Where L = PEt_3, we observe reproducible reaction chemistry with the C–H and/or C–C bonds of acetonitrile and the tetra-*n*-butylammonium cation, depending upon the experimental conditions. A separate report will describe this chemistry in detail.[19]

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Registry No. *cis*-$[PtCl_2(PPh_3)_2]$, 15604-36-1; $[PtO_2(PPh_3)_2]$, 29894-57-3; $[Pt(CO_3)(PPh_3)_2]$, 17030-86-3; $OPPh_3$, 791-28-6; $[Pt(PPh_3)_3]$, 13517-35-6; $[Pt(PEt_3)_2]$, 66916-63-0; [Pt(dppe)], 101519-43-1; $[Pt(PPh_3)_2(PhC{\equiv}CPh)]$, 15308-61-9; PhC≡CPh, 501-65-5; $[Pt(PPh_3)_2(MeOOCC{\equiv}CCOoMe)]$, 22853-55-0; MeOOCC═CCOOMe, 762-42-5; *trans*-$[PtI(Me)(PPh_3)_2]$, 28850-19-3; *trans*-$[PtCOC_6H_5(Cl)(PPh_3)_2]$, 18421-48-2; *trans*-$[Pt(CO)(C_6H_5)(PPh_3)_2][Cl]$, 101519-44-2.

Synthesis of Some Arsinogallanes and the Novel Rearrangement of a Dimeric Bis(arsino)gallane, Bis{bis[bis[(trimethylsilyl)methyl]arsino]chlorogallane}

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Summary: Silylarsines, $R_2AsSiMe_3$ (R = Me_3SiCH_2 and mesityl), have been used to synthesize (arsino)gallanes. Dynamic NMR spectroscopy studies of one of these, $\{[(Me_3SiCH_2)_2As]_2GaCl\}_2$, show it has fluxional properties.

Despite the importance of gallium arsenide in emerging semiconductor technology,[1] the chemistry of this elemental combination had, until recently,[2] been restricted to the studies of Coates et al.[3] in the 1960s. They prepared two mono(arsino)gallanes by cleavage of one Ga–C bond in Me_3Ga with secondary arsines, resulting in the elimination of methane (eq 1). In our hands, this method became

$$\begin{gathered}\mathrm{R_2AsH + Me_3Ga \rightarrow 1/\mathit{n}(R_2AsGaMe_2)_{\mathit{n}} + CH_4} \qquad (1)\\ \mathrm{R = Me;}\ n = 3\\ \mathrm{R = Ph;}\ n = 2\end{gathered}$$

impractical, and eventually failed, as the steric bulk of the substituents was increased;[4] it was also found to be limited to the cleavage of a single Ga–C bond, and bis- and tris(arsino)gallanes, $[(R_2As)_{3-x}GaR_x]_n$ (x = 0, 1), were inaccessible by this route.[5] A number of reports of the synthesis of main-group compounds by metathetical elimination of trimethylchlorosilane[6] prompted us to evaluate this route to (arsino)gallanes. Here we report its successful application (eq 2–4), as well as the fluxional properties of a dimeric bis(arsino)gallane.

$$\begin{gathered}\mathrm{R_2AsSiMe_3 + GaCl_3 \rightarrow 1/\mathit{n}(R_2AsGaCl_2)_{\mathit{n}} + Me_3SiCl} \qquad (2)\\ \mathrm{R = Me_3SiCH_2;}\ n = 3\\ \mathrm{R = Mes = mesityl;}\ n = ?\end{gathered}$$

$$\begin{gathered}\mathrm{2R_2AsSiMe_3 + GaCl_3 \rightarrow 1/\mathit{n}[(R_2As)_2GaCl]_{\mathit{n}} + 2Me_3SiCl} \qquad (3)\\ \mathrm{R = Me_3SiCH_2;}\ n = 2\\ \mathrm{R = Mes;}\ n = ?\end{gathered}$$

$$\begin{gathered}\mathrm{R_2AsSiMe_3 + 1/\mathit{n}[(R_2As)_2GaCl]_{\mathit{n}} \rightarrow (R_2As)_3Ga + Me_3SiCl} \qquad (4)\\ \mathrm{R = Mes}\end{gathered}$$

Silylarsines[7] are readily available from lithium arsenides and trimethylchlorosilane, and their reaction with trichlorogallane proceeds stepwise in hydrocarbon solvents.[8]

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(1) Keyes, R. W. *Science (Washington, D.C.)* **1985**, *230*, 138.

