Synthesis and structural characterisation of the 3,5-di-*tert*-butyl-1,2,4-triphospholyl complexes of monovalent gallium and thallium, $[M(\eta^5\text{-}P_3C_2Bu_2^t)]$, M = Ga, Tl

Matthew D. Francis [a], Peter B. Hitchcock [a], John F. Nixon [a],*,
Hansgeorg Schnöckel [b],*, Jochen Steiner [b]

[a] *School of Chemistry, Physics and Environmental Science, University of Sussex, Brighton, Sussex BN1 9QJ, UK*
[b] *Institut für Anorganische Chemie der Universität Karlsruhe, Engesserstraße, Geb. 30.45, D-76128 Karlsruhe, Germany*

Dedicated to Professor François Mathey on the occasion his 60th birthday

Abstract

Treatment of a metastable toluene–THF solution of GaBr with $KP_3C_2Bu_2^t$ led to the monomeric triphospholyl gallium(I) complex $[Ga(\eta^5\text{-}P_3C_2Bu_2^t)]$ (**3**). The corresponding thallium complex $[Tl(\eta^5\text{-}P_3C_2Bu_2^t)]$ (**4**) was prepared in a similar manner by treatment of TlCl with $[Li(tmeda)_2][(P_3C_2Bu_2^t)]$. Both complexes, which are monomeric in solution and in the gas phase, were characterised by mass spectrometry and multinuclear NMR spectroscopy. X-ray structure analyses of both complexes showed them to consist of weakly interacting monomeric half sandwich units in the solid state. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

In recent years there has been much interest in the use of cyclopentadienyl ligands as a method of stabilising the heavier Group 13 elements (Al, Ga, In, Tl) in low oxidation states. Despite this attention, complexes derived from hetero-cyclopentadienyl rings remain rare. Of the known examples, most have been derived from Group 15 substituted cyclopentadienyls such as phospholyl, polyphospholyl and phosphastibolyl anions e.g. $[Ga(\eta^5\text{-}PC_4Bu_2^tH_2)]$ [1] and $[\{Tl(\eta^5\text{-}P_2SbC_2Bu_2^t)\}_\infty]$ [2]. In addition, Rheingold and co-workers [3] have described the unusual indium(III) ate complex $[In(\eta^1\text{-}PC_4Me_4)_2(\mu\text{-}Cl)_2K(18\text{-}crown\text{-}6)]$ from the reaction between InCl and $[K(8\text{-}crown\text{-}6)][PC_4Me_4]$, thought to

be formed from a ligand induced disproportionation of the intermediate half sandwich complex $[In(\eta^5\text{-}PC_4Me_4)]$.

We recently addressed the paucity of examples of compounds of this type with the synthesis and characterisation of $[In(\eta^5\text{-}P_3C_2Bu_2^t)]$ (**1**) [4], which could be synthesised directly from the potassium salt of the triphospholyl anion $P_3C_2Bu_2^t$ **2** and InI or by the co-condensation of indium vapour [5] with the phosphaalkyne P≡CBu^t. Moreover, we have recently shown that **1** is an excellent precursor to crystalline indium phosphide under remarkably mild conditions [6]. On account of the success of this work, we have now extended our study of the use of **2** as a ligand towards Group 13 elements with the synthesis of $[Ga(\eta^5\text{-}P_3C_2Bu_2^t)]$ (**3**) and $[Tl(\eta^5\text{-}P_3C_2Bu_2^t)]$ (**4**). Further motivation has been derived from the potential of **3** as a precursor to gallium phosphide and because of the interest in organometallic chemistry of monovalent Group 13 elements in general.

* Corresponding authors. Fax: + 44-1273-677196 (J.F.N.).
E-mail address: j.nixon@sussex.ac.uk (J.F. Nixon).

