

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): $R_f \sim 0.4$; 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 $\text{C}_{11}\text{H}_9\text{NO}_2\text{PW}$: 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): $R_f \sim 0.5$; 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 ($R_f \sim 0.8$) 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 ($^1J(^{183}\text{W}-^{31}\text{P}) = 341.8$ Hz); IR (decalin) $\nu(\text{CO})$ 2084 (w), 1978 (s),

1967 (vs) cm^{-1} . The second product ($R_f \sim 0.4$) was (phenylphosphine)pentacarbonyltungsten (14): yield, 44%; ^1H NMR (C_6D_6) δ 4.77 (d, $^1J(\text{H}-\text{P}) = 343$ Hz, 1 H, PH), 6.91-7.16 (m, 5 H, Ph); ^{31}P NMR (hexane) δ -87.7 ($^1J(^{183}\text{W}-^{31}\text{P}) = 224.6$ Hz) (these NMR data are very similar to those reported in the literature for this compound⁹); IR (decalin) $\nu(\text{CO})$ 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): $(\text{PhPH}_2)_2\text{W}(\text{CO})_4$ 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 acetylenedicarboxylate, 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 $[2\text{-Me}_2\text{NCH}(\text{Z})\text{C}_6\text{H}_4]\text{Me}_2\text{In}$ and Five-Coordinate $[2\text{-Me}_2\text{NCH}(\text{Z})\text{C}_6\text{H}_4]_2\text{InCl}$ (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- $\text{Me}_2\text{NCH}_2\text{C}_6\text{H}_4$ or (S)-2- $\text{Me}_2\text{NCH}(\text{Me})\text{C}_6\text{H}_4$, 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 $[(\text{CH}_3)_2\text{InCl}]_2$,¹ $[\text{CH}_3\text{InCl}_2]_2$,² $(\text{C}_2\text{H}_5)_2\text{InO}$

SCCH_3 ,³ and $[(\text{CH}_3)_2\text{In}(\text{ON}=\text{CHC}_5\text{H}_4\text{N})_2]_2$.⁴ The tri-organoindium(III) compounds $(\text{CH}_3)_3\text{In}$ ⁵ and $(\text{C}_6\text{H}_5)_3\text{In}$ ⁶ also involve five-coordinate indium in the solid state, although $(\text{CH}_3)_3\text{In}$ is a trigonal-planar monomer in the gas phase,^{7,8} and both compounds are monomeric in various

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Table II. ^{13}C NMR Spectra of Diaryliindium Chlorides I and II and Dimethylaryliindium 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 ₆ D ₅ CD ₃	151.2	146.4	138.5	67.1	46.1		
I	-50	C ₆ D ₅ CD 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 ₆ D ₅ CD ₃	150.9	151.7				138.8	66.9	44.9	16.2	
II	-40	C ₆ D ₅ CD ₃	149.6	151.3				138.7	65.5	46.0	16.1	
										40.4		
II	-80	C ₆ D ₅ CD ₃	all signals very broad ≥ 100 Hz; solvent sharp									
II	amb	C ₅ D ₅ N	149.4	151.1				138.2	66.2	43.0	15.8	
II	-20	C ₅ D ₅ N	148.5	150.6				138.1	65.0	42.4	14.9	
II	-40	C ₅ D ₅ N	148.7	150.3				138.2	64.6	42.2	14.3	
III	amb	C ₆ D ₅ CD ₃	159.4	144.5				138.6	68.1	45.4		-3.3
IV	amb	C ₆ D ₅ CD ₃	158.6	151.6				139.5	70.9	46.9	19.7	-6.0
										41.4		
IV	-50	C ₆ D ₅ CD ₃	157.8	151.9				139.4	70.7	46.7	19.3	-4.8
										41.5		-7.1
IV	-40	C ₅ D ₅ N	158.2	152.6				138.4	68.6	43.0 (sh)	19.0	-7.7