(2) (a) Wells, R. L.; Purdy, A. P.; McPhail A. T.; Pitt, C. G. *Abstracts of Papers, 189th National Meeting of the American Chemical Society*, Miami Beach, FL; American Chemical Society: Washington, DC, 1985; INOR 26. (b) Wells, R. L.; Purdy, A. P.; McPhail, A. T.; Pitt, C. G. *J. Chem. Soc., Chem. Commun.* **1986**, 487. (c) Wells, R. L.; Purdy, A. P.; McPhail, A. T.; Pitt, C. G. *J. Organomet. Chem.*, in press. (d) Pitt, C. G.; Higa, K. T.; McPhail, A. T.; Wells, R. L., submitted for publication in *Inorg. Chem.*

(3) (a) Coates, G. E.; Graham, J. J. *J. Chem. Soc.* **1963**, 233. (b) Beachley, O. T.; Coates, G. E. *J. Chem. Soc.* **1965**, 3241.

(4) For example, $[(Me_3SiCH_2)_2AsGaPh_2]_2$ was prepared by this method;[2c] however, heating Ph_2AsH and $(Me_3SiCH_2)_3Ga$ (1:1 molar ratio) at 60 °C for 2 days afforded impure $[(Ph_2AsGa(CH_2SiMe_3)_2]_n$, $Ph_2AsAsPh_2$, Me_4Si, H_2, and unreacted $(Me_3SiCH_2)_3Ga$; no evidence for the desired product was obtained when $(Me_3SiCH_2)_2AsH$ and $(Me_3SiCH_2)_3Ga$ (1:1 molar ratio) were heated at 100–120 °C for 1 month.

(5) For example, when Ph_2AsH and Me_3Ga (2:1 molar ratio) were heated at 80–100 °C for 2 days, no evidence for any product other than CH_4, $(Ph_2AsGaMe_2)_n$, and unchanged Ph_2AsH was obtained.

(6) See, for example: (a) Abel, E. W.; Armitage, D. A.; Willey, G. R. *J. Chem. Soc.* **1965**, 57. (b) Wells, R. L.; Collins, A. L. *Inorg. Chem.* **1966**, *5*, 1327. (c) Abel, E. W.; Illingsworth, S. M. *J. Chem. Soc. A* **1969**, 1094. (d) Harman, J. S.; McCartney, M. E.; Sharp, D. W. A. *J. Chem. Soc. A* **1971**, 1547. (e) Goetze, R.; Noeth. H. *Z. naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1975**, *30B*, 875. (f) Nutt, W. R.; Stimson, R. E.; Leopold, M. F.; Rubin, B. H. *Inorg. Chem.* **1982**, *21*, 1909. (g) Hoffmann, G. G. *J. Organomet. Chem.* **1984**, *273*, 187.

