through a toluene solution of complex **9** (1.2 g, 2.6 mmol) at room temperature. After filtration, toluene was evaporated and the residue was chromatographed with hexane–toluene (60:40): R_f ~0.4; yield, 0.82 g (69%) of colorless solid; mp 68 °C; mass spectrum (^{184}W), m/e (relative intensity) 449 (M, 91), 421 (M – CO, 31), 393 (M – 2CO, 31), 365 (M – 3CO, 14), 337 (M – 4CO, 34), 309 (M – 5CO, 100). Anal. Calcd for $C_{11}H_8NO_5PW$: C, 29.43; H, 1.79; N, 3.12; P, 6.90. Found: C, 29.74; H, 1.32; N, 2.79; P, 6.80.

Bis[(phenylphosphido)pentacarbonyltungsten] Sulfide (13). Complex **9** (1 g, 2.1 mmol) was treated with anhydrous NaSH (0.28 g, 5 mmol) in toluene at room temperature for one night. After filtration and evaporation the residue was chromatographed with hexane–toluene (90:10): R_f ~0.5; yield 0.41 g (43%) of colorless solid; mp 157 °C (hexane–toluene); mass spectrum (chemical ionization with NH_3, ^{184}W), m/e 914 (relative intensity) (M + NH_2, 100), 899 (M + 1, 16). There was no SH stretch on the IR spectrum around 2550 cm^{-1}.

Dismutation of Complex 9. Complex **9** (2 g, 4.2 mmol) was treated with $AlCl_3$ (0.6 g, 4.5 mmol) in dichloromethane for 3 h at room temperature. After hydrolysis, the organic phase was evaporated. The organic residue was chromatographed with hexane. The first recovered product (R_f ~0.8) was (phenyldichlorophosphine)pentacarbonyltungsten (**15**): yield 38%; mass spectrum (70 eV, ^{35}Cl, ^{184}W), m/e 502 (M, 90), 467 (M – Cl, 66), 362 (M – 5CO, 100), 327 (362 – Cl, 50); ^{31}P NMR (hexane) δ 126.2 ($^1J(^{183}W-^{31}P)$ = 341.8 Hz); IR (decalin) ν(CO) 2084 (w), 1978 (s), 1967 (vs) cm^{-1}. The second product (R_f ~0.4) was (phenylphosphine)pentacarbonyltungsten (**14**): yield, 44%; ^1H NMR (C_6D_6) δ 4.77 (d, ^1J(H–P) = 343 Hz, 1 H, PH), 6.91–7.16 (m, 5 H, Ph); ^{31}P NMR (hexane) δ –87.7 ($^1J(^{183}W-^{31}P)$ = 224.6 Hz) (these NMR data are very similar to those reported in the literature for this compound[9]); IR (decalin) ν(CO) 2077 (w), 1948 (vs) cm^{-1}; KBr ν (PH) 2325 cm^{-1}. An easy dismutation of **14** seemed to occur in the mass spectrometer (electronic impact, 70 eV, ^{184}W): $(PhPH_2)_2W(CO)_4$ was thus obtained (m/e 516). Both complexes (**14** and **15**) have been already described in the literature.[9,10]

Registry No. 1a, 82265-63-2; **1b**, 82265-64-3; **1c**, 82265-65-4; **2a**, 82839-06-3; **2b**, 82265-66-5; **3a**, 82839-07-4; **3b**, 82839-08-5; **4a**, 82839-09-6; **4b**, 82839-10-9; **4c**, 82839-11-0; **5**, 82839-12-1; **7**, 82839-13-2; **8**, 82839-14-3; **9**, 82839-15-4; **10**, 82839-16-5; **11**, 82839-17-6; **12**, 82839-18-7; **13**, 82839-19-8; HCl, 7647-01-0; HBr, 10035-10-6; HI, 10034-85-2; NaSH, 16721-80-5; $AlCl_3$, 7446-70-0; (1-phenyl-3,4-dimethylphosphole)pentacarbonylchromium, 74363-90-9; dimethyl acetylenedicarboxalate, 762-42-5; (1-phenyl-3,4-dimethylphosphole)pentacarbonyltungsten, 74363-95-4; (1,3,4-trimethylphosphate)pentacarbonyltungsten, 82849-01-2; methanol, 67-56-1; water, 7732-18-5; aniline, 62-53-3; diethylamine, 109-89-7; methyl iodide, 74-88-4; benzophenone, 119-61-9; ammonia, 7664-41-7.

