Organometallics **2009,** *28,* 2091–2095

Steric Enhancement of Group 12 Metal Hydride Stability and the Reaction of an Arylzinc Hydride with Tetramethylpiperidinyl Oxide (TEMPO)

Zhongliang Zhu, James C. Fettinger, Marilyn M. Olmstead, and Philip P. Power*

Department of Chemistry, University of California Davis, One Shields Avenue, Davis, California 95616

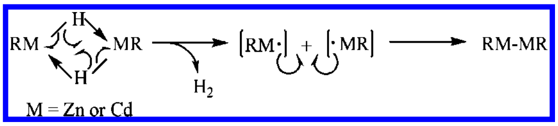
Received January 5, 2009

The synthesis and characterization of arylzinc hydrides Ar*Zn(μ-H)$_2$ZnAr* (Ar* = C_6H_3-2,6-(C_6H_2-2,4,6-Pr^i_3)$_2$, **5**) and {(4-Me_3Si-Ar*)Zn(μ-H)$_2$Zn(Ar*-4-$SiMe_3$)} (4-Me_3Si-Ar* = C_6H_2-2,6-(C_6H_2-2,4,6-Pr^i_3)$_2$-4-$SiMe_3$, **7**) as well as the monomeric arylcadmium hydride Ar*CdH (**9**) are described. They were prepared by the transmetalation of the corresponding aryl metal iodides with NaH. The Ar*CdH monomer displayed significantly greater thermal stability than its recently reported dimeric congener Ar′Cd(μ-H)$_2$CdAr′ (Ar′ = C_6H_3-2,6-(C_6H_3-2,6-Pr^i_2)$_2$), which decomposed at room temperature to afford Ar′CdCdAr′. This result supports the proposal that decomposition of the metal hydrides occurs by an associative mechanism. The reactions of these compounds with TEMPO (2,2,6,6-tetramethylpiperidinyl oxide) were also examined, but the only crystalline product obtained was 4-Me_3Si-Ar*ZnTEMPO, in which the metal is bound to the TEMPO ligand in a quasi side-on fashion primarily through the oxygen but with a significant zinc−nitrogen interaction.

Introduction

The synthesis of molecular compounds featuring homonuclear metal−metal bonds between the group 12 elements (Zn, Cd, and Hg) has proven to be a considerable synthetic challenge and has attracted great interest in the bonding between these metal centers.[1−8] Recent work has shown that the synthesis of related organometal hydrides $(RMH)_2$ (M = Zn or Cd; R = organic or related substituent) followed by their rearrangement with the concomitant elimination of H_2 can be an effective route for the formation of M−M bonded compounds (Scheme 1).[1b,3,7] However, the pathway in Scheme 1, where a homolytic cleavage of M−H bonds occurs to produce radical intermediates, is normally disfavored by a substantial energy barrier and usually becomes effective only for the heavier metals, where M−H bonds are weaker.[9] Furthermore, as pointed out by Downs and co-workers, the homolytic cleavage of M−H bonds probably occurs via an associative mechanism and depends on the ability of hydrides to form at least a transient bridge between the metal atoms.[10] Recently, our group reported the synthesis and characterization of the homologous organo group 12 hydrides $(\text{Ar}'\text{MH})_{1\text{ or }2}$ (M = Zn, Cd, or Hg; Ar′ = C_6H_3-2,6-(C_6H_3-2,6-Pr^i_2)$_2$) via a transmetalation of the aryl metal halides $(\text{Ar}'\text{MI})_{1\text{ or }2}$ and NaH or KH.[3] Studies on these metal hydrides showed that the dimeric zinc hydride Ar′Zn(μ-H)$_2$ZnAr′ (**1**) can be further reduced by NaH to afford the unusual sodium hydride-bridged species, Ar′Zn(μ-H)(μ-Na)ZnAr′ (**2**),[3a] which features a new type of Zn−Zn bond, while Ar′Cd(μ-H)$_2$CdAr′ (**3**) rapidly rearranges to metal−metal bonded Ar′CdCdAr′ at room temperature.[3b] In both reactions a homolytic cleavage of M−H bonds was proposed, and the coupling of highly reactive radical intermediates is, apparently, the key step on the pathway to the final products. However, a greater understanding of the chemical reactivity of organo group 12 hydrides is limited by their scarcity.[3,7,11,12] We now report the synthesis and characterization of further examples of the zinc hydrides Ar*Zn(μ-H)$_2$ZnAr* (**5**) and {(4-Me_3Si-Ar*)Zn(μ-H)$_2$Zn(Ar*-4-$SiMe_3$)} (**7**) as well as a monomeric cadmium hydride Ar*CdH (**9**) (Scheme 2) by the use of Ar*-type ligands (Ar* = C_6H_3-2,6-(C_6H_2-2,4,6-Pr^i_3)$_2$).

Scheme 1. Synthetic Route to Metal−Metal Bonded Group 12 Elements via the Homolytic Cleavage of M−H Bonds Followed by the Radical Coupling between Two ArM$^\bullet$ Fragments



These Ar* ligands are bulkier than the previously used Ar′, as a result of which they provide more steric protection of metal centers and hence greater stability by blocking associative decomposition. The derivatized Ar* ligand Ar*-4-$SiMe_3$ (Ar*-4-$SiMe_3$ = C_6H_2-2,6(C_6H_2-2,4,6-Pr^i_3)$_2$-4-$SiMe_3$) was employed in the case of zinc in order to obtain crystals suitable for

---

* Corresponding author. E-mail: pppower@ucdavis.edu.

(1) (a) Resa, I.; Carmona, E.; Gutierrez-Puebla, E.; Monge, A. *Science* **2004**, *305*, 1136. (b) del Río, D.; Galindo, A.; Resa, I.; Carmona, E. *Angew. Chem., Int. Ed.* **2005**, *44*, 1244. (c) Grirrane, A.; Resa, I.; Rodriguez, A.; Carmona, E.; Alvarez, E.; Gutierrez-Puebla, E.; Monge, A.; Galindo, A.; del Río, D.; Andersen, R. A. *J. Am. Chem. Soc.* **2007**, *129*, 693.

(2) Wang, Y.; Quillian, B.; Wei, P.; Wang, H.; Yang, X.-J.; Xie, Y.; King, R. B.; Schleyer, P. v. R.; Schaefer, H. F., III; Robinson, G. H. *J. Am. Chem. Soc.* **2005**, *127*, 11944.

