

Reaction of M(II) Diaryls (M = Mn or Fe) with Ammonia to Afford Parent Amido Complexes

Chengbao Ni, Hao Lei, and Philip P. Power*

Department of Chemistry, University of California, Davis, California 95616

Received January 21, 2010

Summary: The reaction of the two-coordinate diaryls MAr', $(M = Mn \text{ or } Fe; Ar' = C_6H_3 - 2,6 - (C_6H_3 - 2,6 - Pr_2))$ with excess NH₃ below room temperature afforded the parent amido complexes $\{Ar' Mn(\mu - NH_2)(NH_3)\}_2(1)$ and $\{Ar' Fe(\mu - NH_2)\}_2(2)$ in good yields. The reactions were accompanied by elimination of the arene Ar'H. Both complexes were obtained as dimers in which the metals are bridged by two NH_2 ligands. The complex 1 also includes an ammonia (NH_3) ligand bound to each manganese. Ammonia complexation did not occur in 2, and the metals remained three-coordinate. The metal electron configurations are high-spin and antiferromagnetically coupled.

Cleavage of the N-H bond in ammonia under mild conditions either by insertion of a transition metal atom or by metathetical exchange with other ligands is attracting increasing interest¹⁻²¹ because NH₃ is an inexpensive potential precursor for a variety of amino compounds that may be accessible by transition metal

- (1) Bryan, E. G.; Johnson, B. F. G.; Lewis, J. J. Chem. Soc., Dalton Trans. 1977, 1328.
- (2) Armor, J. N. Inorg. Chem. 1978, 17, 203.
- (3) Süss-Fink, G. Z. Naturforsch., B: J. Chem. Sci. 1980, 35, 454.
- (4) Johnson, B. F. G.; Lewis, J.; Odiaka, T. I.; Raithby, P. R. J. Organomet. Chem. 1981, 216, C56.
- (5) Süss-Fink, G.; Khan, L.; Raithby, P. R. J. Organomet. Chem. 1982, 228, 179.
- (6) Hillhouse, G. L.; Bercaw, J. E. J. Am. Chem. Soc. 1984, 106, 5472. (7) Bercaw, J. E.; Davies, D. L.; Wolczanski, P. T. Organometallics
- 1986, 5, 443. (8) Casalnuovo, A. L.; Calabrese, J. C.; Milstein, D. Inorg. Chem.
- 1987, 26, 971.
- (9) Roesky, H. W.; Bai, Y.; Noltemeyer, M. Angew. Chem., Int. Ed. Engl. 1989, 28, 754.
- (10) Holl, M. M. B.; Wolczanski, P. T.; Vanduyne, G. D. J. Am. Chem. Soc. 1990, 112, 7989.
 - (11) Koelliker, R.; Milstein, D. Angew. Chem., Int. Ed. Engl. 1991, 30, 707.
- (12) Schulz, M.; Milstein, D. J. Chem. Soc., Chem. Commun. 1993, 318. (13) Koszinowski, K.; Schlangen, M.; Schroder, D.; Schwarz, H. Int.
- J. Mass Spectrom. 2004, 237, 19. (14) Zhao, J.; Goldman, A. S.; Hartwig, J. F. Science 2005, 307, 1080.
- (15) Nakajima, Y.; Kameo, H.; Suzuki, H. Angew. Chem., Int. Ed. 2006, 45, 950.
- (16) Frey, G. D.; Lavallo, V.; Donnadieu, B.; Schoeller, W. W.; Bertrand, G. Science 2007, 316, 439.
- (17) Peng, Y.; Ellis, B. D.; Wang, X. P.; Power, P. P. J. Am. Chem. Soc. 2008, 130, 12268.
- (18) Jana, A.; Schulzke, C.; Roesky, H. W. J. Am. Chem. Soc. 2009, 131, 4600.
- (19) Jana, A.; Ghoshal, D.; Roesky, H. W.; Objartel, I.; Schwab, G.; Stalke, D. J. Am. Chem. Soc. 2009, 131, 1288.
- (20) Zhu, Z. L.; Wang, X. P.; Peng, Y.; Lei, H.; Fettinger, J. C.; Rivard, E.; Power, P. P. Angew. Chem., Int. Ed. 2009, 48, 2031.
- (21) Kanzelberger, M.; Zhang, X. W.; Emge, T. J.; Goldman, A. S.; Zhao, J.; Incarvito, C.; Hartwig, J. F. J. Am. Chem. Soc. 2003, 125,
- 13644
 - 22) Roundhill, D. M. Chem. Rev. 1992, 92, 1.
 - (23) Eller, K.; Schwarz, H. Chem. Rev. 1991, 91, 1121.

