) Å in **4** are only marginally longer than the 2.229(4) Å in **5** and the 2.431(3) Å In – C distance to the bridging Cp is somewhat shorter than the 2.482(4) Å in **5**.

The empirical formula for **4** is $\text{C}_{10}\text{H}_{10}\text{In}$ and thus the compound is an isomeric form of “ Cp_2In ”. The structures of the ions in **4** are clearly consistent with the salt being described as a mixed valence indium species containing In^{I} and In^{III} centers in the solid state. In solution, however, only one signal is observed in both the ^1H and ^{13}C NMR spectra (even at -90°C) indicating that all of the Cp rings are equivalent on the NMR timescale and thus an alternative structural arrangement is present in solution. Such behavior is thus reminiscent of the chemistry of the In^{II} halides [4] and it is important to note that the chemical shifts observed for **4** are virtually identical to those reported by Beachley et al. [16] for the mixture of CpIn and Cp_3In . In that case, it was postulated that the mechanism that renders each of the Cp groups equivalent may involve the formation of the In^{II} intermediate Cp_2In – InCp_2 . However, since it has been demonstrated that the presence of cyclopentadienyl groups tend to destabilize such $\text{E}^{\text{II}}\text{E}^{\text{II}}$ arrangements (for $\text{E} = \text{B}, \text{Al}$) in favor of possible $\text{E}^{\text{I}}\text{E}^{\text{III}}$ valence isomers [17–19], and given the structure of the anion in **4** found in the solid state, we propose that perhaps a more likely mechanism involves the formation of ions of $[\text{In}^{\text{I}}]^+$ and $[\text{Cp}_4\text{In}^{\text{III}}]^-$. The relationship between the various likely valence isomers of **4** is outlined in Scheme 3. We believe that the rearrangement of the simple $\text{In}^{\text{I}}\text{In}^{\text{III}}$ salt into the inverse-sandwich cation and bridging anion may aid in the solid state packing of the salt by providing cations and anions that are more similar in size; such a process appears to require less rearrangement for the

simple ionic isomer than for either the donor–acceptor or the covalent isomers.

While the process through which **4** is formed from Cp_2Mn and **1** requires further elucidation, the reaction clearly entails the cleavage of Cp rings from the metallocene in addition to the oxidation of some of the indium(I) centers. We are currently investigating the possibility of making **4** from In_2Cl_4 however our attempts to date have not been successful thus it appears as if the best current method of its preparation is the reaction of CpIn with Cp_3In [16].

Because of the unexpected nature of the reaction of InOTf with manganocene, we examined the reaction of our indium(I) source with a salt containing a metallocenium cation isoelectronic with manganocene, namely the ferricenium salt $[\text{Cp}_2\text{Fe}]^+[\text{PF}_6]^-$. The reaction of an equimolar amount of **1** with $[\text{Cp}_2\text{Fe}]^+[\text{PF}_6]^-$ results in the formation of an intense blue solution. Filtration of the reaction mixture and slow concentration of the filtrate yielded a mixture of colorless and orange crystalline materials. The orange crystals were identified as ferrocene and the colorless crystals were characterized as the mixed-valent salt $[\text{In}]_3^+[\text{In}(\text{OTf})_6]^{-3}$, **6**. Although the other reaction product(s) remain unidentified, a possible balanced equation for the reaction is:



The unique components of the structure of the indium “subtriflate” **6** are depicted in Fig. 3 and important metrical parameters are collected in Table 2. The formula unit of the structure contains three distinct indium environments: there is a distorted octahedral $[\text{In}(\text{OTf})_6]^{-3}$ anion labeled In(1); there is an In^{I} cation labeled In(3) that is also coordinated by a roughly octahedral array of O atoms from the triflate groups; and there are two In^{I} cations (labeled In(2)) that are η^6 -coordinated by the toluene molecules in the structure and have close contacts with some of the O atoms from the triflate groups. The crystalline arrangement, as illustrated in Fig. 4, can be rationalized in the following manner: (1) the In^{III} octahedra are linked to one another by the In^{I} ions to form alternating $\text{In}^{\text{I}}\text{–In}^{\text{III}}$ chains along the crystallographic *c* axis; (2) the remaining In^{I} ions are attached to the alternating chain through close contacts

with the OTf groups; and (3) the coordination sphere of the “external” In^{I} ions is capped by the interactions with the toluene molecules.

