Inorg. Chem. **1998,** *37,* 5097−5101 **5097**

Perfluorinated Diindacycles

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Received April 9, 1998

The reaction of 1,2-bis(halomercurio)tetrafluorobenzene (halide = chloride (**3**) or bromide (**4**)) with the corresponding indium(I) halide in THF results in spontaneous ring closure and formation of the tetrakis(THF) adducts of 9,10-dichloro-9,10-dihydro-9,10-diindaoctafluoroanthracene (**5**) and 9,10-dibromo-9,10-dihydro-9,10-diindaoctafluoroanthracene (**6**), respectively. Diindacycle **6** can also be prepared by reaction of indium(I) bromide with trimeric perfluoro-*o*-phenylenemercury in refluxing toluene, followed by treatment with THF. Upon addition of pyridine, the ligated THF molecules of **6** are readily displaced and 9,10-dibromo-9,10-dihydro-9,10-diindaoctafluoroanthracene tetrakis(pyridine) (**7**) is obtained. Compounds **5**−**7** have been characterized by ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy, MSCI, and elemental analysis, and their molecular structure has been determined by single-crystal X-ray analysis. All compounds crystallize in monoclinic space groups. Two modifications of compound **6** have been analyzed. **5**: space group $P2_1/c$ with $a = 9.686(1)$ Å, $b = 11.071(1)$ Å, $c = 15.725(2)$ Å, $\beta = 105.55(1)°$, $V = 1624.5(3)$ Å^3, and $Z = 2$. **6**: space group $P2_1/c$ with $a = 9.636(1)$ Å, $b = 11.129(1)$ Å, $c = 16.029(2)$ Å, $\beta = 104.40(1)°$, $V = 1664.9(3)$ Å^3, and $Z = 2$; space group $P2_1/n$ with $a = 10.258(1)$ Å, $b = 13.926(1)$ Å, $c = 11.892(2)$ Å, $\beta = 97.86(1)°$, $V = 1682.8(2)$ Å^3, $Z = 2$. **7**: space group $P2_1/c$ with $a = 17.632(2)$ Å, $b = 15.010(1)$ Å, $c = 14.562(1)$ Å, $\beta = 101.72(1)°$, $V = 3773.6(6)$ Å^3, and $Z = 4$. The perfluorination of the phenylene rings in **5**−**7** has a consequent effect on the Lewis acidity of the indium centers which is reflected by the relatively short O−In and N−In dative bond distances.

Introduction

The design of a useful polyfunctional Lewis acid[1] necessitates a judicious choice of the molecular backbone holding the Lewis acidic centers. In polydentate Lewis acids capable of chelating neutral[2−4] or anionic[5−10] nucleophilic substrates, an organic backbone bringing the binding sites into convergence is usually chosen. On the other hand, when the binding sites are located at opposite positions of the organic backbone, the resulting systems can be used as Lewis acidic spacers and constitute

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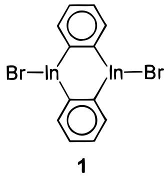
S0020-1669(98)00403-0 CCC: $15.00

powerful building blocks for the preparation of various self-assembled supramolecules.[11] Furthermore, in any of these cases, the electronic properties of the organic backbone can be used to tune the acceptor character of the electrophilic centers. By application of this latter concept, efficient mercury-based anion receptors with electron-withdrawing backbones have been discovered.[3,6,7] We have recently synthesized 9,10-dibromo-9,10-dihydro-9,10-diindaanthracene (**1**).[12] As a result of the unique spatial arrangement of the two indium centers, this diindacycle[13] behaves as a versatile bifunctional Lewis acid, which can be used both as a Lewis acidic spacer[14] and as a selective bidentate receptor for nucleophiles.[15] With the prospect of increasing the Lewis acidity of the indium centers, we endeavored to prepare perfluorinated analogues of **1**. This investigation was further motivated by the growing use of perfluorinated group 13 organometallic compounds as Ziegler–Natta cocatalysts.[16]