pubs.acs.org/Organometallics

Published on Web 03/23/2010

catalytic routes.²²⁻²⁴ Currently known metathetical exchange reactions of NH₃ with transition metal organometallic complexes mainly involve derivatives of the early first-row metals. For example, group 3–5 metal complexes, such as $(\eta^5-Cp^*)_2$ ScMe $(Cp^* = C_5Me_5)$, $(\eta^5-Cp)Ti(\mu:\eta^1,\eta^5-Cp)$ ₂ $(Cp = C_5H_5)$, (η^5-Cp) ₂ $(Cp = C_5H_5)$, (η^5-Cp) ₂ $(Dp^* = C_5H_5)$, $(Dp^* = C_5H_$ $Cp^{*}_{2}MH_{2}$ (M = Zr or Hf),⁶ (η^{5} -Cp^{*})TiMe₃,⁹ and (^{*i*}BuCH₂)₃-Ta=CH'Bu,¹⁰ react with NH₃ to form bridging amido, imido, or nitrido complexes with elimination of alkane or H₂. NH₃ has also been shown to react with some late second- or third-row transi- $Cp^*Ru_3(\mu_3-H)_2(\mu-H)_3$ shows reversible reactivity toward NH₃ to form a μ_3 -imido cluster {(η^5 -Cp*Ru)₃(μ -H)₃(μ_3 -NH)} and H₂.¹⁵ Cooperative action of the multiple metal centers in metal clusters such as $\{Os_3(CO)_{11}(L)\}$ (L = cyclo-C₆H₈, CH₃CN, or NH_3 ^{1,3-5} effectively activates NH_3 to form bridging amido species. Milstein and Hartwig reported the oxidative addition of NH₃ to iridium complexes to afford μ_2 -NH₂ species or terminal amido/hydride complexes.^{8,12,14} Furthermore, oxidative addition reactions of NH₃ with low-valent main group metal species have been reported.^{16,18,20} The mechanisms and thermodynamics of NH₃ reactions with transition metal complexes have been investigated by spectroscopy $^{13,25-30}$ and computational studies. $^{30-41}$ Nonetheless, little attention has been given to

(24) van Santen, R. A.; Neurock, M. Molecular Heterogeneous Catalysis, 1st ed.; Wiley-VCH: Weinheim, 2006.

- (25) Clemmer, D. E.; Sunderlin, L. S.; Armentrout, P. B. J. Phys. Chem. 1990, 94, 3008.
- (26) Clemmer, D. E.; Sunderlin, L. S.; Armentrout, P. B. J. Phys. Chem. 1990, 94, 208.
- (27) Clemmer, D. E.; Armentrout, P. B. J. Phys. Chem. 1991, 95, 3084. (28) Liyanage, R.; Griffin, J. B.; Armentrout, P. B. J. Chem. Phys.
- 2003, 119, 8979. (29) Liyanage, R.; Armentrout, P. B. Int. J. Mass Spectrom. 2005,
- 241.243.
- (30) Chen, M. H.; Lu, H.; Dong, J.; Miao, L.; Zhou, M. F. J. Phys. Chem. A 2002, 106, 11456.
- (31) Blomberg, M. R. A.; Siegbahn, E. M.; Svensson, M. Inorg. Chem. 1993, 32, 4218.
- (32) Musaev, D. G.; Morokuma, K. J. Am. Chem. Soc. 1995, 117, 799
- (33) Fahmi, A.; vanSanten, R. A. Z. Phys. Chem., J. Res. Phys. Chem. *Chem. Phys.* **1996**, *197*, 203. (34) Hendrickx, M.; Ceulemans, M.; Gong, K.; Vanquickenborne, L.
- J. Phys. Chem. A 1997, 101, 8540.
- (35) Nakao, Y.; Taketsugu, T.; Hirao, K. J. Chem. Phys. 1999, 110, 10863.
- (36) Matsubara, T. Organometallics 2001, 20, 1462.
- (37) Sicilia, E.; Russo, N. J. Am. Chem. Soc. 2002, 124, 1471.
- (38) Michelini, M. D. C.; Russo, N.; Sicilia, E. Inorg. Chem. 2004, 43, 4944.
- (39) Reddy, S. Y.; Bruice, T. C. Proc. Natl. Acad. Sci. U. S. A. 2004, 101. 15887.
- (40) Xia, F.; Chen, J.; Zeng, K.; Cao, Z. X. Organometallics 2005, 24, 1845
- (41) Ochi, N.; Nakao, Y.; Sato, H.; Sakaki, S. J. Am. Chem. Soc. 2007, 129, 8615.