Although there are many instances of In^{III} coordinated by octahedral arrays of oxygen atoms in the Cambridge Structural Database (CSD) [20], the tri-anion in **6** is unique and appears to be one of the only examples containing six triflate anions coordinated to any kind of metal atom listed in the CSD. Examination of the metrical parameters in the anion show that the distances

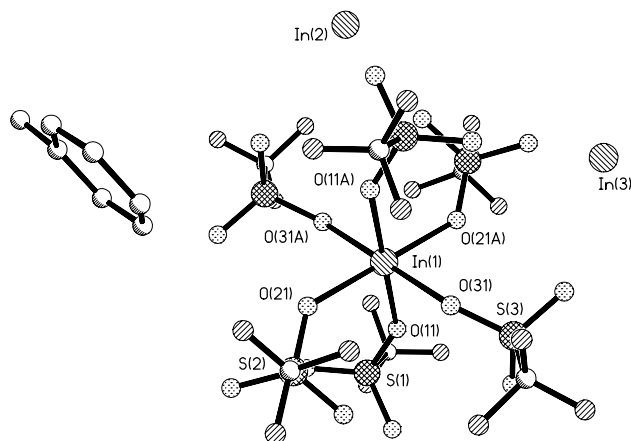
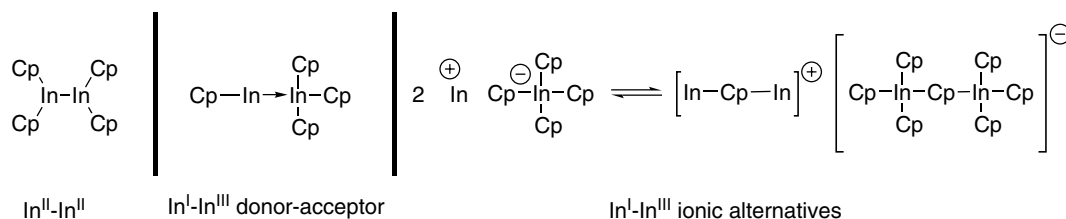


Fig. 3. Ball and stick representation of the components of **6**.

Table 2
Selected bond distances in (Å) for $[\text{In}]_3^+[\text{In}(\text{OTf})_6]^{-3} \cdot 2$ toluene, **6** · 2 toluene

Parameter	Distance	Parameter	Distance
In(1)–O(11)	2.113(4)	S(1)–O(11)	1.457(5)
		S(1)–O(12)	1.422(6)
		S(1)–O(13)	1.405(7)
In(1)–O(21)	2.126(5)	S(2)–O(21)	1.451(5)
		S(2)–O(22)	1.429(6)
		S(2)–O(23)	1.421(6)
In(1)–O(31)	2.121(4)	S(3)–O(31)	1.462(5)
		S(3)–O(32)	1.414(6)
		S(3)–O(33)	1.412(7)
In(3)–O(13)	2.880(7)	In(3)–O(23)	2.902(7)
In(3)–O(33)	2.920(7)		
In(2)–O(12)	2.705(6)	In(2)–O(22)	2.770(5)
In(2)–O(32)	2.847(6)		
In(2)–C(2n)cent	2.998(7)	In(2)–C(3n)cent	2.983(10)



Scheme 3.