^a Me₄Si 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 dimethylaryliindium compounds III and IV are distillable liquids. Molecular weight determinations showed that these compounds exist as monomers in benzene. ¹H and ¹³C 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-Me₂NCH(Z)C₆H₄ ligand in a variety of organometallic compounds including [2-Me₂NCH(Z)C₆H₄]₂Cu_{4-n}M_n (M = Li, n = 2; M = Cu, n = 0),¹⁸ [2-Me₂NCH(Z)C₆H₄]₂MePhSnBr,¹⁷ [2-Me₂NCH(Z)C₆H₄]₂RSnX₂ (R = Me, Ph, or 2-Me₂NCH(Z)C₆H₄),¹⁹ (2-Me₂NCH(Z)C₆H₄)₂HgX,²⁰ and [2-Me₂NCH(Z)C₆H₄]_{2-n}TiX_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 CH₂NMe₂ groupings, the CH₂ and NMe₂ groups will be diastereotopic. In the absence of metal-nitrogen coordination only the CH₂ group will be diastereotopic, since rapid inversion at the N center will render the NMe₂ groups homotopic. In contrast, when molecular mirror planes containing the N atom are present, metal-nitrogen coordination can be detected when the CH₂ group is changed into a chiral CH(Me) group. Coordination of the N center will then result in diastereotopic NMe₂ groups.

The ¹H and ¹³C NMR spectra of III and IV provide a clear illustration of these principles. The CH₂ and NMe₂ ¹H resonances, as well as the NMe₂ ¹³C 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 CH₂ and NMe₂ 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 ¹³C NMR spectra of IV at room temperature and below reveal anisochronous (CH₃)₂N ¹³C resonances that indicate that the N atom has a stable tetrahedral config-

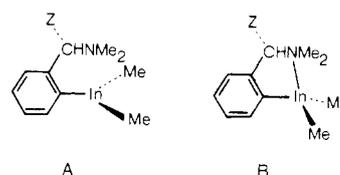


Figure 1. Possible structures for III (Z = H) and IV (Z = (S)-Me).

uration as a result of In-N coordination (Figure 1, B). The prochiral InMe₂ 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 InMe₂ and NMe₂ groups homotopic. The two InMe₂ singlet resonances coalesce at a lower temperature (~25 °C) than do the two NMe₂ singlet resonances (>100 °C), due to the smaller Δδ. (see Table II).

The occurrence of intramolecular In-N coordination in IV (and by inference in III) is perhaps not surprising because trialkyl- and triaryliindium compounds have been reported to form 1/1 complexes with a variety of monodentate ligands¹⁴ in which the indium is most likely tetrahedrally surrounded (cf. Introduction). Considerable distortion from tetrahedral symmetry will occur in tetra-coordinate III and IV, because the bite angle of the Me₂NCH(Z)C₆H₄ ligand in III and IV will be close to 75°, as is observed in other Me₂NCH(Z)C₆H₄M (LM) complexes, e.g., 75.3° in Ph₂LSnBr,²³ 75.2° in PhMeLSnBr,¹⁷ 73° in CpLTi,²⁴ 77° in L₂InCl,²² and 73.4° in CpL₂Ti.²⁵

The observation that In-N coordination nevertheless occurs points to relatively strong acceptor behavior at the indium center in the Me₂ArIn compounds III and IV.

In coordinating solvents the In-N bond in III and IV weakens. Whereas the NMe₂ 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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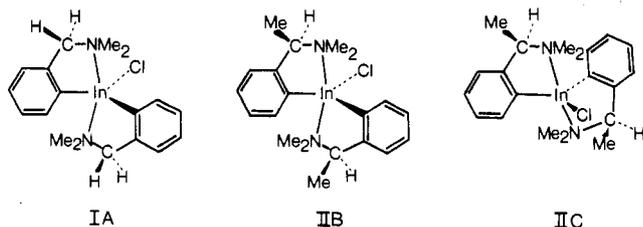
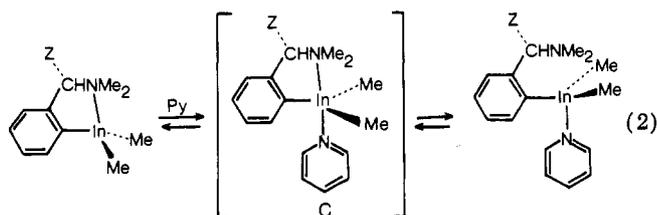


