J|A|C|S
ARTICLES

Synthesis and Reactivity of Dimeric Ar′TlTlAr′ and Trimeric $(Ar''Tl)_3$ (Ar′, Ar″ = Bulky Terphenyl Group) Thallium(I) Derivatives: Tl(I)−Tl(I) Bonding in Species Ligated by Monodentate Ligands

Robert J. Wright, Andrew D. Phillips, Shirley Hino, and Philip P. Power*

Contribution from the Department of Chemistry, One Shields Avenue, University of California, Davis, California 95616

Received November 10, 2004; E-mail: pppower@ucdavis.edu

Abstract: The synthesis and characterization of three new organothallium(I) compounds are reported. Reaction of $(Ar'Li)_2$ ($Ar' = C_6H_3$-2,6-$(C_6H_3$-2,6-$Pr^i{}_2)_2$) and $Ar''Li$ ($Ar'' = C_6H_3$-2,6-$(C_6H_3$-2,6-$Me_2)_2$) with TlCl in Et_2O afforded $(Ar'Tl)_2$ (**1**) and $(Ar''Tl)_3$ (**2**). The "dithallene" **1** is the heaviest group 13 dimetallene and features a planar, trans-bent structure with Ar′Tl−Tl = 119.74(14)° and Tl−Tl = 3.0936(8) Å. Compound **2** is the first structurally characterized neutral, three-membered ring species of formula *c*-$(MR)_3$ (M = Al−Tl; R = organo group). The Tl_3 ring has Tl−Tl distances in the range ca. 3.21−3.37 Å as well as pyramidal Tl geometries. The Tl−Tl bonds in **1** and **2** are outside the range (2.88−2.97 Å) of Tl−Tl single bonds in R_2TlTlR_2 compounds. The weak Tl−Tl bonding in **1** and **2** leads to their dissociation into Ar′Tl and Ar″Tl monomers in hexane. The Ar′Tl monomer behaves as a Lewis base and readily forms a 1:1 donor−acceptor complex with $B(C_6F_5)_3$ to give $Ar'TlB(C_6F_5)_3$, **3**. Adduct **3** features an almost linear thallium C(ipso)−Tl−B angle of 174.358(7)° and a Tl−B distance of 2.311(2) Å, which indicates strong association. Treatment of **1** with a variety of reagents resulted in no reactions. The lower reactivity of **1** is in accord with the reluctance of Tl(I) to undergo oxidation to Tl(III) due to the unreactive character of the $6s^2$ electrons.

Introduction

Metal−metal σ and π bonding in neutral, heavier group 13 metal (Al−Tl; i.e., heavier triels) clusters is an area that has received considerable attention over the past decade.[1−9] The M−M bonded clusters, in which the triel metal has a +1 oxidation state and weakly interacting ns^2 lone pairs, are of particular interest due to the nature of the bonding and the unusual optical properties that can be produced by M−M interactions, in particular those in thallium(I) centers.[10] Although, stable thallium(I) clusters with as many as six[11] or eight[12] thallium atoms have been isolated, the bonding in the simplest dimeric species of formula RTlTlR has generated the most theoretical interest. Several calculations on various thallium model species have been carried out to obtain a clearer picture of the metal bonding.[13−17] The computational work was prompted initially by the synthesis of $[Tl\{\eta^5\text{-}C_5(CH_2Ph)_5\}]_2$ and its indium analogue by Schumann and co-workers.[7] These compounds crystallized as trans-bent dimers which had almost identical In−In and Tl−Tl distances near 3.63 Å. Later experimental work demonstrated that several other molecular compounds have "close" Tl(I)−Tl(I) interactions.[18] These

---

(1) (a) Uhl, W. *Coord. Chem. Rev.* **1997**, *163*, 1. (b) Janiak, C. *Coord. Chem. Rev.* **1997**, *163*, 107. (c) Uhl, W. *Rev. Inorg. Chem.* **1998**, *18*, 239. (d) Linti, G.; Schnöckel, H. *Coord. Chem. Rev.* **2000**, *206−207*, 285. (e) Schnöckel, H.; Schnepf, A. *Adv. Organomet. Chem.* **2001**, *47*, 235. (f) Power, P. P. *Struct. Bonding* **2002**, *103*, 57.

(2) Loos, D.; Baum, E.; Ecker, H.; Schnöckel, H.; Downs, A. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 860.

(3) Beachley, O. T.; Churchill, M. R.; Fettinger, J. L.; Pazik, J. C.; Victoriano, L. *J. Am. Chem. Soc.* **1986**, *108*, 4666.

(4) Dohmeier, C.; Robl, C.; Tacke, M.; Schnöckel, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 564.

(5) (a) Uhl, W.; Hiller, M.; Layh, M.; Schwarz, W. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1364. (b) Schluter, R. O.; Cowley, A. H.; Atwood, D. A.; Jones, R. A.; Atwood, J. L. *J. Coord. Chem.* **1993**, *30*, 25. (c) Uhl, W.; Graupner, R.; Layh, M.; Schütz, U. *J. Organomet. Chem.* **1995**, *493*, C1. (d) Schultz, S.; Roesky, H. W.; Koch, H. J.; Sheldrick, G. M.; Stalke, D.; Kuln, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1729. (e) Schnitter, C.; Roesky, H. W.; Röpken, C.; Herbst-Irmer, R.; Schmidt, H.-G.; Noltemeyer, M. *Angew. Chem., Int. Ed.* **1998**, *37*, 1952. (e) Brothers, P. J.; Power, P. P. *Adv. Organomet. Chem.* **1996**, *39* 1.

(6) Schumann, H.; Janiak, C.; Görlitz, F.; Loebel, J.; Dietrich, A. *J. Organomet. Chem.* **1989**, *363*, 243.

(7) Schumann, H.; Janiak, C.; Pickhardt, J.; Börner, U. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 789.

(8) Beachley, O. T.; Noble, M. J.; Allendoerfer, R. D. *J. Organomet. Chem.* **1999**, *582*, 32.

(9) Uhl, W.; Cuypers, L.; Harms, K.; Kaim, W.; Wanner, M.; Winter, R.; Koch, R.; Saak, W. *Angew. Chem., Int. Ed.* **2001**, *40*, 566.

(10) Fernández, E. J.; López-de-Luzuriaga, J. M.; Monge, M.; Olmos, M. E.; Pérez, J.; Laguna, A. *J. Am. Chem. Soc.* **2002**, *124*, 5942.