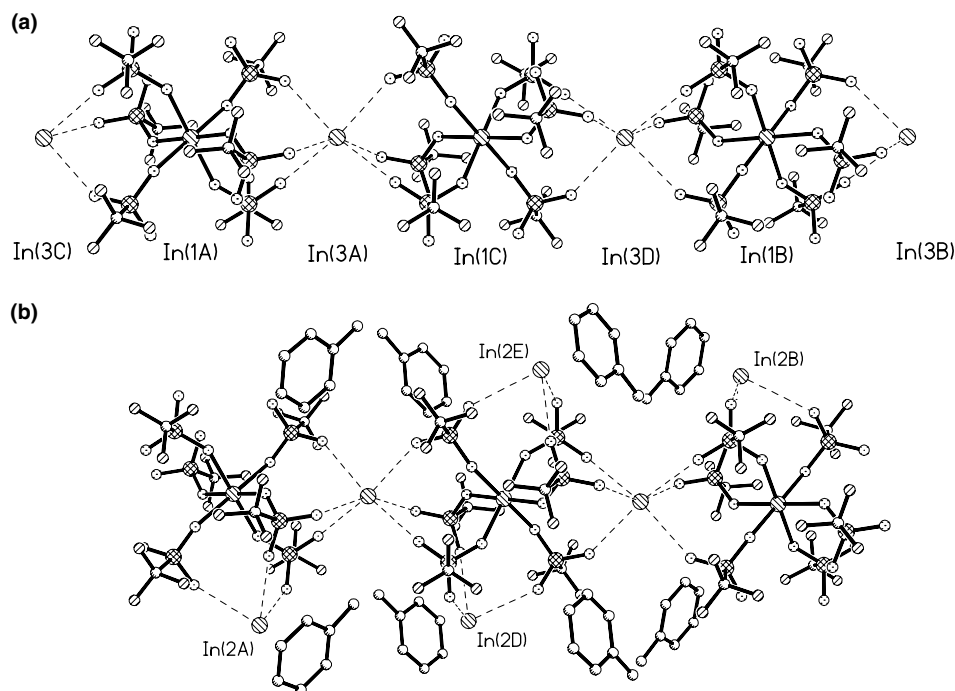


Fig. 4. Crystalline structure of **6** · 2 toluene (a) shows the alternating chain of In^{III} and In^I centers and (b) shows the location of the In^I · toluene fragments around the chain.

between In(1) and the nearest O atoms, which range from 2.113(4) to 2.126(5) Å, are typical of In^{III}–O interactions; the average In–O distance in the CSD is around 2.14 Å and the covalent radii for In and O are 1.44 and 0.73 Å, respectively [21]. Furthermore, the bonding within the triflate ions appears to be somewhat more localized than delocalized in the SO₃ framework in the sense that each anion has one longer S–O bond to the O(n1) atoms that are bonded to the In(1) atom and the two remaining S–O bonds are significantly shorter.

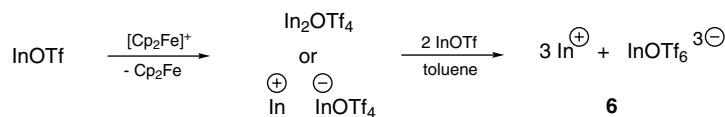
The coordination environments around the indium(I) atoms within the chain are also approximately octahedral however the shortest In(3)–O distances, which range from 2.880(7) to 2.920(7) Å, are significantly longer than those to the indium(III) center. In fact, while these In^I–O distances do fall within the sum of the van der Waals radii for In (1.93 Å) and O (1.52 Å), all of the distances are significantly longer than sum of the covalent radii for the elements or the sum of the ionic radii estimated for In^I (1.04 Å) and O^{-II} (1.40 Å) [21].

The coordination environment around the indium(I) ions external to the chain are less symmetric than those of the other indium centers. Each of the ions labeled In(2) has three In–O contacts ranging from 2.705(6) to 2.847(6) Å which are, again, significantly longer than the distance predicted for typical single bonds between these elements. The coordination sphere of In(2) also includes an η⁶-toluene molecule; the distance from the ring centroid to In(2) is around 2.983(10) Å which is only somewhat longer than the 2.83 and 2.89 Å dis-

tances reported for [In(mesitylene)₂]⁺ by Schmidbauer et al. [22].

While the identities of all of the by-products in the reaction that generates **6** have yet to be established, the isolation of Cp₂Fe and the composition of **6** suggest that a plausible process for the reaction almost certainly involves the oxidation of InOTf to In₂OTf₄ by the Fe^{III} to Fe^{II} couple. As suggested in Scheme 4, we surmise that the In^{II} compound would rearrange to the ionic In^IIn^{III} alternative in the toluene solution and the interaction of the salt with two additional equivalents of the InOTf starting material would yield **6**. We are currently endeavoring to synthesize **6** by the direct reaction of 3 equivalents of InOTf and one equivalent of InOTf₃.

In conclusion, our initial examination of some of the chemistry of InOTf with some first row metallocenes has yielded some surprising results. In particular, while the reactions of **1** with 18-electron and 19-electron species are predictable, the reactions with the 17-electron metallocenes result in the oxidation of the In^I center and the formation of products with unprecedented structures. It appears that the nature of the oxidized or partially oxidized products in both **4** and **6** is readily understood in the context of the relative stabilities of the possible valence isomeric forms. In particular, the putative In^{II}In^{II} products appear to be less stable than the alternative In^IIn^{III} products under the reaction conditions in this investigation. The most obvious difference between the reactions that produced **4** and **6** is



Scheme 4.

the cleavage of the cyclopentadienyl rings from manganocene and the retention of the Cp ligands in the ferricenium system.