(3) (a) Zhu, Z.; Wright, R. J.; Olmstead, M. M.; Rivard, E.; Brynda, M.; Power, P. P. *Angew. Chem., Int. Ed.* **2006**, *45*, 5807. (b) Zhu, Z.; Fischer, R. C.; Fettinger, J. C.; Rivard, E.; Brynda, M.; Power, P. P. *J. Am. Chem. Soc.* **2006**, *128*, 15068. (c) Zhu, Z.; Brynda, M.; Wright, R. J.; Fischer, R. C.; Merrill, A. W.; Rivard, E.; Wolf, R.; Fettinger, J. C.; Olmstead, M. M.; Power, P. P. *J. Am. Soc. Chem.* **2007**, *129*, 10847.

(4) (a) Yang, X.-J.; Yu, J.; Liu, Y.; Xie, Y.; Schaefer, H. F., III; Liang, Y.; Wu, B. *Chem. Commun.* **2007**, 2363. (b) Yu, J.; Yang, X.-J.; Liu, Y.; Pu, Z.; Li, Q.-S.; Xie, Y.; Schaefer, H. F.; Wu, B. *Organometallics* **2008**, *27*, 5800.

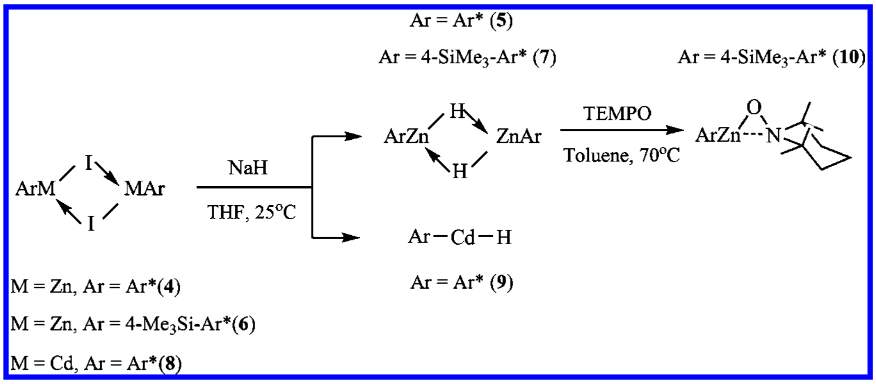
(5) Fedushkin, I. L.; Skatova, A. A.; Ketkov, S. Y.; Eremenko, O. V.; Piskunov, A. V.; Fukin, G. K. *Angew. Chem., Int. Ed.* **2007**, *46*, 4302.

(6) Tsai, Y.-C.; Lu, D.-Y.; Lin, Y.-M.; Hwang, J.-K.; Yu, J.-S. K. *Chem. Commun.* **2007**, 4125.

(7) Reger, D. L.; Mason, S. S.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 10406.

10.1021/om900005t CCC: $40.75

Scheme 2. Synthetic Routes to 5, 7, 9, and 10



crystallographic studies. We also report the reaction between **7** and the radical species TEMPO (2,2,6,6-tetramethylpiperidinyl oxide), which affords 4-Me_3Si-Ar*ZnTEMPO (**10**) (Scheme 2).

Experimental Section

General Procedures. All manipulations were carried out by using modified Schlenk techniques under an atmosphere of N_2 or in a Vacuum Atmospheres HE-43 drybox. Solvents were dried according to the method of Grubbs and degassed prior to use.[13] The chemicals used in this study were purchased from Aldrich or Acros and used as received. The salts LiAr*·OEt_2,[14] Li(Ar*-4-$SiMe_3$)·OEt_2,[15] and {Ar*Zn(μ-I)}$_2$ (**4**)[16] were prepared as previously described. ^{1}H, ^{13}C, ^{29}Si, and ^{113}Cd NMR spectra were recorded on 300 or 600 MHz spectrometers, and the ^{113}Cd NMR spectra were referenced externally to 0.01 M $Cd(ClO_4)_2$. Infrared data were recorded as Nujol mulls using a Perkin-Elmer 1430 instrument. Melting points were recorded in sealed capillaries using a Meltemp apparatus and are uncorrected.

Ar*Zn(μ-H)$_2$ZnAr* (5). {Ar*Zn(μ-I)}$_2$ (2.50 g, 1.87 mmol, **4**) and NaH (0.074 g, 5.61 mmol) were combined with THF (50 mL) at ambient temperature. After stirring for 2 days, the solvent was removed, and the residue was extracted with ca. 70 mL of toluene. The solid was allowed to settle, and the mother liquor was separated from the precipitate (NaI and excess NaH). The solution was then concentrated under reduced pressure to afford the product **5** as a white powder. Yield: 1.32 g, 65% (based on **4**). Anal. Calcd for $C_{72}H_{100}Zn_2$: C, 78.90; H, 9.20. Found: C, 78.16; H, 9.38. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 1.08 (d, 24H, *o*-CH(CH_3)$_2$, $^3J_{HH}$ = 6.9 Hz), 1.17 (d, 24H, *p*-CH(CH_3)$_2$, $^3J_{HH}$ = 7.2 Hz), 1.30 (d, 24H, *o*-CH(CH_3)$_2$, $^3J_{HH}$ = 7.2 Hz), 2.87 (sept, 4H, *p*-C*H*(CH$_3$)$_2$, $^3J_{HH}$ = 6.6 Hz), 2.99 (sept, 8H, *o*-C*H*(CH$_3$)$_2$, $^3J_{HH}$ = 7.2 Hz), 4.93 (s, 2H, Zn*H*), 7.10−7.26 (m, 14H, *m*-C_6H_3, *p*-C_6H_3, and *m*-Dipp). ^{13}C{^{1}H} NMR (C_6D_6, 75.4 MHz, 25 °C): δ 24.4 (*p*-CH(*C*H$_3$)$_2$), 24.9 (*o*-CH(*C*H$_3$)$_2$), 25.1 (*o*-CH(*C*H$_3$)$_2$), 30.8 (*o*-*C*H(CH$_3$)$_2$), 34.7 (*p*-*C*H(CH$_3$)$_2$), 121.1, 126.4, 141.3, 146.7, 148.1, 149.0, and 155.7 (Ar*C*), one Ar*C* resonance is likely obscured by the C_6H_6 signal. IR (Nujol): ν Zn(μ-H)$_2$Zn bands were not identified and may be very weak or obscured by overlapping ligand absorptions.