(11) (a) Hellmann, K. W.; Gade, L. H.; Fleischer, R.; Kottke. *Chem. Eur. J.* **1997**, *3*, 1801. (b) Galka, C. H.; Gade, L. H. *Inorg. Chem.* **1999**, *28*, 1038. See also: (c) Wiberg, N.; Blank T.; Lerner, H. W.; Fenske, D.; Linti G. *Angew. Chem., Int. Ed.* **2001**, *40*, 1232, for the structures of $R^*{}_6Tl_6Cl_2$ and $R_4{}^*Tl_3Cl$ ($R^* = SiBu^t{}_3$) in which the Tl oxidation state is slightly > 1.

(12) Boesveld, W. M.; Hitchcock, P. B.; Lappert, M. F.; Nöth, H. *Angew. Chem., Int. Ed.* **2000**, *39*, 222.

(13) Janiak, C.; Hoffmann, R. *J. Am. Chem. Soc.* **1990**, *112*, 5924.

(14) (a) Schwerdtfeger, P. *Inorg. Chem.* **1991**, *30*, 1660. (b) Schwerdtfeger, P.; Heath, G. A.; Dolg, M.; Bennett, M. A. *J. Am. Chem. Soc.* **1992**, *114*, 7518.

(15) Treboux, G.; Barthelat, J. C. *J. Am. Chem. Soc.* **1993**, *115*, 4870.

(16) Pyykkö, P.; Straka, M.; Tamm, T. *Phys. Chem. Chem. Phys.* **1999**, *1*, 3441.

(17) Han, Y.-K.; Bae, C.; Lee, Y. S.; Lee, S. Y. *J. Comput. Chem.* **1998**, *19*, 1526.

(18) See: Ghosh, P.; Rheingold, A. L.; Parkin, G. *Inorg. Chem.* **1999**, *28*, 5464, for a useful summary of the structures of species with Tl···Tl interactions. Tl(I) amides have been reviewed in: Gade, L. H. *J. Chem. Soc., Dalton Trans.* **2003**, 267.

10.1021/ja0432259 CCC: $30.25

include dimers $Tl_2B_2H_9C_2Me_2$ (Tl−Tl = 3.67 Å),[19] $Tl_2(\eta^5{:}\eta^5\text{-}Bu^t_4C_{10}H_4)_2$ (Tl−Tl = 3.76 Å),[20] $\{\{Tl(Tp^{p-tol})\}_2$ (Tp^{p-tol} = hydridotris(3-*p*-tolyl)pyrazolyl borate; Tl−Tl = 3.86 Å),[21] $\{Tl(Bp\}_2$ (Bp = hydridobis(pyrazolyl) borate; Tl−Tl = 3.70 Å),[18] $\{MeSi[N(Tl)Bu^t]_3\}_2$ (Tl−Tl = 3.15 Å),[22] and the tetramers $[Tl\{N(SiMe_3)C_6H_3\text{-}2,6\text{-}Pr^i_2\}]_4$ (Tl−Tl = 4.06 Å),[23] $\{TlC(SiMe_3)_3\}_4$ (Tl −Tl = 3.32−3.64 Å),[24] and $\{Tl(Tp^{cpr})\}_4$; (Tp^{cpr} hydrotris(3-cyclopropylpyrazol-1-yl) borate) (Tl − Tl = 3.64 Å).[25] These intermetallic distances may be compared to the 3.46 Å observed for the pure metal,[26] but they are much longer than the single Tl−Tl bonds observed in $R_2Tl{-}TlR_2$ (R = $Si(SiMe_3)_3$, 2.914 Å;[27] $SiBu^t_3$, 2.97 Å; and $SiBu^t_2Ph$, 2.881(2) Å),[28] which result from overlap of formally sp^2 orbitals. Despite the interest in Tl−Tl bonded compounds, there has been no structural characterization of a stable dimeric Tl(I)−Tl(I) bonded species in which thallium is bound only to a monodentate ligand. In parallel work it has been demonstrated that terphenyl ligands were effective in the isolation of a variety of low coordinate group 13 element compounds.[29] Moreover, it has been shown by Niemeyer and Power that, if the terphenyl ligand was sufficiently large, the monomer TlAr* (Ar* = $C_6H_3\text{-}2,6(C_6H_2\text{-}2,4,6\text{-}Pr^i{}_2)_2$), with one-coordinate thallium, could be isolated.[30] Recently we reported that terphenyl ligands with slightly less crowding aryl rings permitted the isolation of the first neutral, metal−metal bonded gallium[31] or indium[32a] dimers; i.e., Ar′GaGaAr′ and Ar′InInAr′ (Ar′ = $C_6H_3\text{-}2,6\text{-}(C_6H_3\text{-}2,6\text{-}Pr^i{}_2)_2$). We now show that the first "dithallene" analogue of these, Ar′TlTlAr′ (**1**), can be isolated. In addition, it is shown that the introduction of the less crowded ligand Ar″ (Ar″ = $C_6H_3\text{-}2,6\text{-}(C_6H_3\text{-}2,6\text{-}Me_2)_2$) results in the synthesis of the first neutral trimeric group 13 metal ring derivative $(TlAr'')_3$, **2**. Furthermore, the lower reactivity of **1**, in comparison to the lighter element dimetallenes, is demonstrated.

Experimental Section

General Procedures. All manipulations were carried out using modified Schlenk techniques under an atmosphere of N_2 or in a Vacuum Atmospheres HE-43 drybox. All solvents were distilled from molten Na/K alloy and degassed three times prior to use. $(LiAr')_2$ was prepared according to the literature procedure.[33] Ar″I and Ar″Li was synthesized in a manner anlagous to that of Ar′I and $(LiAr')_2$.[34] TlCl (99%; Acros) was dried at 100 °C under reduced pressure (0.01 mmHg) for 15 min prior to use. Tris(pentafluorophenyl)borane (Albemarle Corp.) was used as received. ^1H, ^{11}B, ^{13}C, and ^{19}F NMR were recorded on Varian 300 and 400 spectrometers and referenced to known standards. UV/vis data were recorded on a Hitachi-1200, and the melting points were recorded using a Meltemp apparatus and were not corrected.

