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Journal of Organometallic Chemistry 582 (1999) 32–39

Journal of Organo metallic Chemistry

Synthesis of an organogallium(I) compound $[Ga(CH_2CMe_2Ph)]_n$ with EPR spectral evidence for gallium clusters

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Received 1 September 1998

Abstract

The organogallium(I) compound $[Ga(CH_2CMe_2Ph)]_n$ has been prepared by the reduction of $Ga(CH_2CMe_2Ph)_2Cl$ by using either sodium or lithium with naphthalene in THF. The yellow dihydronaphthalene gallium(III) intermediate $M_2\{C_{10}H_8[Ga(CH_2CMe_2Ph)_2Cl]_2\}$ initially formed at −78°C but then decomposed at higher temperatures to form $[Ga(CH_2CMe_2Ph)]_n$, $Ga(CH_2CMe_2Ph)_3$ and MCl. EPR spectra, which were recorded as the two yellow intermediates $Na_2\{C_{10}H_8[Ga(CH_2CMe_2R)_2Cl]_2\}$ (R = Ph, Me) decomposed, indicated the presence of radicals. The first and second derivatives of the EPR signals, line-widths, *g*-values and hyperfine coupling constants are consistent with the radicals being clusters of organogallium species. The experimental spectra were simulated by the superposition of two spectra, a single Gaussian shaped line with a peak-to-peak width of 14 mT (92%) with the spectrum of five equivalent gallium nuclei, $A = 2.1$ mT (8%). The even number of lines observed in the experimental spectra indicate an odd number of gallium nuclei with at least five being required to give the number of observed lines. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Organogallium compounds; Gallium clusters; EPR spectra; Gallium radicals

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The syntheses of organogallium compounds in oxidation states other than the typical +3 present interesting challenges. The most common preparative route has been the reaction of a low oxidation state gallium halogen compound with an organo lithium or sodium reagent [1–4]. An alternative route to low oxidation state compounds involves the reduction of an organogallium(III) halide with a metal. Sodium/potassium alloy [5] reduced $Ga[C_6H_2(CF_3)_3]_2Cl$ at 25°C in hexane to form $Ga_2[C_6H_2(CF_3)_3]_4$. When $Ga[C_6H_3(C_6H_2Me_3)_2]Cl_2$ was reacted with sodium [6], or potassium [7] metal, $M_2\{Ga[C_6H_3(C_6H_2Me_3)_2]\}_3$ (M = Na, K), compounds with triangular arrays of gallium atoms were formed whereas reduction with sodium of a derivative with more bulky substituents [8] $Ga\{C_6H_3[C_6H_2(2,4,6\ i\text{-}Pr)_3]_2\}Cl_2$ produced $Na_2[Ga\{C_6H_3[C_6H_2(2,4,6\ i\text{-}Pr)_3]_2\}]_2$. The gallium(I) compound $Ga(C_5Me_5)$ was formed by a reductive dehalogenation of $Ga(C_5Me_5)I_2$ with potassium [9], whereas the reduction of $LiGaCl_3[C(SiMe_2R)_3]$ (R = Me, Et) with Rieke magnesium produced $[GaC(SiMe_2R)_3]_4$ [10]. When sodium naphthalenide [11] was the potential reducing agent and was reacted with $Ga(CH_2CMe_3)_2Cl$ at −78°C, the initial product was a bright yellow dihydronaphthalene gallium(III) derivative $Na_2\{C_{10}H_8[Ga(CH_2CMe_3)_2Cl]_2\}$ rather than a low oxidation state compound. However, this intermediate decomposed at room temperature (r.t.) to form the gallium(I) compound $[Ga(CH_2CMe_3)]_n$ ($n = 6$–12), $Ga(CH_2CMe_3)_3$ and NaCl. The product $[Ga(CH_2CMe_3)]_n$ was confirmed as gallium(I) by oxidation with aqueous DCl to form D_2 and with $HgCl_2$ to form $Ga(CH_2CMe_3)Cl_2$ and mercury metal and was believed to exist as clusters with

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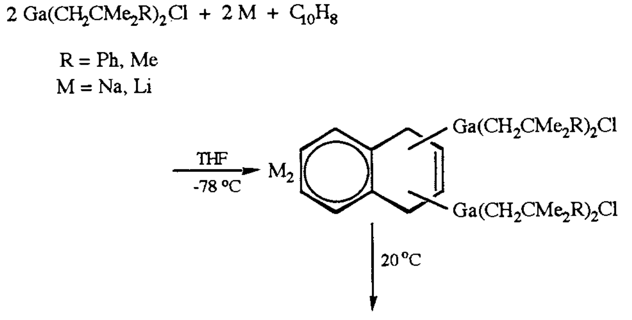
PII: S0022-328X(98)01182-6

different numbers of $Ga(CH_2CMe_3)$ moieties. However, the only experimental evidence for clusters was the cryoscopic molecular weight data which indicated an average association of nine $Ga(CH_2CMe_3)$ moieties. Thus, rings and chains could not be ruled out.

In this paper, we report the synthesis of $[Ga(CH_2CMe_2Ph)]_n$ and the results of our investigations of the EPR spectra which were recorded as the yellow neophyl and neopentyl dihydronaphthalene gallium(III) intermediates $M_2\{C_{10}H_8[Ga(CH_2CMe_2R)_2Cl]_2\}$ (R = Ph, Me; M = Li, Na) were transformed into the final reddish–brown gallium(I) products. It is of interest that $Na_2\{C_{10}H_8[Ga(CH_2CMe_2R)_2Cl]_2\}$ formed the gallium(I) compound faster than $Li_2\{C_{10}H_8[Ga(CH_2CMe_2R)_2Cl]_2\}$.