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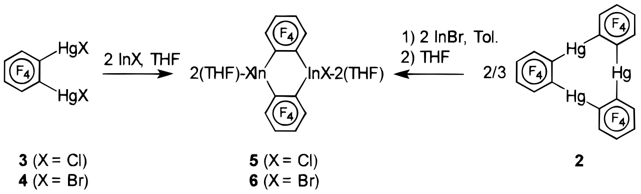
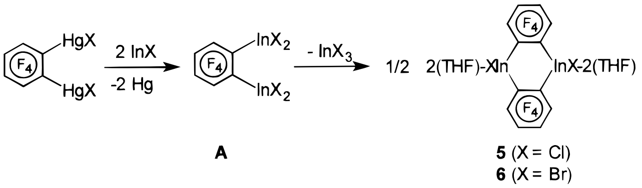
Results and Discussion

Synthesis and Characterization. It was originally thought that the target compounds could be prepared by rigorously following the procedure used for the preparation of **1**. However, treatment of trimeric perfluoro-*o*-phenylenemercury[17] (**2**) with InCl or InBr in THF results in rapid disproportionation of the indium(I) halide InX to In(0) and InX_3. Alternatively, 1,2-bis-(halomercurio)tetrafluorobenzene[18] (halide = chloride (**3**) or bromide (**4**)) react with 2 equiv of the corresponding indium(I) halide in THF at 25 °C to afford the tetrakis(THF) adducts of the 9,10-dihalo-9,10-dihydro-9,10-diindaoctafluoroanthracene (halide = chloride (**5**) or bromide (**6**)) (Scheme 1). Compound **6** can also be prepared by the reaction of **2** with InBr in refluxing toluene followed by treatment with THF (Scheme 1).

Scheme 1



Scheme 2. Proposed Ring Closure Mechanism



The formation of the diindacycles **5** and **6** in the reaction of **3** and **4** with 2 equiv of the corresponding indium(I) halide is surprising since, in principle, bis(indium dihalide) complexes of type **A** would be the expected products. Most probably, the formation of **5** and **6** proceeds through the intermediacy of a complex of type **A** which undergoes ring closure through InX_3 elimination (Scheme 2). These spontaneous ring closure reactions are reminiscent of those observed in the formation of mercuraindacycles where an InX_3 elimination has also been postulated.[19]

Compounds **5** and **6** are stable tetrakis(THF) adducts which do not lose THF under normal conditions. Thus, their behavior is different from that of **1**·4(THF) which was found to spontaneously lose 2 equiv of THF under ambient conditions.[12] In the presence of a better donor, the THF ligands can be displaced. By addition of pyridine, **6** can be quantitatively converted into the tetrakis(pyridine) adduct **7**.

The nature of the halide has no detectable influence on the ^{13}C and ^{19}F NMR spectroscopic features of compounds **5** and **6**, since essentially similar ^{13}C and ^{19}F NMR spectra are obtained for those two compounds. As a result of the C–F coupling and C–In quadrupolar interactions, extended accumulation was necessary to detect the *C*F and *C*In carbon nuclei in compounds **5**–**7**. The ^{19}F NMR spectra of compounds **5**–**7** exhibit two resonances whose multiplicity is consistent with the existence of a higher order AA′BB′ spin system. The mass spectra of compounds **5**–**7** do not allow the detection of the molecular peaks, and the highest assignable peaks correspond to the naked diindacycles which result from the loss of the four coordinated solvent molecules.

Structural Studies. The X-ray crystal structures of compounds **5**–**7** have been determined (Table 1). Important bond lengths and angles have been assembled in Tables 2 and 3. Compounds **5** and **6** crystallize in the space group $P2_1/c$ with very similar unit cell parameters (Figure 1). The molecular structures of the isomorphous complexes are almost identical. A second modification of compound **6** crystallizes in the space group $P2_1/n$. Its molecular structure remains, however, almost unaffected. Molecules of **5** and **6** are centrosymmetrical. The indium centers adopt a trigonal bipyramidal coordination geometry with the THF ligands at the axial positions and the two phenylene rings as well as the halogen atom at the equatorial positions. The indium atoms are displaced by 0.089 Å (**5**), 0.114 Å (**6** in $P2_1/c$), and 0.167 Å for (**6** in $P2_1/n$) out of the plane

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Table 1. Crystal Data, Data Collection, and Structure Refinement for Compounds 5−7

