

thiolane becomes evident from the separation of 3.59 Å between the terminal atoms in the curled chain.¹⁵ The successful isolation of 1, 2, and 3 suggests that the introduction of group 14 metals with tetrahedral environment and the longer M-S bonds compared to the S-S bond in orthorhombic sulfur (2.037 (5) Å)¹⁶ eases the ring strain of these unprecedented tetrathiametallolane ring systems.¹⁷

Further investigation of the formation mechanism and reactivity of the novel 1,2,3,4,5-tetrathiametallolanes is currently in progress.

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Supplementary Material Available: Spectral data of 1-6, ORTEP drawings of 2 and 3 along with the selected bond lengths and angles, and crystallographic data with tables of thermal and positional parameters for 1, 2, and 3 (25 pages). Ordering information is given on any current masthead page.

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(17) No 1,2,3,4-tetrathiolane derivative (R_2CS_4) has been isolated so far as we know.

An Unusual 17-Electron Organometallic Radical, $CpCr(NO)(PPh_3)(CH_2SiMe_3)^1$

F. Geoffrey Herring, Peter Legzdins,* W. Stephen McNeil,
and Michael J. Shaw

Department of Chemistry
The University of British Columbia
Vancouver, British Columbia, Canada V6T 1Z1

Raymond J. Batchelor and Frederick W. B. Einstein*

Department of Chemistry, Simon Fraser University
Burnaby, British Columbia, Canada V5A 1S6
Received April 16, 1991

Paramagnetic organometallic complexes of the transition metals have recently been the focus of considerable attention primarily because of their demonstrated involvement as reaction intermediates and their importance in various catalytic processes.²⁻⁴ Despite the relatively large number of organotransition-metal radicals that have been identified to date, few have also been structurally characterized in the solid state.^{2,5} We wish to report the synthesis, characterization, and some unusual chemical properties of the thermally stable 17-electron radical $CpCr(NO)(PPh_3)(CH_2SiMe_3)$ [$Cp = \eta^5-C_5H_5$].^{6,7} This radical is a convenient precursor to previously unknown chromium nitrosyl

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(7) For a recent review of aspects of the organometallic nitrosyl chemistry of the group 6 elements, see: Legzdins, P. *Can. Chem. News* 1990, 42 (10), 19.

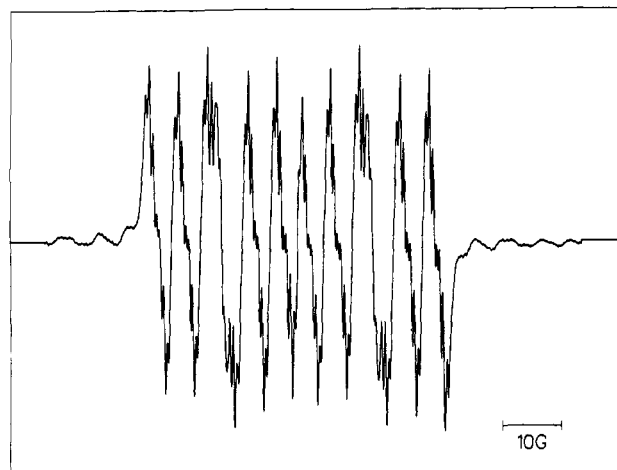
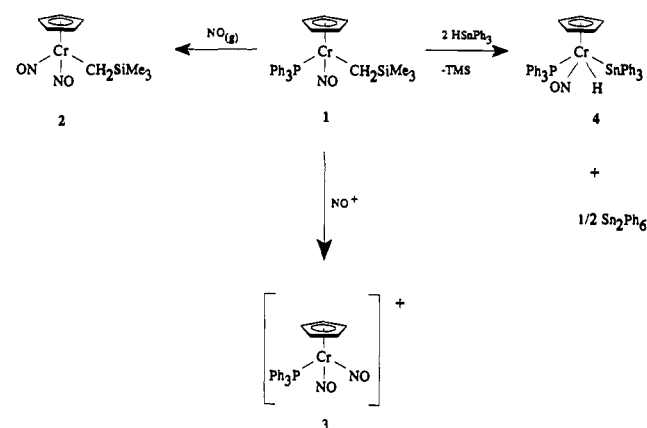
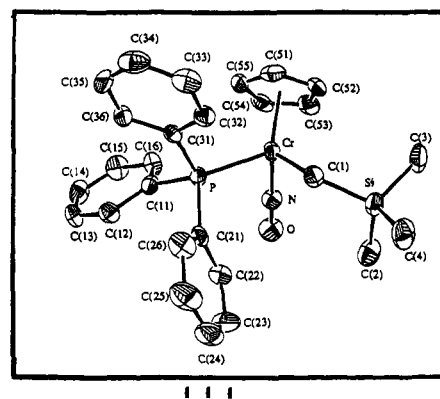