(1)

The strong Lewis base tetramethylethylenediamine also retarded the rate at which the intermediate was converted to the gallium(I) product. The EPR spectra are consistent with the presence of radicals as gallium clusters. The EPR signals grew in intensity, decreased, and then finally disappeared after 6–10 h. A typical EPR spectrum for the neophyl system is shown in Fig. 1. All observations suggest that the main signal arises from the presence of gallium based radicals rather than from hydrocarbon radicals. The *g*-value is approximately 2.07 and the peak-to-peak first derivative linewidth is 14 mT, whereas *g*-values for the hydrocarbon radicals which might be possible for these systems, $C_{10}H_8^{\bullet -}$ and $PhMe_2CCH_2^{\bullet}$, occur in the range of 2.002–2.006 [12,13], and are typically 2–3 mT wide. A second small EPR signal is observed at $g = 2.003$ with a peak-to-peak linewidth of 0.24 mT. Its width is distorted by the large field modulation used to observe the main signal in Fig. 1. This small signal, which never amounts to more than 0.1% of the total signal, disappears from view as the NaCl formed as a product in the reaction settles to the bottom of the EPR tube. Based on its *g*-value and linewidth, we believe this radical is an insoluble Na^+ or Cl^- salt of an organic radical ion.

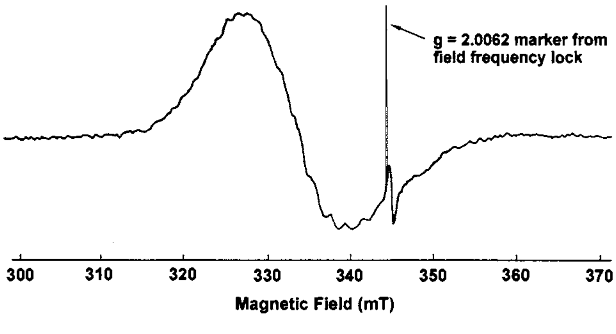


Fig. 1. EPR signal as $Na_2\{C_{10}H_8[Ga(CH_2CMe_2Ph)_2Cl]_2\}$ decomposed at room temperature.

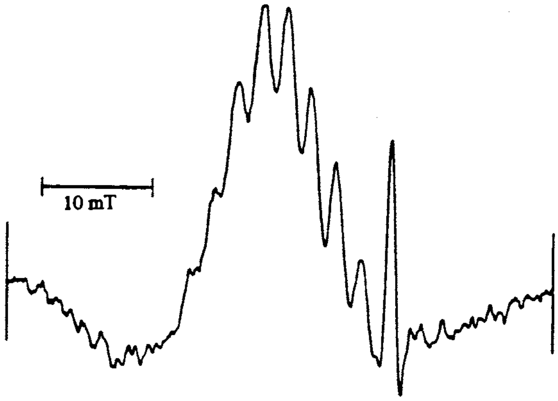


Fig. 2. EPR spectrum (second derivative) for the decomposition of the yellow intermediate formed from the reaction of $Ga(CH_2CMe_2Ph)_2Cl$ with $Na(C_{10}H_8)$.

The EPR line in Fig. 1 reveals a series of ripples which can be resolved into a distinct hyperfine splitting pattern by taking the second derivative of the EPR signal. The second derivative of the EPR signal for the neophyl system reveals an unsymmetrical hyperfine splitting pattern with nine or ten easily identifiable lines (Fig. 2), whereas the spectrum for the neopentyl system exhibits an unsymmetrical pattern with 12 or 13 lines (Fig. 3). The unsymmetrical shape of the main EPR signal, Figs. 2 and 3, could arise from a superposition of signals from more than one radical with different *g*-values or it could be caused by the lack of rotational averaging of the anisotropic component of the hy-

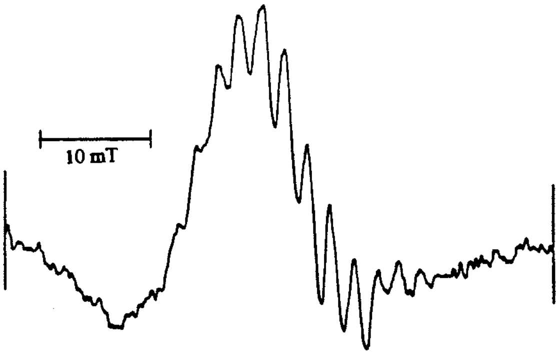


Fig. 3. EPR spectrum (second derivative) for the decomposition of the yellow intermediate formed from reaction of $Ga(CH_2CMe_3)_2Cl$ with $Na(C_{10}H_8)$.