(7) See for example: (a) Abel, E. W.; Honigschmidt-Grossich, R.; Illingworth, S. M. *J. Chem. Soc. A* **1968**, 2623. (b) Abel, E. W.; Crow, J. P. *J. Organomet. Chem.* **1969**, *17*, 337. (c) Mislow, K.; Senkler, G. H.; Cook, R. J.; Casey, J. P.; Baechler, R. D. *J. Am. Chem. Soc.* **1972**, *94*, 2859. The new silylarsines used in this work were prepared under strict inert atmospheric conditions as follows. $(Me_3SiCH_2)_2AsSiMe_3$. A mixture of $(Me_3SiCH_2)_2AsH$[2c] (6.0 g, 24 mmol) and *n*-BuLi (10 mL, 2.4 M in hexane) was stirred at 60 °C for 1 day under nitrogen pressure and then cooled to 0 °C, before excess Me_3SiCl (4 mL in 20 mL pentane) was added dropwise. After refluxing for 0.5 h, addition of 10 mL of Et_2O, and standing at room temperature for 1 day, the mixture was filtered; following solvent removal, distillation afforded the silylarsine as a colorless liquid (5.8 g, 75% yield), bp 40 °C (0.04–0.35 torr). Anal. Calcd (Found) for $C_{11}H_{31}AsSi_3$: C, 40.96 (40.83); H, 9.69 (9.82). NMR: ^1H (80 MHz, C_6D_6) δ 0.80 and 0.46 [AB pattern ($^2J_{HH}$ = 13.6 Hz), 4 H, CH_2], 0.18 (s, 9 H, $AsSiMe_3$), 0.15 (s, 18 H, $CSiMe_3$); ^{13}C (22.5 MHz, C_6D_6) δ 5.7 (s, CH_2), –1.5 (s, $AsSiMe_3$), 0.37 (s, $CSiMe_3$). $Mes_2AsSiMe_3$. (a) Mesitylmagnesium bromide (274 mmol) in THF (200 mL) was added over a 45-min period, with stirring, to $AsCl_3$ (25.0 g, 138 mmol) in THF; after 12 h, degassed water (125 mL) and concentrated HCl (60 mL) were added, and the mixture was stirred for 1 day. Following extraction with benzene, the volatiles were removed by distillation leaving crude, solid Mes_2AsCl (45.1 g, 94% yield). NMR: ^1H (80 MHz, C_6D_6) δ 6.60 (s, 4 H, ring CH), 2.35 (s, 12 H, Me), 2.02 (s, 6 H Me). (b) The crude Mes_2AsCl was dissolved in THF (500 mL), and $LiAlH_4$ (10.0 g, 263 mmol) was added. After the solution was stirred for 46 h, addition of water (220 mL), extraction with benzene, and removal of volatiles, distillation afforded Mes_2AsH as a colorless liquid (14.6 g, 58% yield), bp 145–150 °C (0.01 torr). Anal. Calcd (Found) for $C_{18}H_{23}As$: C, 68.79 (68.66); H, 7.38 (7.55). NMR: ^1H (80 MHz, C_6D_6) δ 6.70 (s, 4 H, ring CH), 4.83 (s, 1 H, AsH), 2.27 (s, 12 H, Me), 2.07 (s, 6 H, Me). IR (Nujol): 2130 cm^{-1} (s, AsH). (c) A mixture of Mes_2AsH (14.62 g, 46.42 mmol), *n*-BuLi (20 mL, 2.4 *M* in hexane), and ligroin (150 mL) was heated at 50 °C for 20 min. Filtration gave solid, yellow Mes_2AsLi which was dried under vacuum (14.41 g, 96.7% yield). Anal. Calcd (Found) for $C_{18}H_{22}AsLi$: C, 67.51 (67.15); H, 7.82 (7.95). NMR: ^1H (80 MHz, C_6D_6 + 1 drop THF) δ 6.93 (s, 4 H, ring CH), 2.61 (s, 12 H, Me) 2.29 (s, 6 H, Me). (d) A mixture of Mes_2AsLi (3.79 g, 11.8 mmol), Me_3SiCl (10 mL), and ligroin (100 mL) was heated to reflux, stirred at room temperature for 12 h, and filtered. The filtrate was concentrated in vacuo to an oil which eventually crystallized as colorless $Mes_2AsSiMe_3$ (4.46 g, 98% yield), mp 62–66 °C. Anal. Calcd (Found) for $C_{21}H_{31}AsSi$: C, 65.26 (65.53); H, 8.08 (8.24). NMR: ^1H (80 MHz, C_6D_6) δ 6.74 (s, 4 H, ring CH), 2.31 (s, 12 H, Me), 2.10 (s, 6 H, Me), 0.28 (s, 9 H, $SiMe_3$).

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The only byproduct trimethylchlorosilane is easily removed in vacuo, a considerable advantage when handling these air- and moisture-sensitive materials. This method did not yield $[(Me_3SiCH_2)_2As]_3Ga$; however, it did afford the sterically hindered tris(arsino)gallane $(Mes_2As)_3Ga$ (eq 4) which was first prepared by us from lithium dimesitylarsenide and trichlorogallane and shown to be monomeric by single-crystal X-ray analysis.[2d] Lack of suitable crystals and the very low solubility of the mono- and bis(arsino)gallanes containing mesityl groups (eq 2 and 3), also prepared from lithium dimesitylarsenide and trichlorogallane),[2d] prohibited determination of their degree of oligomerization.