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Intramolecular In–N Coordination. Synthesis and NMR Study of Four-Coordinate $[2\text{-}Me_2NCH(Z)C_6H_4]Me_2In$ and Five-Coordinate $[2\text{-}Me_2NCH(Z)C_6H_4]_2InCl$ (Z = H or (*S*)-CH_3)

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Arylindium compounds of the type Ar_2InCl and $ArMe_2In$, in which the Ar group is either 2-$Me_2NCH_2C_6H_4$ or (*S*)-2-$Me_2NCH(Me)C_6H_4$, have been synthesized by the organolithium route and characterized by ^1H and ^{13}C NMR spectroscopy. The NMR results clearly reveal that intramolecular In–N coordination occurs in solution, resulting in five-coordinate Ar_2InCl and four-coordinate $ArMe_2In$ structures. In pyridine solution, the In–N bond in the four-coordinate $ArMe_2In$ compounds weakens as the result of the formation of a five-coordinate intermediate in which the NMe_2 and pyridine ligand are in axial positions.

Introduction

There has recently been considerable interest in the structural properties of organoindium(III) compounds and their derivatives, and X-ray crystallographic and other studies have revealed a variety of coordination numbers and stereochemistries at the indium atom. Distorted trigonal-bipyramidal geometry is found in a number of compounds in which intermolecular coordination takes place, including $[(CH_3)_2InCl]_2$,[1] $[CH_3InCl_2]_2$,[2] $(C_2H_5)_2InOSCCH_3$,[3] and $[(CH_3)_2In(ON{=}CHC_5H_4N)_2]_2$.[4] The triorganoindium(III) compounds $(CH_3)_3In$[5] and $(C_6H_5)_3In$[6] also involve five-coordinate indium in the solid state, although $(CH_3)_3In$ is a trigonal-planar monomer in the gas phase,[7,8] and both compounds are monomeric in various

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Table I. ^{1}H NMR Spectra of Diarylindium Chlorides I and II and of the Dimethylarylindium Compounds III and IV

compd[g]	solvent (temp, °C)	δ[a] NMe$_2$	NCH$_2$	α-CH$_3$	H$_6$[b]	In-CH$_3$
I, Ar$_2$InCl	$CDCl_3$ (amb)	2.60 s	3.71 s	...	7.61	...
I, Ar$_2$InCl	$CDCl_3$ (−40)	2.49 s[c] 2.78 s[c]	3.28 d[c,d] 4.29 d[c,d]	...	7.67	...
I, Ar$_2$InCl	$C_6H_5CD_3$ (amb)	2.21 s[e]	3.42 s[e,d]	...	7.55	...
I, Ar$_2$InCl	$C_6H_5CD_3$ (−35)	2.06 s[e] 2.63 s	2.81 d[e,d] 4.33 d	...		...
II, [(*S*)-Ar]$_2$InCl	$CDCl_3$ (amb)	2.53 s	...	1.45	7.87	...
II, [(*S*)-Ar]$_2$InCl	$CDCl_3$ (−10)	2.42 s[f] 2.67 s[f]	...	1.47	7.87	...
II, [(*S*)-Ar]$_2$InCl	$C_6H_5CD_3$ (amb)	2.23 s	...	1.15	7.71	...
III, ArInMe$_2$	$C_6H_5CD_3$ (amb)	1.95 s	3.15 s	...	7.75	0.05
IV, (*S*)-ArInMe$_2$	$C_6H_5CD_3$ (amb)	2.05 s		1.20	7.80	0.05