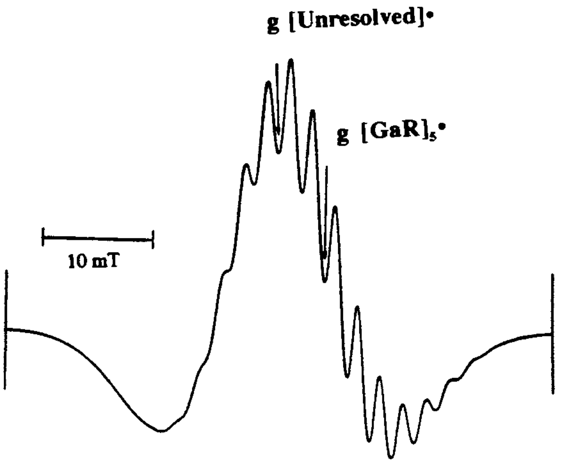


Fig. 4. Computer simulated EPR spectrum of overlapping signals for $[GaR]_5^\bullet$ (8%) and (unresolved)$^\bullet$ (92%), one unpaired electron, $A = 2.1$ mT.

perfine splittings. Low-temperature EPR experiments tested the hypothesis based on the lack of rotational averaging but failed to show any evidence of hyperfine anisotropy. Thus, the asymmetry in the signal is believed to arise from a mixture of radicals. If the experimental spectrum arises from a superposition of only two spectra, it may be simulated by combining the spectrum of a single Gaussian shaped line with a peak-to-peak width of 14 mT (92%) with the spectrum of five equivalent gallium nuclei, $A = 2.1$ mT (8%) [14] as shown in Fig. 4. The even number of lines in the hyperfine pattern indicates that an odd number of gallium nuclei are involved in the cluster and at least five nuclei are required to give the number of observed lines. Five equivalent gallium nuclei ($I = 3/2$) should give 16 lines while 9–13 lines are readily observed.

Since the species responsible for the EPR signal are transient intermediates in low concentration, their identity cannot yet be confirmed chemically. Thus, we suggest one plausible hypothesis to explain the above observations. The decomposition of $Na_2\{C_{10}H_8[Ga(CH_2CMe_2R)_2Cl]_2\}$ might involve the formation of neutral $Ga(CH_2CMe_2R)_2^\bullet$ radicals by homolytic cleavage of the bond between gallium and the dihydronaphthalene moiety. The majority of these neutral radicals could undergo ligand redistribution and/or disproportionation reactions to form the observed products $Ga(CH_2CMe_2R)$ and $Ga(CH_2CMe_2R)_3$ whereas a small concentration of these radicals could form clusters. Those clusters with an odd number of units $[Ga(CH_2CMe_2R)_2]_n^\bullet$ ($n = 1, 3, 5, 7,\ldots$) would be paramagnetic and would be expected to be observed by EPR spectroscopy. If the clusters with $n = 1$ and 3 are too reactive to be observed, the cluster with $n = 5$ could be the 8% of the observed radical with the remaining 92% being accounted for by clusters with $n > 5$ ($n = 7, 9, 11,\ldots$) whose spectra would be expected to be too complex to be resolved. The observed coupling constants for $[Ga(CH_2CMe_2R)_2]_5^\bullet$ (R = Me, Ph) agree well with that found for the Ga_4 radical $\{Ga[C(SiMe_3)_3]\}_4^\bullet$ and is about half of that found for the Ga_2 radicals, $Ga_2[Si(t\text{-}Bu)_3]_3^\bullet$ [15] and $[Li(12\text{-}crown\text{-}4)_2]\{Ga_2[(2,4,6\text{-}(i\text{-}Pr)_3C_6H_2]_4\}^\bullet$, [16] as expected.

1. Experimental

1.1. General

Compounds described in this investigation were extremely sensitive to oxygen and moisture and were handled with a standard vacuum line or under a purified argon atmosphere in a Vacuum Atmospheres drybox. The starting compounds $Ga(CH_2CMe_2Ph)_2Cl$ [17], $Ga(CH_2CMe_2Ph)Cl_2$ [17], $Ga(CH_2CMe_3)_2Cl$ [11], and $Ga(CH_2CMe_3)Cl_2$ [11] were prepared and purified by literature methods. Elemental analyses were performed by either Schwarzkopf Microanalytical Laboratory, Woodside, NY or E&R Microanalytical Laboratory, Corona, NY. IR spectra of Nujol mulls between CsI plates were recorded by means of a Perkin–Elmer 683 spectrometer. The ^{1}H-NMR spectra were recorded at either 300 or 400 MHz by using either a Varian Gemini 300 or a Varian VXR-400 spectrometer, respectively. Proton chemical shifts (δ) were referenced to C_6H_6 at 7.15 ppm and $SiMe_4$ at 0.00 ppm. All samples for NMR spectra were contained in sealed NMR tubes. Melting points were observed for sealed capillaries under purified argon.

1.2. Reaction of $Ga(CH_2CMe_2Ph)_2Cl$ with $Na[C_{10}H_8]$

In a typical experiment, a side-arm dumper with $Ga(CH_2CMe_2Ph)_2Cl$ (1.87 g, 5.03 mmol) was attached to a reaction flask charged with finely cut sodium metal (0.116 g, 5.03 mmol) and naphthalene (0.645 g, 5.03 mmol). After THF (50 ml) was vacuum distilled into the reaction flask, the reaction mixture was stirred for 18 h to form the dark green sodium naphthalenide solution. Then, a small amount of THF (10–20 ml) was transferred by vacuum distillation from the flask to the side-arm dumper. The solutions in the reaction flask and the side-arm dumper were simultaneously cooled to − 78°C and the $Ga(CH_2CMe_2Ph)_2Cl$/THF solution was added to the sodium naphthalenide solution over 30 min. The resulting solution was stirred for 18 h at − 78°C. The color of the solution changed from brown/green to bright yellow. No precipitate was observed. As the yellow solution was slowly warmed to ambient temperature, a large amount of a colorless precipitate formed between − 10 and 0°C. Then, the solution slowly changed from bright yellow to dark brown over 2–5 h at ambient temperature. The solution was stirred for an additional 12 h followed by the removal of THF by vacuum distillation. The material remaining after all visible THF had been removed was subjected to dynamic vacuum for 24 h. These volatile materials were weighed in a small trap (1.41 g) and identified by ^{1}H-NMR spectroscopy as $C_{10}H_8$ (0.482 g, 3.76 mmol, 74.8% recovered based on the initial amount of $C_{10}H_8$), and THF. The nonvolatile material was separated into benzene soluble and insoluble fractions after 3–4 extractions. The dark brown, soluble product was identified as an equimolar mixture of $Ga(CH_2CMe_2Ph)$ and $Ga(CH_2CMe_2Ph)_3$ by ^{1}H-NMR spectroscopy. The benzene insoluble, light brown solid was identified as impure NaCl (0.276 g, 4.72 mmol, 93.9% yield based on Na). The reaction of $Ga(CH_2CMe_2Ph)_2Cl$ with $Na[C_{10}H_8]$ at −78°C was repeated multiple times and identical observations and results were obtained.

