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Synthesis and Molecular Structure of $[2,4,6\text{-}t\text{-}Bu_3C_6H_2]_2InBr$. An Example of a Very Sterically Hindered Molecule

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*Summary: The Grignard reagent Mes*MgBr (Mes* = 2,4,6-t-$Bu_3C_6H_2$) was reacted with $InCl_3$. The crystalline product, Mes*$_2$InBr, was isolated in nearly quantitative yield. This compound crystallizes in the monoclinic space group $P2_1/c$ with unit cell parameters a = 10.421(2) Å, b = 22.894(8) Å, c = 16.082(2) Å, β = 107.51(1)°, V = 3659(2) Å^3, and D_{calcd} = 1.244 g cm^{-3} for Z = 4. Least squares refinement based on 4280 observed reflections ($I \geq 3\sigma(I)$) converged at R = 6.0% (R_w = 6.5%). The geometry around the indium center is trigonal bipyramidal with three short equatorial bonds and two long interactions to methyl groups on the ortho tert-butyl groups of one of the Mes* moieties. Evidence supports an interaction between the two axial methyl groups and the indium atom, but the nature of this interaction, i.e. agostic versus steric, cannot be unequivocally established by the available IR and NMR data.*

Introduction

The synthesis and characterization of group 13 derivatives bound to sterically-demanding ligands are of major interest. These substituents make it possible to generate species with lower coordination numbers,[1-6] and the diorganometallic halides are valuable synthons for compounds with oxidation states of +1 and +2.[7-15]

With such objectives in mind, we have employed 2,4,6-*t*-$Bu_3C_6H_2$ (supermesityl, Mes*) as a ligand because the *ortho tert*-butyl groups provide substantial protection to the metal center. Recent work by Power[16] and Schulz[17] yielded the dihalides Mes*MX_2 (M = Al, Ga, In; X = Cl, Br), by reaction of Mes*Li with MX_3, but neither group reported the formation of the bis(supermesityl) derivative, even when the stoichiometry of Mes*Li to InX_3 (X = Cl, Br) was (2.5:1). In a very recent paper called to our attention by a referee, Meller et al.[18] reported the synthesis and structure of chlorobis(2,4,6-*tert*-butylphenyl)gallane which is isostructural with the indium derivative we report here.

Experimental Section

The compounds are extremely sensitive to both air and water so standard Schlenk line techniques were employed. $InCl_3$ (Aldrich) was used as received. Mes*Br was made according to the literature.[19] The Grignard reagent was prepared by reaction of 3.33 g (10.2 mmol) of Mes*Br and 0.25 g (10.2 mmol) of Mg turnings in 150 mL of THF and refluxed for 24 h. The Grignard reagent was added dropwise to a solution of $InCl_3$ (0.755 g, 3.4 mmol) in THF. After complete addition, the mixture was refluxed for 24 h and decanted to another flask and all volatile materials were removed. The pasty yellowish solid was extracted with two 150-mL portions of hexane. The volume of hexane was reduced to about 70 mL and left undisturbed. Colorless crystals were produced overnight at room temperature. The ^1H and ^{13}C NMR spectra were obtained on General Electric QE-300 and GN-300 and Varian Unity 500 NMR spectrometers. The room temperature spectra were obtained on benzene-d_6 solutions referenced to benzene at δ = 7.15 and 128 ppm for ^1H and ^{13}C, respectively. The low temperature data were obtained on toluene-d_8 solutions and referenced to the methyl line in toluene at δ = 2.09 and 20.4 ppm, respectively. The mass spectrum was obtained in the EI mode on a Kratos a MS-80 mass spectrometer. The melting point was obtained using a Haake Buchler apparatus and is uncorrected. The infrared spectrum was recorded using a KBr pellet on a Nicolet Dx20 FTIR spectrometer.

