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.

---

[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.

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

K. Angermund, A. Döhring, P. W. Jolly,* C. Krüger, and C. C. Romão[1]

Max-Planck-Institut für Kohlenforschung
D-4330 Mülheim a.d. Ruhr, West Germany

Received February 3, 1986

Summary: The title compound has been prepared by reacting $[CrCl_2(\eta^5-C_5H_5)]$ 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 $[Cr(L)(\eta^2,\eta^2-1,5-C_6H_{10})(\eta^5-C_5H_5)]$ complexes while treatment with butadiene or alkynes leads to their displacement and the formation of mono- and binuclear $Cr(\eta^5-C_5H_5)$ species.

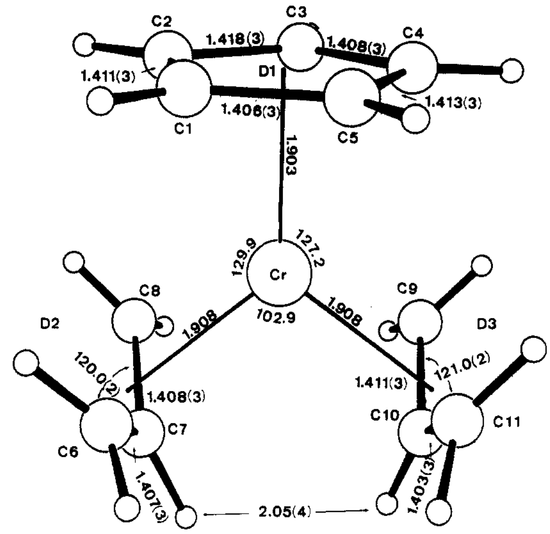
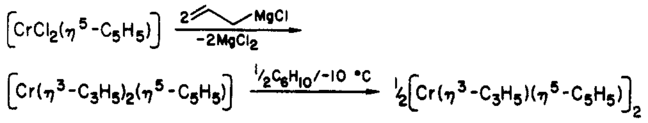


Figure 1. The molecular structure of $[Cr(\eta^3-C_3H_5)_2(\eta^5-C_5H_5)]$ (2).

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 $[CrCl_2(\eta^5-C_5H_5)]$[5] reacts with allylmagnesium chloride in THF at room temperature to give a black binuclear species, $[Cr(\eta^3-C_3H_5)(\eta^5-C_5H_5)]_2$, (1), in low yield. The presumed intermediate in this reaction $[Cr(\eta^3-C_3H_5)_2(\eta^5-C_5H_5)]$ (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 $[Mo(\eta^3-C_3H_5)_2(\eta^5-C_5H_5)]$.[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



---

[1] Present address: Instituto Superior Tecnico, Lisbôa, Portugal.

[2] Jolly, P. W.; Krüger, C.; Romão, C. C.; Romão, M. J. *Organometallics* **1984**, *3*, 936.

[3] Benn, R.; Holle, S.; Jolly, P. W.; Krüger, C.; Romão, C. C.; Romão, M. J.; Rufinska, A.; Schroth, G. *Polyhedron* **1986**, *5*, 461.

[4] Nieman, J.; Pattiasina, J. W.; Teuben, J. H. *J. Organomet. Chem.* **1984**, *262*, 157.

[5] Prepared by reacting $[Cr(\eta^5-C_5H_5)_2]$ 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$^+$; $\mu(MoK\alpha) = 11.14$ cm^{-1}; empirical absorption correction (0.890_{min}–1.243_{max}); $F(000) = 420$, Enraf-Nonius CAD-4 diffractometer; graphite-monochromated Mo radiation ($\lambda = 0.71069$ 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 ($I \geqslant 2\sigma(I)$); 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}.

[9] Shannon, R. D. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1976**, *A32*, 751.

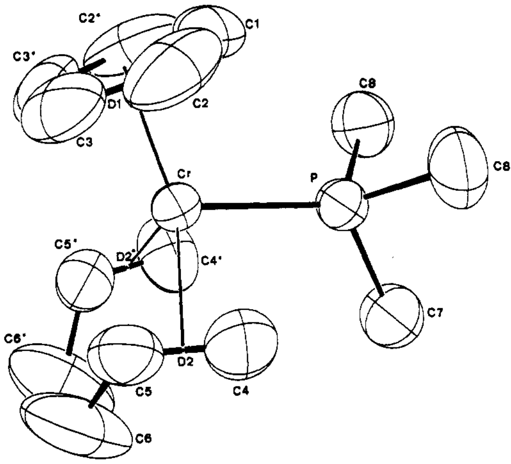


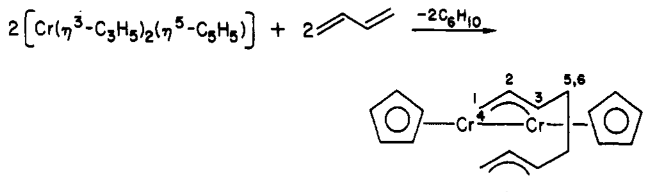
Figure 2. The molecular structure of [Cr(PMe$_3$)(η^2, η^2-1,5-C$_6$H$_{10}$)(η^5-C$_5$H$_5$)] (3).

organic ligands are ca. 0.1 Å closer to the metal in the case of the chromium complex, and the meso H atoms (C7–H, C10–H) are separated by only 2.05 Å (2.17 Å for Mo). The η^5-C$_5$H$_5$ ring is essentially symmetrical whereas in the case of the Mo complex the Cp C–C bond distances vary between 1.410 (4) and 1.373 (5) Å.