Figure 1. X-band ESR spectrum of $CpCr(NO)(PPh_3)(CH_2SiMe_3)$ in hexanes at 25 °C; $a_{CH_2CH_3} = 12.0$ G, $a_{CH_3CH_3} = 1.0$ G, $a_P = 26.0$ G, $a_N = 5.0$ G, and $a_{Cp} = 0.6$ G; $g_{iso} = 1.9979$.

Scheme 1



complexes such as neutral hydrides and cationic dinitrosyl phosphine species.

In a typical experiment, treatment of a green suspension of $CpCr(NO)(PPh_3)I^8$ (1.00 g, 1.86 mmol) in THF (20 mL) with Me_3SiCH_2MgCl (2 mL of 1.0 M solution in Et_2O , 2.0 mmol) resulted in the formation of a red-brown solution which became dark green and deposited a white precipitate over 24 h. The solvent was removed in vacuo. The residues were extracted with Et_2O , and the extracts were filtered through alumina. Addition of hexanes and cooling to -20 °C afforded analytically pure $CpCr(NO)(PPh_3)(CH_2SiMe_3)$ (1) as clusters of needles (0.61 g, 66% yield).⁹ Dark green 1 is a paramagnetic solid ($\mu = 1.47 \mu_B$)¹⁰

(8) Legzdins, P.; Nurse, C. R. *Inorg. Chem.* 1985, 24, 327.

(9) Anal. Calcd for $C_{23}H_{20}NOSiPCr$: C, 51.51; H, 3.76; N, 2.61. Found: C, 51.22; H, 3.77; N, 2.65. IR (KBr) ν_{NO} 1611 cm^{-1} . IR (hexanes) ν_{NO} 1631 cm^{-1} . FAB-MS m/z 498 [P^+], 409 [$P^+ - CH_2SiMe_3$].

which is soluble in common organic solvents to produce dark green solutions. Chlorinated solvents, such as CH_2Cl_2 , convert **1** cleanly to $\text{CpCr}(\text{NO})(\text{PPh}_3)\text{Cl}$ within 1 week at ambient temperatures. As a solid, **1** is moderately stable in air at room temperature for short periods of time and is stable indefinitely under an inert atmosphere.

A single-crystal X-ray crystallographic analysis of **1**¹¹ confirmed its monomeric nature and revealed its "three-legged piano-stool" molecular structure (Scheme I). The most interesting feature of this structure is that there are no unusual bond distances or angles, the intramolecular dimensions¹² being comparable to those exhibited by related 18-electron cyclopentadienylchromium nitrosyl complexes.¹³⁻¹⁷ This feature contrasts with that exhibited by most other structurally characterized 17-electron, metal-centered organometallic radicals which generally display distortions in the metal's coordination-sphere geometry consistent with the unpaired electron being localized primarily at one site.⁵ The relatively complicated ESR spectrum of **1** in hexanes (Figure 1) also indicates that there is considerable delocalization of the unpaired electron throughout the molecule. Thus, the spectrum exhibits signals manifesting couplings of the unpaired electron to the five Cp ring protons, to the ³¹P nucleus, to the ¹⁴N nucleus,¹⁸ to both of the diastereotopic methylene protons, and to ⁵³Cr. This spectrum contrasts with the ESR spectra exhibited by the $\text{CpCr}(\text{NO})(\text{PPh}_3)\text{X}$ (X = Cl, Br, I) precursor complexes, all of which display features indicative of more localization of their unpaired electrons.⁸