2. Results and discussion

Treatment of a metastable toluene–THF solution of GaBr [7] with [K][2] led quantitatively to the gallium triphospholyl complex $[Ga(\eta^5-P_3C_2Bu_2^t)]$ (3) after extraction with pentane and crystallisation. Interestingly, and in contrast, the analogous thallium complex $[Tl(\eta^5-P_3C_2Bu_2^t)]$ (4) could not be prepared from an appropriate thallium(I) halide and [K][2]. All such attempts led to the production of an insoluble grey precipitate of thallium metal and a mixture of neutral organo-phosphorous cage materials. This problem was overcome by using instead, the lithium salt of 2 as its tmeda adduct, $[Li(tmeda)_2][2]$ (Scheme 1). Complex 4 has been previously described in the Sussex laboratory some time ago but was only identified spectroscopically and by its ability to act as a triphospholyl ring transfer agent in the formation of a number of transition metal com-
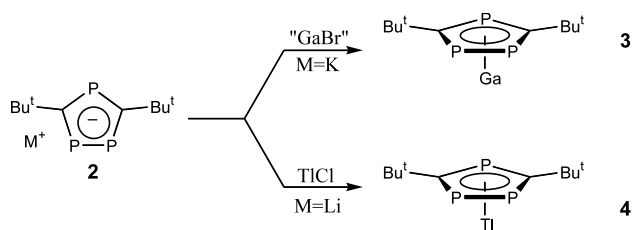
Scheme 1. Reaction scheme for the synthesis of 3 and 4.

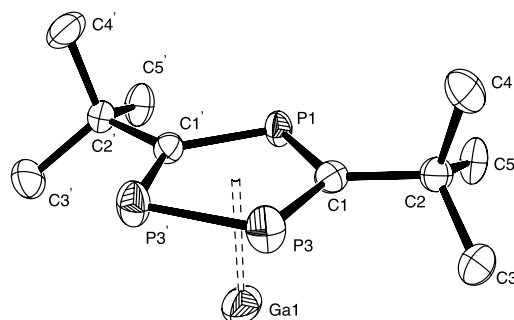Fig. 1. ORTEP diagram of the molecular structure of 3.

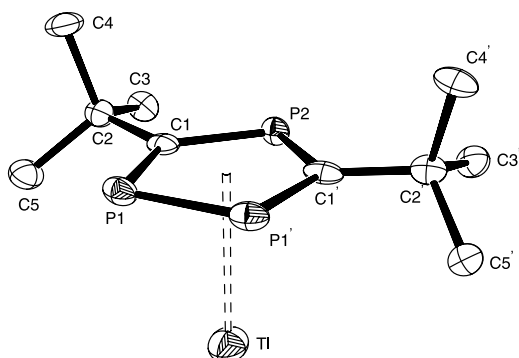Fig. 2. ORTEP diagram of the molecular structure of 4.

plexes including *trans*-$[PtCl(\eta^1-P_3C_2Bu_2^t)(PEt_3)_2]$ [8]. Both 3 and 4 were characterised by multinuclear NMR and mass spectroscopy. In addition, their solid state structures were determined by single crystal X-ray diffraction studies.