The bis(arsino)gallane $[(Me_3SiCH_2)_2As]_2GaCl$ was shown by cryoscopic measurements to exist predominantly as the dimer (eq 3) in benzene. Its ^1H (300-MHz) NMR spectrum in toluene at 22 °C, reproduced in Figure 1a, consisted of singlets at δ 0.25 and 0.27 (72 H, Me_3Si) and 1.65 (8 H, *endo*-CH_2As) and doublets (AB quartet, $^2J_{HH}$ = 13.5 Hz) at δ 0.94 and 1.76 (8 H, *exo*-CH_2As). The ^{13}C NMR spectrum at 21 °C consisted of four singlets at δ 0.05 and 1.15 (Me_3Si) and δ 7.87 and 8.78 ($SiCH_2As$). Only a single isomer was detected, assigned the trans structure on steric grounds. The ^1H NMR spectrum was measured by using a range of concentrations (5.9–111 mM) in an attempt to detect equilibria with monomeric or other oligomeric species; no significant changes in peak intensities of the dimer were observed. However, the relative intensities of the peaks due to trace impurities $(Me_3SiCH_2)_2AsH$ and $(Me_3SiCH_2)_2AsAs(CH_2SiMe_3)_2$, resulting from slight hydrolysis and decomposition of the dimer, respectively,[9] increased somewhat with decreasing concentrations.

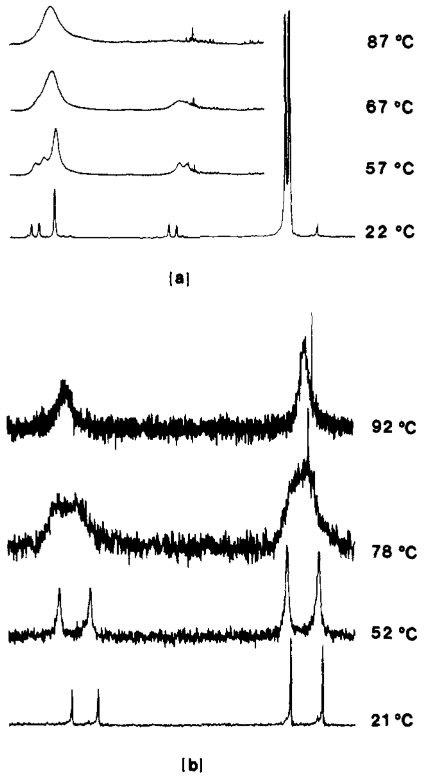

Figure 1. (a) ^1H NMR spectra and (b) ^{13}C NMR spectra of $\{[(Me_3SiCH_2)_2As]_2GaCl\}_2$.

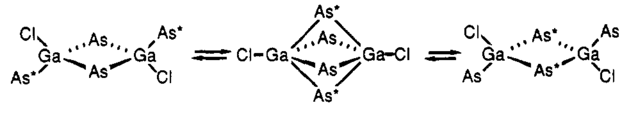

Figure 2. Exchange of the endo- and exocyclic arsino groups.

When the temperature was raised from 22 to 97 °C, the ^1H AB quartet collapsed to a broadened doublet which then approached coalescence with the singlet. Likewise, the ^{13}C methyl peaks broadened and coalesced at 78 °C (Figure 1b). This spectroscopic behavior was reversible, with the exception of the formation of a small amount of the above diarsine. These changes of ^1H and ^{13}C spectra, when coupled with the dimeric molecular weight and the absence of other species in the spectra, can only be reconciled by rapid exchange of the endo- and exocyclic bis[(trimethylsilyl)methyl]arsino groups. Spectra simulated on this basis were in excellent agreement with the experimental data. A $\Delta G^{\ddagger}$ of 17.0 ± 0.0 kcal/mol for the ^{13}C exchange was obtained by line-shape analysis[10] and was

