Organometallics **1999,** *18,* 793−795

Notes

(Phosphacyclopentadienyl)indium(I) Derivatives: Synthesis and X-ray Crystal Structure of $[\mathrm{In}(\eta^5\text{-}\mathrm{P_3C_2Bu^t_2})]$

Charlotte Callaghan, Guy K. B. Clentsmith, F. Geoffrey N. Cloke,*
Peter B. Hitchcock, John F. Nixon,* and David M. Vickers

*The Chemistry Laboratory, School of Chemistry, Physics and Environmental Sciences,
The University of Sussex, Falmer, Brighton, Sussex BN1 9QJ, U.K.*

Received October 26, 1998

Summary: Co-condensation of indium vapor and tert-butylphosphaethyne at 77 K yields two new, volatile In(I) complexes: $[\mathrm{In}(\eta^5\text{-}\mathrm{P_3C_2Bu^t_2})]$ *(**1**) and* $[\mathrm{In}(\eta^5\text{-}\mathrm{P_2C_3Bu^t_3})]$ *(**2**). A single-crystal X-ray diffraction experiment on **1** reveals a discrete molecular structure, involving half-sandwich coordination of the* $\mathrm{P_3C_2Bu^t_2}$ *ring around the indium center. **1** may be independently prepared by treating InI with the newly synthesized, base-free ligand salt* $\mathrm{K(P_3C_2Bu^t_2)}$*.*

Introduction

An early and now classic example of subvalent main-group-metal chemistry is the reaction of $\mathrm{InCl_3}$ with an excess of $\mathrm{NaC_5H_5}$ to give $[\mathrm{In}(\eta^5\text{-}\mathrm{C_5H_5})]$ upon sublimation.[1] For many years $[\mathrm{In}(\eta^5\text{-}\mathrm{C_5H_5})]$ remained the sole representative of this class of compounds,[2−8] and despite recent interest in subvalent main-group chemistry in which ligands other than cyclopentadienyl derivatives are utilized,[9−11] examples of In(I) complexes are less numerous compared to those of In(III) due to the propensity of the former to undergo disproportionation to the zerovalent metal and In(III).[12] The revival in low-valent indium chemistry and the appearance of further examples of In(I) and In(II) complexes in the literature is due in part to the potential of indium compounds to act as precursors for semiconducting films and devices.[13−19] Our success in the synthesis of unusual,[20−22] low-valent transition metal complexes by metal vapor synthesis (MVS) techniques provided the incentive to apply these methods to main-group metals. In this work we report the synthesis and structure of new, volatile, and thermally stable In(I) complexes, $[\mathrm{In}(\eta^5\text{-}\mathrm{P_3C_2Bu^t_2})]$ (**1**) and $[\mathrm{In}(\eta^5\text{-}\mathrm{P_2C_3Bu^t_3})]$ (**2**), by MVS techniques and the determination of the molecular structure of **1**. In addition we report the independent synthesis of **1** by more conventional means, utilizing the newly synthesized, base-free ligand salt $\mathrm{K(P_3C_2Bu^t_2)}$.

Results and Discussion

Co-condensation of indium vapor and $\mathrm{Bu^tC{\equiv}P}$ at 77 K afforded a deep brown matrix, which gave a brown oil after workup. The mass spectrum of this material gave signals at *m/z* 384 and 346, consistent with the formation of $\mathrm{In(P_2C_3Bu^t_3)^+}$ and $\mathrm{In(P_3C_2Bu^t_2)^+}$, respectively, along with the spectrum base peak at *m/z* 115, representing $\mathrm{In^+}$. Evidently the naked metal atoms in the matrix had cyclized $\mathrm{Bu^tC{\equiv}P}$ units to give both $\mathrm{(P_2C_3Bu^t_2)}$ and $\mathrm{(P_2C_3Bu^t_3)}$ rings.[23] Sublimation of the MVS product yielded a yellow powder which gave the same mass spectrum, and the more soluble component, $[\mathrm{In(P_2C_3Bu^t_3)}]$ (**2**), could be removed by recrystallization of

---

[1] Fischer, E. O.; Hofmann, H. P. *Angew. Chem.* **1957**, *69*, 639.