Complex **1**, like most odd-electron metal complexes, is substitutionally labile.^{5b} However, unlike these other complexes, its lability is not restricted solely to the replacement of two-electron ligands. Hence, with the sagacious choice of reagents, this property of **1** can be exploited to produce novel diamagnetic complexes (Scheme I). For instance, reaction of **1** with the NO radical results in replacement of PPh_3 to produce the known alkyl dinitrosyl complex $\text{CpCr}(\text{NO})_2(\text{CH}_2\text{SiMe}_3)$ (**2**)¹⁹ in good yield. In contrast, exposure of **1** to NOPF_6 in CH_2Cl_2 results in the loss of the alkyl ligand as Me_4Si (established by GC) and the formation of $[\text{CpCr}(\text{NO})_2(\text{PPh}_3)]\text{PF}_6$ (**3**),²⁰ a previously inaccessible salt.²¹ Both of these conversions could conceivably proceed through an intermediate dinitrosyl species. Finally, treatment of **1** with 2 equiv of HSnPh_3 results in loss of the alkyl group as Me_4Si and subsequent addition of the Sn-H bond to the Cr center, thereby producing $\text{CpCr}(\text{NO})(\text{PPh}_3)(\text{H})(\text{SnPh}_3)$ (**4**),²² and Sn_2Ph_6 .

(10) Measured on a solid sample with a Johnson Matthey magnetic susceptibility balance.

(11) Crystals of **1** are monoclinic; space group $P2_1/c$; $a = 7.962$ (3) Å, $b = 15.440$ (4) Å, $c = 20.883$ (6) Å, $\beta = 90.31$ (3)°; $V = 2567.0$ Å³; $Z = 4$; absorption coefficient = 5.6 cm⁻¹; diffractometer, Enraf Nonius CAD-4F; radiation, Mo $K\alpha$ ($\lambda = 0.71069$ Å); $2\theta_{\text{max}} = 46^\circ$; $T = 200$ K; reflections = 2128 with $I > 2.5\sigma(I)$; variable parameters = 293; goodness of fit = 1.36; $R_F = 0.048$; $R_{wF} = 0.052$. The non-hydrogen atoms were refined anisotropically, and hydrogen atom coordinate shifts were linked with those of the carbon atoms to which they were bonded.

(12) Selected bond lengths (Å) and angles (deg) for **1** are Cr-P = 2.386 (2), Cr-N = 1.678 (5), Cr-C(1) = 2.096 (5), Cr-CP = 1.898, N-O = 1.216 (6), CP-Cr-P = 121.4, CP-Cr-N = 126.4, CP-Cr-C(1) = 119.0, N-Cr-P = 91.3 (2), C(1)-Cr-P = 91.2 (2), C(1)-Cr-N = 99.2 (2) where CP represents the center of mass of the cyclopentadienyl ring.

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(17) Herrmann, W. A.; Hubbard, J. L.; Bernal, I.; Korp, J. D.; Haymore, B. L.; Hillhouse, G. L. *Inorg. Chem.* 1984, 23, 2978.

(18) The couplings to the ¹⁴N and the ³¹P nuclei are similar in magnitude to those observed previously in related systems.⁸

(19) Legzdins, P.; Richter-Addo, G. B.; Wassink, B.; Einstein, F. W. B.; Jones, R. H.; Willis, A. C. *J. Am. Chem. Soc.* 1989, 111, 2097.