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(8) The (arsino)gallanes were prepared under strict inert atmospheric conditions as follows. $[(Me_3SiCH_2)_2AsGaCl_2]_3$. A solution of $(Me_3SiCH_2)_2AsSiMe_3$ (0.5 g, 1.55 mmol) in pentane (6 mL) was added to a solution of $GaCl_3$ (0.27 g, 1.55 mmol) in pentane (6 mL). After several minutes, a precipitate formed. Removal of the liquid phase, washing with pentane, and drying in vacuo gave the (arsino)gallane as a white solid (0.40 g, 67% yield), mp 170–184 °C dec. Anal. Calcd (Found) for $C_{24}H_{66}As_3Cl_6Ga_3Si_6$: C, 24.64 (24.82); H, 5.68 (5.97); Cl, 18.18 (17.84); mol wt (cryoscopic in benzene), 1170 (1070) ± 80); NMR spectrum shows one species. NMR: ^1H (250 MHz, C_6D_6) δ 1.78 (s, 12 H, CH_2), 0.23 (s, 54 H, $SiMe_3$); ^{13}C (22.5 MHz, C_6D_6) δ 7.4 (s, CH_2) 1.2 (s, $SiMe_3$). $\{[(Me_3SiCH_2)_2As]_2GaCl\}_2$. A solution of $(Me_3SiCH_2)_2AsSiMe_3$ (1.0 g, 3.10 mmol) in pentane (10 mL) was added to a solution of $GaCl_3$ (0.27 g, 1.55 mmol) in benzene (10 mL), and, after 1 day, the mixture was brought to a boil. Removal of the volatiles under vacuum gave a white solid that on slow recrystallization from ligroin (bp 95–110 °C) afforded the bis(arsino)gallane as colorless crystals that were dried in vacuo (0.67 g, 80% yield): mp 101–128 °C dec. Anal. Calcd (Found) for $C_{32}H_{88}As_4Cl_2Ga_2Si_8$: C, 31.82 (31.66); H, 7.34 (7.23); mol wt (cryoscopic in cyclohexane), 1207 (1100 ± 55). $(Mes_2AsGaCl_2)_n$.[2d] A solution of $Mes_2AsSiMe_3$ (0.39 g, 1.0 mmol) in pentane (3 mL) was added to a solution of $GaCl_3$ (0.24 g, 1.36 mmol) in pentane (5 mL), and, after 5 min, the volatiles were removed. Washing the remaining solid with ligroin and drying in vacuo gave the (arsino)gallane as a white solid (0.46 g, 100% yield), mp 145–146 °C dec. Anal.[2d] Calcd (Found) for $C_{18}H_{22}AsCl_2Ga$: C, 47.63 (47.91); H, 4.89 (5.07). NMR: ^1H (80 MHz, C_6D_6 + 2 drops THF) δ 6.69 (s, 4 H, ring CH), 2.45 (s, 12 H, Me), 2.06 (s, 6 H, Me). $[(Mes_2As)_2GaCl]_n$.[2d] Addition of a solution of $Mes_2AsSiMe_3$ (0.82 g, 2.1 mmol) in benzene (10 mL) to a solution of $GaCl_3$ (0.35 g, 2.0 mmol) in benzene (10 mL) gave a white precipitate of $(Mes_2AsGaCl_2)_n$. Addition of more $Mes_2AsSiMe_3$ (0.75 g, 1.9 mmol) resulted in a yellow-orange solution. Removal of volatiles after 3 h gave a yellow solid that on recrystallization from ligroin/benzene (1:1) afforded the bis(arsino)gallane as a yellow solid (0.35 g, 24% yield), mp 120–125 °C dec. Anal. Calcd (Found) for $C_{36}H_{44}As_2ClGa$: C, 59.09 (59.27); H, 6.06 (6.02). NMR: ^1H (80 MHz, C_6D_6) δ 6.68 (s, 8 H, ring CH), 2.31 (s, 24 H, Me), 2.06 (s, 12 H, Me). $(Mes_2As)_3Ga$.[2d] Addition of a solution of $Mes_2AsSiMe_3$ (0.67 g, 1.7 mmol) in benzene (10 mL) to a solution of $GaCl_3$ (0.15 g, 0.85 mmol) in benzene (10 mL) gave a yellow solution. Removal of volatiles after 3 days gave a yellow solid which was shown by NMR to be an impure mixture of mono- and bis(arsino)gallane. Addition of more $Mes_2AsSiMe_3$ (0.21 g, 0.54 mmol) dissolved in benzene (10 mL) gave a yellow solid and orange solution. Filtration and removal of volatiles gave an orange oil to which ligroin (10 mL) was added. The resulting mixture was heated and allowed to cool; after 1 day the tris(arsino)gallane precipitated as an orange solid (0.11 g, 13% yield), mp 130–160 °C dec; Anal.[2d] Calcd (Found) for $C_{54}H_{66}As_3Ga$: C, 64.24 (64.55); H, 6.59 (6.59). NMR: ^1H (80 MHz, C_6H_6) δ 6.63 (s, 12 H, ring CH), 2.32 (s, 36 H, Me) 2.05 (s, 18 H, Me).