[a] Me_4Si internal, δ (ppm). [b] Multiplet resonances. [c] T(coal.) = −10 °C. [d] J_{AB} = 14 Hz. [e] T(coal) = ~0 °C. [f] T(coal) = 12 °C. [g] Spectra of I and II were run on a 90 MHz, and spectra of III and IV were run on a 60-MHz spectrometer.

organic solvents.[9-11] In the lattice of $(CH_3)_2InBr$,[12] the indium atom achieves tetragonal-bipyramidal stereochemistry, with an InC_2Br_4 kernel, and six-coordination is also found in the polymeric $(CH_3)_2InO_2CCH_3$,[13] where the coordination kernel is $InC_2O_2O'_2$. Tetrahedral structures have been proposed for 1:1 adducts of triorganoindium compounds with monodentate ligands[14] and have been identified by X-ray crystallographic methods for the anions $[In(CH_3)_4]^-$[15] and $[In(C_6H_5)_4]^-$.[16]

In recent years, the coordination behavior of organometallic compounds containing the potentially bidentate ligand 2-$Me_2NCH(Z)C_6H_4$ (Z = H or (*S*)-Me) has been the focus of extensive studies. Both ^{1}H and ^{13}C NMR spectroscopy have proven to be particularly valuable tools for establishing whether or not the Me_2N group is involved in metal–nitrogen coordination.[17-21] We have now extended this work to include two types of organoindium compounds containing this ligand, namely, Ar_2InCl and $ArMe_2In$ (Ar = 2-$Me_2NCH(Z)C_6H_4$; Z = H or (*S*)-Me). Depending on whether Ar acts as a mono- or bidentate ligand, the indium atom in these compounds may be three-, four-, or five-coordinate and three- or four-coordinate, respectively. In this paper we report investigations of the coordination behavior of these compounds in solution. The results of an X-ray crystallographic study, which showed a distorted trigonal-bipyramidal structure for Ar_2InCl (Z = H) in the solid, have already been published.[22]

Experimental Section

All reactions were carried out under dry oxygen-free nitrogen. Solvents were carefully purified and distilled before use under nitrogen. {2-[(Dimethylamino)methyl]phenyl}lithium and {2-[(*S*)-1-(dimethylamino)ethyl]phenyl}lithium were as reported elsewhere.[18]

^{1}H NMR spectra were recorded on Varian EM 390 and T 60 and Bruker WH 90 NMR spectrometers; ^{13}C NMR spectra were obtained with a Bruker WP 80 NMR spectrometer.

Bis{2-[(dimethylamino)methyl]phenyl}indium Chloride (I). A suspension of freshly prepared {2-[(dimethylamino)methyl]phenyl}lithium (40 mmol) in diethyl ether (80 mL) was added during 45 min to a suspension of $InCl_3$ (20 mmol) in the same solvent (100 mL). This mixture was stirred during 24 h. The solvent was removed in vacuo and the resulting gray solid extracted with warm benzene (3 × 80 mL). The benzene extract was concentrated until dryness, and the white residue was washed twice with pentane (50 mL) and dried in vacuo: yideld 72%; mol wt (by ebulliometry in benzene) found (calcd), 437 (418.7); mp 191 °C. (Anal. Calcd for $C_{18}H_{24}ClIn$: C, 51.64; H, 5.78; N, 6.69; Cl, 8.47; In, 27.42. Found: C, 51.17; H, 5.91; N, 6.51; Cl, 8.63; In, 27.7.)