The $^{31}P\{^1H\}$-NMR spectra of 3 and 4 are similar and not significantly different from that of the parent potassium complex. Both show a characteristic AB_2 spin system at 262.5 and 259.2 ppm for 3 ($^2J_{PP} = 51.7$ Hz) and 262.9 and 254.5 ppm for 4 ($^2J_{PP} = 49.4$ Hz) (c.f. 252.8 and 244.8 ppm, $^2J_{PP} = 48.7$ Hz in [K][2]) [4]. This observation, which is also true for 1 and $[Ga(\eta^5-PC_4H_2Bu_2^t)]$ [9], contrasts with the general and significant upfield shift usually observed upon coordination of phospholyl anions to transition metals, e.g. in $[Ru(\eta^5-P_3C_2Bu_2^t)_2]$ ($[AB_2]_2$ multiplet centred at 65 ppm) [10]. This may indicate a significant degree of ionic character in the bonding between the metal and triphospholyl rings in 3 and 4. This possibility is supported for 4 by the fact that satellites resulting from coupling to $^{(203)205}Tl$ are not observed either in the $^{31}P\{^1H\}$- or ^1H-NMR spectra of 4. The absence of thallium couplings as an indication of the ionic nature of the bonding in cyclopentadienyl thallium complexes has been previously described [11] and only when the bonding becomes significantly covalent as a consequence of the presence of electron donating groups on the cyclopentadienyl ring such as $SiMe_3$, do $^{(203)205}Tl$ couplings become evident [12]. The ^{71}Ga chemical shift of 3 at -619.4 ppm ($W_{1/2} \approx 1910$ Hz) is somewhat lower than those seen in other cyclopentadienyl gallium(I), compounds e.g. -653 ppm in $[Ga(\eta^5-C_5Me_5)]$ and -714 ppm in $[Ga(\eta^5-C_5H_5)]$ [13]. The ^1H-NMR spectra of 3 and 4 are as expected, each showing one peak corresponding to the two equivalent Bu^t groups. Both 3 and 4 show strong molecular ions in their EI mass spectra, indicating that the compounds exist essentially as monomers in the gas phase.

The structures of 3 and 4 in the solid state were subsequently determined by single crystal X-ray diffraction studies. Figs. 1 and 2 show the individual half sandwich units of 3 and 4, respectively while Fig. 3 shows the packing of molecules of 3 into chains in the crystalline state (the packing of 4 is analogous).

In both cases, the triphospholyl ring is η^5 bound to the metal and the individual monomeric units are linked into almost linear chains by weak interactions between the metal centre and alternate rings. This arrangement is different from that seen in $[Ga(\eta^5-PC_4Bu_2^tH_2)]$ which forms zig-zag chains of gallium atoms flanked by alternate phospholyl rings on either side of the chain [1]. The gallium-ring centroid distance in 3 of 2.261 Å is marginally longer than that of 2.142 Å in $[Ga(\eta^5-PC_4Bu_2^tH_2)]$ [1] and is significantly longer that of 2.081 Å in $[\{Ga(\eta^5-C_5Me_5)\}_\infty]$ [14]. In fact, 3 is only the third structurally characterised compound of a
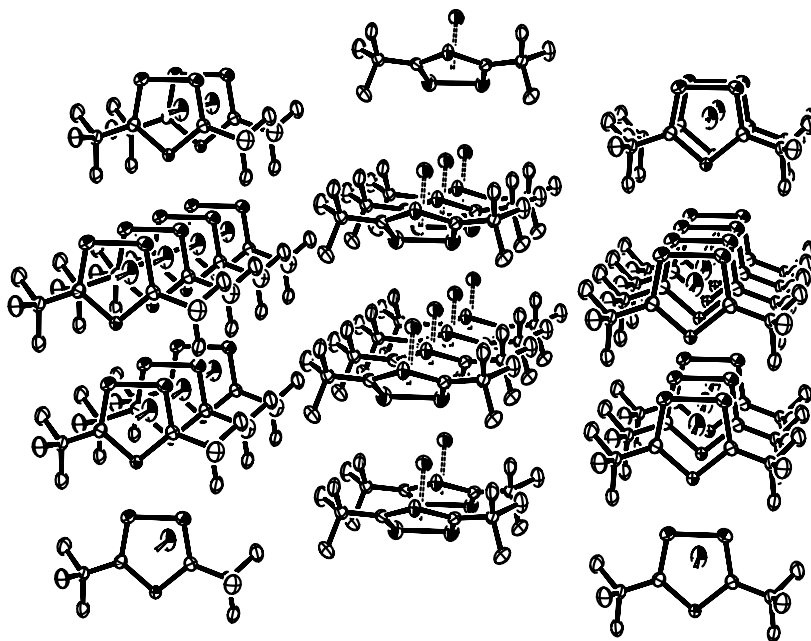
Fig. 3. Diagram of the packing of molecules of **3** in the crystal lattice.