(9) Based on NMR, same peaks as in spectra of authentic samples of the arsine[2c] and the diarsine. The diarsine was prepared by the reduction of $(Me_3SiCH_2)_2AsCl$[2c,13] with zinc amalgam in refluxing methanol. Anal. Calcd (Found) for $C_{16}H_{44}As_2Si_4$: C, 38.54 (38.11); H, 8.89 (8.61). NMR: ^1H (80 MHz, C_6D_6) δ 0.75 and 0.61 [AB pattern ($^2J_{HH}$ = 13.6), 8 H, CH_2], 0.12 (s, 36 H, $SiMe_3$); ^{13}C (22.5 MHz, C_6D_6) δ 10.2 (s, CH_2), 0.5 (s, $SiMe_3$).

(10) (a) The ^{13}C (75.429 MHz) Me_3Si resonances from spectra at 11 temperatures (304, 309, 314, 319, 325, 330, 349, 350, 351, 352, an 365 K) were compared with the simulations from the modified DNMR3[10b] program, using $\Delta\nu$ = 83.5 Hz and a natural line width of 1.0 Hz, and the rate constants (5, 5, 11, 14.5, 29, 35, 150, 170, 185, 195, and 500 s^{-1}) were obtained. A plot and least-squares analysis of $\ln (k/T)$ vs. $1/T$ yielded a slope ($m = -8295 \pm 218$) and an intercept ($b = 22.98 \pm 0.66$). The equations[10c] $\Delta H^{\ddagger} = -mR$, $\Delta S^{\ddagger} = R(b - 23.76)$, and $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$ were used to obtain $\Delta H^{\ddagger}$ (16.5 ± 0.4 kcal/mol), $\Delta S^{\ddagger}$ (−1.55 ± 1.3 cal/(mol K)), and $\Delta G^{\ddagger}$. (b) Binsch, G.; Kleier, D. A. *The Computation of Complex Exchange-Broadened NMR Spectra, Program 165*, Quantum Chemistry Program Exchange, Indiana University, 1970; revised by: Bushweller, C. H.; Bhat, G.; Letendre. L. J.; Brunelle, J. A.; Bilofsky, H. S.; Ruben, H.; Templeton, D. H.; Zalkin, A. *J. Am. Chem. Soc.* **1975**, *97*, 65 and by: Caves, T., North Carolina State University. (c) Sandstrom, J. *Dynamic NMR Spectroscopy*; Academic: London, England, 1982.

in agreement with the estimate derived from the coalescence temperature.[11] The ^1H exchange process between 22 and 57 °C could be simulated by using the same kinetic parameters, without invoking pyramidal inversion of the exocyclic arsenics. Evidently, the latter is not a significant process in this temperature range, despite the fact that the electropositive gallium might be expected to reduce the inversion barrier.

The equivalency of the bis[(trimethylsilyl)methyl]arsino groups can be achieved by associative or dissociative mechanisms. The associative mechanism is intuitively more attractive, involving an intermediate in which one or both gallium atoms assume a five-coordinate square-pyramidal configuration (Figure 2). There is ample precedent for five-coordinate gallium.[12] The dissociative mechanism requires cleavage of one endocyclic Ga–As bond and then reclosure of the ring in a trans–cis–trans equilibrium process. Dissociation into two monomers is considered energetically improbable.

