

Note

# Synthesis and structure of an indium(I) “crown sandwich”

Benjamin F.T. Cooper, Charles L.B. Macdonald \*

*Department of Chemistry and Biochemistry, University of Windsor, Windsor, Ontario, Canada N9B 3P4*

Received 28 September 2007; received in revised form 23 October 2007; accepted 24 October 2007

Available online 30 October 2007

This work is dedicated to the memory of F. Albert Cotton: A giant of Inorganic Chemistry.

## Abstract

The treatment of the soluble reagent indium(I) trifluoromethanesulfonate, InOTf, with the crown ether 15-crown-5 generates the salt  $[\text{In}(\text{15-crown-5})_2][\text{OTf}]$  regardless of the stoichiometry employed. The toluene-soluble salt has been characterized by single-crystal X-ray diffraction and features a cation that may be described as containing an  $\text{In}^{\text{I}}$  center that is “sandwiched” by the two crown ethers.

© 2007 Elsevier B.V. All rights reserved.

**Keywords:** Indium; Low oxidation state; Main group; Crown ether chemistry; Sandwich compounds

## 1. Introduction

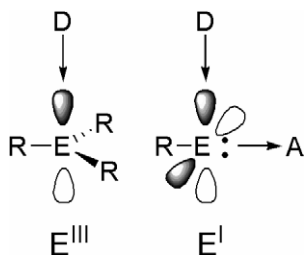
The idea of an element existing in a particular oxidation state (or, perhaps more appropriately, valence state) [1] is one of the most simple and ubiquitous models employed by chemists to explain the structural characteristics and chemical behavior of a molecule containing that element. An element in a lower oxidation state is, by definition, more electron-rich than it would be in a higher oxidation state and the presence of these additional electrons can alter dramatically the chemistry of compounds containing such centers [2,3]. For this reason, the investigation of main group elements in unusually low oxidation states has been a very active area of research since the 1990s. For example, for the group 13 elements other than thallium, the +3 oxidation state ( $\text{E}^{\text{III}}$ , E = B, Al, Ga, In) is the most stable which explains the Lewis-acidic behavior of the electron-deficient neutral molecules containing these elements. Conversely, the considerably less-common compounds that contain a group 13 element in the +1 oxidation state ( $\text{E}^{\text{I}}$ ) can behave either as Lewis bases or Lewis acids, as illustrated in Scheme 1. Because of the presence of the

“lone-pair” of electrons in  $\text{E}^{\text{I}}$  compounds, such reagents, especially cyclopentadienyl ( $\text{C}_5\text{R}_5$ , Cp') compounds of the type  $\text{Cp}'\text{E}^{\text{I}}$  [4] and, more recently, *N*-heterocyclic  $\text{E}^{\text{I}}$  compounds bearing ligands such as  $\alpha$ -dimimines, amidines, guanidines and  $\beta$ -diketimines [5], have been employed as donors for transition metal and main group acceptors to generate new types of catalysts or materials precursors [5–9]. It should be emphasized that  $\text{R}-\text{E}^{\text{I}}$  compounds most obviously exhibit acceptor behavior in situations where the substituent R is not a  $\pi$ -donor, which can partially populate the formally vacant orbitals on the  $\text{E}^{\text{I}}$  center [10]. In a similar vein, the  $\text{R}-\text{E}^{\text{I}}$  ligands in the numerous reported transition metal complexes can act as acceptors, for electrons from the transition metal center or from an external donor, when R is a hydrocarbyl group or a halogen [11–16].

For indium in particular, it is also worth noting that the unique behavior and redox properties of  $\text{In}^{\text{I}}$  compounds (sometimes generated *in situ*) render such species useful as either reagents or catalysts used to effect several types of organic transformations; such reactions almost always proceed through the formation of organoindium intermediates or by-products [17–24]. In a similar vein, inorganic and organometallic  $\text{In}^{\text{I}}$  reagents have been shown to insert into reactive carbon-element bonds to generate new  $\text{In}^{\text{III}}$  species [2,3].

\* Corresponding author. Fax: +1 5199737098.

E-mail address: [cmacd@uwindsor.ca](mailto:cmacd@uwindsor.ca) (C.L.B. Macdonald).



Scheme 1. Drawings depicting the differing behavior of compounds containing group 13 elements (E) in the +3 and +1 oxidation states with electron donors (D) or acceptors (A).