		6		
	5	$P2_1/c$	$P2_1/n$	**7**·py
Crystal Data				
formula	$C_{28}H_{32}Cl_2F_8In_2O_4$	$C_{28}H_{32}Br_2F_8In_2O_4$	$C_{28}H_{32}Br_2F_8In_2O_4$	$C_{37}H_{25}Br_2F_8In_2N_5$
M_r	885.08	974.00	974.00	1081.08
crystal syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_1/c$
a (Å)	9.686(1)	9.636(1)	10.258(1)	17.632(2)
b (Å)	11.071(1)	11.129(1)	13.926(1)	15.010(1)
c (Å)	15.725(2)	16.029(2)	11.892(2)	14.562(1)
β(deg)	105.55(1)	104.40(1)	97.86(1)	101.72(1)
V (Å^3)	1624.5(3)	1664.9(3)	1682.8(2)	3773.6(6)
ρ_{calc} (gcm^{-3})	1.809	1.943	1.922	1.903
Z	2	2	2	4
F(000) (e)	872	944	944	2088
Data Collection				
T (°C)	−70	−70	−78	−78
scan mode	ω/θ	ω	ω	ω
hkl range	$-12 \rightarrow 11$	$-12 \rightarrow 12$	$-13 \rightarrow 13$	$0 \rightarrow 22$
	$0 \rightarrow 14$	$0 \rightarrow 14$	$0 \rightarrow 18$	$0 \rightarrow 19$
	$0 \rightarrow 20$	$0 \rightarrow 21$	$0 \rightarrow 8$	$-18 \rightarrow 18$
sin((/()$_{max}$ (Å^{-1})	0.62	0.64	0.64	0.64
measd reflns	3522	4129	3113	8448
unique reflns, [R_{int}]	3522, [0]	4000, [0.021]	2935, [0.034]	8193, [0.026]
reflns used for refinement	3333	3542	2602	7233
abs correction	DIFABS	DIFABS	DIFABS	DIFABS
Refinement				
refined params	199	195	199	481
final R values [$I > 2\sigma(I)$]:				
R1^a (%)	2.75	4.11	3.88	3.24
wR2^b (%)	6.84	10.01	9.83	7.26
ρ_{fin} (max/min) (e Å^{-3})	0.50/−0.55	1.06/−1.23	0.75/−0.80	0.58/−0.64

[a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. [b] $wR2 = \{[\sum w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$; $a = 0.0334$ (**5**), 0.0505 (**6** in $P2_1/c$), 0.0568 (**6** in $P2_1/n$), 0.0403 (**7**); $b = 1.85$ (**5**), 2.52 (**6** in $P2_1/c$), 2.65 (**6** in $P2_1/n$), 2.91 (**7**).

Table 2. Selected Bond Distances (Å) and Angles (deg) for **5** and **6**^{a}

		6	
	5	in $P2_1/c$	in $P2_1/n$
In−C(1)	2.166(3)	2.164(5)	2.165(5)
In(1)−C(2a)	2.168(3)	2.164(5)	2.166(5)
In−X	2.370(1)	2.505(1)	2.502(1)
In−O(1)	2.395(2)	2.408(3)	2.429(4)
In−O(2)	2.330(2)	2.328(4)	2.324(4)
O(1)−In-O(2)	177.3(1)	177.8(2)	179.5(1)
Br(1)−In−C(1)	119.9(1)	120.8(1)	120.0(1)
Br(1)−In−C(2a)	121.1(1)	119.7(1)	120.5(2)
C(1)−In−C(2a)	118.3(1)	118.4(2)	118.7(2)

[a] **5**, X = Cl; **6**, X = Br.

Table 3. Selected Bond Distances (Å) and Angles (deg) for 7

In(1)−C(1)	2.181(3)	In(1)−C(7)	2.176(3)
In(2)−C(2)	2.181(4)	In(2)−C(8)	2.180(4)
In(1)−Br(1)	2.544(1)	In(2)−Br(2)	2.535(1)
In(1)−N(1)	2.385(3)	In(1)−N(2)	2.514(3)
In(2)−N(3)	2.451(3)	In(2)−N(4)	2.384(3)
N(1)−In(1)−N(2)	177.1(1)	N(3)−In(2)−N(4)	177.0 (1)
Br(1)−In(1)−C(1)	119.6(1)	Br(1)−In(1)−C(7)	121.5 (1)
Br(2)−In(2)−C(2)	121.8(1)	Br(2)−In(2)−C(8)	120.5(1)
C(1)−In(1)−C(7)	118.3(1)	C(2)−In(2)−C(8)	117.5(1)