{(4-SiMe$_3$-Ar*)Zn(μ-H)$_2$Zn(Ar*-4-SiMe$_3$)} (7). Li(Ar*-4-$SiMe_3$)·OEt_2 (1.46 g, 2.43 mmol) and ZnI_2 (0.78 g, 2.43 mmol) were combined with diethyl ether (50 mL) and stirred for 2 days. The solvent was removed under reduced pressure, and the residue was extracted with toluene (50 mL) and separated from the precipitate (LiI) by filtration. Removal of the solvent gave {4-$SiMe_3$-Ar*Zn(μ-I)}$_2$ (**6**) as a white powder. The procedure for the reaction of **6** (1.53 g, 1.03 mmol) with NaH (0.074 g, 3.08 mmol) was conducted in a similar way to that described for **5**. The crude compound was extracted with ca. 50 mL of hexane. Storage of the concentrated hexane solution (ca. 15 mL) for 2 days in a freezer (ca. −18 °C) afforded colorless, X-ray quality crystals of **7**. Yield: 0.72 g, 48% (based on Li(Ar*-4-$SiMe_3$)·OEt_2); mp 212−213 °C. **7**: ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 0.29 (s, 18H, Si(CH_3)$_3$), 1.13 (d, 24H, *o*-CH(CH_3)$_2$, $^3J_{HH}$ = 6.6 Hz), 1.22 (d, 24H, *p*-CH(CH_3)$_2$, $^3J_{HH}$ = 7.2 Hz), 1.39 (d, 24H, *o*-CH(CH_3)$_2$, $^3J_{HH}$ = 7.2 Hz), 2.94 (sept, 4H, *p*-C*H*(CH$_3$)$_2$, $^3J_{HH}$ = 6.6 Hz), 3.03 (sept, 8H, *o*-C*H*(CH$_3$)$_2$, $^3J_{HH}$ = 7.2 Hz), 5.08 (s, 2H, Zn*H*), 7.20 (s, 4H, *m*-C_6H_2), 7.49 (s, 8H, *m*-Dipp). ^{13}C{^{1}H} NMR (C_6D_6, 75.4 MHz, 25 °C): δ −0.99 ((*C*H$_3$)$_3$Si), 24.5 (*p*-CH(*C*H$_3$)$_2$), 24.8 (*o*-CH(*C*H$_3$)$_2$), 25.1 (*o*-CH(*C*H$_3$)$_2$), 30.8 (*o*-*C*H(CH$_3$)$_2$), 34.7 (*p*-*C*H(CH$_3$)$_2$), 121.0, 131.1, 139.4, 141.6, 146.7, 148.0, 148.3 and 156.0 (Ar*C*). ^{29}Si{^{1}H} NMR (C_6D_6, 119.2 MHz, 25 °C): δ −4.63. IR (Nujol): $\nu_{(Zn-H)}$ bands were not observed and may be very weak or obscured by overlapping ligand absorptions. **6**: ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 0.27 (s, 18H, Si(CH_3)$_3$), 1.18 (d, 24H, *o*-CH(CH_3)$_2$, $^3J_{HH}$ = 7.2 Hz), 1.29 (d, 24H, *p*-CH(CH_3)$_2$, $^3J_{HH}$ = 7.8 Hz), 1.38 (d, 24H, *o*-CH(CH_3)$_2$, $^3J_{HH}$ = 6.6 Hz), 2.92 (sept, 4H, *p*-C*H*(CH$_3$)$_2$, $^3J_{HH}$ = 7.2 Hz), 3.06 (sept, 8H, *o*-C*H*(CH$_3$)$_2$, $^3J_{HH}$ = 7.2 Hz), 7.24 (s, 4H, *m*-C_6H_2), 7.52 (s, 8H, *m*-Dipp). ^{13}C{^{1}H} NMR (C_6D_6, 75.4 MHz, 25 °C): δ −1.04 ((*C*H$_3$)$_3$Si), 24.4 (*o*-CH(*C*H$_3$)$_2$), 24.7 (*o*-CH(*C*H$_3$)$_2$), 25.4 (*p*-CH(*C*H$_3$)$_2$), 30.7 (*o*-*C*H(CH$_3$)$_2$), 35.1 (*p*-*C*H(CH$_3$)$_2$), 121.5, 128.9, 131.9, 140.9, 146.8, 147.7, 148.6 and 219.8 (Ar*C*). ^{29}Si{^{1}H} NMR (C_6D_6, 119.2 MHz, 25 °C): δ −4.60.

Ar*CdH (9). Compound **9** was prepared in a similar way to that described for **7** from the reaction of LiAr*·OEt_2 (1.54 g, 2.73 mmol) with CdI_2 (1.00 g, 2.73 mmol) followed by the transmetalation of {Ar*Cd(μ-I)}$_2$ (**8**) (1.26 g, 0.88 mmol) with NaH (0.063 g, 2.62 mmol). Storage of a benzene solution for 1 day in a refrigerator (ca. 7 °C) afforded colorless plates of **9** suitable for crystallographic studies. Anal. Calcd for $C_{36}H_{50}Cd$: C, 72.65; H, 8.47. Found: C, 72.01; H 8.48. Yield: 0.42 g, 26% (based on LiAr*·OEt_2); compound **6** is thermally stable at room temperature; however, at ca. 110 °C it decomposes to a black solid. **9**: ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 1.17 (d, 12H, *o*-CH(CH_3)$_2$, $^3J_{HH}$ = 7.2

---

(8) Bravo-Zhivotovskii, D.; Yuzefovich, M.; Bendikov, M.; Klinkhammer, K.; Apeloig, Y. *Angew. Chem., Int. Ed.* **1999**, *38*, 1100.

(9) Downs, A. J.; Pulham, C. R. *Chem. Soc. Rev.* **1994**, *23*, 175.

(10) Aldridge, S.; Downs, A. J. *Chem. Rev.* **2001**, *101*, 3305.

(11) Some organozinc hydride examples other than those in ref 3: (a) Bell, N. A.; Moseley, P. T.; Shearer, H. M. M.; Spencer, C. B. *J. Chem. Soc., Chem. Commun.* **1980**, 359. (b) Looney, A.; Han, R.; Gorrell, I. B.; Cornebise, M.; Yoon, K.; Parkin, G.; Rheingold, A. L. *Organometallics* **1995**, *14*, 274. (c) Kläui, W.; Schilde, U.; Schmidt, M. *Inorg. Chem.* **1997**, *36*, 1598. (d) Krieger, M.; Neumüller, B.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1998**, *624*, 1563. (e) Hao, H. J.; Cui, C. M.; Roesky, H. W.; Bai, G. C.; Schmidt, H.-G.; Noltemeyer, M. *Chem. Commun.* **2001**, 1118.