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



the reactions of first-row mid to late metal complexes, e.g., manganese, iron, cobalt, or nickel complexes with NH₃, and only limited spectroscopic studies, e.g., guided ion beam tandem mass spectrometry of iron species, have been reported.^{28,29} We now show that the reactions of two-coordinate M(II) diaryls MAr'₂ (M = Mn or Fe;⁴² Ar' = C₆H₃-2,6-(C₆H₃-2,6-ⁱPr₂)₂) with NH₃ readily afford rare examples of parent amido derivatives of manganese and iron as the complexes {Ar'Mn(μ -NH₂)(NH₃)}₂ (1) and {Ar'Fe(μ -NH₂)}₂ (2) with arene (Ar'H) elimination.

Results and Discussion

Exposure of hexane solutions of MAr'_2 (M = Mn or Fe) to a dry NH₃ atmosphere at ca. -78 °C afforded the product 1 or 2 in moderate to high yields. For MnAr'₂, the pink solution gradually changed to pale yellow in ca. 30 min, and extremely air- and moisture-sensitive crystals of 1 were obtained from the solution. For iron, large pale yellow crystals were obtained from hexanes in high yield (77%). Similar reactions were also attempted with cobalt(II) diaryl species; however, no crystalline product was isolated in that case.

The mechanism for the formation of 1 and 2 is currently unknown. It is probable (Scheme 1) that the first step may involve generation of the Lewis base adduct Ar'₂M(NH₃), which is energetically favored according to theoretical studies (two-coordinate iron diaryls and diamides are also known to form isolable complexes with Lewis bases such as nitriles,⁴³ pyridine,⁴⁴ or phosphines⁴⁵).³⁸ The N-H bond may then be cleaved in concert with elimination of an arene molecule to afford the M(II) amido species Ar'MNH₂, which then dimerizes to form $\{Ar'M(\mu-NH_2)\}_2$. For manganese, the dimer $\{Ar'Mn(\mu-NH_2)\}_2$ complexes a further NH₃ at each metal to form the adduct $\{Ar'Mn(\mu-NH_2)(NH_3)\}_2$ (1); however, this complexation was not observed for iron. A possible alternative, if less likely, pathway also involves the initial generation of Ar'2M(NH3), which may undergo oxidative addition of NH₃ to give the M(IV) amido hydride species Ar'₂M(H)(NH₂), followed by reductive elimination of an arene (ArH) molecule. In both cases, the byproduct Ar'H was confirmed by NMR spectroscopy. However, without the identification of intermediates, other reaction pathways cannot be ruled out. The facile reaction of the MAr'_{2} molecules with NH₃ may be contrasted with the behavior of



Figure 1. Thermal ellipsoid (30%) plot of 1 at 190(2) K without H atoms (except N–H). Selected bond lengths (Å) and angles (deg): $Mn1 \cdots Mn1A$ 3.0686(5), Mn1-C1 2.162(2), Mn1-N1 2.093(2), Mn1-N1A 2.093(2), Mn1-N2 2.241(2), Mn1-N1-Mn1A 94.29(6), N1-Mn1-N1A 85.71(6), C1-Mn1-N1 126.33(6), C1-Mn1-N1A 129.81(5).