2 reacts readily with inorganic and organic nucleophiles. A number of donor ligands induce reductive coupling of the allyl groups to give dark green, paramagnetic, η^2, η^2-1,5-hexadiene chromium complexes (**3**) in high yield.[10] The crystal structure of the PMe$_3$ adduct has been established by X-ray diffraction (Figure 2).

$$[\mathrm{Cr}(\eta^3\text{-}\mathrm{C_3H_5})_2(\eta^5\text{-}\mathrm{C_5H_5})] + \mathrm{L} \xrightarrow[-10\ ^\circ\mathrm{C}]{\text{pentane}} [\mathrm{Cr}(\mathrm{L})(\eta^2,\ \eta^2\text{-}1,5\text{-}\mathrm{C_6H_{10}})(\eta^5\text{-}\mathrm{C_5H_5})]$$
$$\mathbf{3}\ (\mathrm{L} = \mathrm{CO},\ \mathrm{P(OMe)_3},\ \mathrm{PMe_3})$$

Unsaturated organic compounds displace the allyl groups to give mono- and binuclear chromium complexes. For example, the product of the reaction with butadiene is a yellow, diamagnetic binuclear complex, [{Cr(η^5-C$_5$H$_5$)}$_2$(μ-η^3, η^3-C$_8$H$_{12}$)] (**4**), whose ^{1}H NMR spectrum indicates that an octadienediyl moiety bridges the metal atoms.[11] Alkynes react to give both mononuclear, e.g.,



4

[Cr(η^5-C$_5$H$_5$)(η^6-C$_6$Me$_6$)], and binuclear, e.g., [{(Cr(η^5-C$_5$H$_5$)}$_2$(μ-C$_6$Et$_6$)], species which are presumably related to the η^5-pentamethylcyclopentadienyl chromium complexes reported by Wilke et al.[12] Details will be reported later.

Acknowledgment. C.C.R. thanks the Alexander von Humboldt Stiftung for the award of a stipend (1983–1984).

Registry No. 1, 90636-08-1; 2, 89922-80-5; 3 (L = PMe$_3$), 101860-22-4; 3 (L = P(OMe)$_3$), 101860-23-5; 3 (L = CO), 101860-24-6; 4, 101860-25-7; CrCl$_2$(η^5-C$_5$H$_5$), 54235-50-6; Cr(η^5-C$_5$H$_5$)$_2$, 1271-24-5; butadiene, 106-99-0; allylmagnesium chloride, 2622-05-1.

Supplementary Material Available: Listings of observed and calculated structure factors, anisotropic thermal papameters, atomic coordinates, interatomic distances, and bond angles (31 pages). Ordering information is given on any current masthead page.

---

[10] 3, L = PMe$_3$: yield 95%. Anal. Found (Calcd): Cr, 18.75 (18.99); P, 11.29 (11.25); c, 60.95 (61.08); H, 9.04 (8.79). MS: m/e 275 (M$^+$). Paramagnetic: 1.9 μ_B. X-ray diffraction data for C$_{14}$H$_{24}$CrP (**3**, L = PMe$_3$): dark green; crystal size (mm) 0.36 × 0.72 × 0.36, crystal system orthorhombic; space group *Pnma* (no. 62); a = 13.937 (2) Å, b = 11.540 (2) Å, c = 9.136 (2) Å; V = 1469.4 Å^3; Z = 4; d_{calcd} = 1.24 g/cm^3; μ(MoKα) = 8.4 cm^{-1}; no absorption correction; F(000) = 588; Enraf-Nonius CAD-4 diffractometer; graphite-monochromated Mo radiation (λ = 0.710 69 Å); Zr filter; scan mode = θ–2θ; T = 293 K, θ range = 1.5–30.8° measured reflections 4182 ($\pm h,\pm k,\pm l$); unique reflections 2416, observed reflections 1558 ($I \geqslant 2\sigma(I)$); structure solved by heavy-atom method; hydrogen atom positions calculated; number of variables 79; R = 0.055, R_w = 0.076 ($w = 1/\sigma^2(F_o)$); EOF = 3.6; residual electron density = 0.57 e Å^{-3}. Cl, Cr, and P$_{(\mathrm{average})}$ located on a mirror plane. Some distances (C6,C6* (1.277 (9) Å) and Cp–ring distances) are artificially shortened by thermal motion (or disorder in $Pn^2{}_1a$): Cr–P = 2.316 (2), C4–C5 = 1.370 (7), C5–C6 = 1.470 (7), C6-C6* = 1.277 (9), Cr–D1 = 1.900 (8), Cr–D2 = 2.047 (9) Å; P–Cr–D1 = 113.5 (2), P–Cr–D2 = 97.1 (2), D2–Cr–D2* = 99.5 (2), C4–C5–C6 = 122.3 (5)°. **3**, L = P(OMe)$_3$: dark green (90% yield). Anal. Found (Calcd): Cr, 16.03 (16.08); P, 9.54 (9.58). MS: m/e 323 (M$^+$). Paramagnetic: 1.9–2.0 μ_B. Structure confirmed by X-ray diffraction study (disorder prevented refinement). **3**, L = CO: dark green (85% yield). Anal. Found (Calcd): Cr, 22.82 (22.88); C, 65.10 (63.42); H, 7.13 (6.65). MS: m/e 227 (M$^+$). Paramagnetic: 1.61–1.58 μ_B. IR (KBr): ν(CO) 1870 vs, 1830 sh cm^{-1}.