For indium, a major obstacle to research and development of the chemistry of +1 oxidation state has been the paucity of convenient starting materials [2,25]. For while the simple halide salts of both +1 and +3 oxidation states are commercially available, the  $\text{In}^{\text{I}}$  salts are either insoluble or decompose in most common organic solvents [2,25]. In this context, several research groups have pursued a protonolytic approach to sources of  $\text{In}(\text{I})$  with improved stabilities and/or solubilities [9]. In our laboratory, we have discovered two routes to the unusually soluble indium(I) trifluoromethanesulfonate salt (indium(I) triflate,  $\text{InOS-O}_2\text{CF}_3$ ,  $\text{InOTf}$ , **1**); the most effective synthesis of **1** involves the protonolysis of  $\text{Cp}^*\text{H}$  from the organometallic precursor  $\text{Cp}^*\text{In}$  [26]. As summarized in Scheme 2, this  $\text{In}^{\text{I}}$  reagent has already exhibited interesting and sometimes unique chemistry, including the formation of new In-carbon and In-element bonds [24,27–30].

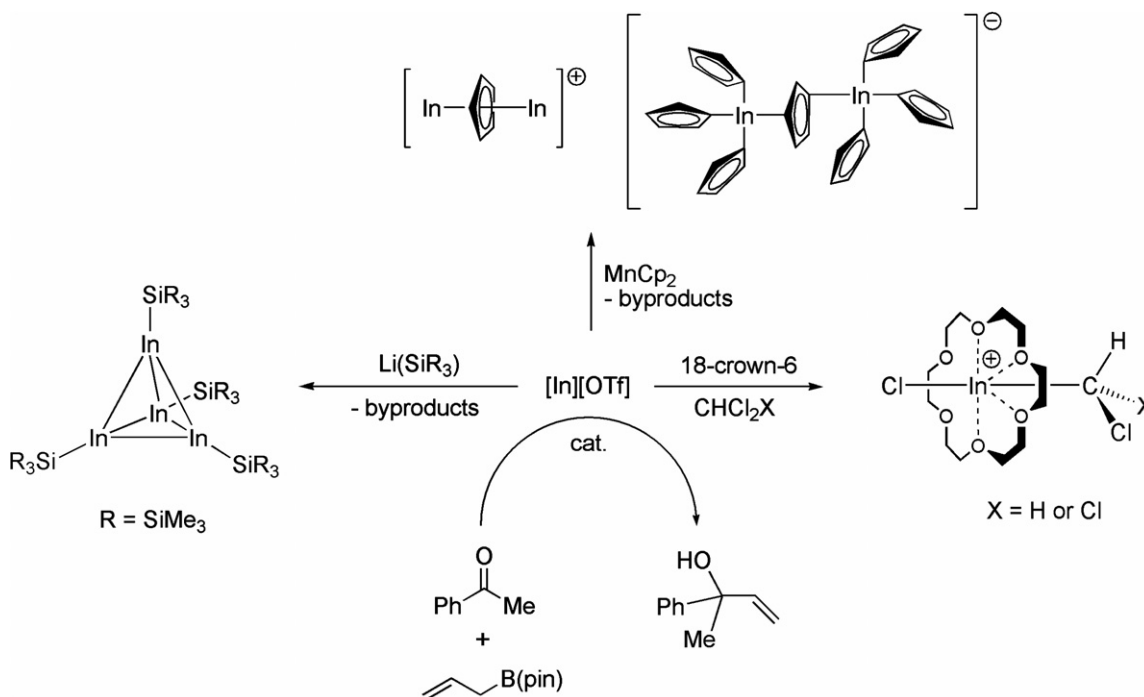
Of particular import to the work reported herein, we have previously reported that the ligation of **1** with cyclic

polyethers 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6) or 2,3,11,12-dibenzo-1,4,7,10,13,16-hexaoxacyclooctadecane (dibenzo-18-crown-6) generates unambiguously monomeric indium(I) compounds  $[\text{In}(\text{18-crown-6})][\text{OTf}]$  (**2a** $[\text{OTf}]$ ) and  $[\text{In}(\text{dibenzo-18-crown-6})][\text{OTf}]$  (**2b** $[\text{OTf}]$ ) [27]. In contrast to most other donors, the ligation of the  $\text{In}^{\text{I}}$  center by the crown ethers occurs without any evidence of disproportionation [31,32] and it also changes the reactivity of the  $\text{In}(\text{I})$  reagent dramatically [30]. In this note, we present the results of some of our investigations concerning the ligation of  $\text{InOTf}$  with the smaller crown ether 1,4,7,10,13-pentaoxacyclopentadecane (15-crown-5) that results in the formation of a new, and potentially more reactive,  $\text{In}^{\text{I}}$  reagent.