[2] See, A.; Schumann, H.; Ghodsi, T.; Esser, L. *Acta Crystallogr., Sect. C* **1992**, *C48*, 618.

[3] Schumann, H.; Kucht, H.; Kucht, A.; Görlitz, F. H.; Dietrich, A. Z. *Z. Naturforsch.* **1992**, *47B*, 1241.

[4] Beachley, T. O., Jr.; Lees, J. F.; Rogers, R. D. *J. Organomet. Chem.* **1991**, *418*, 165.

[5] Beachley, T. O., Jr.; Lees, J. F.; Glassman, T. E.; Churchill, M. R.; Buttrey, L. A. *Organometallics* **1990**, *9*, 2488.

[6] Beachley, T. O., Jr.; Blom, R.; Churchill, M. R.; Faegri, K. J.; Fettinger, J. C.; Pazik, J. C.; Victoriano, L. *Organometallics* **1989**, *8*, 346.

[7] See, A.; Schumann, H.; Janiak, C.; Görlitz, F.; Loebel, J.; Dietrich, A. *J. Organomet. Chem.* **1989**, *363*, 243.

[8] Beachley, T. O., Jr.; Pazik, J. C.; Glassman, T. E.; Churchill, M. R.; Fettinger, J. C.; Blom, R. *Organometallics* **1988**, *7*, 1051.

[9] Haubrich, S. T.; Power, P. P. *J. Am. Chem. Soc.* **1998**, *120*, 2202.

[10] Kuchta, M. C.; Dias, H. V. R.; Bott, S. G.; Parkin, G. *Inorg. Chem.* **1996**, *35*, 943.

[11] Frazer, A.; Piggot, B.; Hursthouse, M. B.; Mazid, M. *J. Am. Chem. Soc.* **1994**, *116*, 4127.

[12] Tuck, D. G. *Chem. Soc. Rev.* **1993**, *22*, 269 and references therein.

[13] Fischer, R. A.; Schulte, M. M.; Herdtweck, E.; Mattner, M. R. *Inorg. Chem.* **1997**, *36*, 2010.

[14] Olazábal, C. A.; Gabbaï, F. P.; Cowley, A. H.; Carrano, C. J.; Mokry, L. M.; Bond, M. R. *Organometallics* **1994**, *13*, 421.

[15] Fischer, R. A.; Herdtweck, E.; Priermeier, T. *Inorg. Chem.* **1994**, *33*, 934.

[16] Fischer, R.; Scherer, W.; Kleine, M. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 748.

[17] Fischer, R. A.; Behm, J.; Priermeier, T.; Scherer, W. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 746.

[18] Chen, Y.-J.; Kaesz, H. D.; Kim, Y. K.; Müller, H.-J.; Williams, R. S.; Xue, Z. *Appl. Phys. Lett.* **1989**, *55*, 2760.

[19] Boocock, S. K.; Shore, S. G. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1982; Vol. 6, p 947.

[20] Arnold, P. L.; Cloke, F. G. N.; Nixon, J. F. *Chem. Commun.* **1998**, 797.

[21] Arnold, P. L.; Cloke, F. G. N.; Hitchcock, P. B.; Nixon, J. F. *J. Am. Chem. Soc.* **1996**, *118*, 7630.

[22] Cloke, F. G. N. *Chem. Soc. Rev.* **1993**, *22*, 17 and references therein.

[23] Nixon, J. F. *Chem. Soc. Rev.* **1998**, *27*, 319.

