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Oxidative Addition Reactions of Alkyl Halides with the Group 13 Carbene Analogue [In{N(Dipp)C(Me)}$_2$CH] (Dipp = 2,6-^{i}Pr$_2$C$_6$H$_3$)

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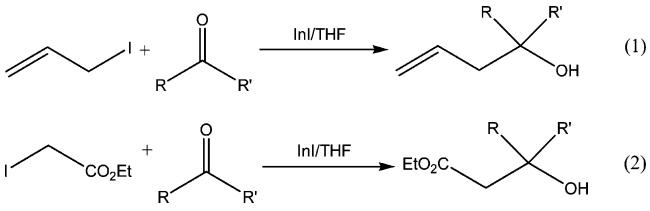
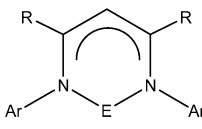
Reactions of the well-defined two-coordinate indium "carbene analogue" [In{N(Dipp)-C(Me)}$_2$CH] (Dipp = 2,6-^{i}Pr$_2$C$_6$H$_3$) have been studied. Reactions of MeI, ^{i}PrI, and ^{t}BuI with [In{N(Dipp)C(Me)}$_2$CH] formed by the in situ reaction of InI, [K{N(SiMe$_3$)$_2$}], and the iminoenamine ligand precursor successfully yielded the oxidative addition products [InRI{N(Dipp)C(Me)}$_2$CH] (R = Me, ^{i}Pr, ^{t}Bu). The results of NMR investigations, which indicated the formation of a series of four-coordinate indium(III) complexes in C_6D_6 solution, were confirmed in the solid-state by single-crystal X-ray diffraction. Similar reactions employing alkyl bromides were unsuccessful and resulted in the isolation of the corresponding iodides, apparently by metathesis of the bromide oxidative addition product with KI formed during the initial InI metathesis. Reactions of isolated samples of [In{N(Dipp)C(Me)}$_2$CH] with ^{i}PrBr and ^{t}BuBr, however, were straightforward and resulted in the successful isolation of the analogous *iso*-propyl and *tert*-butyl indium(III) bromide complexes. These were also fully characterized by ^{1}H and ^{13}C NMR and single-crystal X-ray diffraction experiments. In contrast, no reaction was observed between [In{N(Dipp)-C(Me)}$_2$CH] and aryl halides or alkyl chlorides.

Introduction

Elemental indium and the indium(I) halides, InCl, InBr, and InI, are achieving increasing prominence as stoichiometric and catalytic reagents in C−C coupling reactions.[1] Especially suitable for Barbier and Reformatsky-type reactivity (for example, eqs 1 and 2),[2]



the In0/In1 reduction potential is ideally suited for reactions involving single-electron transfer (SET), while a reduced heterophilicity, in comparison to more electropositive elements, confers greater functional group and substrate tolerance. Extensive investigations of the oxidation of refractory indium(I) halides by substituted *o*-quinones using electron paramagnetic resonance (EPR) spectroscopy revealed the formation of intermediates in which an *o*-semiquinonate ligand is attached to the central element.[3] The reaction pathway was explained in terms of indium(I), (II), and (III) species in solution, and the first steps in the reactions are presumed to involve one-electron transfer and the formation of short-lived radical and radical ion intermediates. Although related reactions of the refractory monohalides with simple, alkyl and aryl halides were first studied some 30 years ago, and it was considered likely that these reactions proceed via similar single-electron pathways,[4,5] the rapidity and effectively heterogeneous nature of these transformations hindered any definitive mechanistic rationale.



I: E = In; Ar = Ar' = 2,6-^{i}Pr$_2$C$_6$H$_3$; R = CH$_3$
II: E = In; Ar = Ar' = 2,6-^{i}Pr$_2$C$_6$H$_3$; R = CF$_3$
III: E = In; Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$; Ar' = 2-CH$_3$OC$_6$H$_4$; R = CH$_3$
IV: E = In; Ar = Ar = 2,4,6-(CH$_3$)$_3$C$_6$H$_2$; R = CH$_3$
V: E = In; Ar = Ar = 2,6-(CH$_3$)$_2$C$_6$H$_3$; R = CH$_3$
VI: E = Al; Ar = Ar' = 2,6-^{i}Pr$_2$C$_6$H$_3$; R = CH$_3$
VII: E = Ga; Ar = Ar' = 2,6-^{i}Pr$_2$C$_6$H$_3$; R = CH$_3$

