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tert-Butylindium Compounds. X-ray Crystal Structure of $(t\text{-}Bu_2InOEt)_2$

Donald C. Bradley,* Dario M. Frigo, Michael B. Hursthouse,* and Bilquis Hussain

Department of Chemistry, Queen Mary College, Mile End, London E1 4NS, U.K.

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Reaction of t-BuMgCl with $InCl_3$ in 2:1 and 3:1 molar ratio gave $(t\text{-}Bu_2InCl)_2$ and $t\text{-}Bu_3In$, respectively; the latter is believed to be monomeric in solution. Reaction of t-BuLi with $InCl_3$ in 2:1 molar ratio gave mainly indium metal with a small amount of $(t\text{-}Bu_2InCl)_2$. Reaction of $(t\text{-}Bu_2InCl)_2$ with LiOEt gave $(t\text{-}Bu_2InOEt)_2$, the X-ray crystal structure of which shows an ethoxo-bridged dimer. The geometry around the indium atom is distorted tetrahedral with C–In–C = 127.2 (4)° and O–In–O′ = 75.2 (3)°. The In–C distances are 2.21 (1) and 2.22 (1) Å; the alkoxy bridge is symmetrical with In–O distances of 2.15 (1) and 2.17 (1) Å and In–O–In′ = 104.8 (4)°. Reaction of $(t\text{-}Bu_2InCl)_2$ with the N-lithiated derivative of $\overline{NHCMe_2(CH_2)_3C}Me_2$ gave $t\text{-}Bu_2In\overline{NCMe_2(CH_2)_3C}Me_2$, a yellow liquid believed to be a monomer.

Introduction

The use of organoindium compounds for the metal organic chemical vapor deposition (MOCVD) of III–V semiconductors[1] has led to renewed interest in this area of chemistry. The desire to produce nonpyrophoric, volatile indium compounds, which thermolyze without excessive incorporation of carbon into the semiconducting material, has prompted the present work. One approach to this has been the use of bulky ligands which shield the metal centers from attack by atmospheric oxygen and water and also reduce the tendency of these compounds to oligomerize, thus enhancing volatility. An additional feature of alkyl substituents with β-hydrogens is the relatively facile β-elimination of olefins to give the metal hydride, thereby reducing carbon incorporation in the MOCVD process.

A number of types of organoindium compounds are known including the following: the trialkyls R_3In (e.g., R = Me,[2] Et, n-Pr, i-Pr, n-Bu, i-Bu, *sec*-Bu[3]); the dialkyl halides (e.g., R_2InX: R = Me; X = Cl, I[4]); the dialkyl alkoxides (e.g., R_2InOR': R = Me; R′ = Me,[5] t-Bu,[6] $SiMe_3$[7]); and the alkyl dialkylamides [e.g., $(Me_2InNMe_2)_2$,[5] $MeIn\{Me\overline{NC(CH)_4N}\}_2$[8]]. Only one example of a compound in which *tert*-butyl groups are bonded to indium, viz., $t\text{-}Bu_2InCH_2SnMe_3$, has been reported.[9] In the synthesis of this compound, $t\text{-}Bu_2InCl$ was referred to as an isolated intermediate, but no analytical data were reported on the halide.

Results and Discussion

Reaction of t-BuMgCl with $InCl_3$ in 3:1 molar ratio in OEt_2 gave the yellow, crystalline $t\text{-}Bu_3In$ which is pyrophoric and very sensitive to daylight. A solution of $t\text{-}Bu_3In$ in C_6D_6 in a Pyrex tube was exposed to bright sunlight, and after 5 min the yellow color had darkened considerably. After 60 min a metallic mirror had been deposited on the glass walls, and after several hours the ^1H NMR showed the presence of a mixture of alkanes and alkenes which, upon comparison of chemical shift data, were found to include butane, isobutane, and isobutene. A very weak signal was also found at δ 4.49 which is believed to be due to molecular hydrogen (δ 4.50 in C_6D_6). A sample of $t\text{-}Bu_3In$ in $C_6D_5CD_3$ in a Pyrex tube was irradiated with a high-pressure mercury discharge lamp in situ in an X-band ESR spectrometer. No signal was detected in the region of ±200 G away from $g = 2$ where $t\text{-}Bu^\bullet$ or $C_6D_5CD_2^\bullet$ radicals would normally be found. Virtually no UV radiation would penetrate the Pyrex tube, but the normal photolysis products were detected after irradiation. This indicates that either the photolysis does not generate radicals or, more likely, they are too short-lived to allow the generation of a detectable steady-state concentration.