the low (three)-coordinate iron(II) species {HC(CMeNAr)₂-Fe}₂(μ -S) (Ar = C₆H₃-2,6-^{*i*}Pr₂), which forms the stable NH₃ adduct {HC(CMeNAr)₂Fe(NH₃)}₂(μ -S).⁴⁶ The driving force for the formation of **1** and **2** may be the greater strength of the M–N bond versus the M–C bond together with the elimination of the arene (Ar'H) molecule. A similar parent amido complex formation, together with arene elimination, is observed when the two-coordinate diarylstannylene SnAr'₂ is treated with NH₃.¹⁷

Structures. The structure of 1 (Figure 1) shows that it is dimerized through bridging of the two manganese atoms by two NH₂ groups. Each manganese is terminally bound to an Ar' ligand as well as an NH3 molecule and thus has a distorted tetrahedral geometry. Complex 1 appears to be the first structurally characterized manganese complex with parent amido (NH₂) ligands. It is also a rare example of a structurally authenticated organometallic manganese-ammonia adduct.47-50 In 1, the Mn–C bond length (2.162(2) Å) is somewhat longer than those in the two-coordinate species $Mn(C_6H_2-2,4,6^{-t}Bu_3)_2$ (2.108(2) Å)⁴⁸ and Ar'MnN(H)Ar[#] (Ar[#] = C₆H₃-2,6-(C₆H₂-2,4,6- Me_{3}_{2} ; 2.095(2) Å),⁵² probably due to the higher coordination number of the manganese atoms in 1. The $Mn-N(NH_2)$ bond lengths (2.093(2) Å) are essentially indistinguishable from that (av 2.0938 Å) in the analogous complex $\{Ar'Mn(\mu-NMe_2)\}_2$, which was synthesized by salt elimination.53 The terminal $Mn-N(NH_3)$ bond length of 2.241(2) Å is, as expected, significantly longer than the Mn-N(NH₂) distances and is comparable to that in the fulleride salt $[Mn(NH_3)_6]C_{60}$

(53) Ni, C. B.; Long, G. J.; Grandjean, F.; Power, P. P. *Inorg. Chem.* **2009**, *48*, 11594.

⁽⁴²⁾ Ni, C. B.; Power, P. P. Chem. Commun. 2009, 5543.

⁽⁴³⁾ Ni, C.; Power, P. P. Unpublished work.

⁽⁴⁴⁾ Panda, A.; Stender, M.; Olmstead, M. M.; Klavins, P.; Power, P. P. *Polyhedron* **2003**, *22*, 67.

⁽⁴⁵⁾ Ni, C.; Rekken, B.; Fettinger, J. C.; Long, G. J.; Power, P. P. Dalton Trans. 2009, 8349.

⁽⁴⁶⁾ Vela, J.; Stoian, S.; Flaschenriem, C. J.; Munck, E.; Holland, P. L. J. Am. Chem. Soc. 2004, 126, 4522.

⁽⁴⁷⁾ Kuroda, R.; Sasaki, Y. Acta Crystallogr. B: Struct. Sci. 1974, B 30, 687.

⁽⁴⁸⁾ Nakano, T.; Miyoshi, T.; Iwamoto, T.; Sasaki, Y. Bull. Chem. Soc. Jpn. 1967, 40, 1297.

⁽⁴⁹⁾ Herberhold, M.; Wehrmann, F.; Neugebauer, D.; Huttner, G. J. Organomet. Chem. **1978**, 152, 329.

⁽⁵⁰⁾ Klaus Himmel, M. J. Eur. J. Inorg. Chem. 1998, 1998, 1183.

⁽⁵¹⁾ Wehmschulte, R. J.; Power, P. P. Organometallics 1995, 14, 3264.
(52) Ni, C. B.; Fettinger, J. C.; Long, G. J.; Power, P. P. Inorg. Chem.
2009, 48, 2443.