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We have recently described the syntheses of several univalent indium complexes supported by β-diketiminate ligands of suitable steric demands.[6−8] The *N*-Dipp (Dipp = 2,6-$^{i}Pr_2C_6H_3$)-substituted compounds, **I**−**III**,[6,7] exist as mononuclear species in both solution and solid states, while the *N*-(2,4,6-$Me_3C_6H_2$)-and *N*-(2,6-$Me_2C_6H_3$)-substituted derivatives, **IV** and **V**, are dimeric in the solid state but mononuclear in solution.[8] We have speculated that this behavior mirrors that of the isoelectronic and well-studied stannanediyls, R_2Sn. In common with the In(I) halides outlined above, these latter species react readily with a great variety of reducible substrates including halogens, alkyl halides, organic cummulenes, diazoalkanes, 1,2-diketones, and 1,3-dienes.[9−15] Stannylenes react with organic halides, RX (R = alkyl or aryl, X = halide) by oxidative addition,[10] a process that, on the basis of product and EPR spectroscopic studies, has again been reasoned to occur via a radical process.[16] Although a comparable oxidative addition chemistry of the aluminum and gallium analogues of **I**, compounds **VI** and **VII**,[17,18] has begun to emerge, no comparable indium chemistry has been reported. To address this deficiency, we have started to study the chemistry of **I**−**V**, and report here upon the reactivity of **I** with a variety of alkyl and aryl halides.

Experimental Section

All manipulations were carried out using standard Schlenk and glovebox techniques under an inert atmosphere of dinitrogen. All solvents were distilled under dinitrogen and dried over conventional drying agents. Compound **I** was synthesized by a literature procedure.[6] All reagents were purchased from Sigma-Aldrich. Liquid alkyl halides were freeze−thaw degassed but were otherwise used as received. NMR spectra were recorded at 270 or 400 (^{1}H) or 125.8 (^{13}C) MHz from samples in C_6D_6; chemical shifts are given relative to $SiMe_4$. $^{13}C\{^1H\}$ assignments were performed using standard DEPT pulse sequences. Elemental analyses were carried out by Mr. Stephen Boyer at London Metropolitan University.

General Procedure for the Synthesis of the Iodide Compounds 1−3. A solution of compound **I** was prepared in situ in THF at −78 °C as described previously.[6] When it was warmed to room temperature, a slight excess of the appropriate alkyl iodide was added via syringe, and the resultant gray slurry was stirred overnight. The removal of the volatiles and extraction into hexane, followed by filtration, produced a pale yellow solution. Concentration and storage at 5 °C overnight yielded compounds **1**−**3** as well-formed pale yellow crystals.

1. Yield: 1.0 g, 74%. mp: 222 °C. Anal. Calcd for $C_{30}H_{44}IInN_2$: C, 53.59; H, 6.52; N, 4.14. Found: C, 53.27; H, 6.40; N, 4.07. ^{1}H NMR (270 MHz, C_6D_6, 298 K): δ 0.03 (s, 3H, InCH_3), 1.07 (d, 6H, $^3J_{HH}$ = 6.5 Hz, CH(CH_3)$_2$), 1.21 (d, 6H, $^3J_{HH}$ = 4.1 Hz, CH(CH_3)$_2$), 1.23 (d, 6H, $^3J_{HH}$ = 4.0 Hz, CH(CH_3)$_2$), 1.44 (d, 6H, $^3J_{HH}$ = 6.6 Hz, CH(CH_3)$_2$), 1.56 (s, 6H, C(CH_3)), 3.20 (m, 2H, CH(CH$_3$)$_2$), 3.83 (m, 2H, CH(CH$_3$)$_2$), 4.83 (s, 1H, C(CH$_3$)CH), 7.00−7.15 (m, 6H, ArH). $^{13}C\{^1H\}$ NMR (125.8 MHz, C_6D_6, 298 K): δ 24.2 (CH(*C*H$_3$)$_2$), 24.3 (CH(*C*H$_3$)$_2$), 24.4 (CH(*C*H$_3$)$_2$), 24.7 (CH(*C*H$_3$)$_2$), 28.1 (*C*H(CH$_3$)$_2$), 28.5 (*C*H(CH$_3$)$_2$), 28.9 (C(CH$_3$)), 97.1 (C(CH$_3$)C*H*), 123.9 (ArH), 125.3 (ArH), 142.3 (Ar), 142.7 (Ar), 144.9 (Ar), 170.2 (*C*N).