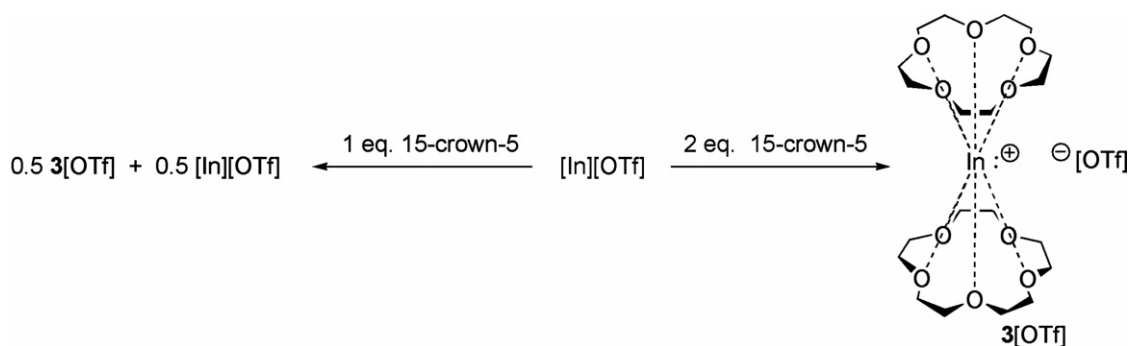
## 2. Results and discussion

Whereas the treatment of a toluene solution of the indium(+1) reagent  $\text{InOTf}$  with a solution containing an equimolar amount of the crown ether 18-crown-6 (or dibenzo-18-crown-6) results in the quantitative formation of the complexes **2a** $[\text{OTf}]$  (or **2b** $[\text{OTf}]$ ) [27], the corresponding reaction of **1** with 15-crown-5 did not form a similar 1:1 complex. Instead, the resultant solid was characterized using physical methods and X-ray crystallography as being composed of a 1:1 mixture of the starting material **1** and the new complex  $[\text{In}(\text{15-crown-5})_2][\text{OTf}]$ , **3** $[\text{OTf}]$  as illustrated in Scheme 3. Predictably, the production of **3** $[\text{OTf}]$  is quantitative when 2 equiv. of 15-crown-5 per indium atom are used in the preparation.

The salt **3** $[\text{OTf}]$  is very soluble in toluene and the slow concentration of a toluene solution of the material yields



Scheme 2. Some of the reported organometallic chemistry of  $\text{InOTf}$ .



Scheme 3.

colorless crystals suitable for examination by single-crystal X-ray diffraction experiments. Details of the data collection, solution and refinement of the crystal structure are listed in Table 1, the structures of the cation and anion are depicted in Fig. 1, and the values of selected metrical parameters are listed in the figure caption. The salt crystallizes in the centro-symmetric space group  $P\bar{1}$  with a total of one cation and anion in the unit cell. The indium atom

resides on an inversion center thus the  $[\text{In}(\text{15-crown-5})_2]$  cation complex is rendered perfectly centro-symmetric. The In–O distances in the cation range from 2.9802(19) to 3.0954(18) Å with an average of 3.031 Å; these values fall well within the sum of the van der Waals radii for In (1.93 Å) and O (1.52 Å) [33]. Finally, it must be noted that the triflate anion is disordered about one of the inversion centers (located roughly between the S and C atoms) and does not appear to have any unusually short contacts with the cation.

Interestingly, **3[OTf]** is the first compound reported containing a bond between indium and 15-crown-5 as confirmed by a search of the Cambridge Structural Database (CSD) [34] thus structural comparisons must be made to other, potentially related complexes. Given the superficially similar appearance of the structures of  $\text{In}^{\text{I}}$  ligated by 18-crown-6 and the corresponding potassium 18-crown-6 complexes, it is not surprising that the structure of the cation **3** is almost indistinguishable from the  $[\text{K}(\text{15-crown-5})_2]^+$  cations in the more than 30 salts containing such ions in the CSD. The average K–O distances in these cations is 2.906 Å, which is only marginally shorter than the average In–O distance found in **3** and thus emphasizes the similarity of the sizes of  $\text{K}^+$  and  $\text{In}^{\text{I}}$ .