Reaction of 2 equiv of t-BuMgCl with $InCl_3$ gave $(t\text{-}Bu_2InCl)_2$ in high yield (78% based upon $InCl_3$), whereas with use of t-BuLi instead of the Grignard reagent, low yields were obtained (less than 28%) due to the production of large amounts of a black precipitate of metallic indium, even when the reaction was carried out at −78 °C in the absence of light. This is presumably due to the lithium reagent being a more powerful reducing agent than the Grignard. Recently Schumann et al., who used the lithium reagent to prepare $(t\text{-}Bu_2InCl)_2$ en route to $t\text{-}Bu_2InCH_2SnMe_3$, did not report this side reaction.[9] Even $(t\text{-}Bu_2InCl)_2$ appears to possess only limited stability since the white crystals darkened slightly over a period of several weeks, which probably accounts for the consistently low elemental analyses obtained for this compound (Table I).

When $(t\text{-}Bu_2InCl)_2$ was treated with the N-lithiated derivative of 2,2,6,6-tetramethylpiperidine using pentane as the solvent, a yellow liquid was obtained which was characterized as $t\text{-}Bu_2In\overline{NCMe_2(CH_2)_3C}Me_2$. This compound was very air-sensitive and darkened upon exposure to sunlight, depositing a metallic mirror and giving rise to (inter alia) very similar peaks due to alkanes and alkenes in the ^1H NMR as were found upon irradiation of $t\text{-}Bu_3In$ (vide supra). However, when diethyl ether was used as the solvent in the above synthesis, a colorless, crystalline solid was isolated which was identified as the dimeric ethoxo compound $(t\text{-}Bu_2InOEt)_2$ by spectroscopic and X-ray structure analysis (see below). Presumably, lithium ethoxide was produced by reaction of the lithium amide with diethyl ether since the reagent was kept overnight before it was added to $(t\text{-}Bu_2InCl)_2$, e.g.

$$Li\overline{NCMe_2(CH_2)_3C}Me_2 + OEt_2 \rightarrow Et\overline{NCMe_2(CH_2)_3C}Me_2 + LiOEt$$

$$(t\text{-}Bu_2InCl)_2 + 2LiOEt \rightarrow (t\text{-}Bu_2InOEt)_2 + 2LiCl$$

When $t\text{-}Bu_2In\overline{NCMe_2(CH_2)_3C}Me_2$ was dissolved in di-

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[1] Manasevit, H. M.; Simpson, W. I. *J. Electrochem. Soc.* **1969**, *116*, 1725.

[2] Dennis, L. M.; Work, R. W.; Rochow, E. G. *J. Am. Chem. Soc.* **1934**, *56*, 1047.

[3] Todt, E.; Dotzer, R. *Z. Anorg. Allg. Chem.* **1963**, *321*, 120.

[4] Clark, H. C.; Pickard, A. L. *J. Organomet. Chem.* **1967**, *8*, 427.

[5] Coates, G. E.; Whitcombe, R. A. *J. Chem. Soc.* **1956**, 3351.

[6] Schmidbaur, H. *Angew. Chem.* **1965**, *77*, 169.

[7] Armer, B.; Schmidbaur, H. *Chem. Ber.* **1967**, *100*, 1521.

[8] Arif, A. M.; Bradley, D. C.; Frigo, D. M.; Hursthouse, M. B.; Hussain, B. *J. Chem. Soc., Chem. Commun.* **1985**, 783.

[9] Schumann, H.; Mohtachemi, R. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1984**, *39B*, 798.

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Table I. Physical and Analytical Data

compd	appearance	mp, °C	accurate mass[a] m/z	anal.[a] C	H	^{1}H NMR (C_6D_6) δ (Me_3CIn)	IR $\nu(Me_3C)$, cm^{-1}
t-Bu_3In	yellow	53–57.5	286.116 10 (286.11514)	49.8 (50.4)	9.16[b] (9.51)	1.30	1363 s, 1384 m sh
(t-$Bu_2InCl)_2$	white	212–212.5[c]	264.012 99[d] (264.013 56)	33.9 (36.3)	6.65 (6.86)	1.40	1365 s, 1369 s sh, 1387 m sh
(t-$Bu_2InOEt)_2$	white	ca. 175[e]	548.154 43[f] (548.157 50)	44.0 (43.8)	8.39 (8.46)	1.45	1361 s
t-$Bu_2In\overline{NCMe_2(CH_2)_3C}Me_2$	yellow	<–25	369.188 14 (369.188 64)	55.2 (55.3)	9.63[g] (9.83)	1.34	1352 s,[h] 1366 s, 1372 s