$(TlAr')_2$ (1). With the exclusion of as much light as possible, $(LiAr')_2$ (2.01 g, 2.50 mmol) in Et_2O (25 mL) was added dropwise to a rapidly stirred −10 °C slurry of TlCl (1.20 g, 5.0 mmol) in Et_2O (75 mL). The resulting mixture was stirred for ca. 4 h during which the cooling bath naturally warmed to 10 °C. The stirring was discontinued, and the flask was immediately placed in the refrigerator (ca. 4 °C) for overnight storage. The pale red mother liquor was removed from the precipitate (LiCl) and decanted into a precooled (−10 °C) aluminum foil wrapped Schlenk tube. The solution was concentrated to ca. 30 mL and placed in the freezer (ca. −25 °C) overnight, which afforded dark red, almost black, X-ray quality crystals of the product. Yield: 1.20 g, 40%; mp 173−174 °C. ^1H NMR (400 MHz, C_6D_6, 25 °C): δ 1.115 (d, 12H, *o*-$CH(CH_3)_2$, $^3J_{HH}$ = 6.9 Hz), 1.181 (d, 12H, *o*-$CH(CH_3)_2$, $^3J_{HH}$ = 6.9 Hz), 3.160 (sept, 4H, $CH(CH_3)_2$, $^3J_{HH}$ = 6.9 Hz), 7.228 (s, 4H, *m*-Dipp), 7.20−7.32 (m, 7H, *p*-C_6H_3, *m*-Dipp, and *p*-Dipp), 7.931 (d, 2H, *m*-C_6H_3). ^{13}C $\{^1H\}$NMR (C_6D_6, 100.6 MHz, 25 °C): δ 24.21 ($CH(CH_3)_2$), 25.17 ($CH(CH_3)_2$), 30.41 ($CH(CH_3)_2$), 123.02 (*m*-Dipp), 125.05 (*p*-C_6H_3), 140.30 (*i*-Dipp), 145.10 (*o*-C_6H_3), 147.50 (*o*-Dipp); *m*-C_6H_3 and *p*-Dipp are likely obscured by the C_6D_6 signal. UV/vis (hexanes; λ_{max}, nm (ϵ, mol^{-1} L cm^{-1})): 364 (2900), 492 (1400).

$(TlAr'')_3$ (2). The trimer **2** was synthesized in a manner analogous to that of **1**.Yield: 0.86 g, 35%; mp 153−154 °C. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ 2.107 (s, 12H, *o*-CH_3), 7.066 (s, 6H, *m*-Xyl and *p*-Xyl), 7.310 (t, 1H, *p*-C_6H_3, $^3J_{HH}$ = 7.5 Hz), 7.739 (d, 2H, *m*-C_6H_3, $^3J_{HH}$ = 7.5 Hz). ^{13}C $\{^1H\}$NMR (C_6D_6, 75.46 MHz, 25 °C): δ 21.34 (*o*-CH_3), 125.88 (*p*-Xyl), 126.98 (*m*-Xyl), 127.45 (*p*-C_6H_3), 127.98 (*m*-C_6H_3), 136.32 (*o*-Xyl), 143.86(*i*-Xyl), 147.62 (*o*-C_6H_3). UV/vis (hexanes; λ_{max}, nm (ϵ, mol^{-1} L cm^{-1})): 368 (2600), 492 (1100).

$Ar'TlB(C_6F_5)_3$ (3). $(TlC_6H_3\text{-}2,6\text{-}Dipp_2)_2$ (0.40 g, 0.33 mmol) and $B(C_6F_5)_3$ (0.425 g, 0.83 mmol) were combined in a foil wrapped Schlenk tube. Toluene (60 mL) cooled to −78 °C was added, and the precipitate was stirred for ca. 12 h. The stirring was discontinued, and the solution was allowed to settle. The pale yellow mother liquor was transferred from a small amount of precipitate (TlOH) into another vessel. The volume was concentrated to ca. 15 mL, and overnight storage in a freezer (ca. −20 °C) afforded large colorless X-ray quality crystals. Yield: 0.26 g, 35 %; mp 165−167 °C, turns deep red at 175 °C. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ 0.957 (d, 12H, *o*-$CH(CH_3)_2$, $^3J_{HH}$ = 6.9 Hz), 1.097 (d, 12H, *o*-$CH(CH_3)_2$, $^3J_{HH}$ = 6.9 Hz), 2.803 (sept, 4H, $CH(CH_3)_2$, $^3J_{HH}$ = 6.9 Hz), 7.035 (d, 4H, *m*-Dipp, $^3J_{HH}$ = 7.5 Hz), 7.16−7.23 (m, 3H, *p*-C_6H_3 and *p*-Dipp, $^3J_{HH}$ = 7.5 Hz), 7.465 (d, 2H, *m*-C_6H_3). ^{13}C $\{^1H\}$NMR (C_6D_6, 75 MHz, 25 °C): δ 23.29 ($CH(CH_3)_2$), 25.49 ($CH(CH_3)_2$), 30.85 ($CH(CH_3)_2$), 123.78 (*m*-Dipp), 129.34 (*p*-Dipp), 130.16 (*p*-C_6H_3), 132.64 (*m*-C_6H_3), 135.88 (br, C_6F_5), 139.18 (br, C_6F_5), 137.93 (*i*-Dipp), 142.23 (br, C_6F_5), 145.50 (br, C_6F_5), 146.87 (*o*-C_6H_3), 147.85 (*o*-Dipp), 149.43 (br, C_6F_5). ^{11}B NMR (128 MHz, C_6D_6, 25 °C): −11.3. ^{19}F $\{^1H\}$ NMR (376 MHz, C_6D_6, 25 °C): δ −128.44 (broad, 6F, o-C_6F_5), −153.59 (t, 3F, p-C_6F_5, ^3J = 25.0 Hz), −159.57 (d, 6F, m-C_6F_5, ^3J = 25.0 Hz).

X-ray Crystallographic Studies. Sample preparation consisted of removing the crystal from the Schlenk tube under a rapid flow of argon and immediately submerging it in hydrocarbon oil. A suitable crystal was selected, mounted on a glass fiber attached to a copper pin, and rapidly placed in a cold stream of N_2 (−183 °C) of the diffractometer for data collection.[35] Data were collected on a Bruker SMART 1000 diffractometer with use of Mo Kα (λ = 0.710 73 Å) radiation and a CCD area detector. Data collection and processing were performed