This solid was identified as Mes*$_2$InBr. Yield: 85%. Mp: 174 °C. Anal. (Galbraith Laboratories) Calcd (found) for Mes*$_2$InBr: C, 63.07 (63.43); H, 8.53 (8.24); In, 16.75 (16.97); Br (by difference), 11.65 (11.36). ^1H NMR (C_6D_6): δ 1.30 (s, 18H, *p*-$C(CH_3)_3$), 1.58 (s, 36H, *o*-$C(CH_3)_3$), 7.60 (s, 4H, aromatic H). ^{13}C NMR (C_6D_6): δ 31.4 ($^1J_{^1H-^{13}C}$ = 124 Hz, $^3J_{^1H-^{13}C}$ = 5 Hz), 34.8 ($^2J_{^1H-^{13}C}$ = 4 Hz) (*p*-$(CH_3)_3C$); 33.5 ($^1J_{^1H-^{13}C}$ = 124 Hz, $^3J_{^1H-^{13}C}$ = 5 Hz), 38.3 ($^2J_{^1H-^{13}C}$ = 4 Hz) (*o*-$(CH_3)_3C$); 123.4 (*meta* aromatic C); 140.9 (*ipso* aromatic C); 150.3 (*para* aromatic C); 156.3 (*ortho* aromatic C). MS (70 eV), *m/z*: 605, $[InMes^*_2]^+$; 439, $[InMes^*Br]^+$; 359, $[InMes^*]^+$. IR (KBr pellet), cm^{-1}: 2740 (w), 2713 (w), 1585 (m), 1466 (m), 1365 (m), 1242 (m), 1210 (m), 1125 (m), 1024 (s), 937 (s), 882 (m), 740 (m), 646 (m), 567 (m), 474 (s).

A crystal of Mes*$_2$InBr was mounted in a thin walled capillary in a drybox and mounted on a goniometer head. X-ray intensity data were collected on Nicolet P3/V diffractometer. Crystal and X-ray data collection parameters are listed in Table 1. The

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[1] Sierra, M. L.; de Mel, V. S. J.; Oliver, J. P. *Organometallics* **1989**, *8*, 2312.

[2] De Mel, V. S. J.; Oliver, J. P. *Organometallics* **1989**, *8*, 827.

[3] Leman, J. T.; Barron, A. R. *Organometallics* **1989**, *8*, 2214.

[4] Healy, M. D.; Wierda, D. A.; Barron, A. R. *Organometallics* **1988**, *7*, 2543.

[5] Petrie, M. A.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1991**, *113*, 8704.

[6] Jerius, J. T.; Hahn, J. M.; Rahman, A. F. M. M.; Mols, O.; Ilsley, W. H.; Oliver, J. P. *Organometallics* **1986**, *5*, 1812.

[7] Beachley, O. T., Jr.; Churchill, M. R.; Fettinger, J. C.; Pazik, J. C.; Victoriano, L. *J. Am. Chem. Soc.* **1986**, *108*, 4666.

[8] Beachley, O. T., Jr.; Blom, R.; Churchill, M. R.; Faegri, K., Jr.; Fettinger, J. C.; Pazik, J. C.; Victoriano, L. *Organometallics* **1989**, *8*, 346.

[9] Wehmschulte, R. J.; Ruhlandt-Senge, K.; Olmstead, M. M.; Hope, H.; Sturgeon, B. E.; Power, P. P. *Inorg. Chem.* **1993**, *32*, 2983.

[10] Uhl, W.; Vester, A.; Kaim, W.; Poppe, J. *J. Organomet. Chem.* **1993**, *454*, 9.

[11] Uhl, W. Z. *Naturforsch.* **1988**, *43B*, 1113.

[12] Uhl, W.; Layh, M.; Hildenbrand, T. *J. Organomet. Chem.* **1989**, *364*, 289.

[13] Uhl, W.; Layh, M.; Hiller, W. *J. Organomet. Chem.* **1989**, *368*, 139.

[14] Schluter, R. D.; Cowley, A. H.; Atwood, D. A.; Jones, R. A.; Bond, M. R.; Carrano, C. J. *J. Am. Chem. Soc.* **1993**, *115*, 2070.

[15] Scholz, M.; Noltemeyer, M.; Roesky, H. W. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1383.

[16] Petrie, M. A.; Power, P. P.; Dias, H. V. R.; Ruhlandt-Senge, K.; Waggoner, K. M.; Wehmschulte, R. J. *Organometallics* **1993**, *12*, 1086.

[17] Schulz, S.; Pusch, S.; Pohl, E.; Dielkus, S.; Herbst-Irmer, R.; Meller, A.; Roesky, H. W. *Inorg. Chem.* **1993**, *32*, 3343.

[18] Meller, A.; Pusch, S.; Pohl, E.; Häming, L.; Herbst-Irmer, R. *Chem. Ber.* **1993**, *126*, 2255.

[19] Pearson, D. E.; Frazer, M. G.; Frazer, V. S.; Washburn, L. C. *Synthesis* **1976**, 621.