Table 1

Summary of collection and refinement data for the X-ray diffraction investigation of **3[OTf]**

Compound	$[\text{In}(\text{15-cr-5})_2][\text{OTf}], \mathbf{3}[\text{OTf}]$
Empirical formula	$\text{C}_{21}\text{H}_{40}\text{F}_3\text{InO}_{13}\text{S}$
Formula weight	704.41
Temperature (K)	173(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
<i>Unit cell dimensions</i>	
<i>a</i> (Å)	8.7238(10)
<i>b</i> (Å)	9.0650(10)
<i>c</i> (Å)	9.4298(10)
$\alpha$ (°)	102.375(1)
$\beta$ (°)	91.359(1)
$\gamma$ (°)	97.681(1)
Volume (Å <sup>3</sup> )	720.80(14)
<i>Z</i>	1
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.623
Absorption coefficient (mm <sup>-1</sup> )	0.972
<i>F</i> (000)	362
$\theta$ Range for data collection (°)	2.32–27.49
Limiting indices	$-11 \leq h \leq 11, -11 \leq k \leq 11,$ $-12 \leq l \leq 12$
Reflections collected	7926
Independent reflections	3184
<i>R</i> <sub>int</sub>	0.0199
Data/restraints/parameters	3184/6/175
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )] <sup>a</sup>	<i>R</i> <sub>1</sub> = 0.0329, <i>wR</i> <sub>2</sub> = 0.0778
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0340, <i>wR</i> <sub>2</sub> = 0.0785
Goodness-of-fit ( <i>S</i> ) <sup>b</sup> on <i>F</i> <sup>2</sup>	1.128
Largest difference in peak and hole (e Å <sup>-3</sup> )	1.005 and -0.386

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

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

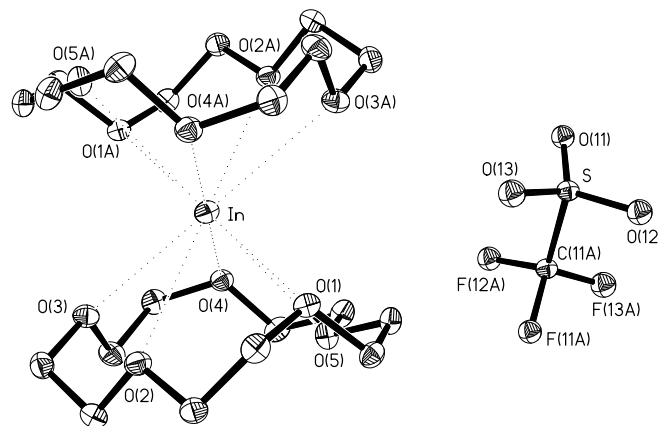
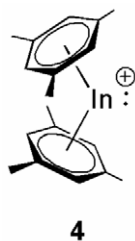


Fig. 1. Thermal ellipsoid plot (30% probability surface) of the molecular structure of the salt **3[OTf]**. Important bond distances (Å): In–O(1) 2.9819(18), In–O(2) 3.0954(18), In–O(3) 3.0103(19), In–O(4) 2.9802(19), In–O(5) 3.0857(19).

In a somewhat different vein, the “sandwich”-like appearance of  $[\text{In}(\text{15-crown-5})_2]^+$  is also reminiscent of the structures observed for certain organometallic arene complexes of  $\text{In}^{\text{I}}$  (and some other  $\text{E}^{\text{I}}$  cations) [35]. It should be noted, however, than in complexes such as Schmidbauer’s salt  $[\text{In}(\text{mesitylene})_2][\text{InBr}_4]$ , **4**  $[\text{InBr}_4]$ , the bent geometry of the cation is consistent with the presence of a stereochemically-active “lone pair” of electrons on the  $\text{In}^{\text{I}}$  center [36]. In contrast, the centro-symmetric nature of the cation **3** does not so obviously emphasize the presence of the two remaining valence electrons on the indium atom.



In conclusion, we have prepared the first coordination complex of indium with the crown ether 15-crown-5. Like the comparably-sized potassium cation,  $\text{In}^{\text{I}}$  is too large for the cavity of 15-crown-5 and is preferentially ligated by two crown ethers in a centro-symmetric “sandwich”-like manner. Given the interesting chemistry already demonstrated by the  $\text{InOTf}$  18-crown-6 derivatives [27,30], we intend to explore the chemistry of this new stable, soluble, monomeric  $\text{In}^{\text{I}}$  reagent.