---

(19) Jutzi, P.; Wegner, D.; Hursthouse, M. B. *Chem. Ber.* **1991**, *124*, 295.
(20) Jutzi, P.; Schnittger, J.; Hursthouse, M. B. *Chem. Ber.* **1991**, *124*, 1693.
(21) Ferguson, G.; Jennings, M. C.; Lalor, F. J. Starahan, C. *Acta Crystallogr.* **1999**, *C47*, 2079.
(22) Veith, M.; Spaniol, A.; Pöhlmann, J.; Gross, F.; Huch, V. *Chem. Ber.* **1993**, *126*, 2625.
(23) Waezsada, S. D.; Belgardt, T.; Noltemeyer, M.; Roesky, H. W. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1351.
(24) Uhl, W.; Keimling, S. U.; Klinkhammer, K. W.; Schwarz, W. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 64.
(25) Rheingold, A. L.; Liable-Sands, L. M.; Trofimenko, S. *Chem. Commun.* **1997**, 1691.
(26) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Clarendon Press: Oxford, U.K., 1984; p 1279.
(27) Henkel, S.; Klinkhammer K W.; Schwarz, W. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 681.
(28) Wiberg, N.; Blank T.; Amelunxen K.; Nöth, H.; Schnöckel, H.; Baum, H.; Purath, A.; Fenske, D. *Eur. J. Inorg. Chem.* **2002**, 341.
(29) (a) Twamley, B.; Haubrich, S. T.; Power, P. P. *Adv. Organomet. Chem.* **1999**, *44*, 1. (b) Clyburne, J. A. C.; McMullen, N. *Coord. Chem. Rev.* **2000**, *210*, 73.
(30) Niemeyer, M.; Power, P. P. *Angew. Chem., Int. Ed.* **1998**, *37*, 1277.
(31) (a) Hardman, N. J.; Wright, R. J.; Phillips, A. D.; Power, P. P. *J. Am. Chem. Soc.* **2003**, *125*, 2667. (b) Hardman, N. J.; Wright, R. J.; Phillips, A. D.; Power, P. P. *Angew. Chem., Int. Ed.* **2002**, *41*, 2842.
(32) (a) Wright, R. J.; Phillips, A. D.; Hardman, N. J.; Power, P. P. *J. Am. Chem. Soc.* **2002**, *124*, 8538. (b) Haubrich, S. T.; Power, P. P. *J. Am. Chem. Soc.* **1998**, *120*, 2202.
(33) Schiemenz, B.; Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2150.
(34) Schiemenz, B.; Power, P. P. *Organometallics* **1996**, *15*, 958.
(35) Hope, H. *Prog. Inorg. Chem.* **1995**, *41*, 1.

Table 1. Selected Crystallographic Data for Compounds **1**−**3**

	Ar′TlTlAr′ (**1**)	(Ar″Tl)$_3$ (**2**)	Ar′TlB(C$_6$F$_5$)$_3$ (**3**)
formula	$C_{60}H_{74}Tl_2$	$C_{66}H_{66}Tl_3$	$C_{55}H_{45}BF_{15}Tl$
fw	1203.93	1469.37	1206.09
color, habit	dark red, block	dark red, block	colorless, block
cryst syst	orthorhombic	monoclinic	monoclinic
space group	Pccn	$P2_1/n$	$P2_1/n$
a, Å	20.648(5)	21.2335(14)	13.0842(7)
b, Å	15.547(4)	14.0989(10)	23.2719(13)
c, Å	16.395(5)	20.1848(13)	16.1097(9)
α, deg	90	90	90
β, deg	90	117.601(3)	94.782(3)
γ, deg	90	90	90
V, Å^3	5263(2)	5355.0(6)	4888.2(5)
Z	2	4	4
cryst dimens, mm	0.62 × 0.43 × 0.26	0.32 × 0.25 × 0.14	0.32 × 0.17 × 0.11
d_{calc}, g cm^{-3}	1.519	1.822	1.639
μ, mm^{-1}	6.151	9.046	3.399
no. of reflns	5168	10 515	15 390
no. of obsd reflns	4378	9434	13 147
R1, obsd reflns[a]	0.0493	0.0232	0.0222
wR2, all[b]	0.1314	0.0593	0.0548

[a] $R1 = \sum||F_o - F_c||/\sum|F_o|$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

using the programs SMART[36a] and SAINT[36b] provided by Bruker AXS. Empirical absorption corrections were applied to all samples using SADABS.[36c] The crystal structures were solved using either direct methods or the Patterson option in SHELXS[37] and refined by the full-matrix least-squares procedure in the SHELXL[37] program. All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were placed at calculated positions and included in refinement using a riding model. Selected crystal data and data collection parameters are provided in Table 1. Further details are given in the Supplementary Information.

Results and Discussion

The extensive theoretical interest in Tl(I)−Tl(I) bonded species, as well as their lighter M(I)−M(I) (M = Al, Ga, or In) homologues, prompted us to investigate the isolation and characterization of unbridged thallium(I) aggregates with low coordination numbers. In particular we were interested in compounds in which the thallium substituent was η^1-bound in order to maximize the metal−metal interaction. Calculations (extended Hückel) by Janiak and Hoffmann on the simplest possible model of this type, i.e., the planar, trans-bent hydride H−Tl−Tl−H, led to the conclusion that there was “strong bonding” when the bending angle was 120°.[13] Later work by Schwerdtfeger involving configurational interactions, relativistic pseudopotentials, and extensive basis sets at various levels of approximation also showed that a maximum interaction between the Tl−H units occurred at a similar trans-bending angle near 115°.[14] But the minimum on the potential plot of the interaction energy versus Tl−Tl distance occurred at only about 3.25 kcal mol^{-1} below the dissociation limit and at a Tl−Tl distance of 3.28 Å. Further analysis showed that the stretching force constant for the bond is below 1 mdyn/Å.[14] Moreover, the difference in the total zero point vibrational energies for the dissociation of $Tl_2H_2 \rightarrow 2TlH$ was ca. 1.2 kcal mol^{-1}. It was predicted that the trans-bent H−Tl−Tl−H species should be observable at low temperature even though the Tl−Tl bond is very weak. In fact, recent experiments by Andrews and Wang showed by infrared spectroscopy that HTlTlH could be formed along with other thallium hydrides and trapped in a solid neon, argon, or hydrogen matrix.[38] In addition, theoretical studies by Treboux and Barthelat using a double-ζ-plus polarization basis set, and QCI energies at Hartree−Fock geometries, treated all the triel hydrides HMMH (M = B−Tl) in terms of the interactions between the two MH fragments and showed that, for the heavier elements, the hydrogen-bridged isomer M(μ-H)$_2$M was the most stable in all cases with the vinylidene isomer H$_2$MM lying next highest in energy.[15] The trans-bent isomers were even higher in energy (by ca. 7−9 kcal mol^{-1}), but a linear HMMH configuration (a triplet) was much less stable. Nonetheless, no minimum on the potential energy surface was found to exist for the trans-bent H−Tl−Tl−H. More recent theoretical studies of the trans-bent HMMH and (η^5-C$_5$H$_5$)MM(η^5-C$_5$H$_5$) model compounds by Pyykkö et al.,[16] with use of ab initio calculations incorporating MP2 and CCSD(I) methods, afforded results that were in broad agreement with those of Schwerdtfeger and which yielded dimerization energies of ca. 4.8 kcal mol^{-1} for the HTlTlH species (Tl−Tl = 3.217 Å) versus ca. 7.1 kcal mol^{-1} for HInInH (In−In = 3.02 Å).[14] Calculations for (η^5-C$_5$H$_5$)MM(η^5-C$_5$H$_5$) yielded M−M distances of (In) 3.96 Å and (Tl) 3.819 Å, which were longer than those experimentally observed (3.63 Å) for the M$_2${η^5-C$_5$(CH$_2$Ph)$_5$}$_2$ species. The calculated M−M−(centroid-η^5-C$_5$H$_5$) angles of (In) 102.8° and (Tl) 94.5° were narrower than the 136.5° and 131.8° found experimentally. As suggested by the longer In−In distance, the interaction energy is less than that predicted for the thallium compounds: 2.96 versus 3.78 kcal mol^{-1}. The longer calculated M−M bonds in comparison to those measured and the narrower M−M−(η^5-C$_5$H$_5$) angles were reasonably attributed to crystal packing effects, although no plausible explanation suggested itself for the longer bonds and weaker interactions of the indium species. As pointed out in the Introduction, the use of terphenyl ligands has allowed the lighter gallium and indium derivatives Ar′GaGaAr′ and Ar′InInAr′ to be synthesized. The use of the