The dark brown soluble product mixture of $Ga(CH_2CMe_2Ph)$ and $Ga(CH_2CMe_2Ph)_3$ was dissolved in 3–5 ml of C_6H_6, chromatographed twice with a Bio-Beads® column and then recrystallized from pentane/benzene (ca. 50 ml/ca. 10 ml, respectively) at −78°C. The recrystallized product was a dark brown, vitreous solid and identified as neophylgallium(I), $[Ga(CH_2CMe_2Ph)]_n$ (0.313 g, 1.54 mm, 60.7% yield based on $Ga(CH_2CMe_2Ph)_2Cl$, Eq. 1).

1.2.1. *$[Ga(CH_2CMe_2Ph)]_n$*

M.p. 69.3–82.4°C (dec.). ^{1}H-NMR (C_6D_6, δ): 7.42, 7.25, 7.15, 7.10, 7.03 (all of the lines are part of br–m, $-C_6H_5$)], 1.89 (s), 1.80 (s), 1.73 (s), 1.68 (s), 1.54 (s), 1.40 (s), 1.38 (s), 1.21 (s) (all of the lines are part of br–m, $-CMe_2$ and $-CH_2-$ of $[Ga(CH_2CMe_2Ph)]_n$)], 0.87 (br, small). IR (Nujol, cm^{-1}): 3100 (s), 3080 (s), 3050 (vs), 3010 (vs), 1938 (m), 1861 (m), 1792 (m), 1739 (m), 1595 (s), 1578 (m), 1490 (vs), 1300 (m), 1272 (vs), 1268 (vs), 1191 (s), 1185 (s), 1152 (m), 1140 (m), 1129 (m), 1082 (s), 1070 (s), 1025 (vs), 1010 (sh, s), 955 (m), 845 (s), 795 (vs), 781 (sh, s), 759 (vs), 730 (m), 718 (s), 690 (vs), 675 (sh, m), 622 (m), 601 (m), 550 (m), 500 (m), 470 (m), 442 (w). Anal. Calc.: C, 59.19; H, 6.45; Ga, 34.36. Found: C, 58.76; H, 6.93; Ga, 34.91. Solubility: soluble in THF and benzene; slightly soluble in pentane.

1.3. *Reaction of $Ga(CH_2CMe_2Ph)_2Cl$ with $Li[C_{10}H_8]$ or $Li_2[C_{10}H_8]$*

Lithium naphthalenide $Li[C_{10}H_8]$ or dilithium naphthalenide $Li_2[C_{10}H_8]$ were reacted with $Ga(CH_2CMe_2Ph)_2Cl$ as described above. The following observations differentiated the reduction reactions with lithium. (1) The yellow intermediates in the lithium reactions formed in 10–20 min after mixing reagents whereas 10–20 h was needed for sodium. (2) No precipitate formed when lithium was used as the reducing agent. (3) The yellow solutions with lithium decomposed more slowly (4–6 h) to the dark brown solution than those with sodium (2–5 h).

1.4. *'In flask' acid hydrolysis of the products from reactions of $Ga(CH_2CMe_2Ph)_2Cl$ with $n(Na/C_{10}H_8)$, $n(Li/C_{10}H_8)$, or $n(Li_2/(C_{10}H_8))$ ($n = 1, 2$)*

Reduction reactions of $Ga(CH_2CMe_2Ph)_2Cl$ with $Na[C_{10}H_8]$ and $Ga(CH_2CMe_2Ph)_2Cl$ with $Li[C_{10}H_8]$ and ($Li_2[C_{10}H_8]$) were performed as previously described, except that the solutions were stirred for 2–3 days to insure complete decomposition of the yellow intermediate before hydrolysis. After removal of the THF and other materials volatile at r.t. by dynamic vacuum distillation for 2–3 days, the dark brown product was reacted with dilute aqueous HCl for 2–4 days in a 60–120°C oil bath. Then the reaction flask was cooled to −196°C and the H_2 was measured with a Toepler pump/gas buret assembly.

$Ga(CH_2CMe_2Ph)_2Cl$ (1.86 g, 5.01 mmol), Na (0.116 g, 5.05 mol), $C_{10}H_8$ (0.645 g, 5.03 mmol) yielded 2.38 mmol H_2 (94.8%). $Ga(CH_2CMe_2Ph)_2Cl$ (1.34 g, 3.61 mmol), Li (0.0254 g, 3.66 mmol), $C_{10}H_8$ (0.470 g, 3.67 mmol) yielded 1.42 mmol H_2 (78.7%). $Ga(CH_2CMe_2Ph)_2Cl$ (1.49 g, 4.01 mmol), Li (0.0278 g, 4.01 mmol), $C_{10}H_8$ (0.257 g, 2.01 mmol) yielded 1.54 mmol H_2 (76.8%).