Bis{2-[(*S*)-1-(dimethylamino)ethyl]phenyl}indium chloride (II) was prepared in essentially the same manner, starting from {2-[(*S*)-1-(dimethylamino)ethyl]phenyl}lithium and $InCl_3$ (2/1 molar ratio): yield 79%; mol wt (by ebulliometry in benzene) found (calcd), 458 (446.3); mp 179 °C. Anal. Calcd for $C_{20}H_{28}N_2ClIn$: C, 53.77; H, 6.32; N, 6.27; Cl, 7.94; In, 25.70. Found: C, 52.59; H, 6.45; N, 6.01; Cl, 8.11; In, 26.04.)

{2-[(Dimethylamino)methyl]phenyl}dimethylindium (III). Me_2InCl (5 mmol) was added at once to a suspension of {2-[(dimethylamino)methyl]phenyl}lithium (5 mmol) in diethyl ether (20 mL). An exothermic reaction occurred resulting in the formation of a light gray suspension. The mixture was stirred for 15 min and then concentrated in vacuo, yielding a white tarry product which was taken up in 20 mL of pentane. The insoluble material (LiCl) was filtered off and the filtrate concentrated at reduced pressure, yielding a colorless oil. According to ^{1}H and ^{13}C NMR spectra this oil appeared to be almost pure III: yield 79%; bp 104 °C (0.1 mm); mol wt (by cryoscopy in benzene) found (calcd), 266 (279.8).

{2-[(*S*)-(1-Dimethylamino)ethyl]phenyl}dimethylindium (IV) was obtained by essentially identical procedures starting from {2-[(*S*)-1-(dimethylamino)ethyl]phenyl}lithium and Me_2InCl (1/1 molar ratio): yield 69%; bp 111 °C (0.1 mm).

Results and Discussion

The diarylindium chlorides I and II were readily obtained via the route shown in eq 1a. The dimethylaryl-

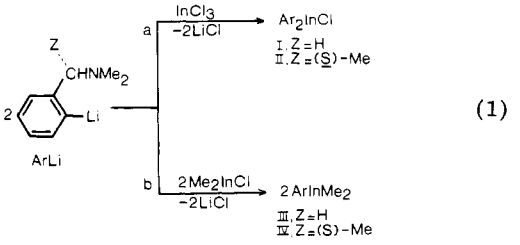

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Table II. ^{13}C NMR Spectra of Diarylindium Chlorides I and II and Dimethylarylindium Chlorides III and IV[a]

	temp, °C	solvent	C_1	C_2	C_3	C_4	C_5	C_6	ArCN	$N(CH_3)_2$	α-CH_3	$InCH_3$
I	amb	$C_6D_5CD_3$	151.2	146.4	...	...	...	138.5	67.1	46.1		
I	−50	$C_6D_5CD_3$	150.1	146.1				138.3	65.9	46.8		
										44.3		
I	amb	$CDCl_3$	149.5	144.9				137.2	65.9	45.5		
I	−50	$CDCl_3$	147.7	144.5				136.9	65.1	46.1		
										44.5		
II	amb	$C_6D_5CD_3$	150.9	151.7				138.8	66.9	44.9	16.2	
II	−40	$C_6D_5CD_3$	149.6	151.3				138.7	65.5	46.0	16.1	
										40.4		
II	−80	$C_6D_5CD_3$	all signals very broad ≥100 Hz; solvent sharp									
II	amb	C_5D_5N	149.4	151.1				138.2	66.2	43.0	15.8	
II	−20	C_5D_5N	148.5	150.6				138.1	65.0	42.4	14.9	
II	−40	C_5D_5N	148.7	150.3				138.2	64.6	42.2	14.3	
III	amb	$C_6D_5CD_3$	159.4	144.5				138.6	68.1	45.4		−3.3
IV	amb	$C_6D_5CD_3$	158.6	151.6				139.5	70.9	46.9	19.7	−6.0
										41.4		
IV	−50	$C_6D_5CD_3$	157.8	151.9				139.4	70.7	46.7	19.3	−4.8
										41.5		−7.1
IV	−40	C_5D_5N	158.2	152.6				138.4	68.6	43.0 (sh)	19.0	−7.7

[a] Me_4Si internal, δ (ppm).

indium compounds III and IV were obtained as pure products from the reaction of dimethylindium chloride with the respective aryllithium compounds (eq 1b), provided that during these reactions dimethylindium chloride was present in excess; i.e., the lithium compound was added to the indium compound. In contrast to I and II, which are white crystalline solids, the dimethylarylindium compounds III and IV are distillable liquids. Molecular weight determinations showed that these compounds exist as monomers in benzene. ^1H and ^{13}C NMR data, which confirm the proposed stoichiometry, are presented in Tables I and II, respectively.