Acknowledgment. The financial support of this work by the Office of Naval Research is gratefully acknowledged. The technical contributions of R. Ernest and C. Foley (Duke University) and T. Caves (North Carolina State University) are similarly recognized.

Registry No. $(Me_3SiCH_2)_2AsSiMe_3$, 101860-04-2; $(Me_3SiCH_2)_2AsH$, 101860-05-3; Me_3SiCl, 75-77-4; $Mes_2AsSiMe_3$, 101860-06-4; MesMgBr, 2633-66-1; $AsCl_3$, 7784-34-1; Mes_2AsCl, 101860-07-5; Mes_2AsH, 101860-08-6; Mes_2AsLi, 101860-09-7; $[(Me_3SiCH_2)_2AsGaCl_2]_3$, 101836-83-3; $GaCl_3$, 13450-90-3; $\{[(Me_3SiCH_2)_2As]_2GaCl\}_2$, 101860-10-0; $(Mes_2AsGaCl_2)_n$, 101836-85-5; $[(Mes_2As)_2GaCl]_n$, 101836-87-7; $(Mes_2As)_3Ga$, 60607-12-7; Ph_2AsH, 829-83-4; $(Me_3SiCH_2)_3Ga$, 72708-53-3; $[(Ph_2AsGa(CH_2SiMe_3)_2]_n$, 101836-89-9; $Ph_2AsAsPh_2$, 2215-36-3; Me_3Ga, 1445-79-0; $(Ph_2AsGaMe_3)_n$, 101836-90-2.

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[11] $\Delta G_c^* = 17.0 \pm 0.1$ kcal/mol; obtained (in cal/mol) from the equation $\Delta G_c^* = T_c[45.67 + 4.58 \log (T_c/\Delta\nu)]$, where $T_c = 351 \pm 1$ K and $\Delta\nu = 83.3 \pm 0.2$ Hz.

[12] See, for example: (a) Pattison, I.; Wade K. *J. Chem. Soc. A* **1968**, 2618. (b) Dymock, K.; Palenik, G. J. *J. Chem. Soc., Chem. Commun.* **1973**, 884. (c) Rettig, S. J.; Storr, A.; Trotter, J. *Can. J. Chem.* **1975**, *53*, 753. (d) Rettig, S. J.; Storr, A.; Trotter, J. *Can. J. Chem.* **1976**, *54*, 1278. (e) McPhail, A. T.; Miller, R. W.; Pitt, C. G.; Gupta, G.; Srivastava, S. C. *J. Chem. Soc., Dalton Trans.* **1976**, 1657.

[13] Seyferth, D. U.S. Patent 2964550, 1960.

$[Cr(\eta^3\text{-}C_3H_5)_2(\eta^5\text{-}C_5H_5)]$: Preparation, Structure, and Reactions

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Summary: The title compound has been prepared by reacting $[CrCl_2(\eta^5\text{-}C_5H_5)]$ with allylmagnesium chloride at −30 °C and the crystal structure determined by X-ray diffraction. Reaction with a variety of donor ligands is accompanied by reductive coupling of the allyl groups to give $[Cr(L)(\eta^2,\eta^2\text{-}1,5\text{-}C_6H_{10})(\eta^5\text{-}C_5H_5)]$ complexes while treatment with butadiene or alkynes leads to their displacement and the formation of mono- and binuclear $Cr(\eta^5\text{-}C_5H_5)$ species.