1.5. *Identification of yellow intermediate from reaction of $Ga(CH_2CMe_2Ph)_2Cl$ with $Na[C_{10}H_8]$ by reaction with anhydrous HCl*

Sodium naphthalenide (0.0358 g, 1.56 mmol Na; 0.200 g, 1.56 mmol $C_{10}H_8$) was reacted with $Ga(CH_2CMe_2Ph)_2Cl$ (0.574 g, 1.55 mmol) in 50 ml of THF at −78°C as previously described to form a clear, bright yellow solution (no precipitate) after 18 h. The yellow solution was cooled to −196°C and then anhydrous HCl (0.066 g, 1.8 mmol) was vacuum distilled into the reaction flask. The solution was slowly warmed to ambient temperature and the solution changed from bright yellow to colorless in 30 min. After the solution was stirred for 12 h, the THF was removed by vacuum distillation. Then, dynamic vacuum for 24 h at r.t. was used to transfer the remaining volatile materials into a small, weighable trap. The contents (0.320 g) were identified by ^{1}H-NMR spectroscopy as $C_{10}H_{10}$ (1,2- and 1,4-dihydronaphthalene), $C_{10}H_8$ (naphthalene) and THF. The nonvolatile material remaining in the flask was separated into pentane soluble and insoluble fractions by extraction through a fine glass frit. The insoluble colorless product was NaCl (0.058 g, 0.99 mmol, 64% yield based on Na). The soluble colorless solid was identified as $Ga(CH_2CMe_2Ph)_2Cl$ (0.538 g, 1.45 mmol, 93.5% yield based on the initial amount of

$Ga(CH_2CMe_2Ph)_2Cl$) by comparison of its melting point and ^1H-NMR spectrum with that of an authentic sample [17].

1.5.1. Colorless solid—$Ga(CH_2CMe_2Ph)_2Cl$

M.p. 83.0–85.3°C (lit. [17] m.p. 86.4–87.8°C). ^1H-NMR (C_6H_6, δ): 1.40 (s, $-CH_2-$ ($Ga(CH_2CMe_2Ph)_2Cl$)), 1.33 (s, $-CMe_3$ ($Ga(CH_2CMe_2Ph)_2Cl$)). Solubility: soluble in THF, pentane, and benzene.

1.5.2. Volatile materials

^1H-NMR (CH_2Cl_2, δ): 7.93 (m, $C_{10}H_8$), 7.57 (m, $C_{10}H_8$), 7.17 (m, $C_{10}H_{10}$), 6.74 (m, $C_{10}H_{10}$), 6.38 (m, s, $C_{10}H_{10}$), 6.10 (m, $C_{10}H_{10}$), 3.77 (m, THF), 3.46 (s, $C_{10}H_{10}$), 2.43 (m, $C_{10}H_{10}$), 1.93 (m, THF).

1.6. Identification of the yellow intermediate from reaction of $Ga(CH_2CMe_2Ph)_2Cl$ with $Li_2[C_{10}H_8]$ by ^1H-NMR spectroscopy

Lithium metal (0.0348 g, 5.01 mmol), naphthalene (0.321 g, 2.51 mmol) and 20 ml of THF were reacted to form the dark purple $Li_2[C_{10}H_8]$ solution (0.25 M). Then, 2 ml (0.501 mmol) of $Li_2[C_{10}H_8]$/THF was added to 2–3 ml of a solution of $Ga(CH_2CMe_2Ph)_2Cl$ (0.186 g, 0.501 mmol) in d_8-THF at −78°C. The bright yellow solution was stirred for ca. 30 min and then a sample of the solution was poured into the NMR tube and cooled to −78°C. The ^1H-NMR spectrum of the yellow solution was recorded immediately after warming to r.t. and at 45 min, 4 h, 5, 15 and 25 days thereafter. The spectra at 5, 15 and 25 days were identical. No precipitate formed in the NMR tube.