0276-7333/94/2313-2123$04.50/0

Table 1. Experimental Parameters for the X-ray Diffraction Study of Mes*$_2$InBr

compd	Mes*$_2$InBr
formula	InBr$C_{36}H_{58}$
mol. wt	685.58
cryst prep:	mounted in capillary
cryst size (mm^3)	0.30 × 0.55 × 0.60
cryst color	colorless crystals
cryst syst	monoclinic
space group	$P2_1/c$ (No. 14)
cell constants	obtained from 24 high angle reflections with $2\theta > 20°$
a (Å)	10.421(2)
b (Å)	22.894(8)
c (Å)	16.082(2)
β (deg)	107.51(1)
vol (Å^3)	3659(2)
dens (calc) (g cm^{-3})	1.244
Z	4
radiation type	Mo K$\bar{\alpha}$, λ = 0.710 73 Å with a graphite monochromator
temp (°C)	22
type of data collcn	$\theta/2\theta$ scan
2θ scan range (deg)	5–50
hkl ranges	$0 \le h \le 12, 0 \le k \le 27, -19 \le l \le 19$
scan rate (deg/min)	3–20
scan width (deg)	1.0 below K$\bar{\alpha}$ to 1.1 above K$\bar{\alpha}$
background/scan ratio	0.5
std reflns	3/97
deviation from the std observed (%)	8 linear
no. of data collcd	7350
no. of unique data	6486
no. of obsd reflns	4280 with ($I \ge 3\sigma(I)$)
linear absn coeff (μ) (cm^{-1})	17.36
$F(000)$	1432
abs corr	ψ scans
transm coeff	0.284–0.624
no. of parms refined	343
obsd/param ratio	12.4
$R = \sum(\lvert F_o\rvert - \lvert F_c\rvert)/\sum\lvert F_o\rvert$	0.060
$R_w = [\sum(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum w\lvert F_o\rvert^2]^{1/2}$ $w = (\sigma_F^2 + 0.0001F^2)^{-1}$	0.065
R (equivalent reflns)	0.029
max shift/esd	0.04σ on methyls; 0.03σ on all other atoms
max/min residual electron dens	+1.4, −2.4 near In, Br

Table 2. Atomic Coordinates and Isotropic Thermal Parameters for the Non-Hydrogen Atoms of Mes*$_2$InBr

atom	x	y	z	U_{eq}[a]
In1	0.33576(5)	0.25757(2)	0.53573(4)	0.0390(2)
Br1	0.54435(9)	0.25335(4)	0.47927(7)	0.0691(4)
C1	0.3138(7)	0.3505(3)	0.5405(5)	0.036(3)
C2	0.2503(7)	0.3821(3)	0.4627(5)	0.038(3)
C3	0.2424(8)	0.4426(3)	0.4655(5)	0.043(3)
C4	0.2895(8)	0.4743(3)	0.5418(5)	0.045(3)
C5	0.3469(8)	0.4432(3)	0.6162(5)	0.046(3)
C6	0.3629(8)	0.3821(3)	0.6182(5)	0.043(3)
C7	0.1885(8)	0.3555(3)	0.3688(5)	0.044(3)
C8	0.1875(8)	0.2891(3)	0.3629(5)	0.048(3)
C9	0.0420(9)	0.3762(3)	0.3336(6)	0.063(4)
C10	0.269(1)	0.3780(4)	0.3103(6)	0.073(4)
C11	0.2788(9)	0.5410(3)	0.5404(6)	0.057(4)
C12	0.324(2)	0.5678(4)	0.6292(8)	0.127(7)
C13	0.132(1)	0.5597(4)	0.4980(9)	0.111(7)
C14	0.357(1)	0.5656(4)	0.4822(9)	0.111(7)
C15	0.435(1)	0.3547(4)	0.7074(5)	0.059(4)
C16	0.559(1)	0.3855(6)	0.7523(9)	0.163(8)
C17	0.350(2)	0.3668(6)	0.7694(8)	0.142(9)
C18	0.449(2)	0.2924(5)	0.7124(7)	0.140(7)
C19	0.2331(7)	0.1748(3)	0.5283(5)	0.038(3)
C20	0.3011(7)	0.1233(3)	0.5211(5)	0.039(3)
C21	0.2346(9)	0.0794(3)	0.4633(5)	0.053(4)
C22	0.1010(9)	0.0832(3)	0.4160(5)	0.055(3)
C23	0.0302(8)	0.1298(4)	0.4354(6)	0.061(4)
C24	0.0893(8)	0.1753(3)	0.4921(5)	0.050(3)
C25	0.4446(8)	0.1062(3)	0.5796(5)	0.047(3)
C26	0.5079(8)	0.1508(4)	0.6489(5)	0.056(3)
C27	0.4292(9)	0.0507(3)	0.6297(5)	0.058(4)
C28	0.5370(9)	0.0933(4)	0.5240(6)	0.061(4)
C29	0.032(1)	0.0378(4)	0.3482(7)	0.085(5)
C30	−0.083(2)	0.0119(9)	0.368(1)	0.25(1)
C31	0.117(2)	−0.0102(7)	0.345(1)	0.27(1)
C32	−0.017(3)	0.0649(8)	0.2645(9)	0.24(1)
C33	−0.0087(9)	0.2171(4)	0.5176(6)	0.063(4)
C34	−0.0822(9)	0.1794(4)	0.5682(7)	0.078(5)
C35	0.054(1)	0.2662(4)	0.5739(8)	0.083(5)
C36	−0.113(1)	0.2434(4)	0.4405(8)	0.098(5)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*\cdot a_j^*\bar{a}_i\cdot\bar{a}_j$.