NMR spectroscopy has proved to be a useful tool for elucidating the coordination behavior (mono- or bidentate) of the 2-$Me_2NCH(Z)C_6H_4$ ligand in a variety of organometallic compounds including [2-$Me_2NCH(Z)C_6H_4]_4Cu_{4-n}M_n$ (M = Li, n = 2; M = Cu, n = 0),[18] [2-$Me_2NCH(Z)C_6H_4$]MePhSnBr,[17] [2-$Me_2NCH(Z)C_6H_4$]-$RSnX_2$ (R = Me, Ph, or 2-$Me_2NCH(Z)C_6H_4$),[19] (2-$Me_2NCH(Z)C_6H_4$)HgX,[20] and [2-$Me_2NCH(Z)C_6H_4]_{2-n}TlX_n$.[21] When metal–nitrogen coordination takes place, so that the molecule lacks molecular mirror planes containing the C and/or N centers of the CH_2NMe_2 groupings, the CH_2 and NMe_2 groups will be diastereotopic. In the absence of metal–nitrogen coordination only the CH_2 group will be diastereotopic, since rapid inversion at the N center will render the NMe_2 groups homotopic. In contrast, when molecular mirror planes containing the N atom are present, metal–nitrogen coordination can be detected when the CH_2 group is changed into a chiral CH(Me) group. Coordination of the N center will then result in diastereotopic NMe_2 groups.

The ^1H and ^{13}C NMR spectra of III and IV provide a clear illustration of these principles. The CH_2 and NMe_2 ^1H resonances, as well as the NMe_2 ^{13}C resonance of III, are isochronous in the temperature range studied (−80 to +100 °C). This can be explained by either a three- or a four-coordinate structure (see Figure 1, Z = H). In structure A, rotation around the (aryl)C–In bond renders the CH_2 and NMe_2 homotopic, while in structure B the C and N centers are in a molecular mirror plane. However, introduction of a methyl group at the benzylic carbon atom allows a choice between structure A and B to be made. In IV the configuration at the benzylic C atom is *S* by choice.

The ^{13}C NMR spectra of IV at room temperature and below reveal anisochronous $(CH_3)_2N$ ^{13}C resonances that indicate that the N atom has a stable tetrahedral configuration as a result of In–N coordination (Figure 1, B). The prochiral $InMe_2$ assembly likewise becomes diastereotopic as a result of In–N coordination. This is confirmed by the observation of two singlets for the In methyl groups in the −50 °C spectrum. The fact that the latter two singlets have coalesced at room temperature points to the occurrence of a dynamic process involving In–N bond dissociation, rapid pyramidal inversion at the N center, rotation around the CH(Z)–N bond and concomitant rotation around the C–In bond, and recoordination. Such a process renders both the $InMe_2$ and NMe_2 groups homotopic. The two $InMe_2$ singlet resonances coalesce at a lower temperature (~25 °C) than do the two NMe_2 singlet resonances (>100 °C), due to the smaller Δδ. (see Table II).

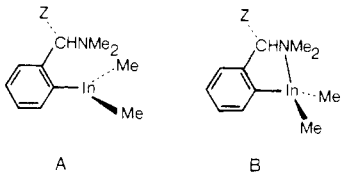

Figure 1. Possible structures for III (Z = H) and IV (Z = (*S*)-Me).