10.1021/om980877v CCC: $18.00

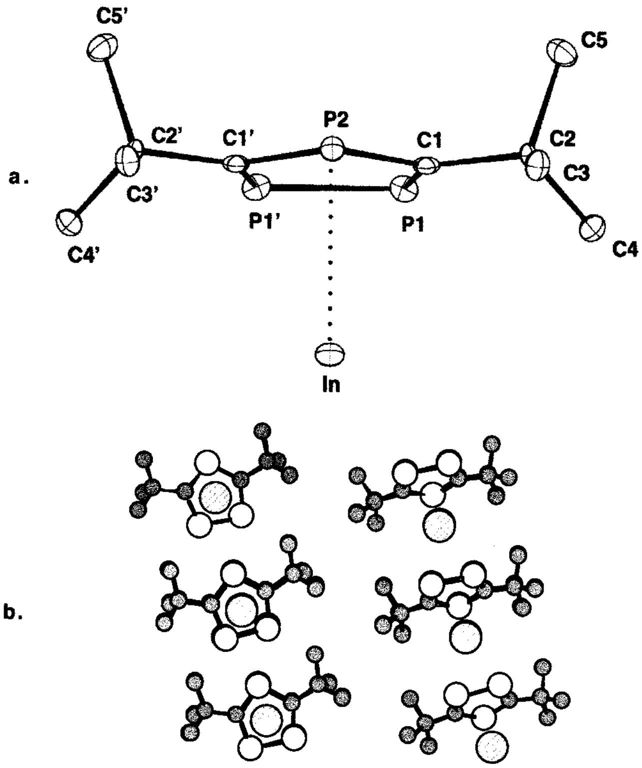
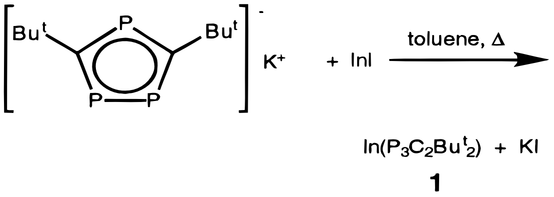


Figure 1. (a) ORTEP view of, and numbering scheme for, $[In(\eta^5\text{-}P_3C_2Bu^t_2)]$ (**1**). (b) Chem 3D view of the crystal packing of **1**.

the sublimate from toluene or petroleum ether to give pure $[In(P_3C_2Bu^t_2)]$ (**1**), identified by means of ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. **1** could be synthesized in near-quantitative yield by heating InI and the base-free ligand salt $K(P_3C_2Bu^t_2)$ in refluxing toluene for 24 h (eq 1). The $^{31}P\{^1H\}$ NMR spectrum of **1** in d_6-benzene



[1]

reveals the typical AB_2 pattern associated with an η^5-ligated, 1,2,4-substituted P_3C_2 ring (a triplet at 259.5 ppm and a doublet at 255.9 ppm, $J_{P-P'} = 50.9$ Hz) or a fluxional η^1 complex undergoing fast 1,2-shifts. The appearance of the $^{13}C\{^1H\}$ NMR spectrum is rather more complicated, since each carbon nucleus couples to sets of one chemically and two magnetically different phosphorus nuclei. Multiplets are observed at 221.4, 41.6, and 37.6 ppm, arising from the ring, quaternary, and methyl carbon nuclei, respectively. Spectral simulation allows extraction of the carbon−phosphorus coupling constants associated with the AM[X]$_2$ spin systems (Table 1).

As expected, the ^1H NMR spectrum of **1** consists of a singlet at 1.37 ppm due to the *tert*-butyl protons. The more soluble indium derivative **2**, presumably the 1,3-diphosphacyclopentadienyl complex $[In(\eta^5\text{-}P_2C_3Bu^t_3)]$, which is recovered from the supernatant of crystalline **1**, could not be isolated as a pure material but was characterized by a singlet in its $^{31}P\{^1H\}$ NMR spectrum at 183.2 ppm, and its ^1H NMR spectrum revealed the expected signals in a 2:1 ratio at 1.52 and 1.36 ppm arising from the chemically different *tert*-butyl groups.