[a] Required values shown in parentheses. [b] Also: In, 40.3 (40.1). [c] Decomposition: goes orange at ca. 208 °C; melts to a red liquid. [d] Monomer peak. [e] Shrinkage to a glassy solid at 133–134 °C; begins to decompose at ca. 162 °C; melts to a black liquid. [f] Dimer peak. [g] Also: N, 3.56 (3.79). [h] Assignment tentative.

ethyl ether and stirred at 30 °C for 16 h, it did not convert to (t-$Bu_2InOEt)_2$, therefore ruling out the possible initial formation of the indium amido compound which was then subsequently solvolyzed by the ether. The (t-$Bu_2InOEt)_2$ showed no detectable photolysis in bright sunlight.

Physical and analytical data of all four compounds are presented in Table I. All of the compounds are volatile: t-Bu_3In and t-$Bu_2In\overline{NCMe_2(CH_2)_3C}Me_2$ are easily volatilized at ca. 20 °C at 10^{-2} mmHg, whereas (t-$Bu_2InCl)_2$ and (t-$Bu_2InOEt)_2$ must be heated to ca. 90 °C at this pressure. The mass spectrum of t-$Bu_2In\overline{NCMe_2(CH_2)_3C}Me_2$ showed no peaks of higher mass number than the molecular ion, whereas most species of the type $R_2InNR'_2$ which are dimeric in the condensed phase show relatively abundant dimers in the mass spectrum.[10] This, coupled with its very low melting point, the high atmospheric sensitivity, its deep color and high volatility, suggests that it is monomeric. The deep yellow color, unprecedented in dialkylindium dialkylamides, may be due to a charge transfer from the nitrogen lone pair into the vacant metal 5p orbital. The monomeric nature of this compound is presumably due to steric hindrance by the bulky ligands preventing dimerization. Its extreme sensitivity to daylight and atmospheric oxidation and hydrolysis has precluded molecular weight determination (cryoscopic or ebullioscopic) since even partial decomposition (which would be unavoidable) would give rise to enormous errors.

The high volatility of t-Bu_3In suggested that it may also be monomeric. Some of the higher trialkyls of indium have been shown to be monomeric, e.g., $(Me_3SiCH_2)_3In$,[11] and t-Bu_3In is probably one of the most sterically crowded trialkyls prepared so far. As with the tetrameric Me_3In,[2] t-Bu_3In is a solid at room temperature, but then so is $[(Me_3Si)_2CH]_3In$ which is monomeric.[12] The mass spectrum of t-Bu_3In contained no peaks of higher mass number than the monomer, but this does not preclude the presence of dimers in the gas phase. Other prominent peaks in the spectrum were due to t-Bu_2In^+, t-$BuInH^+$, t-$BuIn^+$, In^+, t-BuH^+, and t-Bu^+.

The mass spectra of (t-$Bu_2InCl)_2$ and (t-$Bu_2InOEt)_2$ showed peaks due to both the respective monomers and dimers, with predicted fragmentation peaks therefrom; the expected chlorine isotope patterns were observed for (t-$Bu_2InCl)_2$.

The ^{1}H NMR of t-Bu_3In at room temperature showed one singlet, implying either that the compound is monomeric or that rapid exchange between bridging and terminal alkyls is occurring. The ^{13}C NMR showed signals at δ 32.5 and 40.4 due to the methyl and quaternary carbons, respectively, and this spectrum remained essentially unchanged down to −63 °C. This implies that the compound is monomeric in solution rather than the t-Bu groups being equivalent due to fluxionality between bridging and terminal alkyl groups in an oligomeric species. The spectrum of (t-$Bu_2InCl)_2$ also shows a singlet which is slightly downfield of that for t-Bu_3In, while that of (t-$Bu_2InOEt)_2$ shows a singlet flanked by a coupled triplet and quartet, in the correct ratios. The spectrum of t-$Bu_2In\overline{NCMe_2(CH_2)_3C}Me_2$ not only showed two singlets in the correct ratio due to t-Bu and the amide Me groups at δ 1.34 and 1.13, respectively, superimposed on a broad multiplet, but also showed what appeared to be an impurity peak: a singlet slightly upfield of the Me signal at δ 1.09 and approximately half as intense. Upon irradiation, this peak became larger as the other singlets became smaller, and a small, broad peak also appeared at δ 0.31. Comparison with a standard spectrum showed that these new peaks were due to the Me and NH groups of the free amine $\overline{NHCMe_2(CH_2)_3C}Me_2$, showing that it is a photolysis product along with the various hydrocarbons referred to previously.