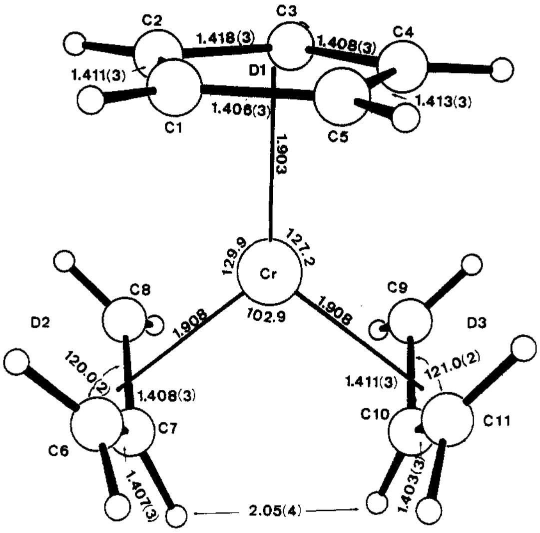
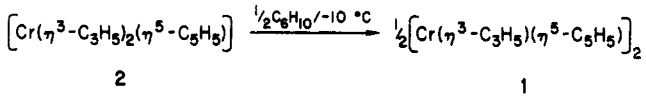


Figure 1. The molecular structure of $[Cr(\eta^3\text{-}C_3H_5)_2(\eta^5\text{-}C_5H_5)]$ (2).

In continuation of our investigation into the chemistry of the η^3-allyl complexes of Cr, Mo, and W,[2,3] we report here the preparation of the title compound and some representative reactions.

It has previously been reported[4] that $[CrCl_2(\eta^5\text{-}C_5H_5)]$[5] reacts with allylmagnesium chloride in THF at room temperature to give a black binuclear species, $[Cr(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)]_2$, (1), in low yield. The presumed intermediate in this reaction $[Cr(\eta^3\text{-}C_3H_5)_2(\eta^5\text{-}C_5H_5)]$ (2) can be isolated in ca. 75% yield by carrying out the reaction at −60 ° in diethyl ether. 2 is an orange-yellow, paramagnetic compound[6] which reacts further in solution above ca. −10 °C to give 1.[7] The crystal structure of 2 has been determined by X-ray diffraction (Figure 1)[8] and should be compared with that of the related molybdenum compound $[Mo(\eta^3\text{-}C_3H_5)_2(\eta^5\text{-}C_5H_5)]$.[2] The organic ligands are arranged in an essentially trigonal-planar geometry about the central metal atom with an angle of ca. 156° between the two allyl planes. Cr is smaller than Mo (covalent radius: Cr(0), 1.15 Å; Mo(0), 1.31 Å), and as a result the



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[5] Prepared by reacting $[Cr(\eta^5\text{-}C_5H_5)_2]$ with HCl (g) in pentane at 0 °C (yield 95%); see also: Klocke, H. J. Dissertation Ruhr-Universität Bochum, 1984.

[6] Anal. Found (Calcd): Cr, 26.02 (26.10); C, 66.24 (66.31); H, 7.60 (7.54). MS: *m/e* 199 (M^+). Paramagnetic: 1.8 μ_B.

[7] Anal. Found (Calcd): Cr, 32.79 (32.87); C, 60.89 (60.79); H, 6.26 (6.37). MS: *m/e* 316 (M^+). Paramagnetic: 4.1 μ_B.

[8] X-ray diffraction data for $C_{11}H_{15}Cr$ (2): orange; crystal size (mm) 0.04 × 0.42 × 0.59; crystal system monoclinic; space group $P2_1/a$ (no. 14); $a = 11.165$ (4) Å, $b = 7.154$ (2) Å, $c = 12.211$ (2) Å, $\beta = 102.40$ (2)°; $V = 952.6$ Å^3; $z = 4$; $d_{calcd} = 1.39$ g/cm$^+$; μ(MoKα) = 11.14 cm^{-1}; empirical absorption correction (0.890_{min}–1.243_{max}); $F(000) = 420$, Enraf-Nonius CAD-4 diffractometer; graphite-monochromated Mo radiation (λ = 0.71069 Å); Zr Filter; scan mode θ–2θ; $T = 100$ K; θ range 1.7–27.3°; measured reflections 4317 ($\pm h,\pm k,+l$); unique reflections 2159, observed reflections 1779 ($I \geq 2\sigma(I)$); structure solved by heavy-atom method; hydrogen positions located and refined isotropically; number of variables 169; $R = 0.030$, $R_w = 0.038$ ($w = 1\sigma^2(F_o)$); EOF = 2.1; residual electron density = 0.55 e Å^{-3}.

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