Table 1. $^{13}C\{^1H\}$ NMR Spectroscopic Data for $[In(\eta^5\text{-}P_3C_2Bu^t_2)]$ (1) in d_6-Benzene at 75.1 MHz

nucleus	chem shift/ppm	$J_{C-P(M)}$/Hz	$J_{C-P(X)} + J_{C-P(X')}$/Hz
C(ring)	221.4	9.5	9.7
C(CH$_3$)$_3$	41.6	20.4	12.8
*C*H$_3$	37.6	67.1	92.1

Table 2. Bond Lengths (Å) and Bond Angles (deg) Observed in $[In(\eta^5\text{-}P_3C_2Bu^t_2)]$ (1)

In−P1	3.035(3)	In−P2	3.108(4)
In−C1	2.981(9)	In−centroid	2.598(9)
P1−C1	1.748(10)	P2−C1	1.781(10)
P1−P1′	2.111(5)		
C1−P1−P1′	100.2(3)	P1−C1−P2	119.8(6)
C2−C1−P1	119.8(6)	C1−P2−C1′	100.0(7)

Single crystals of **1** suitable for an X-ray diffraction experiment were grown from hexanes, and the solid-state structure is shown in Figure 1. Relevant bond distances and angles are listed in Table 2. The $P_3C_2Bu^t_2$ ring is η^5-ligated to the metal, and the $In(P_3C_2Bu^t_2)$ units lie on a crystallographic mirror plane and are linked into chains by weak interactions between the indium centers and alternate $P_3C_2Bu^t_2$ rings. The structure confirms the half-sandwich coordination of the ring around the indium center, and the In−centroid distance is 2.598 Å, which is comparable to metal to ring-centroid distances of cyclopentadienyl complexes of In(I), which range from 2.726 Å (for $[In(\eta^5\text{-}C_5H_5)]$)[24] to 2.53 Å (for $[In(\eta^5\text{-}C_5H_4SiMe_3)]$).[5] However, when intermonomer distance is considered (i.e. the distance between an indium atom and the alternate ligand along the chain), the distance of 3.526 Å observed for **1** is exceptionally long in comparison with the $[In(\eta^5\text{-}C_5H_4R)]$ systems, for which intermonomer distances lie within 0.2 Å of intramolecular indium ring-centroid bond lengths.[4] In addition, the closest In−In contacts of **1** are greater than 6.1 Å, which are comparable to those observed in $[In(pz)_3BH]$ (pz = 3,5-di-*tert*-butylpyrazolyl)[10] and $[In(C_6H_3\text{-}2,6\text{-}Trip_2)]$ (Trip = C_6H_2-2,4,6-Pr^i_3).[9] Evidently the increased steric protection offered by the larger heterocycle and the *tert*-butyl groups is sufficent to diminish aggregation entirely, in contrast to the trend set by the $[In(\eta^5\text{-}C_5H_4R)]$ series in which the tendency to form zigzag polymeric chains is marked; likewise, when more sterically demanding cyclopentadienyl derivatives are employed, aggregation is again observed (cf. the dimeric $[In(\eta^5\text{-}C_5(CH_2Ph)_5)]_2$ and the hexameric $[In(\eta^5\text{-}C_5Me_5)]_6$). As is observed with the tris(pyrazolyl)borate complexes of In(I),[10,11] the solid-state structure of **1** consists of clearly discrete $InP_3C_2Bu^t_2$ units.