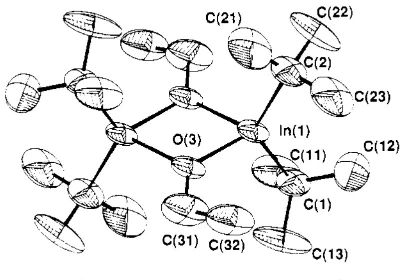

Figure 1. Molecular structure of (t-$Bu_2InOEt)_2$ to show the numbering scheme.

The chemical shifts of the t-Bu groups in these compounds are consistently downfield from the corresponding gallium compounds:[13] δ 1.30 for t-Bu_3In (C_6D_6), δ 1.12 for t-Bu_3Ga (CCl_4); δ 1.40 for (t-$Bu_2InCl)_2$ (C_6D_6); δ 1.25 for (t-$Bu_2GaCl)_2$ (C_6D_6); δ 1.45 for (t-$Bu_2InOEt)_2$ (C_6D_6); δ 1.17 for (t-$Bu_2GaOMe)_2$ ($CDCl_3$). They are also downfield of the signal due to t-Bu in t-$Bu_2InCH_2SnMe_3$, viz., δ 0.14 (C_6D_6).[9]

X-ray Crystal Structure of (t-$Bu_2InOEt)_2$

A diagram of the centrosymmetric dimer is given in Figure 1, with selected bond lengths and angles in Table II. The tetrahedral geometry around the indium atoms is strongly distorted with the bulky alkyls producing a large C–In–C angle of 127.2 (4)°. The small O–In–O′ angle of 75.2 (3)° arises partly as a result of "hybridization compensation" for the large C–In–C angle and partly through the In–In′ nonbonded repulsion requiring the In–In′ vector in the planar In_2O_2 ring to be larger than the O–O′ vector.

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(10) Arif, A. M.; Bradley, D. C.; Dawes, H.; Frigo, D. M.; Hursthouse, M. B.; Hussain, B. *J. Chem. Soc. Dalton Trans.* **1987**, 2159.

(11) Beachley, O. T.; Rusinko, R. N. *Inorg. Chem.* **1979**, *18*, 1966.

(12) Carty, A. J.; Gynane, M. J. S.; Lappert, M. F.; Miles, S. J.; Singh, A.; Taylor, N. *Inorg. Chem.* **1980**, *19*, 3637.

(13) Schwering, H. U.; Jungk, E.; Weidlein, J. *J. Organomet. Chem.* **1975**, *91*, C4.

Table II. Bond Lengths and Angles for $(t\text{-}\mathrm{Bu_2InOEt})_2$[a]

Bond Lengths (Å)			
C(1)–In	2.219 (12)	C(2)–In	2.206 (18)
O(3)–In	2.147 (5)	In(1)–O(3B)	2.165 (5)
C(11)–C(1)	1.53 (2)	C(12)–C(1)	1.56 (2)
C(13)–C(1)	1.52 (2)	C(21)–C(2)	1.49 (2)
C(22)–C(2)	1.54 (2)	C(23)–C(2)	1.57 (2)
C(31)–O(3)	1.41 (1)	C(32)–C(31)	1.37 (2)

Bond Angles (deg)			
C(2)–In(1)–C(1)	127.2 (4)	O(3)–In(1)–C(1)	113.2 (4)
O(3)–In(1)–C(2)	111.3 (4)	C(2)–In(1)–O(3B)	108.1 (4)
O(3)–In(1)–O(3B)	75.2 (2)	C(11)–C(1)–In(1)	110.4 (8)
C(12)–C(1)–In(1)	106.8 (10)	C(12)–C(1)–C(11)	108 (9)
C(13)–C(1)–In(1)	110.5 (8)	C(13)–C(1)–C(11)	112 (2)
C(13)–C(1)–C(12)	109 (1)	C(21)–C(2)–In(1)	113.3 (11)
C(22)–C(2)–In(1)	106.2 (13)	C(22)–C(2)–C(21)	112 (1)
C(23)–C(2)–In(1)	107.8 (13)	C(23)–C(2)–C(21)	109 (2)
C(23)–C(2)–C(22)	109 (1)	C(31)–O(3)–In(1)	131.0 (6)
In(1B)–O(3)–C(31)	131.1 (6)	C(32)–C(31)–O(3)	119 (11)
In(1)–O(3)–In(1B)	104.8 (2)		

[a] Atoms In(1B) and O(3B) are related to In(1) and O(3), respectively, by the symmetry operation $-x, -y, -z$.