Figure 2. Thermal ellipsoid (30%) plot of **2** at 90(2) K without H atoms (except N–H). Selected bond lengths (Å) and angles (deg): Fe1 \cdots Fe1A 2.7334(7), Fe1–C1 2.027(2), Fe1–N1 1.996(2), N1–Fe1–N1 93.57(9), N1–Fe1–C1 133.21(4), Fe1–N1–Fe1A 86.43(9).

(2.298(3) Å).⁵⁰ The Mn₂(μ -N)₂ core is planar with Mn–N–Mn and N–Mn–N angles of 94.29(6)° and 85.71(6)°. The Mn···Mn separation in **1** is 3.0686(4) Å, which is ca. 0.1 Å longer than the 2.9479(3) Å in {Ar'Mn(μ -NMe₂)}₂,⁵³ which is probably a result of the complexation of an additional NH₃ molecule at each manganese atom. The effective magnetic moment (μ_{eff}) of **1** (5.62 μ_B /dimer at 293 K) is significantly lower than the value of 8.36 μ_B expected for two isolated 3d⁵ Mn(II) ions, due to the antiferromagnetic coupling interactions between the metal atoms. The N–H stretching bonds are observed at 3605 and 3355 cm⁻¹ in the IR spectrum.

The structure of 2 (Figure 2) is also dimerized through symmetrically bridging NH2 groups; however, no Fe-NH3 coordination was observed. The absence of NH₃ complexation may be due to steric effects owing to the smaller ionic radius of iron versus manganese.⁵⁴ In addition, for threecoordinate $Fe^{2+}(d^6)$, the d_{z^2} orbital is probably doubly occupied, which would discourage complex formation. Each iron displays a Y-shaped coordination geometry with a relatively narrow N(1)-Fe(1)-N(1A) angle of 93.57(9)° and two ca. 40° wider C(1)-Fe(1)-N angles (133.21(4)°). To our knowledge, iron complexes with parent amido ligands are quite rare, and structurally characterized examples are limited to the higher coordinate Fe complexes, such as the NH2-bridged dimer {Fe(CO)₃(μ -NH₂)}₂,⁵⁵ prepared according to the Hieber–Beutner procedure,⁵⁶ and the monomeric amido hydride complex $(dmpe)_2Fe(H)(NH_2)$ (dmpe = 1.2-bis(dimethylphosphino)ethane),⁵⁷ obtained by reaction of (dmpe)₂Fe(H)(Cl) with NaNH₂. The $Fe_2(\mu-N)_2$ four-membered ring in 2 is strictly planar. This is in contrast to the structure of ${Fe(CO)_3}$ - $(\mu$ -NH₂)₂,⁵⁵ which is folded along the Fe···Fe vector by ca. 86°. Notably, the Fe₂(μ -N)₂ plane is coplanar with the two central rings of the terphenyl ligands (torsion angle = ca. 8°). Such coplanarity is in sharp contrast to the geometry of the analogous amido complex $\{Ar'Fe(\mu-NMe_2)\}_2$, in which the $Fe_2(\mu-N)_2$ plane has a torsion angle of ca. 57.2° to the two

central aryl rings of the terphenyl ligands.⁵³ In **2**, the Fe–C (2.027(2) Å) and the Fe–N (1.996(2) Å) distances are similar to those observed in {Ar'Fe(μ -NMe₂)}₂ (Fe–C = 2.056(2) Å; Fe–N = 2.028 Å (av)).⁵³ As expected, the Fe···Fe separation in **2** (2.7334(7) Å) is essentially the same as that of 2.7239(6) Å in {Ar'Fe(μ -NMe₂)}₂,⁵³ but is significantly longer than that in the heavily folded species {Fe(CO)₃(μ -NH₂)}₂ (2.402(6) Å).⁵⁵ Similar to the antiferromagnetic coupling interactions between the metal atoms in {Ar'Fe(μ -NMe₂)}₂,⁵³ complex **2** has a μ_{eff} of 4.41 μ_{B} /dimer at 293 K. The N–H stretches were located at 3351 and 3247 cm⁻¹ in the IR spectrum, corresponding to the two stretching modes of the N–H bonds.