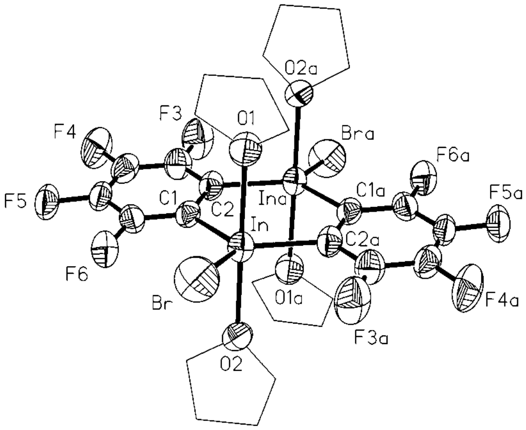

Figure 1. Structure of **5** in the crystal: ORTEP drawing with 50% probability ellipsoids.

containing the perfluorophenylene rings. This distortion is much more pronounced for the halide ligands, which are positioned 0.620 Å (**5**), 0.789 Å (**6** in $P2_1/c$), and 0.884 Å (**6** in $P2_1/n$) above and below the plane of the aromatic rings. As observed in the structure of **1**·4(THF), there is, in the structures of **6**, a detectable dissymmetry in the distances of the In−O bond around a unique indium center (Table 2). Although the origin of this dissymmetry remains unclear, it is manifest that the short In−O bonds of **6** (2.324(4) Å, 2.328(4) Å) are shorter than those of **1**·4(THF) (2.407(3) Å, 2.428(4) Å).[12] Similarly, the long In−O bonds of **6** (2.408(3) Å, 2.429(4) Å) are shorter than those of **1**·4(THF) (2.492(3) Å, 2.488(4) Å).[12] In turn, the relative In−O bond shortening in **6** reflects an increase of the indium center's Lewis acidity which can be associated with the presence of perfluorinated ligands. Note that this conclusion is in agreement with the observation that **5** and **6** are stable tetrakis-(THF) adducts while **1**·4(THF) spontaneously decomposes at 25 °C.[12] The structure of **7** (Figure 2) can be derived from that of **6** by replacing each coordinated THF molecule by a pyridine

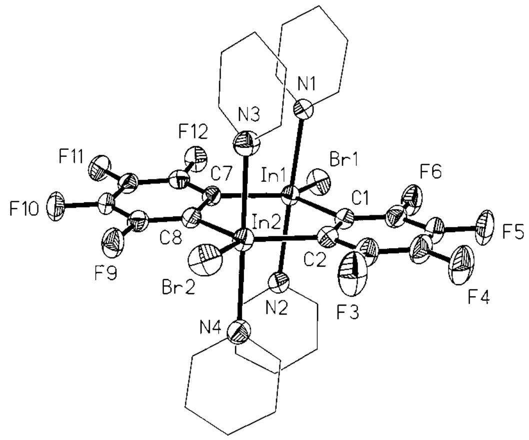

Figure 2. Structure of **7** in the crystal: ORTEP drawing with 50% probability ellipsoids.

ligand. The In−N bond lengths in **7** (average 2.43 Å) are appreciably shorter than those in **1**·4(py) (average 2.48 Å)[14] which further substantiates the electronic influence of the perfluorinated phenylene rings.

Conclusion

Some of our recent investigations demonstrate that the reaction of organometallic bis(mercury halide) complexes with indium(I) halides usually affords the corresponding bis(indium dihalide) complexes.[20] In contrast, the reaction of the bis(mercury halide) complexes **3** and **4** with InX results in the formation of the diindacycles **5** and **6** rather than the bis(indium dihalide) complexes of type **A**. It is in fact most probable that the latter complexes (**A**) are formed as reaction intermediates, but that the proximity of the indium dihalide moieties favors the occurrence of InX_3 elimination followed by dimerization. In fact, examination of the literature indicates that such reactions are known in boron chemistry and that, for example, 9,10-diethyl-9,10-dihydro-9,10-diboraanthracene can be quantitatively obtained by thermal treatment of 1,2-bis(diethylboryl)benzene.[21] It should finally be noted that the perfluorination of the phenylene rings in **5**−**7** has a consequent effect on the Lewis acidity of the indium centers which is reflected by the stability of the tetrakis(THF) adducts as well as by the relatively short In−O and In−N dative bond distances. Our current investigations are focused on the use of those novel diindacycles as halide abstractors.