Experimental Section

All operations were performed under an atmosphere of purified nitrogen by using Schlenk-style apparatus and a glovebox. Solvents were distilled from sodium benzophenone under nitrogen. Anhydrous $\mathrm{InCl_3}$, $\overline{\mathrm{NHCMe_2(CH_2)_3C}}\mathrm{Me_2}$, and solutions of n-BuLi (in hexane), t-BuLi (in pentane), and t-BuMgCl (in diethyl ether) were obtained from commercial sources. ^{1}H NMR spectra were obtained by using a Bruker WP80 FT spectrometer and are quoted referenced to TMS by using the undeuteriated solvent signal as internal reference; infrared spectra were obtained as Nujol mulls or as a neat liquid film between CsI plates by using a Perkin-Elmer 577 spectrophotometer; mass spectra were obtained by using an AEI MS902 spectrometer (only principal peaks are reported; in assignments, unless otherwise stated, In refers to ^{115}In); and microanalyses were by the Micro-analytical Laboratory of University College, London, U.K., and Butterworth Laboratories Ltd., Teddington, U.K.

Tri-*tert*-butylindium(III). To a suspension of $\mathrm{InCl_3}$ (4.6 g, 21 mmol) in diethyl ether (20 cm^3) at 0 °C was added t-BuMgCl (31.5 cm^3 of 2.0 M solution in ether, 63 mmol) dropwise and in the dark. The solvent was removed at 0 °C in vacuo, and the residue was then heated to 30 °C (10^{-2} mmHg) whereupon pale yellow crystals of t-$\mathrm{Bu_3In}$ sublimed: yield 4.3 g, 72% based on $\mathrm{InCl_3}$; ^{1}H NMR ($\mathrm{C_6D_6}$) δ 1.30; IR 2760 m, 2705 m, 1384 m sh, 1363 s, 1260 w, 1241 w, 1176 m, 1155 s, 1012 m, 936 m, 919 m, 804 s, 757 w, 722 w, 570 m, 501 w, 479 w, 464 w, 395 w br sh, 384 m br, 356 w br, 251 m sh, 247 s cm^{-1}; mass spectrum, m/z (relative intensity) 286 (2, M), 229 (29, t-$\mathrm{Bu_2In}$), 173 (11, t-BuInH), 172 (33, t-BuIn), 115 (100, ^{115}In), 113 (5, ^{113}In), 58 (23, t-BuH), 57 (23, t-Bu).

Bis(μ-chloro)tetra-*tert*-butyldiindium(III). $\mathrm{InCl_3}$ (2.35 g, 10.6 mmol) was suspended in diethyl ether (70 cm^3) at −78 °C, and t-BuMgCl (7.75 cm^3 of 2.71 M solution in ether, 21.0 mmol) was added over 5 min. After about half of the addition, the solution began to darken so that on complete addition the precipitate was brown. This initially went black over the next 20 min and finally yellow after 1 h. The precipitate was filtered off, and the colorless filtrate was held at −25 °C whereupon white crystals of $(t\text{-}\mathrm{Bu_2InCl})_2$ were obtained which were sublimed at 100 °C (10^{-2} mmHg): yield 2.2 g, 78% based on $\mathrm{InCl_3}$; ^{1}H NMR ($\mathrm{C_6D_6}$) δ 1.40; IR 2770 m, 2715 m, 1387 m sh, 1369 s sh, 1365 s, 1163 s, 1160 s sh, 1016 m, 943 w, 813 m, 808 w sh, 515 w, 389 w sh, 381 w, 266 m, 243 m, 220 m cm^{-1}; mass spectrum (where ^xM = monomer containing ^xCl isotope), m/z (relative intensity) 530 (1, ^{37}M + ^{35}M), 528 (2, $^{35}\mathrm{M_2}$), 473 (5, ^{37}M + ^{35}M − t-Bu), 471 (9, $^{35}\mathrm{M_2}$ − t-Bu), 381 (12, ^{37}M + In), 379 (37, ^{35}M + In), 266 (16, ^{37}M), 264 (49, ^{35}M), 229 (39, t-$\mathrm{Bu_2In}$), 172 (9, t-BuIn), 114 (29, t-$\mathrm{Bu_2}$), 57 (100, t-Bu).

Alternative Synthesis. $\mathrm{InCl_3}$ (3.50 g, 15.8 mmol) was suspended in diethyl ether (100 cm^3) at 0 °C, and t-BuLi (14.5 cm^3 of 2.2 M solution in ether, 32 mmol) was added dropwise over 60 min. Initially a white precipitate formed which subsequently became yellow, brown, and finally black. The contents were stirred at room temperature for a further 60 min, the precipitate was filtered off, and then the solvent was removed from the filtrate in vacuo to leave a white residue. This was sublimed at 100 °C (10^{-2} mmHg) to give white crystals of $(t\text{-}\mathrm{Bu_2InCl})_2$: yield 1.15 g, 28% based on $\mathrm{InCl_3}$.