In summary, we have shown for the first time that two-coordinate M(II) diaryls (M = Mn or Fe) readily cleave the N-H bond of NH₃ to afford the parent amido (NH₂) dimers 1 and 2. The formation of 1 and 2 emphasizes the importance of coordination numbers in determining the reactivity of metal centers. Complexes 1 and 2 are rare examples of mid to late first-row transition metal complexes with parent amido ligands.

Experimental Details

General Procedures. All manipulations were carried out using Schlenk techniques under an argon atmosphere or in a Vacuum Atmospheres HE-43 drybox. All solvents were dried over an alumina column, stored over 3 Å molecular sieves overnight, and degassed three times (freeze-thaw) prior to use. MAr'_{2} (M = Mn or Fe) were prepared by literature procedures.² Liquid NH₃ (ca. 10 mL) was transferred into a Schlenk flask containing sodium metal with cooling to ca. -78 °C. The resulting deep blue solution was stirred at -78 °C for 30 min and then slowly warmed to ca. -30 °C. The flask containing MAr'₂ solution at ca. -78 °C was evacuated and quickly refilled with NH₃ vapor. The solution was kept under an NH3 atmosphere for at least 30 min. Melting points were recorded in glass capillaries sealed under N2 and are uncorrected. UV-vis data were recorded on a Hitachi-1200 spectrometer. Magnetic susceptibility measurements by Evans' method^{59,60} and the ¹H NMR spectra were recorded on a Bruker 300 MHz spectrometer at ca. 293 K.

{Ar'Mn(NH₃)(μ -NH₂)}₂ (1). A pale pink solution of MnAr'₂ (0.345 g, 0.4 mmol) in ca. 40 mL of hexanes was cooled to ca. -78 °C in a flask, and dry NH₃ was introduced. The solution was kept at ca. -78 °C for ca. 1 h, slowly warmed to ca. 25 °C, and stirred for another 2 h. The pale orange solution was filtered and concentrated to ca. 10 mL, which afforded colorless, X-ray quality crystals of 1 after storage overnight at 7 °C. Yield: 0.106 g (54.4%). Mp: 119-121 °C. ¹H NMR (300 MHz, C₆D₆, 20 °C): δ 1.13 (s, br, 48H, CH(CH₃)₂), 2.91 (s, br, 8H, CH(CH₃)₂). IR in Nujol mull (cm⁻¹) in KBr: ν_{N-H} 3605, 3355. Anal. Calcd for C₆₀H₈₄Mn₂N₄: C, 74.20; H, 8.72; N, 5.77. Found: C, 74.52; H, 9.07; N, 5.44. $\mu_{eff} = 5.6(3) \mu_B$ /dimer at 293 K.

{Ar'Fe(μ -NH₂)}₂ (2). A procedure similar to that of 1, employing FeAt'₂ (0.346 g, 0.40 mmol) instead of MnAr'₂, afforded large pale yellow crystals of **2** from hexanes at 7 °C. Yield: 0.144 g (76.8%). Mp: 137–139 °C. ¹H NMR (300 MHz, C₆D₆, 20 °C): δ –7.61 (s, br, 4H), 1.14 (s, br, 48H, CH(CH₃)₂), 1.90 (s, br, 4H), 2.92 (s, br, 8H, CH(CH₃)₂), 3.46 (s, br, 4H), 5.61 (s, br, 2H), 6.21 (s, br, 8H). IR in Nujol mull (cm⁻¹) in KBr: ν_{N-H} 3351 and 3247. Anal. Calcd for C₆₀H₇₈Fe₂N₂: C, 76.75; H, 8.37; N, 2.98. Found: C, 77.12; H, 8.23; N, 2.79. μ_{eff} = 4.4(2) μ_{B} /dimer at 293 K.

In both cases, after the isolation of the desired products, the mother liquors were concentrated to ca. 2 mL to afford a colorless crystalline product, which was identified as Ar'H according

- (59) Evans, D. F. J. Chem. Soc. 1959, 2003.
- (60) Schubert, E. M. J. Chem. Educ. 1992, 69, 62.