---

(36) (a) *SMART: Area-Detector Software Package*; Bruker AXS, Inc.: Madison, WI, 1993. (b) *SAINT: Area-Detector Integration Software*; Bruker AXS, Inc.: Madison, WI, 1995. (c) *SADABS: Area-Detector Absorption Correction*; Bruker AXS, Inc.: Madison, WI, 1996.

(37) (a) *SHELXL PC*, version 5.03; Bruker AXS, Inc.: Madison, WI, 1994. (b) Cooper, R. I.; Gould, R. O.; Parsons, S.; Watkin, D. J. *J. Appl. Crystallogr.* **2002**, *35*, 168.

(38) Wang, X.; Andrews, L. *J. Phys. Chem. A* **2004**, *108*, 3396.

Table 2. UV/Vis Spectroscopic Data (nm) (ϵ, mol^{-1} L cm^{-1}) for TlAr*, **1**, and **2** in Hexane Solution

TlAr*	367 (1200)	492 (640)
TlAr′	364 (2900)	492 (1400)
TlAr″	368 (2600)	492 (1100)

Ar′ ligand for thallium raised the possibility that the corresponding dimeric species could also be obtained, thereby affording a homologous series of this type for M = Ga, In, or Tl and permitting the M−M distances to be compared.

Synthesis. The thallium(I) aryls **1** and **2** were synthesized under rigorously anaerobic and anhydrous conditions by the treatment of thallium(I) chloride with 1 equiv of the lithium aryl in Et_2O at ca. −78 °C in accordance with the equation.

$$\mathrm{LiAr' \ or \ LiAr'' + TlCl} \rightarrow \underset{\mathbf{1}}{\tfrac{1}{2}(\mathrm{TlAr'})_2} \ \mathrm{or} \ \underset{\mathbf{2}}{\tfrac{1}{3}(\mathrm{TlAr''})_3} + \mathrm{LiCl}$$

The addition, which was carried under conditions of low illumination, resulted in red solutions upon warming to 0 °C. Separation of the precipitated LiCl and concentration of the filtrate under reduced pressure afforded upon storage at ca. −20 °C dark red, almost black, crystals of **1** or **2** in ca. 40% yield. The crystals of the products are soluble in hydrocarbons such as benzene or toluene, but these solutions are prone to decomposition at room temperature to afford a deposit of thallium and a colorless supernatant solution. Analysis of these solutions by ^{1}H and ^{13}C NMR spectroscopy showed the presence of free arene (Ar′H or Ar″H), which is probably a result of hydrogen abstraction from the hydrocarbon solvent. However, storage of **1** and **2** as solids for several months at ca. − 20 °C in the absence of light afforded no evidence of decomposition. The compounds were characterized by ^{1}H and ^{13}C NMR spectroscopy. Attempts to obtain ^{205}Tl NMR data were unsuccessful. This is probably due to broadening of the signal by the large anisotropy of the chemical shift tensor, which shortens the relaxation times.[39] A similar problem was encountered in NMR studies of the monomer TlAr*.[25] The electronic spectra of **1** and **2**, along with those of TlAr*, are presented in Table 2. Each compound displays two absorbances at ca. 366 and 492 nm. Each absorbance has a relatively large ϵ value, which is consistent with orbitally allowed transitions. It is probable that n−p (6s−6p) and σ−σ* (Tl−C) transitions are responsible for these absorptions. The electronic spectra of **1** and **2** are almost identical to that of TlAr*, which has already been shown to be monomeric in both the solid state and in solution. Attempts to measure the molecular weight of **1** by cryoscopy were hampered by the decomposition of the solution with the deposition of Tl metal.

The monomeric character of **1** and **2** in solution is further supported by their immediate reaction with $B(C_6F_5)_3$. The reaction between **1** and $B(C_6F_5)_3$ occurs instantly upon mixing toluene solutions of the reactants and afforded colorless crystals of the 1:1 donor−acceptor complex **3**. Compound **3** displayed three ^{19}F resonances (*o*-F, *m*-F, *p*-F) and a ^{11}B NMR signal at −11.3 ppm, which are similar to those of the analogous lighter element complexes Ar′M→$B(C_6F_5)_3$. (M = Ga, $\delta = -17.73$; In, $\delta = -14.1$). However, the reaction between **2** and $B(C_6F_5)_3$ yielded a very pale yellow oil that was prone to decomposition, which severely hindered attempts to analyze the compound spectroscopically. Attempts to crystallize the oil from common solvents were unsuccessful.