(12) Some spectroscopically characterized organomercury hydrides: (a) Devaud, M. *J. Organomet. Chem.* **1981**, *220*, C27. (b) Bellec, N.; Guillemin, J.-C. *Tetrahedron Lett.* **1995**, *36*, 6883. (c) Greene, T. M.; Andrews, L.; Downs, A. J. *J. Am. Chem. Soc.* **1995**, *117*, 8180. (d) Nakamura, E.; Yu, Y.; Mori, S.; Yamago, S. *Angew. Chem., Int. Ed.* **1997**, *36*, 374.

(13) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

(14) Schiemenz, B.; Power, P. P. *Organometallics* **1996**, *15*, 958.

(15) Wolf, R.; Ni, C.; Nguyen, T.; Brynda, M.; Long, G. J.; Sutton, A. D.; Fischer, R. C.; Fettinger, J. C.; Hellman, M.; Pu, L. H.; Power, P. P. *Inorg. Chem.* **2007**, *46*, 11277.

Hz), 1.24 (d, 12H, *p*-CH(C*H*$_3$)$_2$, $^3J_{HH}$ = 7.2 Hz), 1.24 (d, 12H, *o*-CH(C*H*$_3$)$_2$, $^3J_{HH}$ = 6.6 Hz), 2.84 (sept, 2H, *p*-C*H*(CH$_3$)$_2$, $^3J_{HH}$ = 7.2 Hz), 3.12 (sept, 4H, *o*-C*H*(CH$_3$)$_2$, $^3J_{HH}$ = 6.6 Hz), 6.79 (s, 1H, Cd*H*), 7.19 (s, 4H, *m*-Dipp), 7.24−7.28 (6H, *m*-C$_6$H$_3$ and *p*-C$_6$H$_3$). ^{13}C {^{1}H} NMR (C$_6$D$_6$, 75.4 MHz, 25 °C): δ 24.3 (*o*-CH(*C*H$_3$)$_2$), 24.4 (*o*-CH(*C*H$_3$)$_2$), 24.9 (*p*-CH(*C*H$_3$)$_2$), 30.6 (*o*-*C*H(CH$_3$)$_2$), 34.8 (*p*-*C*H(CH$_3$)$_2$), 121.3, 126.4, 127.9, 142.1, 147.0, 148.5, 148.7, and 167.3 (Ar*C*). ^{113}Cd{^{1}H} NMR (C$_6$D$_6$, 133.1 MHz, 25 °C): δ 410.3. IR (Nujol): $\nu_{(Cd-H)}$ 1735 cm^{-1} (m). **8**: ^{1}H NMR (300 MHz, C$_6$D$_6$, 25 °C): δ 1.16 (d, 24H, *o*-CH(C*H*$_3$)$_2$, $^3J_{HH}$ = 7.2 Hz), 1.27 (d, 24H, *p*-CH(C*H*$_3$)$_2$, $^3J_{HH}$ = 7.2 Hz), 1.37 (d, 24H, *o*-CH(C*H*$_3$)$_2$, $^3J_{HH}$ = 6.6 Hz), 2.90 (sept, 4H, *p*-C*H*(CH$_3$)$_2$, $^3J_{HH}$ = 7.2 Hz), 3.06 (sept, 8H, *o*-C*H*(CH$_3$)$_2$, $^3J_{HH}$ = 7.2 Hz), 7.15 (s, 8H, *m*-Dipp), 7.24−7.26 (6H, *m*-C$_6$H$_3$ and *p*-C$_6$H$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 75.4 MHz, 25 °C): δ 24.6 (*o*-CH(*C*H$_3$)$_2$), 24.7 (*o*-CH(*C*H$_3$)$_2$), 25.3 (*p*-CH(*C*H$_3$)$_2$), 30.6 (*o*-*C*H(CH$_3$)$_2$), 35.1 (*p*-*C*H(CH$_3$)$_2$), 121.6, 126.6, 127.9, 142.1, 146.6, 148.4, 148.6, and 162.9 (Ar*C*).

{4-Me$_3$Si-Ar*Zn(TEMPO)} (10). A solution of **7** (0.46 g, 0.37 mmol) in toluene (50 mL) was added dropwise to a Schlenk tube containing the red solid TEMPO (0.18 g, 1.11 mmol) over 10 min at ambient temperature. The solution was stirred at 70 °C for 1 day, by which time the red color had faded to pale brown. The toluene solvent and excess TEMPO were then removed under reduced pressure, and the residue was redissolved in ca. 15 mL of hexane. Storage for 2 days in a freezer (ca. −18 °C) afforded colorless, X-ray quality crystals of **10**. Yield: 0.26 g, 45%; mp 167 °C. Anal. Calcd for C$_{48}$H$_{75}$NOSiZn: C, 74.33; H, 9.75; N, 1.81. Found: C, 73.89; H, 9.88; N, 1.70. ^{1}H NMR (600 MHz, C$_6$D$_6$, 25 °C): δ 0.27 (s, 9H, Si(C*H*$_3$)$_3$), 1.15 (s, 12H, N(C(C*H*$_3$)$_2$CH$_2$)$_2$CH$_2$), 1.19 (d, 12H, *o*-CH(C*H*$_3$)$_2$, $^3J_{HH}$ = 6.6 Hz), 1.23−1.24 (m, 6H, N(C(CH$_3$)$_2$C*H*$_2$)$_2$C*H*$_2$), 1.32 (d, 12H, *p*-CH(C*H*$_3$)$_2$, $^3J_{HH}$ = 7.2 Hz), 1.39 (d, 12H, *o*-CH(C*H*$_3$)$_2$, $^3J_{HH}$ = 6.6 Hz), 2.87 (sept, 2H, *p*-C*H*(CH$_3$)$_2$, $^3J_{HH}$ = 6.6 Hz), 3.16 (sept, 4H, *o*-C*H*(CH$_3$)$_2$, $^3J_{HH}$ = 7.2 Hz), 7.19 (s, 4H, *m*-Dipp), 7.54 (s, 2H, *m*-C$_6$H$_2$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 150.9 MHz, 25 °C): δ −1.04 ((*C*H$_3$)$_3$Si), 14.4 (N(C(CH$_3$)$_2$-CH$_2$)$_2$*C*H$_2$), 17.5 (N(C(*C*H$_3$)$_2$CH$_2$)$_2$CH$_2$), 24.0 (*o*-CH(*C*H$_3$)$_2$), 24.5 (*o*-CH(*C*H$_3$)$_2$), 25.4 (*p*-CH(*C*H$_3$)$_2$), 30.9 (*o*-*C*H(CH$_3$)$_2$), 32.0 (N(C(CH$_3$)$_2$*C*H$_2$)$_2$CH$_2$), 35.0 (*p*-*C*H(CH$_3$)$_2$), 58.6 (N(*C*(CH$_3$)$_2$CH$_2$)$_2$-CH$_2$), 121.5, 131.8, 139.1, 142.4, 147.0, 148.6, 148.9, and 151.6 (Ar*C*). ^{29}Si{^{1}H} NMR (C$_6$D$_6$, 119.2 MHz, 25 °C): δ −21.9.