2. Yield: 0.50 g, 57%. mp: 245 °C. Anal. Calcd for $C_{32}H_{48}IInN_2$: C, 54.72; H, 6.83; N, 3.99. Found: C, 54.86; H, 7.00; N, 3.94. ^{1}H NMR (270 MHz, C_6D_6, 298 K): δ 0.88 (d, 6H, $^3J_{HH}$ = 7.4 Hz InCH(CH_3)$_2$), 1.07 (d, 6H, $^3J_{HH}$ = 6.5 Hz, CH(CH_3)$_2$), 1.23 (d, 6H, $^3J_{HH}$ = 6.7 Hz, CH(CH_3)$_2$), 1.28 (d, 6H, $^3J_{HH}$ = 6.9 Hz, CH(CH_3)$_2$), 1.44 (d, 6H, $^3J_{HH}$ = 6.7 Hz, CH(CH_3)$_2$), 1.57 (s, 6H, C(CH_3)), 3.29 (m, 2H, CH(CH$_3$)$_2$), 3.89 (m, 2H, CH(CH$_3$)$_2$), 4.85 (s, 1H, C(CH$_3$)CH), 7.00−7.16 (m, 6H, ArH). $^{13}C\{^1H\}$ NMR (125.8 MHz, C_6D_6, 298 K): δ 22.2 (InCH(*C*H$_3$)$_2$, 24.1 (CH(*C*H$_3$)$_2$), 24.2 (CH(*C*H$_3$)$_2$), 24.4 (CH(*C*H$_3$)$_2$), 24.8 (CH(*C*H$_3$)$_2$), 28.0 (*C*H(CH$_3$)$_2$), 28.7 (*C*H(CH$_3$)$_2$), 29.1 (C(*C*H$_3$)), 97.3 (C(CH$_3$)C*H*), 123.6 (ArH), 125.8 (ArH), 127.1 (ArH), 142.3 (Ar), 143.1 (Ar), 144.9 (Ar), 170.1 (*C*N).

3. Yield: 0.35 g, 40%. mp: 198 °C. Anal. Calcd for $C_{33}H_{50}IInN_2$: C, 55.32; H, 6.98; N, 3.91. Found: C, 55.59; H, 7.09; N, 3.83. ^{1}H NMR (270 MHz, C_6D_6, 298 K): δ 0.95 (s, 9H, InC(CH_3)$_3$), 1.07 (d, 6H, $^3J_{HH}$ = 6.5 Hz, CH(CH_3)$_2$), 1.24 (d, 6H, $^3J_{HH}$ = 6.6 Hz, CH(CH_3)$_2$), 1.31 (d, 6H, $^3J_{HH}$ = 7.0 Hz, CH(CH_3)$_2$), 1.42 (d, 6H, $^3J_{HH}$ = 6.8 Hz, CH(CH_3)$_2$), 1.59 (s, 6H, C(CH_3)), 3.35 (m, 2H, CH(CH$_3$)$_2$), 3.96 (m, 2H, CH(CH$_3$)$_2$), 4.94 (s, 1H, C(CH$_3$)CH), 7.04−7.16 (m, 6H, ArH).

General Procedure for the Synthesis of the Bromide Compounds 4 and 5. A slight excess of the appropriate alkyl bromide was added via syringe to a solution of compound **I** in hexane at room temperature. After the mixture was stirred overnight, concentration and storage at 5 °C yielded compounds **4** and **5** as well-formed pale yellow crystals.

4. Yield: 0.28 g, 57%. mp: 195 °C. Anal. Calcd for $C_{32}H_{48}BrInN_2$: C, 58.58; H, 7.32; N, 4.27. Found: C, 58.69; H, 7.41; N, 4.29. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 0.91 (d, 6H, $^3J_{HH}$ = 7.2 Hz InCH(CH_3)$_2$), 1.07 (d, 6H, $^3J_{HH}$ = 6.8 Hz, CH(CH_3)$_2$), 1.26 (d, 6H, $^3J_{HH}$ = 7.0 Hz, CH(CH_3)$_2$), 1.26 (d, 6H, $^3J_{HH}$ = 6.9 Hz, CH(CH_3)$_2$), 1.46 (d, 6H, $^3J_{HH}$ = 6.6 Hz, CH(CH_3)$_2$), 1.57 (s, 6H,

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Table 1. Selected Crystallographic and Data Collection Parameters for Compounds **1**−**5**