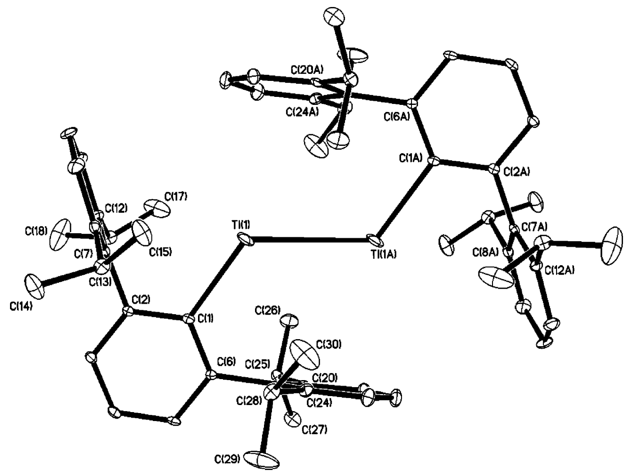

Figure 1. Thermal ellipsoid (30%) drawing of **1**. Hydrogen atoms are not shown. Selected bond lengths (Å) and bond angles (deg) are as follows: Tl(1)−Tl(1A) = 3.0936(8); Tl(1)−C(1) = 2.313(5); C(1)−Tl(1)−Tl(1A) = 119.74(14); C(2)−C(1)−Tl(1) = 117.6(4); C(6)−C(1)−Tl(1) = 122.9(4).

Structure, Bonding, and Reactivity. The structure of **1** is illustrated in Figure 1. It is a centrosymmetric dimer with a planar $Tl_2C(ipso)_2$ core. The Tl−Tl distance, 3.0936(8) Å, is the shortest that has been observed in a molecular Tl(I) species. The only Tl(I)−Tl(I) separation in a molecular species that approaches this value is the 3.15 Å observed in the structure of $\{MeSi[N(Tl)Bu^t]_3\}_2$. The trans-bending angle for the Tl(1A)−Tl(1)−C(1) array is 119.74(14)°. This is in good agreement with the 120, 115, and 119.5° angles calculated for HTlTlH.[13−15] The calculated distances, however, are longer (3.28 and 3.217 Å)[13−15] than the experimentally observed 3.0936(8) Å in **1**. Calculations for the dimerization energies of $(TlH)_2$ have afforded values of 3.35 and 4.78 kcal mol^{-1}. The dissociated structures of **1** and **2** in solution underline the weakness of the Tl(I)−Tl(I) bonding and are consistent with the calculated and experimentally observed bond lengths as well as the calculated low association energies. It is also notable that the Tl(I)−Tl(I) distance in **1**, which contains two-coordinate thallium, is longer than the 2.88−2.97 Å range observed for Tl−Tl single bonds in R_2TlTlR_2 species. This also is indicative of weak bonding[27,28] and suggests that the Tl−Tl bond in such dimers could be shortened by packing forces to values less than the calculated distances which concern gas phase species only.

The Tl−C bond length in **1** is 2.313(5) Å, which is essentially indistinguishable from the 2.34(1) Å seen in TlAr*.[30] This suggests that the electronic arrangement in the valence orbitals surrounding thallium seems little affected by association. This is, of course, also consistent with weak Tl−Tl bonding. In contrast, the Tl−C distance in **1** and TlAr* are ca. 0.09−0.14 Å longer than the Tl(III)−C bond lengths in the compounds $TlMes_3$ (2.169−2.224 Å)[40] and $TlMe_3$ (2.196−2.207 Å).[41] Presumably the smaller size of the Tl^{3+} in comparison to Tl^+ accounts for some of this difference.

---

(39) Poole, C. P.; Farach, H. A. *Relaxation in Magnetic Resonance*; Academic Press: New York, 1971; p 75.

(40) Blumel, J.; Werner, B.; Krauter, T.; Neumüller, B. *Z. Anorg. Allg. Chem.* **1997**, *623*, 309.

(41) Boese, R. Downs, A. J.; Greene, T. M.; Hall, A. W.; Morrison, C. A.; Parsons, S. *Organometallics* **2003**, *22*, 2450.

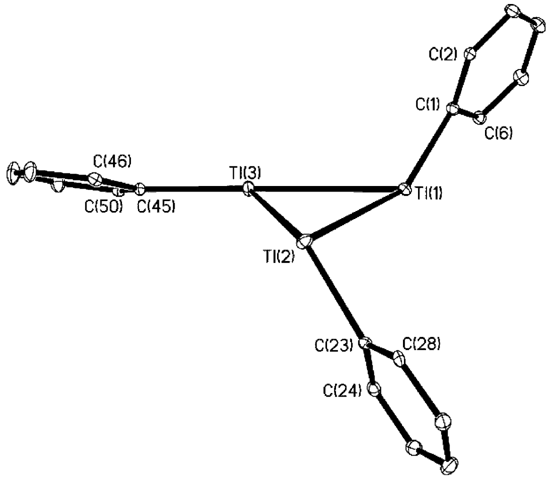

Figure 2. Thermal ellipsoid (30%) drawing of **2**. Hydrogen atoms, as well as the flanking 2,6-dimethylphenyl substituents of the terphenyl groups, are not shown. Selected bond lengths (Å) and bond angles (deg) are as follows: Tl(1)−Tl(2) = 3.2144(3); Tl(1)−Tl(3) = 3.3782(3); Tl(2)−Tl(3) = 3.3590(3); Tl(2)−Tl(1)−Tl(3) = 61.203(6); Tl(1)−Tl(2)−Tl(3) = 61.805(5); Tl(2)−Tl(3)−Tl(1) = 56.992(6); Tl−C(av.) = 2.331(4); C(1)−Tl(1)−Tl(2) = 150.02(10); C(1)−Tl(1)−Tl(3) = 110.93(9); C(23)−Tl(2)−Tl(1) = 96.96(10); C(23)−Tl(2)−Tl(3) = 131.61(9); C(45)−Tl(3)−Tl(2) = 111.9(1); C(45)−Tl(3)−Tl(1) = 168.3(1).

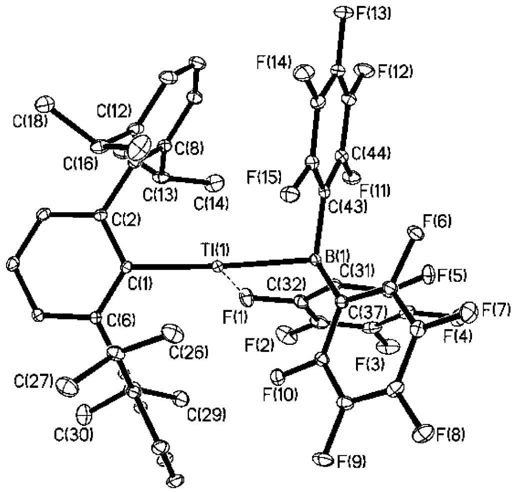

Figure 3. Thermal ellipsoid (30%) drawing of **3**. Hydrogen atoms are not shown. Selected bond lengths (Å) and bond angles (deg) are as follows: Tl(1)−B(1) = 2.31(2); Tl(1)−C(1) = 2.1647(17); Tl(1)···F(1) = 2.6689(13); C(1)−Tl(1)−B(1) = 174.358(7).