X-ray Crystallography. Crystals of **7**, **9**, or **10** were removed from a Schlenk tube under a stream of argon and immediately covered with a thin layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber, and quickly placed in the N$_2$ cold stream on the diffractometer.[17] The data for **7** were recorded near 180 K, and those of **9** and **10** were recorded near 90 K on a Bruker APEX instrument (Mo Kα radiation (λ = 0.71073 Å) and a CCD area detector). The SHELX version 6.1 program package was used for the structure solutions and refinements. Absorption corrections were applied using the SADABS program.[18] The crystal structures were solved by direct methods and refined by full-matrix least-squares procedures. All non-H atoms were refined anisotropically. All carbon-bound H atoms were included in the refinement at calculated positions using a riding model included in the SHELXTL program. The two hydrogen atoms bonded to Zn in **7** were located in the electron density map and refined with similar distance restraints; however, there is a disorder over one hydrogen position with iodine impurity. This is probably due to incomplete transmetalation of **6** by NaH. The occupancy of the iodine was refined to 0.01. The terminal hydrogen atoms bonded to Cd in **9** were also located in the electron density map and refined freely. In **10** the positions of Zn and O atoms are disordered. The occupancy of the second position refined to 0.11. Distance restraints and equal atomic displacement parameters of the two atoms of one position were used for the refinement. A summary of the data collection parameters for **7**, **9**, and **10** is provided in Table 1.

Table 1. Selected Crystallographic Data for 7·3C$_6$H$_{14}$, 9, and10

	7·3C$_6$H$_{14}$	**9**	**10**
formula	C$_{96}$H$_{157.98}$I$_{0.02}$Si$_2$Zn$_2$	C$_{36}$H$_{50}$Cd	C$_{48}$H$_{75}$NOSiZn
fw	1501.66	595.16	775.57
habit	block	plate	block
cryst syst	monoclinic	orthorhombic	monoclinic
space group	*C*2/*c*	*Pnma*	*P*2$_1$/*n*
a, Å	20.7441(10)	7.9195(3)	10.5369(9)
b, Å	17.1921(8)	25.5730(11)	29.196(3)
c, Å	28.8855(17)	16.1398(7)	15.2128(13)
α, deg	90	90	90
β, deg	110.3960(10)	90	93.026(2)
γ, deg	90	90	90
V, Å^3	9655.7(9)	3268.7(2)	4673.5(7)
Z	4	4	4
cryst dimens, mm	0.51 × 0.45 × 0.40	0.30 × 0.28 × 0.16	0.28 × 0.24 × 0.14
d_{calc}, g·cm^{-3}	1.033	1.209	1.102
μ, mm^{-1}	0.567	0.688	0.584
no. of reflns	11 088	3836	10 702
no. of obsd reflns	7918	3402	8793
R1 obsd reflns	0.0536	0.0289	0.0451
wR2, all	0.1663	0.0710	0.1203

Results and Discussion

The compounds **5**, **7**, and **9** were prepared by the treatment of the aryl metal halide with NaH in THF. Attempts to grow crystals of **5** suitable for X-ray crystallography were unsuccessful. The use of the derivatized aryl group Ar*-4-SiMe$_3$ instead of Ar* allowed crystals of **7** to be obtained. We have established elsewhere[15] that derivatization of the *para* position of the central aryl ring in terphenyl ligands exerts essentially no steric and little electronic effect, so that it can be assumed that structures of ZnAr*-4-SiMe$_3$ derivatives are similar to those of ZnAr*. The molecular structure of **7** is shown in Figure 1. It is similar to that previously reported for the Ar′ derivative **1**. The Zn−H distances are 1.62(2) and 1.65(2) Å, which are close to the 1.67(2) and 1.79(3) Å measured in **1**, and the Zn···Zn separation of 2.4102(5) Å is essentially the same as the previously seen 2.4084(3) Å. The terphenyl ligands in **7** are oriented perpendicularly to each other, and the central aryl rings subtend a dihedral angle of 47.1° with respect to the Zn$_2$H$_2$ core. A ^{1}H NMR signal corresponding to the bridging hydride in **7** was located at 5.08 ppm, which is slightly downfield to the 4.84

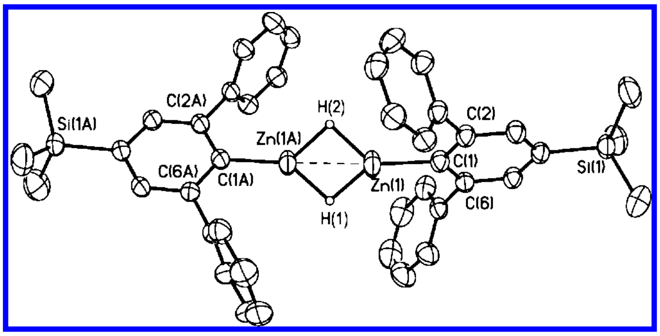


Figure 1. Thermal ellipsoid (50%) plot of **7**. Carbon-bound hydrogen atoms and isopropyl groups on flanking the rings are not shown for clarity. Selected bond lengths [Å] and angles [deg]: Zn(1)···Zn(1A) 2.4102(5), Zn(1)−H(1) 1.65(2), Zn(1)−H(2) 1.62(2), Zn(1)−C(1) 1.924(2), Si(1)−C(4) 1.872(2); C(1)−Zn(1)−Zn(1A) 176.39(7), C(1)−Zn(1)−H(1) 134.1(8), Zn(1A)−Zn(1)−H(1) 43.2(8), Zn(1A)−Zn(1)−H(2) 42.1(8), C(6)−C(1)−Zn(1) 120.89(15), C(2)−C(1)−Zn(1) 120.39(15), C(4)−Si(1)−C(37) 109.65(13), C(37)−Si(1)−C(38) 108.60(16); the dihedral angle between the Zn$_2$H$_2$ and central aryl planes is 47.1°, and the dihedral angle between two central aryl planes is 87.1°.