structure was solved by direct methods using SHELX-76[20] and refined based on 4280 observed reflections with intensities ($I \ge 3\sigma(I)$. Refinement converged at R = 6.00% (R_w = 6.50%). Anisotropic thermal parameters were used for all non-hydrogen atoms. Hydrogen atoms were placed in idealized positions with assigned isotropic temperature factors based on the thermal parameters of the carbon atoms to which they are bound. Atomic coordinates and isotropic thermal parameters are listed in Table 2.

Results and Discussion

We have synthesized Mes*$_2$InBr using the Grignard reagent Mes*MgBr in high yield and have determined its structure from single crystal X-ray diffraction. The reaction proceeds as shown in eq 1.[21]

$$\mathrm{InCl_3 + 2Mes^*MgBr \rightarrow Mes^*{}_2InBr + MgBrCl + MgCl_2} \quad (1)$$

Although both Cl and Br are present in the reaction mixture and either could be bound to the indium, it appears from all data that the bromide is preferentially crystallized from solution and that no THF is bound to the indium.

Meller et al.[18] recently described the synthesis and structure of the analogous gallium derivative Mes*$_2$GaCl from LiMes* and $GaCl_3$, showing that this reaction provides an alternative route to the preparation of bis(supermesityl) derivatives.

The structure of Mes*$_2$InBr was determined by single crystal X-ray diffraction methods, and an ORTEP drawing is shown in Figure 1. The structure consists of a monomeric unit. Selected bond distances and angles are listed in Table 3 and are normal compared to many examples in the literature.[16,17,21] There are two interesting features in the structure. First, one of the Mes* groups is oriented in a normal fashion while the second is tipped at a 15° angle relative to the anticipated linear arrangement for the In–C_{ipso}-C_{para} atoms. This implies severe steric interaction between the *tert*-butyl groups on the two Mes* ligands. This also is reflected in the dislocation of the *ortho tert*-butyl groups in this Mes* moiety, which are bent 5° out of the C_6H_2 plane. These features are shown in Figure 2A. Second, the other Mes* group is oriented so that the *ortho tert*-butyl groups are directly above and below the indium atom with In–C8 = 2.837(8) Å and In–C18 = 2.843(10) Å (Figure 2B). These are very short In–C contact distances, less than those observed in $Me_2InC{\equiv}CPh$,[22] $(Me_3In)_4$,[23]

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(20) Sheldrick, G. M. *SHELX-76*; University Chemical Laboratory: Cambridge, England, 1976.

(21) Porchia, M.; Benetollo, F.; Brianese, N.; Rossetto, G.; Zanella, P.; Bombieri, G. *J. Organomet. Chem.* **1992**, *424*, 1.

(22) Fries, W.; Schwarz, W.; Hausen, H.-D.; Weidlein, J. *J. Organomet. Chem.* **1978**, *159*, 373.

(23) Blake, A. J.; Cradock, S. *J. Chem. Soc., Dalton Trans.* **1990**, 2393.