Bis(μ-ethoxo)tetra-*tert*-butyldiindium(III). The preparation given here is not optimal but was the procedure used. n-BuLi (1.3 cm^3 of 1.99 M solution in hexane, 2.6 mmol) was added to $\overline{\mathrm{NHCMe_2(CH_2)_3C}}\mathrm{Me_2}$ (0.5 g, 3.5 mmol) in diethyl ether (50 cm^3), and the contents were stirred at room temperature for 16 h, after which a white precipitate had appeared. Solvent and excess amine were removed in vacuo, and the resulting clear, yellow gum was redissolved in ether (25 cm^3) and added to a suspension of $(t\text{-}\mathrm{Bu_2InCl})_2$ (0.70 g, 1.3 mmol) in ether (35 cm^3). The resulting white precipitate was filtered off, and the solvent was removed from the filtrate in vacuo to leave a pale yellow residue. This was recrystallized from pentane to give large, colorless crystals of $(t\text{-}\mathrm{Bu_2InOEt})_2$. These were sublimed at 90 °C (10^{-2} mmHg): yield 0.45 g, 63% based on $(t\text{-}\mathrm{Bu_2InCl})_2$; ^{1}H NMR ($\mathrm{C_6D_6}$) δ 1.15 (6 H, t, J = 7 Hz, $\mathrm{OCH_2C}H_3$), 1.45 (36 H, s, t-Bu), 3.80 (4 H, q, J = 7 Hz, $\mathrm{OC}H_2\mathrm{CH_3}$); IR 2765 m, 2705 m, 1450 s sh, 1361 s, 1260 w br, 1160 s, 1097 s, 1061 s, 1012 m, 940 w, 892 m, 809 s, 766 w br, 722 w br, 534 vs br, 521 s sh, 490 w sh, 379 s, 366 s, 261 s br, 257 s sh, 231 m cm^{-1}; mass spectrum ($\mathrm{M_2}$ = dimer), m/z (relative intensity) 549 (1, $\mathrm{M_2}$ + H), 548 (3, $\mathrm{M_2}$), 519 (10 $\mathrm{M_2}$ − Et), 491 (100, $\mathrm{M_2}$ − t-Bu), 435 (5, $\mathrm{M_2}$ − 2t-Bu + H), 389 (5, M + In), 377 (24, $\mathrm{M_2}$ − 3t-Bu), 333 (6, M + OEt + $\mathrm{CH_2}$), 321 (20, M + OEt + 2H), 277 (6, M + 3H), 275 (29, M + H), 114 (22, t-$\mathrm{Bu_2}$), 57 (38, t-Bu).

Di-*tert*-butyl(2,2,6,6-tetramethylpiperidino)indium(III). n-BuLi (0.95 cm^3 of 2.83 M solution in hexane, 2.7 mmol) was added to $\overline{\mathrm{NHCMe_2(CH_2)_3C}}\mathrm{Me_2}$ (0.39 g, 2.8 mmol) in pentane (25 cm^3). Solvent and excess amine were removed in vacuo, and the resulting off-white solid was resuspended in pentane (35 cm^3) and added to a suspension of $(t\text{-}\mathrm{Bu_2InCl})_2$ (0.70 g, 1.3 mmol) in pentane (25 cm^3). The resulting solution immediately turned yellow and gave a fine white precipitate. This was filtered and solvent removed to leave an orange-yellow liquid that distilled at 60 °C (10^{-1} mmHg) to give pure t-$\mathrm{Bu_2In}\overline{\mathrm{NCMe_2(CH_2)_3C}}\mathrm{Me_2}$: yield 0.78g, 81% based on $(t\text{-}\mathrm{Bu_2InCl})_2$; ^{1}H NMR ($\mathrm{C_6D_6}$) δ 1.13 (12 H, s, $\mathrm{CMe_2}$), 1.34 (18 H, s, t-Bu), 1.2–1.9 (6 H, br m, $\mathrm{CH_2}$); IR 3000 m, 2985 m, 2950 s, 2925 s, 2870 s, 2830 s, 2765 m, 2710 m, 1463 s, 1453 s, 1372 s, 1366 s, 1352 s, 1340 m, 1289 m, 1239 s, 1195 w, 1175 w, 1157 s, 1136 s, 1075 m, 1051 m, 1027 s, 1013 m, 983 w, 959 m, 941 m, 923 s, 902 s, 855 m, 804 s, 733 w, 584 w, 532 w, 507 w, 490 m, 455 w, 420 w, 381 w br, 240 s cm^{-1}; mass spectrum [where amine = $\overline{\mathrm{NHCMe_2(CH_2)_3C}}\mathrm{Me_2}$], m/z (relative intensity) 369 (23, M), 312 (42, M − t-Bu), 254 (8, M − 2t-Bu), 240 (22, In + amine − $\mathrm{CH_4}$), 141 (11, amine), 127 (10, amine − $\mathrm{CH_2}$), 126 (100, amine − Me), 115 (37, In), 98 (9, amine − $\mathrm{C_3H_7}$), 70 (37, $\mathrm{Me_2}\overline{\mathrm{CCH_2N}}\mathrm{H}$?), 69 (32, $\mathrm{Me_2}\overline{\mathrm{CCH_2N}}$?), 58 (67, $\mathrm{C_4H_{10}}$), 57 (16, $\mathrm{C_4H_9}$), 56 (23, $\mathrm{C_4H_8}$).