1.6.1. Spectrum immediately after warming to ambient temperature

Solution color: bright yellow. ^1H-NMR (d_8-THF/THF, δ): 7.78 (m, $C_{10}H_8$), 7.42 (m, $C_{10}H_8$), 7.32 (d, o-Ar ($-C_6H_5$, $Li_2\{C_{10}H_8[Ga(CH_2CMe_2Ph)_2Cl]_2\}$), 7.08 (m, m-Ar ($-C_6H_5$, $Li_2\{C_{10}H_8[Ga(CH_2-CMe_2Ph)_2Cl]_2\}$), 6.91 (m, p-Ar($-C_6H_5$, $Li_2\{C_{10}H_8[Ga(CH_2CMe_2Ph)_2Cl]_2\}$), 6.66 (br, (1,4- and 1,2-$C_{10}H_{10}$), 3.58 (m, THF), 1.73 (m, THF), 1.31 (s, $-CMe_2$, $Li_2\{C_{10}H_8[Ga(CH_2CMe_2Ph)_2Cl]_2\}$), 0.88 (s, $-CH_2-$, $Li_2\{C_{10}H_8[Ga(CH_2CMe_2Ph)_2Cl]_2\}$), solution color: dark yellow. 7.78 (m, $C_{10}H_8$), 7.40 (m, $C_{10}H_8$), 7.32 (d, o-Ar ($-C_6H_5$, $Li_2\{C_{10}H_8[Ga(CH_2CMe_2Ph)_2Cl]_2\}$), 7.12 (m, $-C_6H_5$, $Ga(CH_2CMe_2Ph)_3 + [Ga(CH_2CMe_2Ph)]_n$), 7.07 (m, m-Ar ($-C_6H_5$, $Li_2\{C_{10}H_8[Ga(CH_2CMe_2Ph)_2Cl]_2\}$), 6.90 (m, p-Ar($-C_6H_5$, $Li_2\{C_{10}H_8[Ga(CH_2-CMe_2Ph)_2Cl]_2\}$), 6.68 (br, 1,4- and 1,2-$C_{10}H_8$), 3.58 (m, THF), 1.74 (m, THF), 1.31 (s, $-CMe_2$, $Li_2\{C_{10}H_8[Ga(CH_2CMe_2Ph)_2Cl]_2\}$), 1.18 (s, $-CMe_2$, $Ga(CH_2CMe_2Ph)_3$), 0.88 (s, $-CH_2-$, $Li_2\{C_{10}H_8[Ga(CH_2CMe_2Ph)_2Cl]_2\}$), 0.63 (s, $-CH_2-$, $Ga(CH_2CMe_2Ph)_3$).

1.6.2. Spectrum after 4 h

Solution color: light reddish/brown. 7.78 (m, $C_{10}H_8$), 7.40 (m, $C_{10}H_8$), 7.32 (d, o-Ar ($-C_6H_5$, $Li_2\{C_{10}H_8[Ga(CH_2CMe_2Ph)_2Cl]_2\}$), 7.12 (m, $-C_6H_5$, $Ga(CH_2CMe_2Ph)_3 + [Ga(CH_2CMe_2Ph)]_n$), 7.07 (m, m-Ar ($-C_6H_5$, $Li_2\{C_{10}H_8[Ga(CH_2CMe_2Ph)_2Cl]_2\}$), 6.90 (m, p-Ar ($-C_6H_5$, $Li_2\{C_{10}H_8[Ga(CH_2CMe_2Ph)_2Cl]_2\}$), 6.48 (br, 1,4- and 1,2-$C_{10}H_{10}$), 3.58 (m, THF), 1.74 (m, THF), 1.34 (s, $-CMe_2$, $Li_2\{C_{10}H_8[Ga(CH_2CMe_2Ph)_2Cl]_2\}$), 1.18 (s, $-CMe_2$, $Ga(CH_2CMe_2Ph)_3$), 0.88 (S, $-CH_2-$, $Li_2\{C_{10}H_8[Ga(CH_2CMe_2Ph)_2Cl]_2\}$), 0.63 (s, $-CH_2-$, $Ga(CH_2CMe_2Ph)_3$).

1.6.3. Spectra after 5, 15 and 25 days

Solution color: reddish/brown. 7.78 (m, $C_{10}H_8$), 7.40 (m, $C_{10}H_8$), 7.11 (m, $-C_6H_5$, ($Ga(CH_2CMe_2Ph)_3 + [Ga(CH_2CMe_2Ph)]_n$), 6.97 (m, $-C_6H_5$, $Ga(CH_2CMe_2Ph)_3 + [Ga(CH_2CMe_2Ph)]_n$), 3.58 (m, THF), 1.74 (m, THF), 1.19 (s, $-CMe_2$, $Ga(CH_2CMe_2Ph)_3$), 0.64 (s, $-CH_2-$, $Ga(CH_2CMe_2Ph)_3$).

1.6.4. EPR spectroscopic studies of the decomposition of the yellow intermediates, $M_2\{C_{10}H_8[Ga(CH_2CMe_2R)_2Cl]_2\}$), ($M = Na, Li$; $R = Ph, Me$) in THF solution

EPR spectra were recorded with an IBM/Bruker X-band EPR spectrometer model ER200D-SRC by using a TE_{102} mode rectangular cavity model 4102ST. The sample temperature was controlled with an IBM/Bruker ER 4111VT temperature controller. The spectrometer was interfaced to a Nicolet 2090 digital oscilloscope for digital recording of spectra. The g-values were measured with a Magnion G-502 Gaussmeter and a Hewlett Packard 5245L frequency counter by using the procedure described previously [18]. The precision of the g-value measurements is limited to ±0.002 by the broad lines encountered with gallium radicals. The concentration of an observed radical was estimated by comparison of the signal intensity with the signal intensity for a known concentration of the stable free radical 2,2-diphenyl-1-picryl hydrazyl (DPPH) in the same size sample tube. The first-derivative EPR spectrum of a 2.7×10^{-4} M DPPH solution was obtained by using 100 kHz Zeeman field modulation of 0.08 mT and a microwave power of 5 mW. First-derivative spectra of the gallium radicals were obtained with field modulation of 0.8 mT and microwave power of 20 mW. The area under the EPR signal was determined by double integration by using the program STICKS [19] on an IBM-PC/XT. The signal to mol ratio obtained for DPPH was recalculated for the gallium radical conditions before making the comparison.