[11] Anal. Found (Calcd); Cr, 30.24 (30.37); C, 63.16 (63.15); H, 6.47 (6.48). MS: m/e 342 (M$^+$). Diamagnetic. ^{1}H NMR (THF-d_8, −80 °C): δ 5.31, 5.25 (s, C$_5$H$_5$), 3.83 (H$_1$), 2.44 (H$_2$), 3.04 (H$_3$), 2.17 (H$_4$), 2.49 (H$_5$), 2.01 (H$_6$) (provisional assignment, all signals broad). ^{13}C NMR (toluene-d_8, −80 °C): δ 56.08 (C-1, J(CH) = 156 Hz), 72.96/75.79 (C-2/3, J(CH) = 150/156 Hz), 32.05 (C-4, J(CH) = 125 Hz), 98.30 (C$_5$H$_5$, J(CH) = 171 Hz).

[12] Benn, H.; Wilke, G.; Henneberg, D. *Angew. Chem.* **1973**, *85*, 1052. Wilke, G. Proceedings of the *5th IUPAC Symposium on Organic Syntheses*; Freiburg, 1984; p 1 (1985).

Alkylation of Osmium(VI) Nitrido Complexes: Reaction of [Os(N)R$_4$][N-*n*-Bu$_4$] with [Me$_3$O][BF$_4$] and the X-ray Crystal Structures of [Os(N)(CH$_2$SiMe$_3$)$_4$][N-*n*-Bu$_4$] and [Os(NMe)(CH$_2$SiMe$_3$)$_4$]

Patricia A. (Belmonte) Shapley* and Zang-Yuan Own
Department of Chemistry, University of Illinois
Chicago, Illinois 60680

John C. Huffman
Molecular Structure Center, Indiana University
Bloomington, Indiana 47405

Received January 8, 1986

Summary: The nitridoosmium(VI) anion [Os(N)(CH$_2$SiMe$_3$)$_4$][N-*n*-Bu$_4$] can be methylated by Me$_3$OBF$_4$, MeOSO$_2$CF$_3$, or MeI to give Os(NMe)(CH$_2$SiMe$_3$)$_4$ in high yield. The structures of both [Os(N)(CH$_2$SiMe$_3$)$_4$][N-*n*-Bu$_4$] and Os(NMe)(CH$_2$SiMe$_3$)$_4$ were determined by X-ray diffraction. The alkyl complexes [Os(N)R$_4$][N-*n*-Bu$_4$], where R = Me or CH$_2$C$_6$H$_5$, also react with [Me$_3$O][BF$_4$] to form methylimido complexes [Os(NMe)R$_4$]. [Os(N)(CH$_2$SiMe$_3$)$_4$]$^-$ reacts with [Et$_3$O][BF$_4$] or EtOSO$_2$CF$_3$ to form [Os(NEt)(CH$_2$SiMe$_3$)$_4$] and with Me$_3$SiOSO$_2$CF$_3$ to form [Os(NSiMe$_3$)(CH$_2$SiMe$_3$)$_4$].

Reactions of unsaturated nitrogen ligands bound to transition metals are of interest as models for steps in the ammoxidation of olefins[1] and the reduction of dinitrogen.[2]

---

[1] Chang, A. O.; Oshima, K.; Sharpless, K. B. *J. Am. Chem. Soc.* **1977**, *99*, 3420–3426. Grasselli, R. K.; Burrington, J. D.; Brazdil, J. F. *Faraday Dis.* **1981**, *72*, 203–223. Groves, J. T.; Takahashi, T. *J. Am. Chem. Soc.* **1983**, *105*, 2073–2074.

[2] Chatt, J.; Leigh, G. H. *Chem. Soc. Rev.* **1972**, *1*, 121–144. Chatt, J.; Dilworth, J. R.; Richards, R. L. *Chem. Rev.* **1978**, *78*, 589–625.