While the metal center of **1** is expected to be a Lewis base, its reactivity is unremarkable. No evidence for adduct formation was obtained by NMR spectroscopy when solutions of **1** were treated with Lewis acids such as $[Pt(PPh_3)_2Cl_2]_2(\mu\text{-}Cl)_2$ and $[V(\eta^5\text{-}C_5H_5)_2]$. Attempts to oxidize the indium center by addition of iodine led to decomposition. The solubility of **1** tends to suggest a monomer in solution, in agreement with the solid-state

---

(24) Frasson, E.; Menegus, F.; Panattoni, C. *Nature* **1963**, *199*, 1087.

data, and if this is the case, the poor ability of the In center as a Lewis base more likely represents an electronic effect rather than a steric one. In(I) complexes, such as $[\mathrm{In(pz)_3BH}]$[10,25] or $[\mathrm{In(C_6H_3\text{-}2,6\text{-}Trip_2)}]$,[9] contain similarly bulky steric groups but are nevertheless quite potent Lewis bases. It is suggested that the reduced donor ability of the In center of **1** is related to the electronic properties of the $\mathrm{P_3C_2Bu^t{}_2}$ ring, which is overall more electron-withdrawing than the cyclopentadienyl systems.[26]

Conclusions

In this work is presented a well-characterized example of an In(I) complex. Further work, including the extension of this chemistry to gallium and aluminum and an appraisal of **1** as a precursor for the deposition of semiconducting indium phosphide films, is underway.

Experimental Section

General procedures are detailed elsewhere.[22,27] Indium metal and InI (99.999% purity) were supplied by Aldrich. $\mathrm{P(SiMe_3)_3}$, $\mathrm{Bu^tC(OSiMe_3){=}PSiMe_3}$, and $\mathrm{Bu^tC{\equiv}P}$ were synthesized according to literature procedures.[28,29] Solutions of potassium menthoxide (approximately 0.50 mol $\mathrm{L^{-1}}$) in heptane were prepared by treating menthol (Aldrich) in heptane with excess potassium metal (BDH) and heating the mixture to reflux for 24 h, followed by filtration and dilution to a 0.52 mol $\mathrm{L^{-1}}$ titer. $\mathrm{Bu^nLi}$ (Acros) was used as supplied as a 2.5 mol $\mathrm{L^{-1}}$ solution in hexane. Unless otherwise stated, all procedures were carried out under dry dinitrogen or argon. Microanalyses were performed by Mikroanalytisches Labor Pascher.

$[\mathrm{In}(\eta^5\text{-}\mathrm{P_3C_2Bu^t{}_2})]$ (1) and $[\mathrm{In}(\eta^5\text{-}\mathrm{P_2C_3Bu^t{}_3})]$ (2). Cocondensation at 77 K of indium vapor (1.67 g, 14.5 mmol) from a resistively heated alumina crucible with an excess of $\mathrm{Bu^tC{\equiv}P}$ (20 g, 0.20 mol) over 1.5 h resulted in the formation of a deep brown matrix, which was warmed to room temperature under vacuum. The apparatus was then opened to an external trapping system, and unreacted $\mathrm{Bu^tC{\equiv}P}$ (12 g) was collected in an external trap at 77 K. After 4 h the reaction vessel was refilled with dinitrogen and the matrix washed into a Schlenk receiver with hexanes (2 L). This mixture was then filtered through a flame-dried bed of Celite to remove colloidal metal to give a clear dark solution from which the solvent was removed in vacuo. The resultant oil was sublimed onto a liquid-nitrogen cold finger (10^{-3} mBar, 80 °C) to give a yellow oil (40 mg). Extraction of the yellow oil into toluene (2 mL) and cooling to −50 °C yielded pale yellow crystals of **1** (20 mg). ^{1}H NMR (d_6-benzene): δ 1.49 (s, CH_3C). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (d_6-benzene): δ 259.5.(t, 1P, $J_{\mathrm{P-P'}} = 50.8$ Hz), 255.5 (d, 2P, $J_{\mathrm{P-P'}} = 50.8$ Hz). MS (70 eV) (%): m/z 346 (40, $\mathrm{M^+}$), 331 (10, $\mathrm{M^+ - CH_3}$), 231 (10, $\mathrm{M^+ - In}$), 115 (100, $\mathrm{In^+}$). Anal. Calcd for $\mathrm{C_{10}H_{18}InP_3}$: C, 34.71; H, 5.24. Found: C, 34.65; H, 5.18.