Experimental Section

General Procedures. Nuclear magnetic resonance spectra were obtained on a JEOL-GX 400 instrument (400 MHz for ^{1}H, 100.5 MHz for ^{13}C) and on a JEOL-JNM-LA 400 instrument (376.5 MHz for ^{19}F). The proton and carbon signals of the deuterated solvent were used as internal standards for the ^{1}H and ^{13}C NMR spectra, respectively. ^{19}F NMR chemical shifts are reported relative to CF_3COOH. All NMR measurements were carried out at 25 °C. The atom-numbering scheme used to report the NMR data is in accordance with the IUPAC nomenclature.[22] The Laboratory for Microanalysis at Technische Universität München performed the elemental analyses. All experiments were carried out under a dry inert atmosphere of N_2 using standard Schlenk techniques or in a glovebox (Labmaster 130, Fa. M. Braun). All melting points were measured on samples in sealed capillaries and are uncorrected. THF and THF-d_8 were dried over Na/K and distilled prior to use. Toluene was dried over K and distilled prior to use. All other solvents were used without further purification. All commercially available starting materials were purchased from Aldrich Chemicals and used without further purification. InBr was prepared by fusing $InBr_3$ and 2 equiv of In(0) at 375 °C under vacuum and was purified through sublimation under those conditions. Compounds **2**−**4** were synthesized according to the literature procedure.[17,18]

Synthesis of 9,10-Dichloro-9,10-dihydro-9,10-diindaoctafluoroanthracene Tetrakis(THF) Adduct (5). InCl (0.165 g, 1.1 mmol) and **3** (0.310 g, 0.5 mmol) were stirred together in THF (5 mL) under nitrogen for 4 h, after which time the reaction mixture was filtered to remove the metallic precipitate. Concentration of the filtrate followed by cooling to −25 °C afforded crystalline compound **5** (mp 141 °C dec) in 39% yield based on **3** (170 mg). Elemental anal. Calcd for $C_{28}H_{32}Cl_2F_8In_2O_4$: C, 37.98; H, 3.62. Found: C, 37.24; H, 3.66. ^{1}H NMR (THF-d_8): δ 1.77 (m, 16H, OCH_2CH_2), 3.61 (m, 16H, OCH_2). ^{13}C NMR (THF-d_8): δ 24.3 (s, OCH_2CH_2), 66.3 (s, OCH_2), 139.9 (d, $^1J_{C,F}$ = 234 Hz, *C*(1,4,5,8)), 141.8 (br, *C*(4a,8a,9a,10a)), 149.4 (d, $^1J_{C,F}$ = 264 Hz, *C*(2,3,6,7)). ^{19}F NMR (THF-d_8): δ −37.90 (pseudo-dd, 4F, $J_{F,F}$ = 18.0 Hz, $J_{F,F}$ = 6.9 Hz, *F*(1,4,5,8)), −79.55 (pseudo-dd, 4F, $J_{F,F}$ = 18.0 Hz, $J_{F,F}$ = 6.9 Hz, *F*(2,3,6,7)). MS (CI, isobutane) [*m*/*e*]: 596.8 (21.8, M^+ − 4 THF).

Synthesis of 9,10-Dibromo-9,10-dihydro-9,10-diindaoctafluoroanthracene Tetrakis(THF) Adduct (6). From 4 and InBr. Compound **6** was prepared in an analogous way to **5** starting from InBr (0.117 g, 0.6 mmol) and **4** (0.203 g, 0.29 mmol); mp 250 °C dec, 28% yield based on **4** (0.080 g). **From 2 and InBr.** InBr (0.218 g, 1.12 mmol) and **2** (0.355 g, 0.34 mmol) were stirred in refluxing toluene (5 mL) under nitrogen until disappearance of the red InBr (ca. 8 h). The toluene solution was then decanted off and the residue was dissolved in THF (5 mL). Following short warming to 65 °C, the THF solution was filtered and concentrated to 3 mL. Cooling to −25 °C afforded crystalline **6** (mp 250 °C dec) in a 71% yield (0.329 g). Elemental anal. Calcd for $C_{28}H_{32}Br_2F_8In_2O_4$: C, 34.52; H, 3.29. Found: C, 34.65; H, 3.10.^{1}H NMR (THF-d_8): δ 1.77 (m, 16H, OCH_2CH_2), 3.61 (m, 16H, OCH_2). ^{13}C NMR (THF-d_8): δ 24.3 (s, OCH_2CH_2), 66.3 (s, OCH_2), 139.5 (d, $^1J_{C,F}$ = 265 Hz, *C*(1,4,5,8)), 141.6 (br, *C*(4a,8a,9a,10a)), 149.4 (d, $^1J_{C,F}$ = 234 Hz, *C*-(2,3,6,7)). ^{19}F NMR (THF-d_8): δ −37.90 (pseudo-dd, 4F, $J_{F,F}$ = 18.0 Hz, $J_{F,F}$ = 6.9 Hz, *F*-(1,4,5,8)), −79.39 (pseudo-dd, 4F, $J_{F,F}$ = 18.0 Hz, $J_{F,F}$ = 6.9 Hz, *F*(2,3,6,7)). MS (CI, isobutane) [*m*/*e*]: 686.7 (2.2, M^+ − 4 THF).