	1	**2**	**3**	**4**	**5**
chemical formula	$C_{30}H_{44}IInN_2$	$C_{32}H_{48}IInN_2$	$C_{33}H_{50}IinN_2$	$C_{32}H_{48}BrInN_2$	$C_{33}H_{50}BrInN_2$
fw	674.39	702.44	716.47	655.45	669.48
T (K)	173(2)	173(2)	173(2)	173(2)	173(2)
cryst size (mm^3)	0.1 × 0.1 × 0.1	0.20 × 0.15 × 0.15	0.15 × 0.15 × 0.10	0.20 × 0.15 × 0.15	0.2 × 0.2 × 0.1
cryst syst	monoclinic	orthorhombic	monoclinic	orthorhombic	monoclinic
space group	$P2_1/n$ (No. 14)	*Pnma* (No. 62)	$P2_1/m$ (No. 11)	*Pnma* (No. 62)	$P2_1/n$ (No. 14)
a (Å)	19.0020(5)	15.7887(2)	9.1089(3)	15.6859(3)	10.2964(2)
b (Å)	8.6125(1)	21.4997(4)	20.3097(4)	21.4625(3)	27.2575(4)
c (Å)	20.0582(5)	9.5541(2)	10.0983(3)	9.4625(3)	12.2832(3)
α (deg)	90	90	90	90	90
β (deg)	112.882(1)	90	116.040(1)	90	106.063(1)
γ (deg)	90	90	90	90	90
Z	4	4	2	4	4
V (Å^3)	3024.30(12)	3243.16(10)	1678.53(8)	3213.41(10)	3312.74(11)
d_c (Mg m^{-3})	1.48	1.44	1.42	1.36	1.34
μ (mm^{-1})	1.82	1.70	1.65	2.00	1.94
θ range (deg)	3.72−25.07	3.78−25.02	2.01−24.98	3.49−26.01	3.45−26.05
R1, wR2 [$I > 2\sigma(I)$]	0.033, 0.082	0.022, 0.050	0.034, 0.098	0.025, 0.053	0.057, 0.143
R1, wR2 (all data)	0.037, 0.083	0.026, 0.052	0.045, 0.123	0.036, 0.057	0.082, 0.158
measured/indep reflns/R(int)	35 876/5324/0.055	26 148/2931/0.047	20 704/3036/0.077	44 711/3245/0.062	38 664/6515/0.087
reflns with $I > 2\sigma(I)$	4928	2659	2686	2756	5080

Table 2. Selected Bond Lengths (Å) for Compounds **1**−**5**

	1[a]	**2**	**3**	**4**	**5**
In−N(1)	2.145(3)	2.155(2)	2.162(3)	2.1481(16)	2.162(5)
In−N(2)	2.167(3)				2.147(5)
In−C(30)	2.353(2)	2.177(3)[b]	2.221(6)[b]	2.160(3)[b]	2.180(7)
In−I/Br	2.7243(4)	2.7385(3)	2.7581(6)	2.5310(4)	2.5493(8)
N(1)−C(1)	1.333(5)	1.330(3)	1.328(5)	1.330(3)	1.326(7)
N(1)−C(6)	1.448(5)	1.452(3)[c]	1.449(5)[c]	1.447(3)[c]	1.446(7)
N(2)−C(3)	1.323(5)				1.335(7)
N(2)−C(18)	1.445(5)				1.452(7)
C(1)−C(2)	1.408(5)	1.405(3)	1.399(5)	1.403(2)	1.411(8)
C(2)−C(3)	1.401(5)				1.408(8)

[a] For compound **1**, values involving C(30) are unreliable because of disorder. [b] In−C(16). [c] N(1)−C(4).

C(C*H*$_3$)), 3.27 (m, 2H, C*H*(CH$_3$)$_2$), 3.87 (m, 2H, C*H*(CH$_3$)$_2$), 4.80 (s, 1H, C(CH$_3$)C*H*), 7.01−7.15 (m, 6H, Ar*H*). ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6, 298 K): δ 1.4 (InC*H*(C*H*$_3$)$_2$), 22.2 (InC*H*(C*H*$_3$)$_2$), 23.9 (CH(C*H*$_3$)$_2$), 24.0 (CH(C*H*$_3$)$_2$), 24.3 (CH(C*H*$_3$)$_2$), 24.8 (CH(C*H*$_3$)$_2$), 27.4 (C*H*(C*H*$_3$)$_2$), 27.9 (C*H*(C*H*$_3$)$_2$), 29.1 (C(C*H*$_3$)), 97.0 (C(CH$_3$)C*H*), 123.6 (ArH), 125.3 (ArH), 127.0 (ArH), 142.0 (Ar), 143.1 (Ar), 144.8 (Ar), 169.9 (*C*N).