### 3. Experimental

#### 3.1. General methods

All work was carried out using standard inert-atmosphere techniques. All reagents and solvents were obtained from Aldrich and were used without further purification. Preparative methods for **1** are described in a preliminary communication [26]. Solvents were dried on a series of Grubbs'-type columns and were degassed prior to use [37]. 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 ( $\text{SiMe}_4$  for  $^1\text{H}$  and  $^{13}\text{C}$ ;  $\text{CFCl}_3$  for  $^{19}\text{F}$ ). Melting points were obtained using an Electrothermal<sup>®</sup> melting point apparatus on samples sealed in glass capillaries under dry nitrogen.

#### 3.2. Synthesis of $3[\text{OTf}]$

A toluene (25 mL) 15-crown-5 (0.167 g, 0.758 mmol) solution was added to a toluene solution of  $\text{InOTf}$  (0.100 g, 0.379 mmol) in a 100 mL Schlenk flask and stirred overnight. After addition, an orange color was observed

initially, however, after completion of the reaction, all volatile components were removed under reduced pressure and the product was obtained as a white powder. (0.21 g, 78%) m.p. 104–107 °C;  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = 3.48$  (s;  $\text{CH}_2$ );  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta = 70.76$  (s;  $\text{CH}_2$ );  $^{19}\text{F}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta = -76.5$  (s). The powder X-ray diffraction pattern of the solid is consistent with  $3[\text{OTf}]$  being the only crystalline material present.

#### 3.3. Crystallography

The subject crystal was covered in Nujol<sup>®</sup>, mounted on a goniometer head and rapidly placed in the dry  $\text{N}_2$  cold-stream of the low-temperature apparatus (Kryoflex) attached to the diffractometer. The data were collected using the SMART [38] software on a Bruker APEX CCD diffractometer using a graphite monochromator with  $\text{Mo K}\alpha$  radiation ( $\lambda = 0.71073$  Å). A hemisphere of data were collected using a counting time of 10 s per frame at  $-100$  °C. Details of crystal data, data collection and structure refinement are listed in Table 1. Data reduction was performed using the SAINT-PLUS [39] software and the data were corrected for absorption using SADABS [40]. The structure was solved by direct methods using SIR97 [41] and refined by full-matrix least-squares on  $F^2$  with anisotropic displacement parameters for the non-disordered heavy atoms using SHELXL-97 [42] and the WINGX [43] software package and thermal ellipsoid plots were produced using SHELXTL [44]. The trifluoromethanesulfonate anion resides on a crystallographic inversion center and is disordered; the bond distances in the anion were restrained to be similar and appropriate thermal parameters in the anion were constrained to be equal in the solution.

Powder X-ray diffraction experiments were performed with a Bruker D8 Discover diffractometer equipped with a Hi-Star area detector using  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.54186$  Å).

#### Acknowledgements

The funding that has enabled this work has been provided by the Natural Sciences and Engineering Research Council of 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), and the Ontario Ministry of Research and Innovation (Early Researcher Award).

#### Appendix A. Supplementary material

CCDC 661703 contains 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](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2007.10.040](https://doi.org/10.1016/j.jorganchem.2007.10.040).