Figure 2. Proposed structures for the diarylindium chlorides I and II.

at $-40\text{ }^{\circ}\text{C}$ (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 $\text{CH}(\text{Z})\text{NMe}_2$ ligand as essential steps. The weakening of the In-NMe₂ 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 NMe₂ donors occupying mutually trans positions. This type of structure has actually been ob-



served for $(2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4)_2\text{InCl}$ (I) in the solid state.²² With CDCl_3 solutions below $-10\text{ }^{\circ}\text{C}$, the ^1H NMR spectrum consists of two singlets from the NMe₂ resonance (at 2.49 and 2.78 ppm) and an AB pattern for the NCH₂ protons (3.20 + 3.35 and 4.20 + 4.35 ppm). This result demonstrates that under these conditions the NMe₂ and CH₂ hydrogen atoms are diastereotopic, in agreement with the coordination of at least one NMe₂ ligand to the indium atom. Furthermore, the appearance of the diastereotopic NMe₂ 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 $2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4$ 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 InMe₂ and NMe₂ 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-

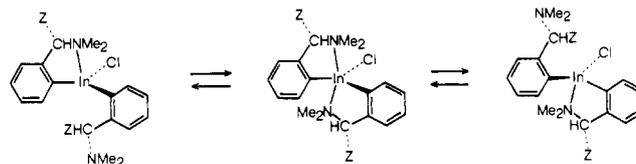
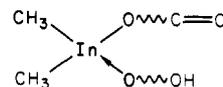


Figure 3. Processes which explain the dynamic NMR spectra of I ($\text{Z} = \text{H}$) and II ($\text{Z} = (\text{S})\text{-Me}$).

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 $[2\text{-Me}_2\text{NCH}(\text{Z})\text{C}_6\text{H}_4]\text{InMe}_2$ have a strong tendency to form four-coordinate complexes via intramolecular In-N coordination. A similar behavior was found for the recently reported $[2\text{-Me}_2\text{NCH}(\text{Z})\text{C}_6\text{H}_4]\text{TlCl}_2$ complexes.²¹ Comparison of the NMR data of the four-coordinate In and Tl derivatives indicates that the M-N bond in $[2\text{-Me}_2\text{NCH}(\text{Z})\text{C}_6\text{H}_4]\text{TlCl}_2$ is weaker than in $[2\text{-Me}_2\text{NCH}(\text{Z})\text{C}_6\text{H}_4]\text{-InMe}_2$, 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 $[2\text{-Me}_2\text{NCH}(\text{Z})\text{C}_6\text{H}_4]_2\text{MCl}$ compounds ($\text{M} = \text{In}, \text{Tl}$)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 $(\text{CH}_3)_2\text{In}(\text{CF}_3\text{COCHCOR})$ and $\text{CF}_3\text{COCH}_2\text{COR}$ ($\text{R} = \text{CH}_3, t\text{-C}_4\text{H}_9$) 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 $(\text{CH}_3)_2\text{In}(\text{CF}_3\text{COCHCOR})(\text{bpy})$ ($\text{bpy} = 2,2'\text{-bipyridine}$). Coordination number changes have also been postulated in ligand exchange reactions²⁷ for $\text{In}(\text{CF}_3\text{COCHCOR})_3$, 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; $\{2\text{-}[(\text{dimethylamino})\text{methyl}]\text{phenyl}\}\text{lithium}$, 27171-81-9; $\{2\text{-}[(\text{S})\text{-}1\text{-}(\text{dimethylamino})\text{ethyl}]\text{phenyl}\}\text{lithium}$, 63072-89-9.

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