3. Experimental

3.1. General methods

All work was carried out using standard inert-atmosphere techniques. Manganocene, ferrocene and cobaltocene were purchased from Strem whereas $[\text{Cp}_2\text{Fe}]^+[\text{PF}_6]^-$ and all solvents were obtained from Aldrich; all reagents were used without further purification. Preparative methods for InOTf are described in a preliminary communication [9]. Solvents were dried on a series of Grubbs' type columns and were degassed prior to use [23]. Unless otherwise noted in the text, NMR spectra were recorded at room temperature on a Bruker Avance 300 MHz spectrometer. Chemical shifts are reported in ppm, relative to external standards (SiMe_4 for ^1H and ^{13}C , CFCl_3 for ^{19}F). Melting points were obtained using an Electrothermal[®] melting point apparatus on samples sealed in glass capillaries under dry nitrogen or argon. The high resolution ESI mass spectra were recorded on a Micromass LCT time-of-flight spectrometer from acetonitrile solutions in "lockmass" mode.

3.2. Specific procedures

3.2.1. Synthesis of $[\text{Cp}_2\text{Co}]^+[\text{OTf}]^-$

The addition of a purple solution of Cp_2Co (398 mg, 2.10 mmol) in dichloromethane to a colorless suspension of InOTf (548 mg, 2.08 mmol) in the same solvent results in the immediate formation of a lemon yellow solution in which was suspended a fine grey powder of metallic In. After filtration and rinsing of the metal with fresh dichloromethane, the solvent was removed in vacuo to yield the product as a bright yellow solid (633 mg, 1.87 mmol, 90.1% yield). Crystalline material is obtained by the slow evaporation of a concentrated CH_2Cl_2 solution. m.p. 330–331 °C. Low resolution mass spectrometry supports the identities of both the $[\text{Cp}_2\text{Co}]^+$ and $[\text{OTf}]^-$ ions. HRMS: Calcd. for $\text{C}_{10}\text{H}_{10}\text{Co}$: 189.0114, found: 189.0110 (2.4 ppm). ^1H NMR (CD_2Cl_2 , 300 MHz): δ 5.77 (s). ^{13}C NMR (CD_2Cl_2 , 300 MHz): δ 85.5 (s). ^{19}F NMR (CD_2Cl_2 , 300 MHz): δ -79.1 (s).

3.2.2. Synthesis of $[\text{In}(\mu^2, \eta^5\text{-Cp})\text{In}]^+[\text{Cp}_3\text{In}(\mu^2, \eta^1\text{-Cp})\text{InCp}_3]^-$, **4**

Toluene (50 mL) was added to a solid mixture of InOTf (527 mg, 2.00 mmol) and Cp_2Mn (372 mg, 2.01 mmol), to result in the immediate formation of a yellow solution. The reaction mixture was left stirring overnight after which a fluffy off-white precipitate and small number of brown particles formed. The reaction mixture was filtered using a fine frit, and the solvent removed in vacuo to isolate the product as a light yellow solid (112 mg, 0.46 mmol, 22.9% yield based on In). Single crystals suitable for X-ray analysis are obtained by the slow evaporation of a concentrated toluene solution at room temperature. d.p. 124–127 °C. ^1H NMR (C_7H_8 , 300 MHz): δ 5.89 (broad, s); (C_6D_6 , 300 MHz): δ 5.98 (broad, s). ^{13}C NMR (C_7H_8 , 300 MHz): δ 105.8 (s).

3.2.3. Synthesis of In_4OTf_6 , **6**

Toluene (50 mL) was added to a solid mixture of InOTf (459 mg, 1.74 mmol) and $[\text{Cp}_2\text{Fe}]^+[\text{PF}_6]^-$ (191 mg, 0.58 mmol), to form a deep blue solution, which became yellow with a blue suspension after stirring under nitrogen overnight. The reaction mixture was filtered and concentrated to produce colorless crystals characterized as **6** · 2 toluene (23 mg, 0.02 mmol, 3.9% isolated crystalline yield based on In after washing 3 times with toluene; the actual yield is considerably greater). d.p. 116–119 °C. ^{19}F NMR (CDCl_3 , 300 MHz): δ -78.8 (s).