In a typical experiment, the gallium reagent $Ga(CH_2CMe_2R)_2Cl$ ($R = Ph, Me$) was added to a THF solution of the alkali metal naphthalenide at −78°C to form the bright yellow intermediate. Details are given below. Then, a portion of the yellow solution at −78°C was poured into a quartz EPR tube which had been precooled to −78°C and then flame sealed. After the sample was rapidly warmed to r.t., EPR spectra (first and second derivative spectra, as appropriate) were recorded. In all cases the EPR signal was observed to grow in intensity with time, decrease until a broad unresolved signal was apparent and then finally disappear. The solution changed color from bright yellow to brown. When sodium was used, a precipitate appeared during the decomposition. However, when lithium was the reducing agent, no precipitate was observed. The following give quantities of reagents, specific experimental observations and details of the EPR spectra for each reagent combination.

1.6.5. $Ga(CH_2CMe_2Ph)_2Cl$—sodium

$Ga(CH_2CMe_2Ph)_2Cl$ (1.88 g, 5.07 mmol), Na (0.117 g, 5.07 mmol), $C_{10}H_8$ (0.650 g, 5.07 mmol), THF (18 ml), the initial gallium concentration (0.28 M); a yellow solution formed after 18 h at −78°C; the time for the EPR signal to reach maximum intensity was 2–3 h; the first derivative spectrum was a broad unresolved signal with a peak-to-peak distance of 13.8 mT and $g = 2.067 \pm 0.002$; the second derivative spectrum was a broad but well resolved signal with an unsymmetrical hyperfine splitting pattern. The center of the hyperfine pattern falls at $g = 2.038 \pm 0.002$, $A_{ave}(Ga) = 2.2$ mT; maximum observed concentration of gallium radicals was 2.5×10^{-5} M; broad unresolved signal remained after 3–6 h; no gallium radicals were observed after an additional 6–10 h.

1.6.6. $Ga(CH_2CMe_2Ph)_2Cl$—lithium

$Ga(CH_2CMe_2Ph)_2Cl$ (1.86 g, 5.01 mmol), Li (0.0349 g, 5.03 mmol), $C_{10}H_8$ (0.645 g, 5.03 mmol), THF (18 ml), initial gallium concentration (0.28 M); a yellow solution formed in less than 1 min but the solution was stirred at −78°C for 12 h before an EPR spectal study; the time for the EPR signal to reach maximum intensity was 2–3 h; the concentration of gallium radicals was so low that only the g-value from the first derivative spectrum could be accurately measured; the first derivative spectrum was a broad unresolved signal with a peak-to-peak distance of 15.4 mT and $g = 2.068 \pm 0.002$; the second derivative spectrum was a small, broad and unresolved signal; the broad unresolved signal remained after 3–6 h; no gallium radicals were observed after an additional 6–12 h.

1.6.7. $Ga(CH_2CMe_2Ph)_2Cl$—lithium

$Ga(CH_2CMe_2Ph)_2Cl$ (1.57 g, 4.22 mmol), Li (0.0293 g, 4.22 mmol), $C_{10}H_8$ (0.272 g, 2.12 mmol), THF (14 ml), initial gallium concentration (0.30 M); the first derivative spectrum of the yellow solution exhibited a small, broad, unresolved signal, whereas no second derivative spectrum was detected; all other experimental observations were identical to those described for the previous experiment.

1.6.8. $Ga(CH_2CMe_2Ph)_2Cl$—sodium (second-derivative spectra at low temperature)

$Ga(CH_2CMe_2Ph)_2Cl$ 2.29 g, 6.18 mmol), Na (0.142 g, 6.19 mmol), $C_{10}H_8$ (0.795 g, 6.20 mmol), THF (23 ml), initial gallium concentration (0.27 M); the second-derivative spectra of the yellow solution were recorded at ambient temperature until the signal reached a maximum intensity at which time the tube was cooled to −50°C; the spectra were recorded at −50, −25, 0 and 20°C; the unresolved signal, $g = 2.067 \pm 0.002$, remained after 3–6 h at 20°C; no gallium radicals were observed after an additional 6–10 h. The second-derivative spectrum at 20°C before cooling was a well resolved signal with an unsymmetrical splitting pattern with the center of the hyperfine pattern at $g = 2.038 \pm 0.002$, $A_{ave}(Ga) = 2.2$ mT. The second-derivative spectrum at −50 and −25°C depicted only an unresolved spectrum. At 0°C, a slightly resolved signal was observed. At 20°C, the spectrum depicted the same well resolved signal as observed previously. At all temperatures, the overall lineshape of the signal is the same and the relative ratios of the individual hyperfine lines, once resolved, appear to be independent of temperature.

1.6.9. $Ga(CH_2CMe_2Ph)_2Cl$—sodium with added TMEDA

$Ga(CH_2CMe_2Ph)_2Cl$ (0.613 g, 1.65 mmol), Na (0.0381 g, 1.66 mmol), $C_{10}H_8$ (0.213 g, 1.66 mmol), THF (30 ml), initial gallium concentration (0.06 M); a yellow solution formed after 18 h at −78°C. The bright yellow solution was cooled to −196°C and TMEDA (2.45 g, 21.1 mmol) was added to the flask. The resulting solution was warmed to −78°C and a heavy, colorless precipitate formed. After stirring for 12 h, a sample was poured into the quartz EPR tube and the tube was flame-sealed. The tube was warmed to r.t. and inserted into the EPR spectrometer. However, no gallium radicals were observed. The solution remained yellow with a colorless precipitate for more than 5 days before slowly turning brown. A signal for an unknown organic radical at a g-value of 2.003 ± 0.001 was observed in the precipitate (NaCl).