## References

- [1] G. Parkin, *J. Chem. Educ.* 83 (2006) 791.
- [2] D.G. Tuck, *Chem. Soc. Rev.* 22 (1993) 269.
- [3] C.L.B. Macdonald, B.D. Ellis, *Encyclopedia of Inorganic Chemistry*, in: R.B. King (Ed.), *Low Oxidation State Main Group Chemistry*, John Wiley & Sons Ltd, 2005.
- [4] P. Jutzi, N. Burford, *Chem. Rev.* 99 (1999) 969.
- [5] R.J. Baker, C. Jones, *Coord. Chem. Rev.* 249 (2005) 1857.
- [6] R.A. Fischer, J. Weiss, *Angew. Chem., Int. Ed.* 38 (1999) 2831.
- [7] G. Linti, H. Schnöckel, *Coord. Chem. Rev.* 206 (2000) 285.
- [8] C. Gemel, T. Steinke, M. Cokoja, A. Kemptner, R.A. Fischer, *Eur. J. Inorg. Chem.* (2004) 4161.
- [9] S. Aldridge, *Angew. Chem., Int. Ed.* 45 (2006) 8097.
- [10] C.L.B. Macdonald, A.H. Cowley, *J. Am. Chem. Soc.* 121 (1999) 12113, and references therein.
- [11] C. Boehme, J. Uddin, G. Frenking, *Coord. Chem. Rev.* 197 (2000) 249.
- [12] J. Uddin, G. Frenking, *J. Am. Chem. Soc.* 123 (2001) 1683, and references therein.
- [13] H. Behrens, M. Moll, E. Sixtus, G. Thiele, *Z. Naturforsch., B: Chem. Sci.* 32 (1977) 1109.
- [14] M.M. Schulte, E. Herdtweck, G. Raudaschl-Sieber, R.A. Fischer, *Angew. Chem., Int. Ed. Engl.* 35 (1996) 424.
- [15] G.N. Harakas, B.R. Whittlesey, *Inorg. Chem.* 36 (1997) 2704 (and references therein).
- [16] R.A. Fischer, M.M. Schulte, J. Weiss, L. Zsolnai, A. Jacobi, G. Huttner, G. Frenking, C. Boehme, S.F. Vyboishchikov, *J. Am. Chem. Soc.* 120 (1998) 1237.
- [17] P. Cintas, *Synlett* (1995) 1087.
- [18] C.J. Li, T.H. Chan, *Tetrahedron* 55 (1999) 11149.
- [19] B.C. Ranu, *Eur. J. Org. Chem.* (2000) 2347.
- [20] J. Podlech, T.C. Maier, *Synthesis* (2003) 633.
- [21] K.K. Chauhan, C.G. Frost, *J. Chem. Soc., Perkin Trans. 1* (2000) 3015.
- [22] V. Nair, S. Ros, C.N. Jayan, B.S. Pillai, *Tetrahedron* 61 (2005) 2725.
- [23] T.P. Loh, G.L. Chua, *Chem. Commun.* (2006) 2739.
- [24] U. Schneider, S. Kobayashi, *Angew. Chem., Int. Ed.* 46 (2007) 5909.
- [25] J.A.J. Pardoe, A.J. Downs, *Chem. Rev.* 107 (2007) 2.
- [26] C.L.B. Macdonald, A.M. Corrente, C.G. Andrews, A. Taylor, B.D. Ellis, *Chem. Commun.* (2004) 250.
- [27] C.G. Andrews, C.L.B. Macdonald, *Angew. Chem., Int. Ed.* 44 (2005) 7453.
- [28] C.G. Andrews, C.L.B. Macdonald, *J. Organomet. Chem.* 690 (2005) 5090.
- [29] M. Buhler, G. Linti, *Z. Anorg. Allg. Chem.* 632 (2006) 2453.
- [30] B.F.T. Cooper, C.G. Andrews, C.L.B. Macdonald, *J. Organomet. Chem.* 692 (2007) 2843.
- [31] R.J. Baker, H. Bettentrup, C. Jones, *Eur. J. Inorg. Chem.* (2003) 2446.
- [32] R.J. Baker, C. Jones, M. Kloth, D.P. Mills, *New J. Chem.* 28 (2004) 207.
- [33] <[www.webelements.com](http://www.webelements.com)>.
- [34] F.H. Allen, *Acta Crystallogr., Sect. B: Struct. Sci.* 58 (2002) 380.
- [35] H. Schmidbaur, *Angew. Chem., Int. Ed. Engl.* 24 (1985) 893.
- [36] J. Ebenhoch, G. Muller, J. Riede, H. Schmidbaur, *Angew. Chem., Int. Ed. Engl.* 23 (1984) 386.
- [37] A.B. Pangborn, M.A. Giardello, R.H. Grubbs, R.K. Rosen, F.J. Timmers, *Organometallics* 15 (1996) 1518.
- [38] SMART, Bruker AXS Inc.: Madison, WI, 2001.
- [39] SAINTPLUS, Bruker AXS Inc.: Madison, WI, 2001.
- [40] SADABS, Bruker AXS Inc.: Madison, WI, 2001.
- [41] A. Altomare, M.C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, M.A.G.G., G. Polidori, R. Spagna, SIR97, CNR-IRMEC: Bari, 1997.
- [42] G.M. Sheldrick, SHELXL-97, Universitat Gottingen, Gottingen, 1997.
- [43] L.J. Farrugia, *J. Appl. Crystallogr.* 32 (1999) 837.
- [44] G.M. Sheldrick, SHELXTL, Bruker AXS Inc., Madison, WI, 2001.