cyclopentadienyl ring bound to gallium(I) without further coordination to a transition metal and so data for further comparison are lacking. This distance between the gallium and the centroid of the adjacent ring is 3.931 Å. The molecules are linked into chains which are almost linear, the centroid–Ga–centroid and Ga–centroid–Ga angles both being 179°. The structure of **4** is similar to that of **3**. The thallium–centroid distance to the bonded ring is 2.85 Å whilst the distance of the thallium to the centroid of the adjacent half sandwich unit is markedly longer at 3.22 Å. In addition, the centroid–Tl–centroid and Tl–centroid–Tl angles are 171°. Although the Tl–centroid distance is comparable with that seen in related systems, both these features are unusual for cyclopentadienyl thallium compounds which usually link together into chains of alternating, almost equally spaced, thallium and ring moieties which are bent at the thallium centre. In [{Tl(η^5-C$_5$Me$_5$)}$_\infty$] [15] the thallium–centroid distances range between 2.91 and 2.99 Å, while the centroid–Tl–centroid angles are 148.2 and 142.8°. Similarly, in the only other homoleptic hetero-cyclopentadienyl thallium complex [{Tl(η^5-P$_2$SbC$_4$Bu$_2^t$)}$_\infty$] [2], the metal–centroid distances lie between 2.835 and 2.935 Å whilst the centroid–Tl–centroid angles are 158.2 and 154.7°. Interestingly, the distance between monomeric units decreases steadily from 3.931 Å in **3** to 3.526 Å in [In(η^5-P$_3$C$_2$Bu$_2^t$)] (**1**) to 3.22 Å in **4**. This trend is paralleled by the observed solubility for the compounds. Whereas, **3** is readily soluble in pentane, **1** is only appreciably soluble in toluene or donor solvents and **4** is soluble only in hot toluene or donor solvents such as dme or pyridine.

3. Experimental

3.1. General procedures

All procedures were carried out with the rigorous exclusion of air and moisture using Schlenk techniques or in an MBraun MB 150B/G or MB 120B/G glove box under an atmosphere of high purity Ar or N$_2$. Toluene, tetrahydrofuran (THF), 1,2-dimethoxyethane (dme) and pentane were dried by refluxing over Na–K alloy or LiAlH$_4$ and were distilled and degassed before use. NMR spectra were recorded in C$_6$D$_6$ or C$_5$D$_5$N on the following instruments: ^{1}H and ^{13}C, Bruker AC-250 or AMX-500 spectrometer; ^{31}P{^{1}H}; Bruker AMX-300 or DPX-300 spectrometer; ^{71}Ga, Bruker AMX-300. Resonances were referenced to the residual ^{1}H resonances of the solvent, the ^{13}C resonances of the deuterated solvent, to external 85% H$_3$PO$_4$ ($\delta = 0.0$, ^{31}P-NMR) or 1.3 M Ga(NO$_3$)$_3$ in D$_2$O ($\delta = 0.0$, ^{71}Ga-NMR). EI mass spectra were recorded on a VG Autospec or Finnigan MS-8230 instrument at 70 eV. Microanalyses were performed by Labor Pascher, Remagen, Germany. TlCl was purchased from Aldrich and used as received. Solutions of metastable GaBr were produced by co-condensation of the high temperature molecule GaBr with THF and toluene (1:3 ratio) at -196 °C and 'trapped' in a flask at -78 °C as previously described [7]. KP$_3$C$_2$Bu$_2^t$ was synthesised by the literature procedure [4] and [Li(tmeda)$_2$][P$_3$C$_2$Bu$_2^t$] by an unpublished modification of this procedure.