3.3. Crystallography

In the dry N_2 atmosphere of a VAC glovebox, each crystal was selected and mounted in thin-walled glass capillary tubes. These were subsequently flame-sealed and glued to brass pins suitable for attachment to a goniometer head. The data were collected using the SMART [24] software on a Bruker APEX CCD diffractometer using a graphite monochromator with Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). A hemisphere of data was collected using a counting time of 10 seconds per frame at 25 °C. Details of crystal data, data collection and structure refinement are listed in Table 3. Data reductions were performed using the SAINT [25] software and the data were corrected for absorption using SADABS [26]. The structures were solved by direct methods using SIR 97 [27] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-disordered heavy atoms using SHELXL-97 [28] and the WINGX [29] software package and thermal ellipsoid

Table 3

Summary of collection and refinement data for the X-ray diffraction investigations of **4** and **6** · 2 toluene

Compound	[InCpIn] [Cp ₃ InCpInCp ₃], 4	[In · toluene] ₂ [In] [In(OTf) ₆], 6 · 2 toluene
Empirical formula	C ₄₀ H ₄₀ In ₄	C ₂₀ H ₁₆ F ₁₈ In ₄ O ₁₈ S ₆
Formula weight	980.00	1537.97
Temperature (K)	298(2)	298(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	C2/c	C2/c
<i>Unit cell dimensions</i>		
<i>a</i> (Å)	15.226(3)	21.291(2)
<i>b</i> (Å)	8.5570(14)	10.4280(13)
<i>c</i> (Å)	28.316(5)	21.014(3)
α (°)	90	90
β (°)	99.089(6)	102.409(3)
γ (°)	90	90
Volume (Å ³)	3643.1(11)	2407.6(2)
<i>Z</i>	4	4
<i>D</i> _{calc} (g cm ⁻³)	1.787	2.242
Absorption coefficient (mm ⁻¹)	2.526	2.411
<i>F</i> (000)	1904	2936
θ Range for data collection (°)	1.46–27.49	1.96–23.31
Limiting indices	–19 < <i>h</i> < 19, –11 < <i>k</i> < 11, –36 < <i>l</i> < 36	–22 < <i>h</i> < 23, –9 < <i>k</i> < 11, –21 < <i>l</i> < 23
Reflections collected	17055	10991
Independent reflections	4178	3287
<i>R</i> _{int}	0.0346	0.0324
Data/restraints/parameters	4178/3/211	3287/10/263
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)] ^a	<i>R</i> ₁ = 0.0280, <i>wR</i> ₂ = 0.0606	<i>R</i> ₁ = 0.0400, <i>wR</i> ₂ = 0.0973
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0442, <i>wR</i> ₂ = 0.0661	<i>R</i> ₁ = 0.0675, <i>wR</i> ₂ = 0.1120
Goodness-of-fit (<i>S</i>) ^b on <i>F</i> ²	1.019	1.027
Largest differences in peak and hole (e Å ⁻³)	0.647 and –0.446	0.598 and –0.456

^a $R_1(F) = \sum(|F_o| - |F_c|) / \sum|F_o|$ for reflections with $F_o > 4\sigma(F_o)$. $wR_2(F^2) = \{\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w(|F_o|^2)^2\}^{1/2}$, where *w* is the weight given each reflection.

^b $S = [\sum w(|F_o|^2 - |F_c|^2)^2 / (n - p)]^{1/2}$, where *n* is the number of reflections and *p* is the number of parameters used.

plots were produced using SHELXTL [30]. In **4** the hydrogen atoms on the *ipso*-carbon atoms of the terminal Cp groups and those of the bridging Cp group in the anion were located in the difference Fourier map and were refined isotropically; all other H atoms in both structures were placed in calculated positions. The centroid of the bridging Cp group in the [In(μ^2, η^5 -Cp)In] cation is located approximately on an inversion center at (0.25, 0.75, 0.5) and the group is thus highly disordered. This ring was modeled as a rigid ring with C–C distances of 1.403 Å and C–C–C angles of 108.0° with a site occupancy factor of 0.5. The disorder in the orientation of the toluene molecules in **6** · 2 toluene was refined with models including rigid 6-membered rings with C–C distances of 1.390 Å and C–C–C angles of 120.0°; refinement of the occupancy of each model yielded an approximate 58:42 ratio.