⁽⁵⁴⁾ Shannon, R. D. Acta Crystallogr. A 1976, 32, 751.

⁽⁵⁵⁾ Dahl, L. F.; Costello, W. R.; King, R. B. J. Am. Chem. Soc. 1968, 90, 5422.

 ⁽⁵⁶⁾ Hieber, W.; Beutner, H. Z. Anorg. Allg. Chem. 1962, 317, 63.
 (57) Fox, D. J.; Bergman, R. G. J. Am. Chem. Soc. 2003, 125, 8984.

⁽⁵⁸⁾ Ni, C. B.; Power, P. P. Chem. Commun. 2009, 5543.

Table 1. Selected Crystallographic Data and Collection Parameters for 1 and 2

	1	$2 \cdot C_6 H_{14}$
formula	C60H84Mn2N4	C66H92Fe2N2
fw	971.19	1025.12
color	colorless	pale yellow
habit	plate	plate
cryst syst	Pbca	I2/m
a, Ă	17.7138(7)	11.963(2)
b, Å	16.2752(7)	20.350(3)
<i>c</i> , Å	19.9105(8)	12.583(2)
α, deg	90	90
β , deg	90	99.002(2)
γ , deg	90	90
V, \tilde{A}^3	5740.1(4)	3025.7(9)
Ź	4	2
$d_{\rm calcd}$, Mg/m ³	1.124	1.125
θ range, deg	2.62 - 27.50	1.92 - 27.5
μ, mm^{-1}	0.478	0.518
no. of obsd data, $I > 2\sigma(I)$	5006	3034
R1 (obsd data)	0.0350	0.0434
wR2 (all data)	0.0961	0.1240

to ¹H NMR spectroscopy. ¹H NMR (300 MHz, C₆D₆, 20 °C): δ 1.12 (d, ³*J*_{H-H} = 6.9 Hz, CH(C*H*₃)₂, 12H), 1.13 (d, ³*J*_{H-H} = 6.9 Hz, CH(C*H*₃)₂, 12H), 2.91 (sept, ³*J*_{H-H} = 6.9 Hz, C*H*(CH₃)₂,

(61) SADABS, version 5.0 package; an empirical absorption correction program from the SAINTPlus NT; Bruker AXS: Madison, WI, 1998.
 (62) SHELVL variations 51: Bruker AXS: Madison, WI, 1998.

(62) SHELXL, version 5.1; Bruker AXS: Madison, WI, 1998.

12H), 7.09 (s, C₆ H_4 , 1H), 7.12 (m, *p*-C₆ H_4 and *p*-C₆ H_3 , 3H), 7.14 (d, ${}^3J_{H-H} = 7.2$ Hz, *m*-C₆ H_3 , 4H), 7.31 (t, ${}^3J_{H-H} = 7.2$ Hz, *m*-C₆ H_4 , 2H).

X-ray Crystallographic Studies. Crystals of 1 and 2 were selected and covered with a layer of hydrocarbon oil under a rapid flow of argon. They were mounted on a glass fiber attached to a copper pin and placed in the cold N_2 stream on the diffractometer. X-ray data for 1 were collected on a Bruker SMART Apex II diffractometer at 190(2) K using Mo Ka radiation ($\lambda = 0.71073$ Å). For **2**, the data were collected on a Bruker SMART 1000 diffractometer at 90(2) K using Mo Ka radiation ($\lambda = 0.71073$ Å). Absorption corrections were applied using SADABS.⁶¹ The structures were solved using direct methods and refined by the full-matrix least-squares procedure in SHELXL.⁶² All of the non-hydrogen atoms were refined anisotropically. The N-hydrogen atoms in 1 were located by a Fourier difference map. All other hydrogen atoms in both structures were placed at calculated positions and included in the refinement using a riding model.

Acknowledgment. We thank the National Science Foundation (CHE-0948417) for financial support and Dr. James C. Fettinger for crystallographic assistance.

Supporting Information Available: Crystallographic information files (CIFs); ¹H NMR and IR spectra for **1** and **2**. These materials are available free of charge via the Internet at http:// pubs.acs.org.