---

(16) Wang, Y.; Quillian, B.; Wannere, C. S.; Wei, P.; Schleyer, P. v. R.; Robinson, G. H. *Organometallics* **2007**, *26*, 3054.

(17) Hope, H. *Prog. Inorg. Chem.* **1995**, *41*, 1.

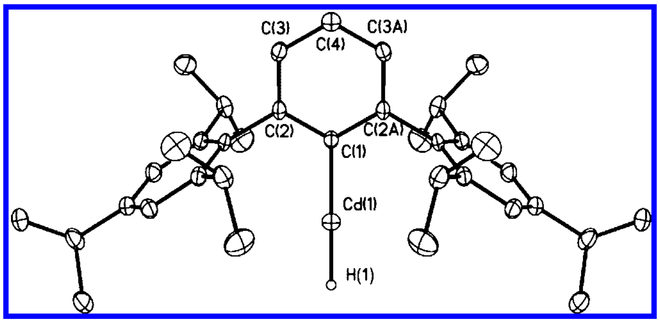


Figure 2. Thermal ellipsoid (50%) plot of **9**. Carbon-bound hydrogen atoms are not shown for clarity. Selected bond lengths [Å] and angles [deg]: Cd(1)−H(1) 1.79(4), Cd(1)−C(1) 2.122(2), C(1)−C(2) 1.404(2); C(1)−Cd(1)−H(1) 174.2(14), C(2)−C(1)−Cd(1) 120.47(11).

ppm shift in **1**, and its intensity was in the correct ratio to the signals of the aryl ligand. In contrast to the behavior of **1**, **7** does not undergo a further reduction with NaH to form a sodium hydride-bridged species {(4-$SiMe_3$-Ar*)Zn(μ-H)(μ-Na)Zn(Ar*-4-$SiMe_3$)}. Presumably such a process is prevented by the more sterically encumbering parent Ar* ligand, which discourages a closer approach of the metal centers.

The monomeric structure of **9**, illustrated in Figure 2, is its most noteworthy feature. Only two molecular cadmium hydride structures have been previously reported. These are the weakly dimerized arylcadmium hydride **3** and the tris(pyrazolyl)borato complex $Tp^{Me}{}_2Cd(\mu\text{-}H)_2BH_2$ (**11**)[7] ($Tp^{Me}{}_2$ = tris(3,5-dimethylpyrazolyl)hydroborate). The former species is an unstable, loosely associated dimer, while the latter complex has two hydrides bridging the Cd and B atoms. The monomeric structure of **9** is thus in sharp contrast to these. The coordination geometry at cadmium is almost linear [C(1)−Cd(1)−H(1) = 174.2(4)°] with Cd(1)−C(1) and Cd(1)−H(1) distances of 2.122(2) and 1.79(4) Å, respectively. The Cd−H distance is comparable to the short Cd−H bond length of 1.78(6) Å in the unsymmetrically bridged cadmium hydride **3**, but is shorter by ca. 0.2 Å than the bridging 1.973 and 2.126 Å Cd−H distances in **11**. Our previous calculations[3c] on model compounds PhM(μ-H)$_2$MPh (M = Zn, Cd, and Hg) showed that the dimerization of organo group 12 hydrides becomes less favored as the group is descended. A similar trend was also found in $(Ar'MI)_{1 \text{ or } 2}$ (M = Zn, Cd, or Hg),[3c] where arylzinc iodide and arylcadmium iodide were dimers in the solid state, while arylmercury iodide existed as a monomer. In **9**, the Ar* ligand increases the preference for a monomeric structure by steric pressure and the unassociated Ar*CdH is the result. This compound also exhibited much higher thermal stability than the dimer **3**. Refluxing compound **9** in toluene overnight led only to partial decomposition of **9** with some precipitation of a black solid. The monomeric structure of **9** is consistent with an increased stability to homolytic M−H cleavage, which is believed to require an associative mechanism.[10] A signal corresponding to the terminal hydride in **9** was located at 6.69 ppm in the ^{1}H NMR spectrum. In the ^{113}Cd NMR spectrum a signal at 410.3 ppm was observed. Both chemical shifts are similar to those of 6.84 and 410.7 ppm observed in the ^{1}H NMR and ^{113}Cd NMR spectra of **3**, suggesting that the compound **3** is dissociated to monomers in solution. The IR spectrum of **9** displayed a medium-intensity absorption band of 1735 cm^{-1} in reasonable agreement with the 1764 and 1771 cm^{-1} observed in frozen matrixes[19] or the gas phase.[20]

Scheme 3. Synthetic Routes to the Zn−Zn Bonded Dimer $Zn_2(\eta^6\text{-}C_5Me_5)_2$ (12)[1]

$$\text{ZnCp*2} + \text{ZnEt2} \xrightarrow[\text{-10°C}]{\text{Diethyl Ether}} \underset{45\%}{\text{Cp*Zn—ZnCp*}} - \text{Cp*ZnEt} \qquad \text{route 1}$$

$$\text{ZnCl}_2 + \text{KCp*} + \text{KH} \xrightarrow[\text{25°C, 3h.}]{\text{THF}} \underset{60\text{-}80\%}{\text{Cp*Zn—ZnCp*}} \qquad \text{route 2}$$

It has been reported that the first Zn−Zn bonded compound (ZnCp*)$_2$ (Cp* = η^5-C_5Me_5, **12**) can be prepared by the reduction of 1:1 ZnCp*$_2$/ZnCl$_2$ mixtures with KH in THF solution (route 2 in Scheme 3).[1b,c] The radical rearrangement of the transient species (Cp*ZnH)$_2$ via homolytic cleavage of the Zn−H bond might be the key step on the pathway to the final product. A similar radical pathway might also exist in the stepwise synthesis of Ar′Zn(μ-H)(μ-Na)ZnAr′ (**2**), where Ar′Zn(μ-H)$_2$ZnAr′ (**1**) can eliminate H$_2$ and then form an adduct with NaH.[3a] However, investigations of CH_3ZnH in argon matrixes showed that this simple zinc hydride species is photostable and will not yield the $CH_3Zn^{\bullet}$ radical when irradiated with the broadband output of a 500 W medium-pressure Hg lamp.[21]Nonetheless we decided to test the reactivity of the arylmetal hydrides with the radical species TEMPO. The reaction of compound **7** with TEMPO at 70 °C for 1 day afforded the derivative **10** (Figure 3) with hydrogen elimination in moderate yield upon concentration and cooling of the hexane solution to −18 °C.