X-ray Crystallography. The crystals of $(t\text{-}\mathrm{Bu_2InOEt})_2$ grown from pentane were obtained as colorless blocks. The specimen used for the X-ray work had the dimensions 0.4 × 0.3 × 0.25 mm. The orientation matrix and cell dimensions were obtained by using standard SEARCH and INDEX routines on an Enraf-Nonius CAD4 diffractomer with graphite-monochromated MoKα radiation (λ = 0.710 69 Å) and refined by using setting angles for 25 well-spaced reflections with $6 < \theta < 15°$. The formula weight of $\mathrm{In_2O_2C_{20}H_{46}}$ is 548.23. The crystals are triclinic, space group $P\bar{1}$, with cell dimensions a = 9.042 (2) Å, b = 9.884 (2) Å, c = 9.915 (1) Å, α = 117.83 (1)°, β = 121.53 (2)°, γ = 75.31 (2)°, V = 667.9 Å^3, Z = 1, D_{calcd} = 1.363 g cm^{-3}, μ(MoKα) = 17.0 cm^{-1}, $F(000)$ = 280, and T = 291 K. Intensity data were recorded by using an $\omega/2\theta$ scan technique with $1.5 \leqslant \theta \leqslant 25°$ (h, 0→11; k, −11→+11; l, −10→+10), ω scan width = 0.8 + 0.35 tan θ, and variable scan speed 1.35–10.15 deg min^{-1} to achieve $I > 33\sigma(I)$ subject to t_{max} = 60 s. A total of 2345 unique reflections were measured, of which 1600 satisfied the condition $I > 1.5\sigma(I)$. Intensity controls indicated that during data collection an almost linear and isotropic decay of the crystal occurred to ~0.36 of the initial value. This was corrected during processing, and an empirical absorption

Table III. Fractional Atomic Coordinates (×10^4) for (t-Bu_2InOEt)$_2$

	x	y	z
In	1255 (1)	1459 (1)	1851 (1)
C(1)	1492 (13)	1741 (12)	4311 (10)
C(11)	2251 (18)	287 (14)	4635 (15)
C(12)	2799 (20)	3062 (17)	5791 (13)
C(13)	−252 (17)	2174 (20)	4295 (18)
C(2)	2677 (15)	2711 (14)	1536 (13)
C(21)	2128 (21)	2308 (21)	−380 (14)
C(22)	4613 (15)	2367 (21)	2541 (22)
C(23)	2332 (23)	4467 (17)	2413 (24)
O(3)	−1335 (7)	950 (6)	−262 (7)
C(31)	−2883 (16)	1833 (17)	−538 (20)
C(32)	−2762 (18)	3393 (16)	290 (20)

correction was also applied (relative maximum and minimum transmission factors were 1.0 and 0.84, respectively). The structure was solved via the heavy-atom method and refined by full-matrix least squares. At the end of isotropic refinement, a further absorption correction was applied by using the DIFABS procedure.[14] All atoms were refined anisotropically, and no hydrogens were included. The final R and R_w values were 0.049 and 0.047, respectively, with 109 parameters and weights $w = 1/[\sigma^2(F) + 0.0005F_o^2]$. The maximum and minimum values on the final difference electron density map were 0.61 and −0.42 e Å^{-3}, respectively. The non-hydrogen coordinates are listed in Table III.