1.6.10. $Ga(CH_2CMe_3)_2Cl$—sodium

$Ga(CH_2CMe_3)_2Cl$ (1.24 g, 5.01 mmol), Na (0.115 g, 5.02 mmol), $C_{10}H_8$ (0.644 g, 5.02 mmol), THF (18 ml), initial gallium concentration (0.28 M); a yellow solution with slight precipitate formed after 18 h at −78°C; the time for EPR signal to reach maximum intensity was 2–3 h; the first-derivative spectrum was broad unresolved signal with a peak to peak distance of 14.7 mT and $g = 2.063 \pm 0.002$; the second-derivative spectrum was a broad but well-resolved signal with an unsymmetrical hyperfine splitting pattern; the center of the hyperfine pattern falls at $g = 2.036 \pm 0.002$, $A_{\mathrm{ave}}(\mathrm{Ga}) = 2.0$ mT; maximum observed concentration of gallium radicals was 1.2×10^{-4} M; a broad unresolved signal remained after 3–6 h; no gallium radicals were observed after an additional 6–10 h.

1.6.11. *$Ga(CH_2CMe_3)_2Cl$—lithium*

$Ga(CH_2CMe_3)_2Cl$ (1.55 g, 6.28 mmol), Li (0.0437 g, 6.30 mmol), $C_{10}H_8$ (0.808 g, 6.30 mmol), THF (23 ml), initial gallium concentration (0.27 M); a yellow solution formed after 15 min at −78°C but the solution was stirred for 12 h before an EPR spectral study; the time for EPR signal to reach maximum intensity was 1–2 h; the concentration of gallium radicals was so low that only the g-value from the first-derivative spectrum could be accurately measured; the first-derivative spectrum was a broad unresolved signal with a peak to peak distance of 12.3 mT and $g = 2.062 \pm 0.002$; the second-derivative spectrum was a small, broad and unresolved signal; no gallium radicals were observed after an additional 6–10 h.

1.6.12. *$Ga(CH_2CMe_3)_2Cl$—lithium*

$Ga(CH_2CMe_3)_2Cl$ (1.57 g, 6.33 mmol), Li (0.044 g, 6.3 mmol), $C_{10}H_8$ (0.406 g, 3.17 mmol), THF (23 ml), initial gallium concentration (0.28 M); the first-derivative spectrum of the yellow solution exhibited a broad, unresolved signal with a peak to peak distance of 11.7 mT and $g = 2.066 \pm 0.002$; the second-derivative spectrum was a small, broad and unresolved signal; all other experimental observations were identical to those described for the previous experiment.

1.6.13. *$Ga(CH_2CMe_3)_2Cl$—sodium (second-derivative spectra at low temperature)*

$Ga(CH_2CMe_3)_2Cl$ (1.98 g, 8.00 mmol), Na (0.184 g, 8.02 mmol), $C_{10}H_8$ (1.03 g, 8.02 mmol), THF (30 ml), initial gallium concentration (0.27 M); the second-derivative spectra of the yellow solution were recorded at ambient temperature until signal reached maximum intensity at which time the tube was cooled to −50°C; spectra were recorded at −50, −35, −20, −5, 15 and 20°C; a broad unresolved signal remained after 1–3 h at 20°C; no gallium radicals were observed after an additional 6–10 h. The second-derivative spectrum at 15°C before cooling was a well-resolved signal with an unsymmetrical splitting pattern. At −50 and −35°C, the signal for the gallium radicals had an unresolved spectrum whereas at −5 and 15°C the signal was well resolved with an unsymmetrical hyperfine splitting pattern; after 1 h at 15°C the hyperfine splitting pattern could no longer be observed. Similar observations were made when 2-methyl-tetrahydrofuran was used instead of THF.

1.6.14. *$Ga(CH_2CMe_3)_2Cl$—sodium with added TMEDA*

$Ga(CH_2CMe_3)_2Cl$ (0.312 g, 1.50 mmol), Na (0.0346 g, 1.51 mmol), $C_{10}H_8$ (0.194 g, 1.51 mmol), THF (30 ml), initial gallium concentration (0.05 M); a yellow solution formed after 18 h at −78°C. The bright yellow solution was cooled to −196°C and TMEDA (3.46 g, 29.7 mmol) was added to the flask. The resulting solution was warmed to −78°C and a heavy, colorless precipitate formed. After stirring for 12 h, a sample was poured into the quartz EPR tube and the tube was flame-sealed. The tube was warmed to r.t. and inserted into the EPR spectrometer. No gallium radicals were observed. The solution remained yellow with a colorless precipitate for more than 5 days before slowly turning brown. A signal for an unknown organic radical at a g-value of 2.003 ± 0.001 was observed in the precipitate (NaCl).

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[14] Gallium has two important isotopes ^{69}Ga (60.4% abundant) and ^{71}Ga (39.6% abundant) with nuclear spins of $I = 3/2$. ^{71}Ga is expected to have a 27% larger hyperfine coupling constant than ^{69}Ga for the same electron density. Thus, the hyperfine splitting pattern for a radical with five or seven equivalent Ga nuclei is expected to be very complex. In the present case, the component linewidth is considerably greater than the difference in the ^{69}Ga and ^{71}Ga hyperfine splittings so that only an average splitting is observed. We have simulated spectra both with a single weighted average coupling constant and with two separate coupling constants for the gallium isotopes. The simulations are indistinguishable. The values reported are for the best match of the single weighted average coupling simulations. The separate isotopic hyperfine values can be calculated as $^{69}A = A_{\mathrm{ave}}0.9033$ and $^{71}A = A_{\mathrm{ave}}1.148$.

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