(20) Isolated in 60% yield. Anal. Calcd for $\text{C}_{23}\text{H}_{20}\text{N}_2\text{O}_2\text{F}_6\text{P}_2\text{Cr}$: C, 47.27; H, 3.44; N, 4.79. Found: C, 47.11; H, 3.47; N, 4.70. IR (Nujol mull) ν_{NO} 1826, 1730 cm⁻¹. FAB-MS m/z 439 [$\text{P}^+ - \text{PF}_6^-$]. ¹H NMR (CD_2Cl_2) δ 7.90-7.10 (m, 15 H, $\text{P}(\text{C}_6\text{H}_5)_3$), 5.70 (s, C_5H_5). ³¹P{¹H} NMR (CD_2Cl_2) δ 68.46 (s, PPh_3), -31.07 (septet, PF_6^- , J(P-F) = 710 Hz).

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Significantly, the synthesis of complex **3** means that it should be possible to incorporate other, more useful, ligands onto the electrophilic chromium dinitrosyl center. Furthermore, complex **4** is the first hydrido nitrosyl complex of chromium to have been isolated,²³ and its chemistry remains to be explored. Nevertheless, its manner of formation suggests that this reactivity of $\text{CpCr}(\text{NO})(\text{PPh}_3)(\text{CH}_2\text{SiMe}_3)$ could be exploited for the activation of other main group-element bonds. Efforts to realize both of these synthetic goals are currently underway.

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Supplementary Material Available: The simulated ESR spectrum of $\text{CpCr}(\text{NO})(\text{PPh}_3)(\text{CH}_2\text{SiMe}_3)$ (**1**) and a table of coupling constants and tables of fractional coordinates, equivalent isotropic thermal parameters, and selected bond distances and bond angles for the non-hydrogen atoms of $\text{CpCr}(\text{NO})(\text{PPh}_3)(\text{CH}_2\text{SiMe}_3)$ (**1**) (6 pages). Ordering information is given on any current masthead page.

(22) Anal. Calcd for $\text{C}_{41}\text{H}_{26}\text{NOPCrSn}$: C, 64.88; H, 4.74; N, 1.84. Found: C, 64.90; H, 4.82; N, 1.90. IR (Nujol mull) ν_{NO} 1620 cm⁻¹. ¹H NMR (C_6D_6) δ 8.09-7.43 (m, 15 H, $\text{Sn}(\text{C}_6\text{H}_5)_3$), 7.40-6.90 (m, 15 H, $\text{P}(\text{C}_6\text{H}_5)_3$), 4.56 (d, C_5H_5 , J(P-H) = 3 Hz), -2.47 (d, Cr-H, J(P-H) = 90.3 Hz, J(Sn-H) = 23.7 Hz). ³¹P{¹H} NMR (C_6D_6) δ 87.94 (s, PPh_3 , J(Sn-P) = 38.6 Hz).

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Synthesis and Structure of the First Base-Free Diphosphadigallate

D. A. Atwood, A. H. Cowley,* R. A. Jones,* and M. A. Mardones

Department of Chemistry
The University of Texas at Austin
Austin, Texas 78712

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Much of the current interest in the chemistry of the heavier group 13 and 15 elements has been spurred on by the desire to develop alternative compound semiconductor precursors.¹ In the context of single source precursors, most of the emphasis has been placed on the chemistry of compounds of empirical formula $\text{R}_2\text{MER}'_2$ (M = Ga, In; E = P, As, Sb).^{1,2} Information concerning less ligated species of the general type $(\text{RMER}')_n$ is much more sparse and base-free examples are confined to the cubanes $[\text{-BuAl}(\mu_3\text{-PSiPh}_3)]_4$ and $[\text{-BuGa}(\mu_3\text{-PSiPh}_3)]_4$.^{3,4} In principle, less aggregated species should be obtainable by increasing the steric demands of the M and/or E substituents. We report (i) the

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