The occurrence of intramolecular In–N coordination in IV (and by inference in III) is perhaps not surprising because trialkyl- and triarylindium compounds have been reported to form 1/1 complexes with a variety of monodentate ligands[14] in which the indium is most likely tetrahedrally surrounded (cf. Introduction). Considerable distortion from tetrahedral symmetry will occur in tetracoordinate III and IV, because the bite angle of the $Me_2NCH(Z)C_6H_4$ ligand in III and IV will be close to 75°, as is observed in other $Me_2NCH(Z)C_6H_4M$ (LM) complexes, e.g., 75.3° in Ph_2LSnBr,[23] 75.2° in PhMeLSnBr,[17] 73° in CpLTi,[24] 77° in L_2InCl,[22] and 73.4° in CpL_2Ti.[25]

The observation that In–N coordination nevertheless occurs points to relatively strong acceptor behavior at the indium center in the Me_2ArIn compounds III and IV.

In coordinating solvents the In–N bond in III and IV weakens. Whereas the NMe_2 groups of IV dissolved in toluene were diastereotopic (up to 100 °C; Δδ = 5), in pyridine as a solvent these groups are already homotopic

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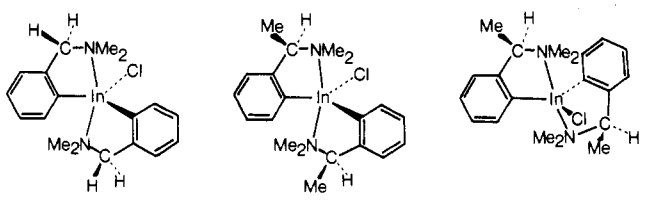
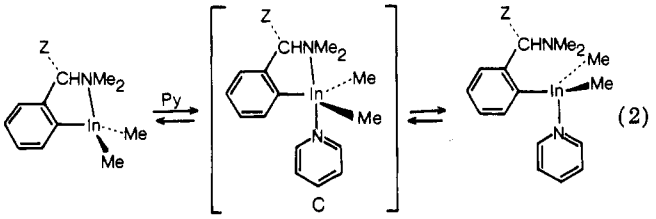


IA IIB IIC

Figure 2. Proposed structures for the diarylindium chlorides I and II.

at −40 °C (one sharp singlet). This points to an increase of the rate of the dynamic process discussed above, which involves initial In–N bond breaking and recoordination of the $CH(Z)NMe_2$ ligand as essential steps. The weakening of the In–NMe_2 bond in pyridine solution is ascribed to the coordination of a pyridine ligand to the indium atom (see eq 2). The resulting five-coordinate intermediate C that is involved in the equilibria shown in eq 2 will most probably have a trigonal-bipyramidal structure with the pyridine and NMe_2 donors occupying mutually trans positions. This type of structure has actually been ob-



(2)

served for $(2\text{-}Me_2NCH_2C_6H_4)_2InCl$ (I) in the solid state.[22] With $CDCl_3$ solutions below −10 °C, the ^1H NMR spectrum consists of two singlets from the NMe_2 resonance (at 2.49 and 2.78 ppm) and an AB pattern for the NCH_2 protons (3.20 + 3.35 and 4.20 + 4.35 ppm). This result demonstrates that under these conditions the NMe_2 and CH_2 hydrogen atoms are diastereotopic, in agreement with the coordination of at least one NMe_2 ligand to the indium atom. Furthermore, the appearance of the diastereotopic NMe_2 proton signals at lower field relative to the chemical shift of these protons in the fast-exchange limit also provides evidence of In–N coordination. Since only one pattern is observed for the two $2\text{-}Me_2NCH_2C_6H_4$ groups, compound I must have the stereochemistry shown in Figure 2 (IA), which is similar to that found in the solid.