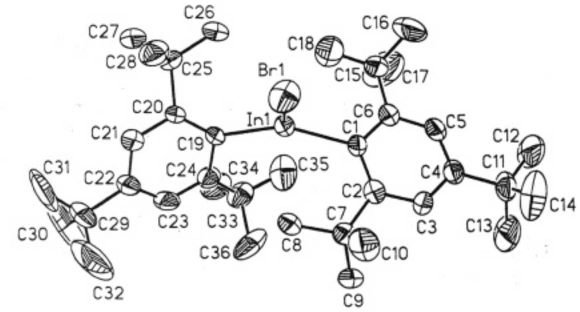

Figure 1. ORTEP diagram of Mes*$_2$InBr showing the atom labeling scheme. Hydrogen atoms are omitted for clarity.

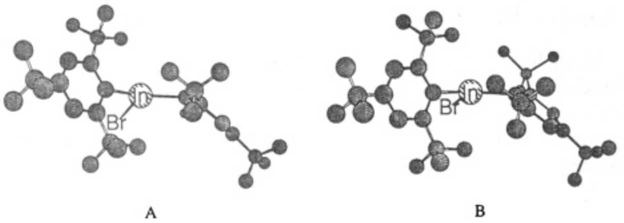

Figure 2. Diagram of Mes*$_2$InBr viewed parallel to the Mes* ring containing C19 with In–C19–C22 = 15° (A) and oriented perpendicular to the ring with agostic interactions (B).

Table 3. Selected Interatomic Distances (Å) and Angles (deg) for Mes*$_2$InBr

	Distances		
In1-Br1	2.597(1)	In1···C8	2.837(8)
In1-C1	2.144(6)	In1···C18	2.843(10)
In1-C19	2.162(7)		
	Angles		
In1-C-C2	119.9(4)	C1-C6-C15	124.5(6)
In1-C19-C20	119.3(5)	C3-C2-C7	113.8(5)
In1-C1-C6	122.0(5)	C5-C6-C15	116.6(6)
In1-C19-C24	117.0(5)	C19-C20-C25	125.4(6)
Br1-In1-C1	99.2(2)	C19-C24-C33	126.2(6)
Br1-In1-C19	113.6(2)	C21-C20-C25	114.5(6)
C1-In1-C19	144.6(3)	C23-C24-C33	116.1(7)
C1-C2-C7	126.5(6)		

and Ph_3In[24] and comparable to those observed in $Me_2(2\text{-}C_4H_3S)In$[25] and in the Mes*MX_2 derivatives reported earlier.[16,17] The gallium derivative, Mes*$_2$GaCl, has very similar features with short gallium–carbon distances for one of the supermesityl groups and shows substantial distortion of the second group, almost identical to that observed in the indium derivative described here.[18] On heating, the gallium derivative undergoes a rearrangement with formation of a new species in which the gallium is bound to a methyl group in one of the supermesityl moieties.

These short In–C contact distances support an agostic or steric interaction between the metal and the *ortho tert*-butyl groups. It should also be noted that the *ortho tert*-butyl groups are bent away from the indium atom by approximately 5° with C1–C6–C15 = 124.5(6)° and C1–C2–C7 = 126.5°, further supporting an interaction between these groups and the metal center. The IR spectrum shows two weak bands at 2740 and 2713 cm^{-1} in the range that has been attributed to agostic interactions.[3] However, there is some question concerning this assignment, and further studies on the IR assignments are required.[26] The ^{1}H and ^{13}C NMR spectra of the compound are normal at room temperature, but at −90 °C the *ortho tert*-butyl groups are selectively broadened. Examination of the ^{1}H NMR spectrum at 500 MHz at room temperature and −90 °C and the 125-MHz ^{13}C NMR spectrum under these conditions (Figure 3) shows similar results, i.e., the proton resonance lines associated with the *ortho tert*-butyl groups are selectively broadened from $\nu_{1/2}$ = 1.85 to 36.5 Hz while those for the *para tert*-butyl group are $\nu_{1/2}$ = 1.30 to 9.7 Hz. The ^{13}C lines increase from $\nu_{1/2}$ = 2.75 to 22.5 Hz and from $\nu_{1/2}$ = 2.64 to 11.0 Hz for the *ortho* and *para tert*-butyl groups, respectively. This selective line broadening indicates an interaction between the *tert*-butyl groups with diminished rotational rates for the *ortho* groups. The rate of rotation is not slowed sufficiently to allow the resolution of individual resonances for the methyl groups but clearly they are rotating at a significantly slower rate than the *para tert*-butyl groups. This implies that the motion of these groups is hindered and further supports an agostic interaction. (See, for example Selnau and Merola.[27]) Alternatively, this line broadening could be attributed to steric interactions which slow the rotation of the groups.