5. Yield: 0.30 g, 63%. mp: 190 °C. Anal. Calcd for $C_{33}H_{50}BrInN_2$: C, 59.21; H, 7.47; N, 4.18. Found: C, 59.12; H, 7.34; N, 4.08. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 0.96 (s, 9H, InC(C*H*$_3$)$_3$), 1.06 (d, 6H, $^3J_{HH}$ = 6.7 Hz, CH(C*H*$_3$)$_2$), 1.21 (d, 6H, $^3J_{HH}$ = 6.6 Hz, CH(C*H*$_3$)$_2$), 1.30 (d, 6H, $^3J_{HH}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.45 (d, 6H, $^3J_{HH}$ = 6.6 Hz, CH(C*H*$_3$)$_2$), 1.59 (s, 6H, C(C*H*$_3$)), 3.32 (m, 2H, C*H*(CH$_3$)$_2$), 3.96 (m, 2H, C*H*(CH$_3$)$_2$), 4.88 (s, 1H, C(CH$_3$)C*H*), 7.01−7.19 (m, 6H, Ar*H*). ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6, 298 K): δ 1.4 (InC(*C*H$_3$)$_3$), 23.7 (CH(*C*H$_3$)$_2$), 24.2 (CH(*C*H$_3$)$_2$), 24.4 (CH(*C*H$_3$)$_2$), 24.9 (CH(*C*H$_3$)$_2$), 27.1 (*C*H(*C*H$_3$)$_2$), 28.1 (*C*H(*C*H$_3$)$_2$), 29.3 (C(*C*H$_3$)), 32.2 (InC(*C*H$_3$)$_3$), 97.7 (C(CH$_3$)C*H*), 123.6 (ArH), 125.3 (ArH), 127.0 (ArH), 142.0 (Ar), 143.8 (Ar), 144.7 (Ar), 170.4 (*C*N).

Crystal Structure Determinations. Data were collected at 173 K on a Nonius KappaCCD diffractometer, λ(Mo Kα) = 0.71073 Å; details are given in Table 1. An absorption correction (MULTISCAN) was applied for compounds **1**−**5**. For **1**, there appeared to be a small amount (∼9%) of iodine at the C(30) position. The disorder could not be resolved and bonds and angles involving C(30) listed in Tables 2 and 3 are, therefore, unreliable. For **3**, the *tert*-butyl group was disordered across the mirror plane and was refined with isotropic C atoms and SADI constraints. The structures were solved by direct methods (SHELXS-97) and refined by full matrix least-squares (SHELXL-97) with non-H atoms anisotropic and H atoms included in riding mode.[19,20]

Results and Discussion

Compound **I** is readily synthesized by the "one-pot" route shown in Scheme 1 and may be isolated as pale yellow crystals by extraction and crystallization from hexane.[6] Isolated crystals of **I**, although readily manipulated, are somewhat light-sensitive and decompose with the formation of indium metal upon storage.[6,7] For this reason, we initially attempted reactions with a variety of alkyl iodides by addition of a slight excess of the appropriate alkyl iodide to a THF solution of **I** formed in situ by the reaction depicted in Scheme 1. This reaction was completely successful for the synthesis of the indium(III) alkyl iodide compounds **1**−**3** (Scheme 1), which were isolated as pale yellow crystalline materials after crystallization from hexane. Compounds **1**−**3** afforded simple ^{1}H and ^{13}C NMR spectra, consistent with the formation of β-diketiminato chelate compounds with differing substituents attached to four-coordinate indium. In all three cases, the ^{1}H NMR spectra featured two well-resolved pairs of doublet signals and two multiplets which were assigned to the diastereotopic disposition of the ligand N-Dipp isopropyl methyl and methine groups, respectively. These data were interpreted as a clear indication that the crystallographically confirmed solid-state structures (vide infra) are retained in solution. The characteristic β-diketiminate γ-C methine signal occurred at ∼4.85 ppm, approximately 0.2 ppm upfield from that observed in the monovalent starting material, **I**.[6] A similar shift has been observed from comparison of monovalent and trivalent dihalo- and dimethylaluminum and gallium derivatives complexed by the same β-diketiminate ligand.[21,22]