Synthesis of 9,10-Dibromo-9,10-dihydro-9,10-diindaoctafluoroanthracene Tetrakis(pyridine) Adduct (7). Dissolution of **6** (0.073 g, 0.075 mmol) in pyridine (1 mL) followed by cooling of the resulting solution to −25 °C afforded crystalline **7**·pyridine (mp 335 °C dec) in a 76% yield (0.057 g). Elemental anal. Calcd for $C_{37}H_{25}Br_2F_8In_2N_5$: C, 41.09; H, 2.31, N, 6.47. Found: C, 41.07; H, 2.37, N, 6.45. ^{1}H NMR (THF-d_8): δ 7.39 (m, 10H, *H*(3,5)-py), 7.82 (m, 5H, *H*(4)-py), 8.59 (m, 10H, *H*(2,6)-py)). ^{13}C NMR(THF-d_8): δ 126.1 (s, *C*(3,5)-py), 139.2 (s, *C*(4)-py), 141.5 (d, $^1J_{C,F}$ = 254 Hz, *C*(1,4,5,8)), 143.5 (br, *C*(4a,8a,9a,10a)), 151.0 (*C*(2,6)-py)), 151.4 (d, $^1J_{C,F}$ = 234 Hz, *C*(2,3,6,7)). ^{19}F NMR (THF-d_8): δ −38.67 (pseudo-dd, 4F, $J_{F,F}$ = 25.7 Hz, $J_{F,F}$ = 6.9 Hz, *F*(1,4,5,8)), −79.47 (pseudo-dd, 4F, $J_{F,F}$ = 25.7 Hz, $J_{F,F}$ = 6.9 Hz, *F*(2,3,6,7)). MS (CI, isobutane) [*m*/*e*]: 686.7 (10.4, M^+ − 4 (py)).

Crystal Structure Determinations. Specimens of suitable quality and size of compounds **5**−**7** were mounted in glass capillaries and used for measurements of precise cell constants and intensity data collection on an Enraf-Nonius CAD4 diffractometer (Mo *K*α radiation, λ(Mo *K*α) = 0.710 73 Å). During data collection, three standard reflections were measured periodically as a general check of crystal and instrument stability. No significant changes were observed for all compounds. Lp correction was applied, and intensity data were corrected for absorption effects. The structures were solved by direct methods (SHELXS-86) and completed by full-matrix least-squares techniques against F^2 (SHELXL-93). The thermal motion of all non-hydrogen atoms was treated anisotropically, except for those of the disordered solvent THF and pyridine molecules in compound **6** (in $P2_1/c$) and **7**. All hydrogen atoms were placed in idealized calculated positions and

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allowed to ride on their corresponding carbon atoms with fixed isotropic contributions ($U_{\mathrm{iso(fix)}} = 1.5U_{\mathrm{eq}}$ of the attached C atom). The hydrogen atoms of the disordered solvent molecule in **6** (in $P2_1/c$) and **7** were neglected. Further information on crystal data, data collection, structure refinement, and metrical parameters are summarized in Tables 1−3.

Acknowledgment. We thank Prof. H. Schmidbaur, who made this work possible. Financial support from the European Commission (Training and Mobility of Researchers Program, grant to F.P.G.), the Deutsche Forschungsgemeinschaft, and the Fonds der Chemischen Industrie is very thankfully acknowledged.

Supporting Information Available: Tables of crystal data, atomic coordinates, thermal parameters, and bond lengths and angles (25 pages). Four X-ray crystallographic files for **5**−**7**, in CIF format, are available on the Internet only. Ordering and access information is given on any current masthead page.

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