The three-membered ring arrangement of **2** (Figure 2) is the first observation of a species of formula c-(MR)$_3$ (M = Al−Tl; R = organo group) for group 13 metals.[42] Cryoscopic measurements of molecular weights of some Ga(I) alkyls have afforded values that correspond to (GaR)$_3$ species.[1c,5a] The data, however, were interpreted in terms of an equilibrium mixture of monomers and tetramers rather than trimers. The observation of dimeric and trimeric structures in our work suggests that such species might also exist in equilibrium alongside the tetramers and monomers in Ga(I) or In(I) alkyl or aryl solutions, even though no trimeric organogallium(I) or organoindium(I) species corresponding to **2** have been isolated to date. The reaction of Ar″Li with InCl did not afford a trimeric indium cluster analogous to **2**, but instead a mixed In(I)−In(II) compound with bridging chlorides of formula Ar″$_4$In$_4$Cl$_2$ was isolated.[43] Moreover, reaction of the mesityl-substituted *m*-terphenyl, ArylLi, (Aryl = C$_6$H$_3$-2,6-(C$_6$H$_2$-2,4,6-Me$_3$)$_2$), a reagent that differs from Ar″ only by the addition of a *p*-Me group on the flanking aryl, with InCl did not generate a trimer like **2**; instead a In$_8$Aryl$_4$ cluster was isolated.[44] In addition, reaction of ArylLi with TlCl generated highly unstable thallium products that readily decomposed above −30 °C.[30]

The three Tl atoms in **2** are arranged as an isosceles triangle in which two Tl−Tl distances (ca. 3.37 Å) are longer than the other (ca. 3.21 Å). This leads to a narrower, 56.992(6)°, angle opposite the shortest Tl−Tl bond. The planarity of the Tl$_3$ array does not extend to their attached ipso carbon atoms. The C(1), C(23), and C(45) carbons lie −1.1479, 1.6734, and −0.1508 Å from the Tl$_3$ plane, the C(23) carbon being on the opposite side of the plane from C(1) and C(45). Each thallium is pyramidally coordinated with the sum of the angles (Σ°) as follows: Tl(1) = 323.15(10)°, Tl(2) = 290.38(10)°, Tl(3) = 337.22(10)°, which is indicative of substantial lone pair character at each metal. This is consistent with weakened Tl−Tl bonding, and it is notable that the Tl−Tl distances in **2** are 0.1−0.25 Å longer than those in **1**. In contrast, the Tl−C bonds, average 2.331(8) Å, are essentially unaltered from those in **1** and TlAr*. As discussed above, the unchanged Tl−C bond length is consistent with weak bonding of the thallium centers and is in agreement with the monomeric character of **2** in solution.

The main reason for the weakness of the metal−metal bonding in **1** and **2** is the large energy difference between the lone pair orbital, mostly 6s in character, and empty valence 6p orbitals in the TlAr′ and TlAr″ moieties. The Tl−H singlet−triplet energy difference (which is somewhat less than the 6s^2−6p energy difference) has been calculated to be 51.9 kcal mol^{-1} by Treboux and Barthelat.[15] Thus, formation of strong covalent bonds between the thalliums require very high preparation energy to induce the s-electrons into combination. This cannot be compensated for by the low inherent strength of the metal−metal bonds that are formed.[14]

The energy difference between the 6s^2 and 6p levels does not prevent the TlAr moiety from behaving as a good Lewis base if a suitable acceptor is available. Thus, when it is treated with B(C$_6$F$_5$)$_3$, the thermally robust complex **3** is formed readily. Complex **3** features an almost linear thallium coordination and a Tl(1)−C(1) distance of 2.1647(17) Å (Figure 3), which is ca. 0.15 Å less than the C(1)−Tl(1) bond in **1**.

The Tl−B distance is 2.311(2) Å, which is in good agreement with the sum of the covalent radii of thallium and boron.[45] Compounds having Tl−B bonds are scarce and limited to various thallium boron cage species, which feature a wide range

---

(42) The alkali metal−gallium clusters M$_2$(GaC$_6$H$_3$-2, 6-Mes$_2$)$_3$ (M = Na or K) have a Ga$_3$ arrangement which can be regarded to have an aromatic (GaC$_6$H$_3$-2,6-Mes$_2$)$^{2-}$ unit: Li, X.-W.; Pennington, W. T.; Robinson, G. H. *J. Am. Chem. Soc.* **1995**, *117*, 7578. Li, X.-W.; Xie, Y.; Schreiner, P. R.; Gripper, K. D.; Crittendon, R. C.; Campana, C. F.; Schaefer, H. F.; Robinson, G. H. *Organometallics* **1996**, *15*, 3798. In addition, free radical aluminum and gallium ring species of formula M$_3$(SiBu$^t_3$)$_4$ (M = Al or Ga) have been synthesized. Wiberg, N.; Blank, T.; Kaim, W.; Schwerdeski, B.; Linti, G. *Eur. J. Inorg. Chem.* **2000**, 1475. Wiberg, N.; Blank, T.; Amelunxen, K.; Nöth, H.; Knizek, J.; Habereder, T.; Kaim, W.; Wanner, M. *Eur. J. Inorg. Chem.* **2001**, 1719.

(43) Fox, A. F.; Wright, R. J.; Richards, A. F.; Power, P. P. Unpublished work, 2004.

(44) Eichler, B. E.; Hardman, N. J. Power, P. P. *Angew. Chem., Int. Ed.* **2000**, *39*, 383. For a recent review of heavier group 14 clusters see: Wiberg, N.; Power, P. P. *Mol. Clusters Main Group Elem.*; Driess, M., Nöth, H., Eds.; WCH-Wiley: Weinheim, 2004; p 188.