The corresponding C-chiral compound II can in principle exist in the two diastereomeric forms shown in Figure 2 (B and C), which differ with respect to the relative orientation of the Me groups connected to the chiral *S* benzylic C center to the In–Cl bond. Tables I and II reveal that only one pattern is observed, also in the slow-exchange limit, which suggests the presence of only one diastereomer in solution. The signals of the diastereotopic groups in I and II coalesce already at room temperature. The In–N bonds in I and II will be weaker than those in III and IV as a result of coordination of two trans-positioned N ligands (cf. the lower coalescence temperatures for the resonances of the diastereotopic $InMe_2$ and NMe_2 groups in IV in pyridine solution and the role of intermediate C in eq 2). The coalescence may be explained in terms of the equilibria shown in Figure 3. One of the two In–N bonds can dissociate with the concomitant processes pointed out for III and IV taking place. Recoordination is then fol-

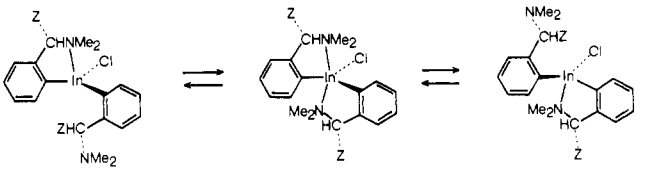
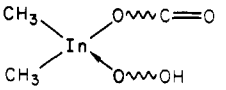


Figure 3. Processes which explain the dynamic NMR spectra of I (Z = H) and II (Z = (*S*)-Me).

lowed either by dissociation of the same or of the trans-positioned In–N bond. Occurrence of an alternative process involving simultaneous In–N bond dissociation seems less likely in view of the relatively strong In–N coordination found for the four-coordinate compounds III and IV but cannot be ruled out completely on the available evidence.

The present results show that triorganoindium compounds $[2\text{-}Me_2NCH(Z)C_6H_4]InMe_2$ have a strong tendency to form four-coordinate complexes via intramolecular In–N coordination. A similar behavior was found for the recently reported $[2\text{-}Me_2NCH(Z)C_6H_4]TlCl_2$ complexes.[21] Comparison of the NMR data of the four-coordinate In and Tl derivatives indicates that the M–N bond in $[2\text{-}Me_2NCH(Z)C_6H_4]TlCl_2$ is weaker than in $[2\text{-}Me_2NCH(Z)C_6H_4]InMe_2$, especially when the presence of Tl–Cl bonds instead of Tl–Me bonds in the Tl compound is taken into account. The observation that with external donor ligands, e.g., pyridine, an exchange process occurs which probably involves the formation of a five-coordinate intermediate indicates that the four-coordinate indium center in $ArInMe_2$ still has Lewis acid activity. The higher stability of the In–N bonds as compared with the Tl–N bonds is also reflected in the related $[2\text{-}Me_2NCH(Z)C_6H_4]_2MCl$ compounds (M = In, Tl)[21] which in the slow-exchange limit both have five-coordinate structures.

It is also worth noting that the Lewis acid properties of diorganoindium(III) compounds have been invoked previously in kinetic studies of the solution properties of such compounds.[26] Ligand exchange between $(CH_3)_2In(CF_3COCHCOR)$ and CF_3COCH_2COR (R = CH_3, $t\text{-}C_4H_9$) is a second-order process in which the proposed transition state is



The proposed increase in coordination number was supported by the isolation of adducts of bidentate ligands such as $(CH_3)_2In(CF_3COCHCOR)(bpy)$ (bpy = 2,2′-bipyridine). Coordination number changes have also been postulated in ligand exchange reactions[27] for $In(CF_3COCHCOR)_3$, and in general the present work confirms earlier statements as to the lability of indium(III) complexes in solution.[28]

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Registry No. I, 74552-66-2; II, 82839-20-1; III, 82839-21-2; IV, 82839-22-3; $InCl_3$, 10025-82-8; Me_2InCl, 14629-99-3; {2-[(dimethylamino)methyl]phenyl}lithium, 27171-81-9; {2-[(*S*)-1-(dimethylamino)ethyl]phenyl}lithium, 63072-89-9.

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