4. Supplementary data

CCDC 261763 and 261764 contain the supplementary crystallographic data for this paper. These data

can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

The funding that has enabled this work has been provided by the Natural Sciences and Engineering Research Council (Canada), the Canada Foundation for Innovation, the Ontario Innovation Trust and the Ontario Research and Development Challenge Fund (University of Windsor Centre for Catalysis and Materials Research).

References

- [1] P. Jutzi, N. Burford, Chem. Rev. 99 (1999) 969.
- [2] R.A. Fischer, J. Weiss, Angew. Chem., Int. Ed. 38 (1999) 2831.
- [3] G. Linti, H. Schnöckel, Coord. Chem. Rev. 206 (2000) 285.
- [4] D.G. Tuck, Chem. Soc. Rev. 22 (1993) 269.
- [5] P.L. Timms, Acc. Chem. Res. 6 (1973) 118.
- [6] C. Dohmeier, D. Loos, H. Schnöckel, Angew. Chem., Int. Ed. Engl. 35 (1996) 129.

- [7] M.L.H. Green, P. Mountford, G.J. Smout, S.R. Speel, *Polyhedron* 9 (1990) 2763.
- [8] M. Kehrwald, W. Kostler, A. Rodig, G. Linti, T. Blank, N. Wiberg, *Organometallics* 20 (2001) 860.
- [9] C.L.B. Macdonald, A.M. Corrente, C.G. Andrews, A. Taylor, B.D. Ellis, *Chem. Commun.* (2004) 250.
- [10] S. Scholz, J.C. Green, H.W. Lerner, M. Bolte, M. Wagner, *Chem. Commun.* (2002) 36.
- [11] H. Schmidbaur, *Angew. Chem., Int. Ed. Engl.* 24 (1985) 893.
- [12] A. Dashti-Mommertz, B. Neumuller, S. Melle, D. Haase, W. Uhl, *Z. Anorg. Allg. Chem.* 625 (1999) 1828.
- [13] O.T. Beachley, J.C. Pazik, T.E. Glassman, M.R. Churchill, J.C. Fetting, R. Blom, *Organometallics* 7 (1988) 1051.
- [14] A.H. Cowley, C.L.B. Macdonald, J.S. Silverman, J.D. Gorden, A. Voigt, *Chem. Commun.* (2001) 175.
- [15] J.N. Jones, C.L.B. Macdonald, J.D. Gorden, A.H. Cowley, *J. Organomet. Chem.* 666 (2003) 3.
- [16] O.T. Beachley, D.J. MacRae, A.Y. Kovalevsky, Y.G. Zhang, X. Li, *Organometallics* 21 (2002) 4632.
- [17] J.D. Gorden, C.L.B. Macdonald, A.H. Cowley, *Chem. Commun.* (2001) 75.
- [18] A.Y. Timoshkin, G. Frenking, *J. Am. Chem. Soc.* 124 (2002) 7240.
- [19] P. Greiwe, A. Bethauser, H. Pritzkow, T. Kuhler, P. Jutzi, A. Siebert, *Eur. J. Inorg. Chem.* (2000) 1927.
- [20] F.H. Allen, *Acta Crystallogr. Sect. B: Struct. Sci.* 58 (2002) 380.
- [21] www.webelements.com.
- [22] J. Ebenhoch, G. Muller, J. Riede, H. Schmidbaur, *Angew. Chem., Int. Ed. Engl.* 23 (1984) 386.
- [23] A.B. Pangborn, M.A. Giardello, R.H. Grubbs, R.K. Rosen, F.J. Timmers, *Organometallics* 15 (1996) 1518.
- [24] SMART, Bruker AXS Inc., 2001.
- [25] SAINTPLUS, Bruker AXS Inc., 2001.
- [26] SADABS, Bruker AXS Inc., 2001.
- [27] A. Altomare, M.C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, M.A.G.G., G. Polidori, R. Spagna, *SIR 97, CNR-IRMEC*, 1997.
- [28] G.M. Sheldrick, *SHELXL-97*, Universitat Gottingen, Gottingen, 1997.
- [29] L.J. Farrugia, *J. Appl. Crystallogr.* 32 (1999) 837.
- [30] G.M. Sheldrick, *SHELXTL*, Bruker AXS Inc., 2001.