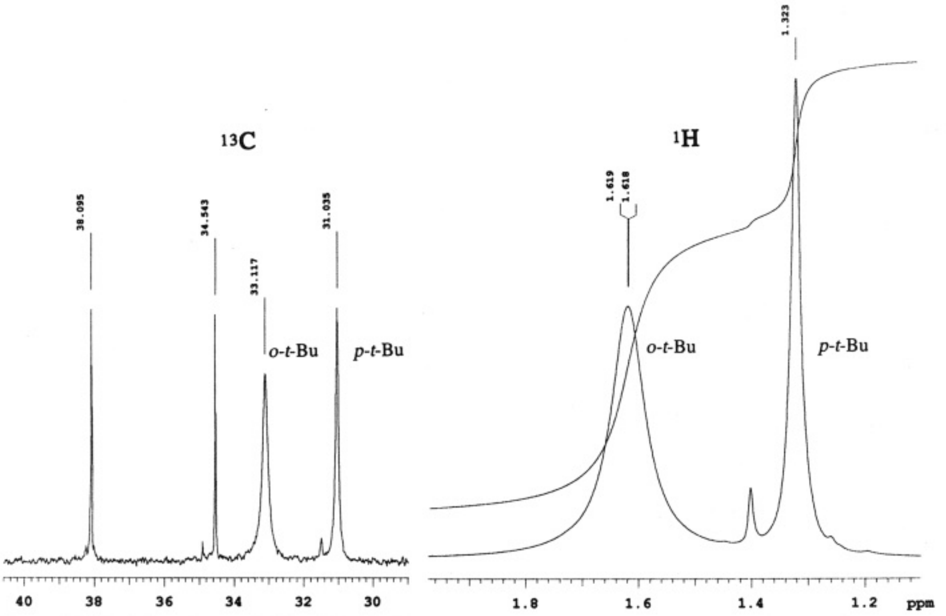

Figure 3. Partial 500-MHz ^{1}H and 125-MHz ^{13}C NMR spectra of Mes*$_2$InBr showing the *tert*-butyl regions of the spectra obtained at −90 °C.

The one-bond $^1H-^{13}C$ coupling constant for systems involving agostic interactions has been used to demonstrate the localized metal proton binding at low temperature. The one-bond $^1H-^{13}C$ coupling constants for the *ortho* and *para tert*-butyl groups in Mes^*_2InBr, determined at 25 °C, were both found to be 124 Hz. Efforts to obtain these coupling constants at low temperature were unsuccessful because of a signal to noise ratio resulting from the limited solubility of the indium derivative in toluene at low temperature.

All of the evidence implies that there is a substantial interaction between the metal atom and the *ortho tert*-butyl groups in Mes^*_2InBr and Mes^*_2GaCl. The question which cannot be answered from the data available is whether this interaction is an agostic interaction or simply a steric interaction between the groups which are in close proximity to one another. The strongest evidence comes from the thermal decomposition of Mes^*_2 GaCl, which yields HCl and the metal hetrocyclic compound Mes*Ga.

In conclusion, we have established the Grignard procedure provides a convenient route for the synthesis of Mes^*_2InX and have shown that this molecule has an unusual structure with strong steric interactions. We are continuing to explore the formation of other supermesityl derivatives and, specifically, to study Mes^*_2InBr as a reagent for formation of In(II) species.

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Supplementary Material Available: Complete listings of bond distances and angles, anisotropic thermal parameters for the non-hydrogen atoms, and atomic coordinates and isotropic thermal parameters for the hydrogen atoms (8 pages). Ordering information is given on any current masthead page.

OM930768A

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(24) Malone, J. F.; McDonald, W. S. *J. Chem. Soc. A* **1970**, 3362.

(25) Rahbarnoohi, H.; Kumar, R.; Heeg, M. J.; Oliver, J. P. Unpublished results.

(26) Kainz, B.; Schmidt, A. *Spectrochim. Acta* **1990**, *46A*, 1361.

(27) Selnau, H. E.; Merola, J. S. *Organometallics* **1993**, *12*, 3800.