3.2. Syntheses

3.2.1. [Ga(η^5-P$_3$C$_2$Bu$^t_2$)] (3)

[K][**2**] (0.4 g, 1.48 mmol) was dissolved in a mixture of toluene (1 ml) and THF (6 ml). The solution was cooled to -78 °C, whereupon a solution of GaBr was added with stirring (6 ml, 0.35 mmol ml^{-1}, 2 mmol). The resulting mixture was stirred at -78 °C for 2 h and was then gradually warmed to room temperature (r.t.) and stirred for a further 18 h. Volatiles were then removed in vacuo and the residue extracted with pentane and filtered to give an orange brown solution. Removal of the solvent afforded **3** as a brown–yellow oil in essentially quantitative yield. NMR (C$_6$D$_6$): ^{31}P{^{1}H} 259.2 (d, $^2J_{PP}$ = 51.7 Hz), 262.5 (tr, $^2J_{PP}$ = 51.7 Hz); ^{71}Ga -619.4 ($W_{1/2} \approx 1910$ Hz); ^{1}H 1.44 (s, 18H, Bu^t); ^{13}C AMXX′ spin system 38.0 (m, $^3J_{P(A)C}$ = 9.4 Hz, $^4J_{P(X)C}$ + $^3J_{P(X')C}$ = 4.7 Hz, C(CH$_3$)$_3$), 37.6 (m, $^2J_{P(A),C}$ = 7.6 Hz, C(CH$_3$)$_3$), 234.2 (m, P*C*P). MS (70 eV) m/z (%): 299 (100) [M$^+$], 284 (44) [M–CH$_3$]$^+$, 200 (33) [GaP$_2$CBu^t]$^+$, 68.9 (85) [Ga]$^+$, 57 (24) [Bu^t]$^+$.

3.2.2. [Tl(η^5-P$_3$C$_2$Bu$^t_2$)] (4)

TlCl (0.356 g, 1.49 mmol) was stirred in dimethoxyethane (30 ml). To this suspension was added a solution of [Li(tmeda)$_2$][**2**] (0.86 g, 1.83 mmol) in dme (20 ml). The resulting mixture was stirred in the absence of light for 3 days. Volatiles were removed in vacuo and the residue extracted with warm toluene and filtered to give an orange solution. Evaporation of the toluene yielded a solid which was washed with pentane to give a yellow powder which was further purified by sublimation to afford **4** as bright yellow crystals, 0.140 g, 21.6%. NMR (C$_5$D$_5$N): ^{31}P{^{1}H} 254.5 (d, $^2J_{PP}$ = 49.4 Hz), 262.9 (tr, $^2J_{PP}$ = 49.4 Hz); ^{1}H 1.69 (s, 18H, Bu^t); ^{13}C AMXX′ spin system 38.1 (m, $^3J_{P(A)C}$ = 10.0 Hz, $^4J_{P(X)C}$ + $^3J_{P(X')C}$ = 10.1 Hz, C(CH$_3$)$_3$), 41.3 (m, $^2J_{P(A)C}$ = 21.4 Hz, $^3J_{P(X)C}$ + $^2J_{P(X')C}$ = 13.43 Hz, C(CH$_3$)$_3$), 218.8 (m, $^1J_{P(A)C}$ = 64.1 Hz, $^2J_{P(X)C}$ + $^1J_{P(X')C}$ = 89.3 Hz P*C*P) (where P(A) is the unique phosphorus and P(X) and P(X′) are the chemically equivalent but magnetically non-equivalent directly bonded phosphorus atoms). MS (70 eV) m/z (%): 436 (62) [M$^+$], 205 (100) [Tl$^+$], 231 (16) [P$_3$C$_2$Bu$^t_2$]$^+$, 169 (9) [PC$_2$Bu$^t_2$]$^+$. Microanalysis: Calc. (Found): C, 27.58 (27.79%); H, 4.17 (4.09%).