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Registry No. t-Bu_3In, 113088-72-5; $InCl_3$, 10025-82-8; t-BuMgCl, 677-22-5; (t-Bu_2InCl)$_2$, 113088-74-7; t-BuLi, 594-19-4; (t-Bu_2InOEt)$_2$, 113088-75-8; $t\text{-Bu}_2\text{In}\overline{\text{NCMe}_2(\text{CH}_2)_3\text{C}}\text{Me}_2$, 113088-73-6; $\overline{\text{NHCMe}_2(\text{CH}_2)_3\text{C}}\text{Me}$, 768-66-1.

Supplementary Material Available: Tables of atomic coordinates, anisotropic temperature factors, and bond distances and angles (4 pages); a listing of structure factor amplitudes (10 pages). Ordering information is given on any current masthead page.

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(14) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1983**, *A39*, 158.

A Triad of Electron-Rich μ_2-Alkylidene Complexes $M_2(CO)_6[\mu\text{-}CHC(Ph)NEt_2](\mu\text{-}PPh_2)$ (M = Fe, Ru, Os) via the Addition of Diethylamine to the Acetylides $M_2(CO)_6(\mu_2\text{-}\eta^2\text{-}C{\equiv}CPh)(\mu\text{-}PPh_2)$: Spectroscopic Properties and Structural Chemistry

Andrew A. Cherkas, Graham N. Mott, Ruthanne Granby, Shane A. Maclaughlin, John E. Yule,
Nicholas J. Taylor, and Arthur J. Carty*

*Guelph-Waterloo Centre for Graduate Work in Chemistry, Waterloo Campus, Department of Chemistry,
University of Waterloo, Waterloo, Ontario, Canada N2L 3G1*

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The synthesis, X-ray structures, and IR and ^1H, ^{13}C, and ^{31}P NMR spectroscopic characterization of a triad of zwitterionic μ-alkylidene compounds, $M_2(CO)_6[\mu\text{-}CHC(Ph)NEt_2](\mu\text{-}PPh_2)$ (**2a**, M = Fe; **2b**, M = Ru; **2c**, M = Os), are described. Complex **2** is formed by addition of diethylamine to the β-carbon atom of the μ_2-η^2-acetylide of **1**, $M_2(CO)_6(\mu_2\text{-}\eta^2\text{-}C{\equiv}CPh)(\mu\text{-}PPh_2)$ (**1a**, M = Fe; **1b**, M = Ru; **1c**, M = Os), with hydrogen transfer across the acetylide triple bond. The ^1H and ^{13}C NMR chemical shifts for **2a–c** indicate a very electron-rich M–C–M core. Crystals of **2a–c** are monoclinic, space group $P2_1/n$, with unit cell dimensions: **2a**, $a = 14.694$ (7) Å, $b = 13.653$ (7) Å, $c = 17.787$ (7) Å, $\beta = 99.03$ (7)°; **2b**, $a = 10.066$ (1) Å, $b = 20.297$ (3) Å, $c = 17.512$ (2) Å, $\beta = 105.90$ (1)°; **2c**, $a = 14.767$ (2) Å; $b = 14.174$ (2) Å, $c = 17.922$ (3) Å, $\beta = 99.92$ (1)°. The structures were solved and refined to the following R and R_w values: **2a**, $R = 0.035$, $R_w = 0.041$, on 3760 observed ($I \geqslant 3\sigma(I)$) data; **2b**, $R = 0.030$, $R_w = 0.037$, on 3494 data; **2c**, $R = 0.043$, $R_w = 0.050$, on 3064 data. The three molecules are isostructural with a metal–metal bond bridged by a phosphido group and an electron-rich μ-alkylidene group. Structural changes down the triad are discussed in the context of metal–alkylidene bonding.

Introduction

Since the discovery of the first transition-metal μ-methylene complex by Herrmann and co-workers in 1975,[1] μ-alkylidene (or carbene) compounds in general have been the targets of considerable synthetic endeavour.[2] Much of the interest can be attributed to two factors: (i) the recognition that the alkylidene ligand is a key intermediate

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(1) Herrmann, W. A.; Reiter, B.; Biersack, H. *J. Organomet. Chem.* **1975**, *97*, 245.

(2) For reviews see: (a) Herrmann, W. A. *Adv. Organomet. Chem.* **1982**, *20*, 159. (b) Herrmann, W. A. *Pure Appl. Chem.* **1982**, *54*, 65. (c) Hahn, J. E. *Prog. Inorg. Chem.* **1984**, *31*, 205. (d) Holton, J.; Lappert, M. F.; Pearce, R.; Yarrow, P. I. W. *Chem. Rev.* **1983**, *83*, 135.

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