2 could be obtained as a pale yellow powder by removing the solvent from the supernatant solution of crystalline **1** (5 mg). ^{1}H NMR (d_6-benzene): δ 1.52 (t, 18H, $^4J_{\mathrm{H-P}} = 1$ Hz, Bu^t), 1.36 (t, 9H, $^4J_{\mathrm{H-P}} = 1$ Hz, Bu'^t). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR: δ 183.2 (s). MS (70 eV) (%): m/z 384 (42%, $\mathrm{M^+}$), 246 (15%, $\mathrm{M^+ - Me_3CC{\equiv}CCMe_3}$), 115 (100, $\mathrm{In^+}$). Analysis was not obtained.

1 could also be synthesized by heating finely ground InI (0.38 g, 1.57 mmol) and $\mathrm{K(P_3C_2Bu^t{}_2)}$ (0.48 g, 1.57 mmol) in toluene (30 mL) at reflux for 24 h. Removal of the solvent and sublimation of the residue gave pure **2** as a pale yellow powder (0.36 g, 92.3%).

$\mathrm{K(P_3C_2Bu^t{}_2)}$. $\mathrm{Bu^nLi}$ (21.3 mL, 0.053 mol) was added to $\mathrm{P(SiMe_3)_3}$ (13.3 g, 0.053 mol) in $\mathrm{Et_2O}$ (100 mL) at 0 °C. Potassium menthoxide in heptane (105 mL, 0.055 mol) was added directly, and the mixture was stirred for 12 h, at the end of which time a caramel color had developed. This solution was then added to $\mathrm{Bu^tC(OSiMe_3){=}PSiMe_3}$ (27.89 g, 0.106 mol) in toluene (40 mL) at 0 °C in an ampule. The ampule was evacuated and heated to 50 °C for 48 h, during which time an orange solid precipitated and the solution became dark red. The orange solid was collected on a frit, washed with toluene (3 × 10 mL volumes), and dried under vacuum to give $\mathrm{K(P_3C_2Bu^t{}_2)}$ as a light beige powder (4.82 g, 33.6%). A second crop of product could be obtained by heating the combined filtrate and toluene washings to 50 °C for a further 36 h (1.89 g, 13.1%). ^{1}H NMR (d_5-pyridine): δ 2.05 (s, Bu^t). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (d_5-pyridine): δ 252.8 (t, 1P, $J_{\mathrm{P-P'}} = 48.7$ Hz), 244.8 (d, 2P, $J_{\mathrm{P-P'}} = 48.7$ Hz). Anal. Calcd for $\mathrm{C_{10}H_{18}KP_3}$: C, 44.44; H, 6.71. Found: C, 44.05; H, 6.76.

Acknowledgment. The advice and assistance of Dr. Tony Avent is acknowledged for the NMR spectra and simulations. Also thanked is Dr. Ali Abdul-Sada for acquiring the mass spectra. Financial assistance was obtained from the EPSRC in the form of a scholarship to D.M.V. and a fellowship to G.K.B.C.

Supporting Information Available: Tables of crystal data, atomic coordinates, bond lengths, and bond angles for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM980877V

---

(25) Kuchta, M. C.; Parkin, G. *Main Group Chem.* **1996**, *1*, 291.

(26) Bartsch, R.; Datsenko, S.; Ignatiev, N. V.; Müller, C.; Nixon, J. F.; Pickett, C. J. *J. Organomet. Chem.* **1997**, *529*, 375.

(27) Cloke, F. G. N.; Hitchcock, P. B.; Love, J. B. *J. Chem. Soc., Dalton Trans.* **1995**, 25.

(28) Becker, G.; Schmidt, H.; Uhl, G.; Uhl, W. *Inorg. Synth.* **1990**, *27*, 243.

(29) Becker, G. *Z. Anorg. Allg. Chem.* **1977**, *430*, 66.