It has been reported that TEMPO can induce fission of p-block M−H bonds by two different radical pathways (Scheme 4). Metal−metal bonded derivatives of group 14 metals R_3MMR_3 (R/M = Ph/Ge or ^{n}Bu/Sn) were formed via hydrogen

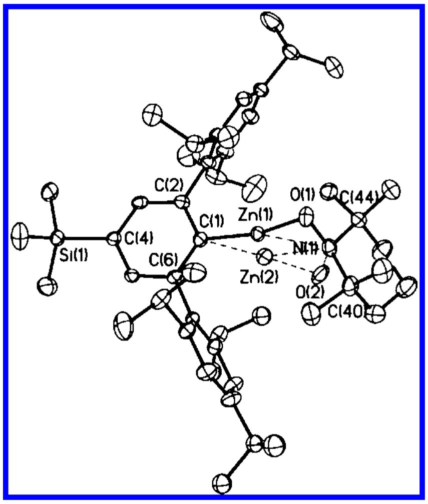


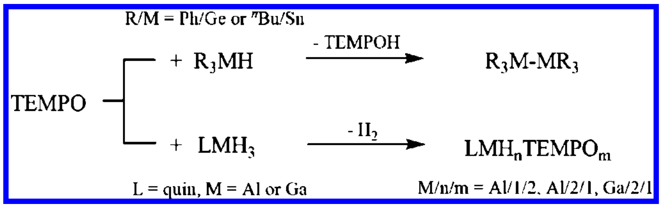
Figure 3. Thermal ellipsoid (50%) plot of **10**, where Zn and O atoms are disordered over two positions with occupancies of 0.89 and 0.11 for Zn(1), O(1) and Zn(2), O(2), respectively. Carbon-bound hydrogen atoms are not shown for clarity. Selected bond lengths [Å] and angles [deg]: Zn(1)−O(1) 1.8450(15), Zn(2)−O(2) 1.831(8), Zn(1)···N(1) 2.2039(16), Zn(2)···N(1) 2.220(3), O(1)−N(1) 1.504(2), O(2)−N(1) 1.552(10), Zn(1)−C(1) 1.9317(18), Zn(2)−C(1) 2.052(3), N(1)−C(40) 1.500(3), N(1)−C(44) 1.488(2); C(1)−Zn(1)−O(1) 163.29(7), C(1)−Zn(2)−O(2) 174.9(4), Zn(1)−O(1)−N(1) 81.62(9), Zn(2)−O(2)−N(1) 81.6(4), C(1)−Zn(1)−N(1) 154.23(7), C(1)−Zn(2)−N(1) 141.32(13), O(1)−N(1)−C(40) 108.04(15), O(2)−N(1)−C(40) 95.2(5), C(44)−N(1)−C(40) 118.18(15) C(2)−C(1)−Zn(1) 117.67(13), C(6)−C(1)−Zn(2) 109.51(14).

---

[18] *SADABS*, An empirical absorption correction program, part of the SAINT-Plus NT version 5.0 package; Bruker AXS: Madison, WI, 1998.

[19] Wang, X.; Andrews, L. *J. Phys. Chem. A* **2004**, *108*, 11006.

Scheme 4. Radical Reaction of TEMPO with p-Block M−H Bonds in Two Pathways[18,19]



transfer to TEMPO.[22] However, TEMPO complexes of group 13 hydrides [MH_2(quin)(TEMPO)] (quin = quinuclidine, M = Al (**13**) or Ga (**14**)) or [AlH(quin)$(TEMPO)_2$] (**15**) were obtained via TEMPO substitution and H_2 elimination.[23]

The formation of **10** apparently occurs by a similar process to that of the group 13 hydrides. However, instead of forming a simple monodentate M−O bonded complex as in **13**−**15**, TEMPO is bound to the Zn center in a quasi "side-on" fashion with a significant secondary interaction between zinc and the nitrogen atom to afford a three-membered Zn−N−O metallacycle as shown in Figure 3. The zinc is disordered over two sites with an occupancy ratio of ca. 9:1. The Zn−N−O metallacycle has Zn−O, O−N, and Zn···N distances of 1.8450(15), 1.504(2), and 2.2039(16) Å (only structural information of the major Zn1 and O1 components is listed), respectively. The Zn···N distance is ca. 0.4 Å longer than Zn−N single bond lengths of 1.81−1.85 Å in monomeric zinc amides,[24] but it is well within the Zn···N distance range of 2.04−2.67 Å in various zinc amine adducts.[25] The C−Zn−O angle is 163.29(7)°, and there is an acute Zn−O−N angle of 81.62(9)°. The relatively long N−O distance indicates that the TEMPO has been reduced so that it behaves as an anionic $[TEMPO]^-$ ligand.