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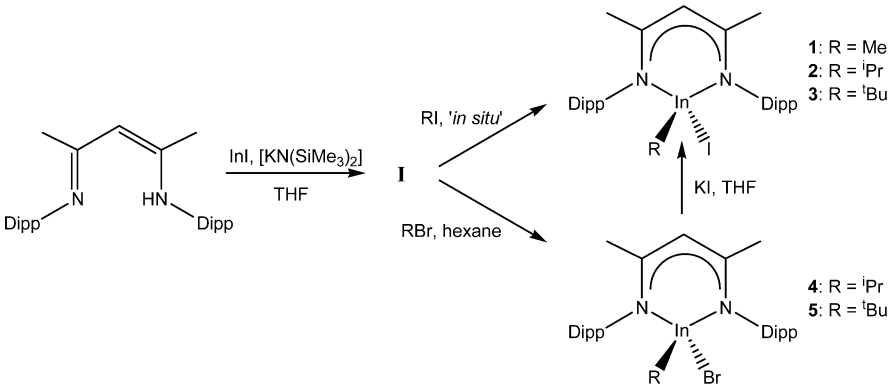
(20) Sheldrick, G. M. *SHELXL-97, Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.

Table 3. Selected Bond Angles (deg) for Compounds **1**−**5**

	1[a]	**2**[b]	**3**[b]	**4**[b]	**5**
N(1)−In−N(2)	90.60(11)	90.53(10)[c]	89.43(17)[c]	89.99(9)[c]	89.50(18)
N(1)−In−C(30)	113.58(10)	117.69(8)[d]	122.01(13)[d]	117.61(8)[d]	122.6(3)
N(2)−In−C(30)	119.69(10)				122.8(3)
N(1)−In−I/Br	109.35(8)	105.50(5)	102.46(9)	104.76(5)	101.59(13)
N(2)−In−I/Br	104.22(8)				102.12(13)
C(30)−In−I/Br	116.25(6)	116.36(11)[e]	114.09(17)[e]	117.93(10)[e]	113.6(2)
C(1)−N(1)−In	121.0(2)	121.17(15)	117.5(3)	121.63(14)	118.4(4)
C(6)−N(1)−In	120.4(2)	119.22(13)[f]	120.9(2)[f]	118.88(12)[f]	118.8(3)
C(3)−N(2)−In	120.7(2)				118.7(4)
C(18)−N(2)−In	116.2(2)				119.7(4)
N(1)−C(1)−C(2)	124.8(3)	124.9(2)	124.5(4)	124.6(2)	124.6(5)
C(1)−C(2)−C(3)	131.0(3)	131.1(3)[g]	131.0(5)[g]	131.0(3)[g]	130.5(5)
C(2)−C(3)−N(2)	125.3(3)				124.5(5)

[a] For compound **1**, values involving C(30) are unreliable because of disorder. [b] Symmetry transformations used to generate equivalent atoms; $'$ x, $-y + {}^1/_2$, z. [c] N(1)$'$−In−N(1). [d] N(1)−In−C(16). [e] C(16)−In−I/Br. [f] C(4)−N(1)−In. [g] C(1)−In−C(1)$'$.

Scheme 1



The use of a similar procedure for the reaction of **I** and ^{t}BuBr also resulted in the isolation of compound **3**. Evidently the presence of KI, formed from the initial metathesis of the InI, in the reaction mixture favors the formation of the indium alkyl iodide rather than the desired bromide. A similar outcome has previously been noted in the attempted synthesis of [$InCl_2${N(Dipp)C(Me)}$_2$CH]. In this latter case the reaction of [Li{N(Dipp)C(Me)}$_2$CH] and $InCl_3$ resulted in the isolation of [$InCl_{1.5}Br_{0.5}${N(Dipp)C(Me)}$_2$CH] because of contamination of the lithium reagent with LiBr.[21] This problem was easily overcome by employing isolated and crystalline samples of compound **I** during the synthesis, and this modified synthetic procedure yielded analytically pure bulk samples of the indium alkyl bromides, compounds **4** and **5** (Scheme 1), in good yield after crystallization from hexane. The indium bromide derivatives again displayed NMR characteristics that were consistent with the formation of stable chelate complexes and only exhibited minor differences in chemical shift data in comparison to the directly analogous iodides **2** and **3**.