(45) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell: Ithaca, NY, 1960; p 246.

of Tl−B distances (2.063−2.772 Å).[19,46] These data suggest that the thallium boron bond in **3** is relatively strong. This is borne out by other structural parameters such as the degree of geometrical change from planarity to tetrahedral in $B(C_6F_5)_3$, which has been used to gauge the strength of donor−acceptor complexes.[47] The sum of the C−B−C angles in **3** is 341.03(15)°, which is just slightly greater than the corresponding angular sums at $B(C_6F_5)_3$ in Ar′MB$(C_6F_5)_3$ (M = Ga, 337.5(3)°[31] and M = In, 339.33 (1)°).[32a] One major fluorine contact Tl(1)···F(1) with a distance of 2.6689(13) Å is present in the solid state. The distance is at least 0.29 Å longer than known Tl(III)−F single bonds that span the range 2.38−2.44 Å.[48] However, the Tl−F interaction lengthens the C(32)−F(1) distance to 1.370(2) Å, which is longer than the 1.347(2) Å average for the 14 remaining ligand C−F bonds. The Tl−F interaction is also preserved in solution as indicated by the broad ortho-chemical shift in the ^{19}F NMR spectra. This is in contrast to the lighter congeners Ar′MB$(C_6F_5)_3$ (M = Ga, In), where three sharp signals are observed for the ortho, meta, and para fluorines in the ^{19}F NMR.[31,32a]

The Tl−C bond in **3** is ca. 6% shorter than that in **1**, despite the increase in coordination number at thallium. The shortening may be rationalized in a number of ways. One involves an increase ionic contribution to the Tl−C bond strength as a result of the donation of the lone pair to boron, which increases the δ^+ at thallium. Alternatively, the removal of charge from thallium by lone pair donation effectively decreases its ionic radius so that shorter bonds are observed. Similar arguments have been used to account for the metal−carbon bond shortening in complexes of gallium(I) and indium(I) aryls which display a Ga−C and In−C bond shortening of at least 0.1 Å upon reaction with acceptors such as $B(C_6F_5)_3$ or metal carbonyls.[31,32] In a similar vein, it can be argued that the absence of shortening in **1** in comparison to TlAr*, and the ready formation of **3** at low temperatures, provides further evidence for the weakness of the Tl−Tl bond in **1**.

The diindene (Ar′InInAr′),[32] digallene (Ar′GaGaAr′),[31] and dialuminene (Ar′AlAlAr′)[49] analogues of **1** have been shown to be highly reactive. For example, the diindene and digallene readily react with bulky azides with the elimination of N_2 to form the imides Ar′MNAr that contain M−N bonds with multiple character.[50] The dialuminene, Ar′AlAlAr′ is so reactive that it forms a cycloaddition product with toluene at room temperature.[49] The diindene and digallene also react with N_2O to form compounds with bridging oxides of formula $(\mathrm{Ar'MO})_2$.[51] However, reaction of Ar′TlTlAr′ with N_3SiMe_3, N_3Ar, N_2O or $W(CO)_5THF$, which yielded isolable and characterizable products with the lighter dimetallenes, afforded no reaction with **1** under the same conditions. The inert nature of the dithallene toward oxidation is in accord with the so-called inert pair effect.[52]

Conclusions

The heaviest group 13 dimetallene of formula Ar′TlTlAr′ has been synthesized. It displays weak Tl−Tl bonding which is manifested by dissociation of Ar′TlTlAr′ into two monomeric Ar′Tl units in hydrocarbon solvent. In solution, the Ar′Tl monomer displays Lewis base character but a lower tendency to form oxidized products in comparison to its Al(I), Ga(I), or In(I) dimetallene analogues. This is in accord with the greater stability of Tl(I) in comparison to Tl(III). Use of the smaller terphenyl ligand Ar″ gave the first example of a neutral group 13 element three-membered ring compound $(\mathrm{Ar''Tl})_3$. The trimer also dissociates to monomeric Ar″Tl units in hydrocarbon solution as shown by its UV/vis spectrum which is very similar to that of the known monomer Ar*Tl.

Acknowledgment. We are grateful to the National Science Foundation for financial support and the Albemarle Corporation for a generous gift of $B(C_6F_5)_3$.

Supporting Information Available: Crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA0432259

---

(46) (a) Yanovsky, A. I.; Antipin, M. Yu.; Struchkov, Yu. T.; Bregadze, V. I.; Usyatinskii, A. Ya.; Godovikov, N. N. *Izv. Akad. Nauk SSSR, Ser. Khim. (Russ.) (Russ. Chem. Bull.)* **1982**, 293. (b) Stumpf, K.; Pritzkow, H.; Siebert, W. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 71. (c) Usyatinskii, A. Ya.; Bregadze, V. I.; Godovikov, N. N.; Vinogradova, L. E. Leites, L. A.; Yanovsky, A. I.; Struchkov, Yu, T. *Izv. Akad. Nauk SSSR, Ser. Khim. (Russ.) (Russ. Chem. Bull.)* **1984**, 2009. (d) Usyatinskii, A. Ya.; Bregadze, V. I.; Godovikov, N. N.; Antonovich, V. A.; Polyakov, A. V.; Yanovsky, A. I.; Struchkov, Yu. T. *Metalloorg. Khim. (Russ.) (Organomet. Chem. (USSR))* **1989**, *2*, 877. (e) Greenwood, N. N.; Howard, J. A. *J. Chem. Soc., Dalton Trans.* **1976**, 177. (f) Colquhoun, H. M.; Greenhough, T. J.; Wallbridge, M. G. H. *Acta Crystallogr, Sect. B: Struct. Crystallogr. Cryst. Chem.* **1978**, *34*, 2373. (g) Manning, M. J.; Knobler, C. B.; Hawthorne, M. F.; Do, Y. *Inorg. Chem.* **1991**, *30*, 3589.

(47) Jacobsen, H.; Berke, H.; Döring, S.; Kerh, G.; Erker, G.; Frölich, R.; Meyer, O. *Organometallics* **1999**, *18*, 1724.

(48) (a) Becker, C.; Kieltsch, I.; Broggini, D.; Mezzetti, A. *Inorg. Chem.* **2003**, *42*, 8417. (b) Coutsolelos, A. G.; Orfanopoulos, M.; Ward, D. L. *Polyhedron* **1991**, *10*, 885. (c) Barthazy, P.; Togni, A.; Mezzetti, A. *Organometallics* **2001**, *20*, 3472.

(49) Wright, R. J.; Phillips, A. D.; Power, P. P. *J. Am. Chem. Soc.* **2003**, *125*, 10784.

(50) Wright, R. J.; Phillips, A. D.; Allen, T. L.; Fink, W. H.; Power, P. P. *J. Am. Chem. Soc.* **2003**, *125*, 1694.

(51) Wright, R. J.; Moody, I. S.; Phillips, A. D.; Power, P. P. Unpublished work, 2003.

(52) (a) Hess, B. A. *Relativistic Effects in Heavy-Element Chemistry and Physics*; Wiley: New York, 2003. (b) Balasubramanian, K. *Relativistic Effects in Chemistry*; Wiley: New York, 1997. (c) Pyykkö, P. *Chem. Rev.* **1988**, *88*, 563.