The "side-on" bonding mode for TEMPO and the Zn center differs from that found in TEMPO complexes of unsaturated transition metals (Mn,[26] Co,[27] Ni,[28] Cu,[29] Mo,[30] and Pd[31]). The difference relates to the coordination mode of the TEMPO ligand, which is fully bidentate in the tranistion metal complexes. Thus, in the [$Mn(CO)_3$(η^2-TEMPO)],[26] [$Co(CO)_2$ (η^2-TEMPO)],[27] [(dtbpe)Ni(Cl)(η^2-TEMPO)] (dtbpe = 1,2-bis(di-*tert*-butylphosphino)ethane),[28] and [CuBr(η^2-TEMPO)][29] complexes, the M−N distances are all relatively short and are less than 2.0 Å. In the manganese complex the Mn−N distance, 1.839(3) Å, is even shorter than the Mn−O distance, 1.981(3) Å. Furthermore the N−O bond lengths in these complexes are in the range 1.304(8)−1.413(3) Å, suggesting that the TEMPO ligand remains unreduced. The coordination mode of TEMPO in **10** most resembles that found in the magnesium dimer [Mg_2(μ_2:η^2-TEMPO)(μ_2:η^1-TEMPO){$N(SiMe_3)_2$}$_2$], where a weak Mg···N interaction (2.395(3) Å) is also observed for one of the two bridging TEMPO ligands.[32] The reaction between TEMPO and Zn{$N(SiMe_3)_2$}$_2$ in the presence of LiN$(SiMe_3)_2$ afforded [Li$(TEMPO)_4$] [Zn{$N(SiMe_3)_2$}$_3$], which has no Zn−TEMPO bonding.[32]

The reaction between $ZnEt_2$ and TEMPO has been reported by Carmona and co-workers.[1c] However, in this case, a TEMPO-bridged compound [ZnEt(TEMPO)]$_2$ was obtained, which is the only previous known Zn-TEMPO complex. The same authors have reported two synthetic routes (Scheme 3) to the Zn−Zn bonded compound **12**. TEMPO can inhibit the synthetic route 1 by a competition reaction with $ZnEt_2$. This inhibition suggests the involvement of radicals in this route. A computational study of $(ZnCp^*)_2$ formation also supported this view.[33] The fact that TEMPO can induce H_2 elimination by **7** also suggests a possible radical formation via Zn−H cleavage. The tendency of zinc hydrides to eliminate H_2 gas and form Zn−Zn bonds thus becomes feasible via this cleavage type. Zinc hydride **5** and cadmium hydride **9** can also react with TEMPO at 70 °C. However, both reactions did not result in any crystals suitable for X-ray crystallographic studies. An attempt to react Zn−Zn bonded compound Ar′ZnZnAr′ with TEMPO did not result any new species. Analysis of the reaction mixtures by ^{1}H NMR spectroscopy afforded resonances assignable only to starting materials.

In summary, dimeric {(4-$SiMe_3$-Ar*)Zn(μ-H)$_2$Zn(Ar*-4-$SiMe_3$)} (**7**) and monomeric Ar*CdH (**9**) were synthesized and structurally characterized. The reaction between **7** and TEMPO was examined. Experimental results showed that the zinc hydride undergoes a Zn−H cleavage to form a complex with the reduction of the radical species TEMPO. This observation supports the involvement of a radical pathway in the synthesis of compounds **2** and **11**. The fact that the monomeric compound **9** is more stable than its dimeric analogue **3** supports the view that homolytic M−H cleavage of group 12 M−H bonds to form M−M bonds requires association of the hydride species.

Acknowledgment. We thank the National Science Foundation (CHE-0641020) and the Department of Energy Office of Basic Energy Sciences (DE-FG02-07ER4675) for financial support. Z.Z. thanks Dr. Eric Rivard for helpful discussions.

Supporting Information Available: X-ray data (CIF) for **7**, **9**, and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM900005T

---

(20) Shayesteh, A.; Yu, S.; Bernath, P. F. *Chem.*−*Eur. J.,* **2005**, *11*, 4709.

(21) Greene, T. M.; Andrews, L.; Downs, A. J. *J. Am. Chem. Soc.* **1995**, *117*, 8180.

(22) Lucarini, M.; Marchesi, E.; Pedulli, G. F.; Chatilialoglu, C. *J. Org. Chem.* **1998**, *63*, 1687.

(23) Jones, C.; Rose, R. P. *New J. Chem.* **2007**, *31*, 1484.

(24) (a) Power, P. P.; Ruhlandt-Senge, K. S.; Shoner, C. *Inorg. Chem.* **1991**, *30*, 5013. (b) Elias, A. J.; Schmidt, H.-G.; Noltemeyer, M.; Roesky, H. W. *Eur. J. Solid State Inorg. Chem.* **1992**, *29*, 23. (c) Rees, W. S., Jr.; Green, D. M.; Hesse, W. *Polyhedron* **1992**, *11*, 1697. (d) Rees, W. S., Jr.; Just, O.; Schumann, H.; Weimann, R. *Polyhedron* **1998**, *17*, 1001. (e) Schumann, H.; Gottfriedsen, J.; Dechert, S.; Girgsdies, F. *Z. Anorg. Allg. Chem.* **2000**, *626*, 747. (f) Margraf, G.; Lerner, H.-W.; Boltea, M.; Wagner, M. *Z. Anorg. Allg. Chem.* **2004**, *630*, 217. (g) Tang, Y.; Felix, A. M.; Boro, B. J.; Zakharov, L. N.; Rheingold, A. L.; Kemp, R. A. *Polyhedron* **2005**, *24*, 1093.

(25) (a) Westerhausen, M.; Wieneke, M.; Rademacher, B. B.; Schwarz, W. *Chem. Ber.* **1997**, *130*, 1499, and references therein. (b) Coward, K. M.; Jones, A. C.; Steiner, A.; Bickley, J. F.; Smith, L. M.; Pemble, M. E. *J. Chem. Soc., Dalton Trans.* **2000**, 3480, and references therein.

(26) Jaitner, P.; Huber, W.; Hunter, G.; Scheidsteger, O. *J. Organomet. Chem.* **1983**, *259*, C1.

(27) Jaitner, P.; Huber, W.; Gieren, A.; Betz, H. *J. Organomet. Chem.* **1986**, *311*, 379.

(28) Mindiola, D. J.; Waterman, R.; Jenkins, D. M.; Hillhouse, G. L. *Inorg. Chim. Acta* **2003**, *345*, 299.

(29) Caneschi, A.; Grand, A.; Laugier, J.; Rey, P.; Subra, R. *J. Am. Chem. Soc.* **1988**, *110*, 2307.

(30) Jaitner, P.; Huber, W.; Gieren, A.; Betz, H. *Z. Anorg. Allg. Chem.* **1986**, *538*, 53.

(31) (a) Dickman, M. H.; Doedens, R. J. *Inorg. Chem.* **1982**, *21*, 682. (b) Porter, L. C.; Doedens, R. J. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1985**, *41*, 838.

(32) Forbes, G. C.; Kennedy, A. R.; Mulvey, R. E.; Rodger, P. J. A. *Chem. Commun.* **2001**, 1400.

(33) Hepperle, S. S.; Wang, Y. A. *J. Phys. Chem. A* **2008**, *112*, 9619.