In contrast to the reactivity of **I** with alkyl iodides and bromides, no reaction was observed with aryl iodides or a variety of alkyl monochlorides. This observation is consistent with reports of previous workers attempting to perform C−C coupling reactions of aryl reagents and alkyl chlorides and may be rationalized as a reflection of the increased sp^2-C−I and sp^3-C−Cl thermodynamic bond strengths versus their respective alkyl and heavier group 17 counterparts.[1]

X-ray Structural Analyses. Single-crystal X-ray diffraction analyses of compounds **1**−**5** were undertaken. The structures of all five compounds were similar, and representative examples are provided for compounds **1** and **5** in Figures 1 and 2, respectively (ORTEP representations of compounds **2**−**4** are provided as Figures S1−S3 in the Supporting Information). Details of the crystallographic analyses for **1**−**5** and selected bond length and angle data are displayed in Tables 1−3, respectively. The structures of **1**−**5** display a number of common features, as well as similarities to previously reported β-diketiminate complexes of trivalent aluminum, gallium, and indium.[21,22] Subtle differences in ligand steric demands do, however, result in minor variations about the indium metal center. Although only the indium isopropyl derivatives **2** and **4** are isostructural, the ring C−N and C−C bond lengths for all five compounds lie within narrow ranges, 1.323(5)−1.333(5) and 1.399(5)−1.411(8) Å. These values are effectively identical within the limits of experimental uncertainty and are consistent with significant multiple-bond character and delocalization about the metallocycle. The In−N distances [av 2.155 Å] and N−In−N bond angles [av 89.9°] are also similar and may be compared to the respective distances and angles within the previously reported complexes [$InCl_{1.5}Br_{0.5}${N(Dipp)C(Me)}$_2$CH] (av 2.117 Å, 92.5°), [InI_2{N(Dipp)C(Me)}$_2$CH] (av 2.134 Å, 92.42°), and [$InMe_2${N(Dipp)-

(21) Stender, M.; Eichler, B. E.; Hardman, N. J.; Power, P. P.; Prust, J.; Noltemeyer, M.; Roesky, H. W. *Inorg. Chem.* **2001**, *40*, 2794.
(22) Quian, B.; Ward, D. L.; Smith, M. R., III. *Organometallics* **1998**, *17*, 3070.

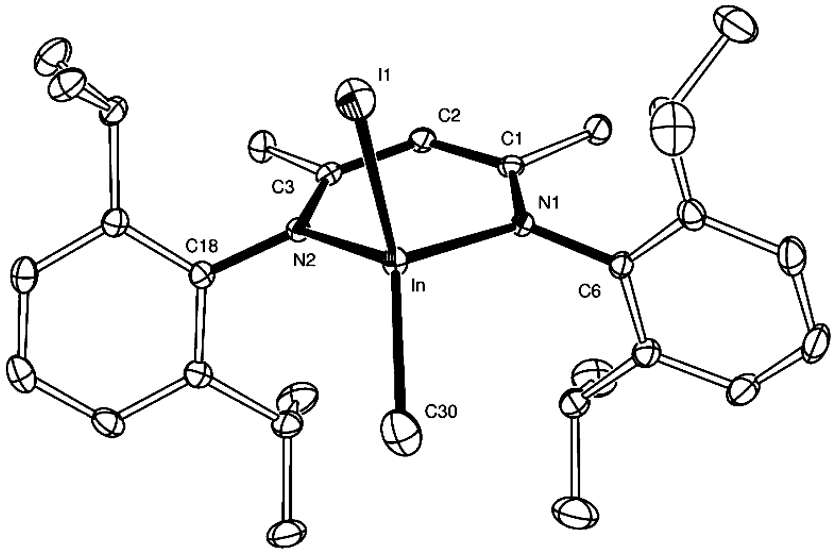


Figure 1. Thermal ellipsoid (30%) plot of compound **1**. Hydrogen atoms omitted for clarity.

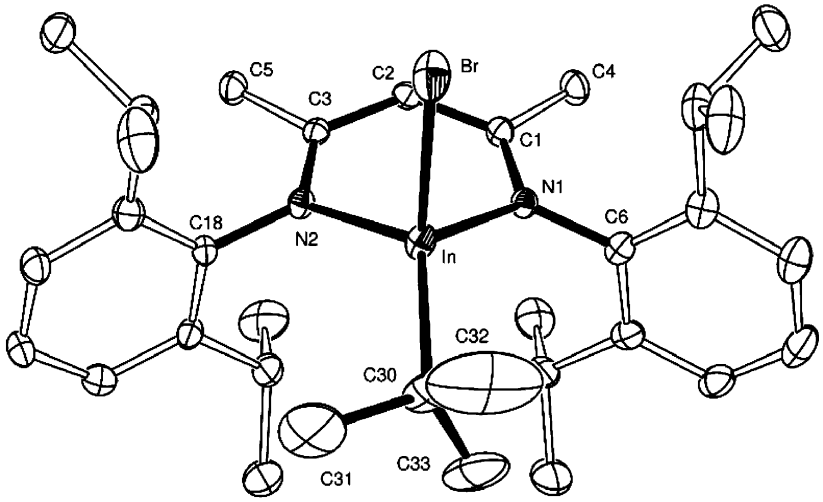


Figure 2. Thermal ellipsoid (30%) plot of compound **5**. Hydrogen atoms omitted for clarity.