3.3. Structure determinations

Crystals of **3** were grown from a slowly evaporated pentane solution whilst those of **4** were grown from a slowly cooled saturated dme solution. Intensity data were measured on a KappaCCD diffractometer for **4** and a STOE-IPDS machine for **3** using Mo–K$_\alpha$ radiation (λ = 0.71069 Å). Both structures were solved by direct methods and refined using full-matrix least-squares on F^2 with SHELX-97 [16] and WINGX [17]. Details of crystal structure data and refinement are collected in Table 1.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 167243 for **3** and 167242 for **4**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk.

Table 1
Crystallographic data for compounds **3** and **4**

	3	**4**
Empirical formula	C$_{10}$H$_{18}$P$_3$Ga	C$_{10}$H$_{18}$P$_3$Tl
Mr	300.87	435.52
Crystal system	Orthorhombic	Orthorhombic
Space group	*Ama*2 (no. 40)	*Ama*2 (no. 40)
a (Å)	20.454(4)	20.3947(16)
b (Å)	6.4427(13)	6.3562(5)
c (Å)	10.533(2)	10.3024(5)
V (Å^3)	1388.0(5)	1335.5(2)
Z	4	4
Absorption correction	Numerical	Multiscan
μ (mm^{-1})	2.293	12.42
Crystal size (mm)	0.65 × 0.5 × 0.25	0.50 × 0.20 × 0.01
Reflections collected	2813	3513
Independent reflections	1217 [R_{int} = 0.0337]	1509 [R_{int} = 0.075]
R_1 [$I > 2\sigma(I)$]	0.0222	0.062
wR_2 [$I > 2\sigma(I)$]	0.0545	0.160
R_1 all data	0.0232	0.065
wR_2 all data	0.0548	0.163

References

[1] J. Chojnacki, E. Baum, I. Krossing, D. Carmichael, F. Mathey, H. Schnöckel, Z. Anorg. Allg. Chem. 627 (2001) 1209.

[2] M.D. Francis, C. Jones, G.B. Deacon, E.E. Delbridge, P.C. Junk, Organometallics 17 (1998) 3826.

[3] T. Douglas, K.H. Theopold, B.S. Haggerty, A.L. Rheingold, Polyhedron 9 (1990) 329.

[4] C. Callaghan, G.K.B. Clentsmith, F.G.N. Cloke, P.B. Hitchcock, D.M. Vickers, Organometallics 18 (1999) 793.

[5] F.G.N. Cloke, M.L.H. Green, J. Chem. Soc. Dalton Trans. (1981) 1938.

[6] M.D. Francis, J.F. Nixon, W.S. Rees, (2000) unpublished results.

[7] C. Dohmeier, D. Loos, H. Schnöckel, Angew. Chem. Int. Ed. Engl. 35 (1996) 129.

[8] G.J.D. Sillett, DPhil Thesis, University of Sussex, 1990.

[9] A. Schnepf, G. Stößer, D. Carmichael, F. Mathey, H. Schnöckel, Angew. Chem. Int. Ed. Engl. 38 (1999) 1646.

[10] P.B. Hitchcock, J.F. Nixon, R.M. Matos, J. Organomet. Chem. 490 (1995) 155.

[11] H.P. Fritz, F.H. Köhler, J. Organomet. Chem. 30 (1971) 177.

[12] P. Jutzi, W. Leffers, J. Chem. Soc. Chem. Commun. (1985) 1735.

[13] D. Loos, H. Schnöckel, J. Organomet. Chem. 463 (1993) 37.

[14] D. Loos, E. Baum, A. Ecker, H. Schnöckel, A.J. Downs, Angew. Chem. Int. Ed. Engl. 36 (1997) 860.

[15] H. Werner, H. Otto, H.J. Kraus, J. Organomet. Chem. 315 (1986) C57.

[16] G. Sheldrick, SHELX-97, Programs for Crystal Structure Analysis, University of Göttingen, Göttingen, Germany, 1998.

[17] L.J. Farrugia, J. Appl. Crystallogr. 32 (1999) 837.