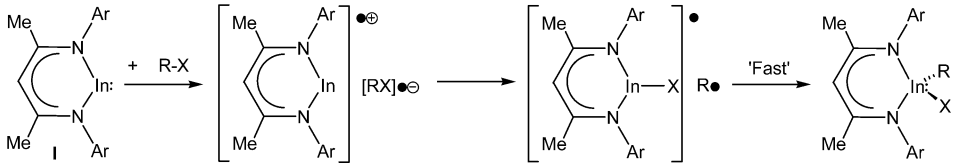
C(Me)}$_2$CH] (av 2.197 Å, 86.76°). These values, therefore, may be described as entirely typical of In(III) derivatives of this ligand and are respectively shorter and more obtuse than those observed in the corresponding In(I) complex (2.268(3), 2.276(3) Å; 81.12(10)°). Although the NCCCN chelates are completely planar (rms deviation of fitted atoms = 0.00°), as is observed in many other derivatives of β-diketiminate ligands, the structures of **1**−**5** display a distinct folding across the N−N vector formed by the nitrogen donors. The structures adopted by all five complexes are dictated by the steric interactions between the *N*-Dipp and alkyl (rather than the halide) substituent. The out-of-plane folding of the indium center occurs in a manner that minimizes possible steric interactions between the *N*-Dipp ligand substituents and the indium alkyl group. The dihedral angles between the planes defined by the NCCCN and NInN fragments are displayed in Table 4, and it is readily apparent from inspection of these data that the presence of the bulky *tert*-butyl substituent within the structures of compounds **3** and **5** has the most meaningful structural consequence.

Table 4. Dihedral Angle (φ) (deg) Formed by Intersection of the NCCCN and NInN Planes of Compounds **1**−**5**

	1	**2**	**3**	**4**	**5**
φ	160.0	160.6	148.2	159.6	149.6

Mechanistic Considerations. NMR scale studies of the oxidative addition reactions described above indicated that the reactions were effectively complete with 15 min of mixing at ambient temperatures. Additionally, all the reactions studied in this manner resulted in quantitative conversion to compounds of the form [LInRX] (L = diketiminate ligand, R = alkyl, X = Br or I) as the *only* indium-containing product. Lappert's observation of low, but observable, concentrations of E_2SnX_2 products (E = alkyl or amide) from reactions of stabilized stannylenes and alkyl halides was cited as evidence for the dominance of radical pathways some 30 year ago,[12] a hypothesis strongly supported by the direct observation of tin- and carbon-centered radicals in parallel EPR investigations of the same reactions.[16a] Although our failure to observe anything other than indium alkyl halide formation in any of the reactions that we have studied thus

Scheme 2



far could be interpreted as evidence of a contrasting concerted mechanism, the literature precedents in both low valent group 13 and 14 chemistry lead us to conclude that the rate of $[LinI]^{\bullet}/R^{\bullet}$ radical recombination is simply too rapid to allow formation of anything but the observed unsymmetrically substituted products. This hypothesis has been supported by preliminary X-band EPR experiments on the reaction of compound **I** with MeI. The addition of an excess of the alkyl iodide to a toluene glass containing compound **I** at 77 K, followed by warming in 5 K increments within the cavity of the EPR spectrometer, gave a very weak but persistent signal at 190 K (coincidentally the melting point of toluene) at around the *g* value for the free electron (see Figure S4, Supporting Information). This signal rapidly disappeared upon any further increase of temperature and did not reappear upon recooling of the samples. Similarly, more rapid warming of the sample to temperatures in excess of 195 K gave no evidence of radical intermediates and leads us to propose the tentative mechanism illustrated in Scheme 2 where rapid recombination of the indium- and carbon-centered radicals predominates over other recombination processes which are probably impeded by the steric effects of the bulky supporting ligand.

We are continuing our experimental and theoretical studies this well-defined reactivity as well as related reaction chemistry of the In(I) compounds **I**−**V**.

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Supporting Information Available: ORTEP figures of compounds **2**−**4**, representative EPR spectrum, and crystallographic data for **1**−**5** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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