Synthesis and Structure of a Five-Coordinate Organochromium(III) Thiolate Complex from a Chromium(II) Alkyl Precursor

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Summary: The reaction of the Cr(II) methyl complex, CrMe[N(SiMe$_2$CH$_2$PPh$_2$)$_2$], with diphenyl disulfide (PhSSPh) leads to the formation of the five-coordinate, paramagnetic complex CrMe(SPh)[N(SiMe$_2$CH$_2$PPh$_2$)$_2$] by an overall one-electron oxidation. The complex is unusual in that the phenyl thiolate moiety is terminal and does not engage in bridging to generate a dinuclear system having octahedral Cr(III) centers. The complex was characterized both in solution and in the solid state.

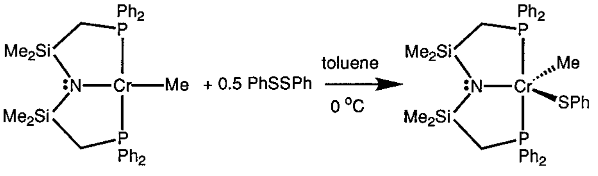
Introduction

Oxidative addition is considered to be one of the fundamental processes in organometallic chemistry.[1,2] In this reaction, a substrate interacts with a transition metal complex in an overall two-electron redox process in which the formal oxidation state of the metal center is increased by two. One-electron oxidation processes, on the other hand, have been less-studied in an organometallic context.[3] However, divalent first-row transition metals, in particular Cr, Fe, and Co, generally undergo one-electron redox processes to yield M(III) systems and not M(IV) complexes.[1,4]

One type of reagent that easily undergoes both one- and two-electron oxidation reactions with transition metals are diaryl disulfides, ArSSAr.[4] The S−S bond in diphenyl disulfide in particular is known to be easily cleaved, resulting in the formation of PhS$^\bullet$ radicals.[5] Complexes which undergo this formal one-electron oxidation with PhSSPh include [CpM(CO)$_3$]$_2$ (M = Cr,[6,7] Mo,[6] W[8,9]), [Cp*Cr(CO)$_3$]$_2$,[10] and W(^{i}Pr$_3$P)$_2$(CO)$_3$.[11] The one-electron oxidative addition of disulfides to a formally divalent first-row transition metal seems to be restricted to two studies; the dinuclear complex Cp$_2$Ta(μ-CH$_2$)$_2$-CoCp was shown to react via initial attack of the cobalt(II) center on the disulfide; in the same paper, PhSSPh was shown to react with cobaltocene, Cp$_2$Co, via an outer-sphere electron-transfer mechanism.[12] The other example is the one-electron oxidation of [Cr(H$_2$O)$_6$]$^{2+}$ by PhSSPh,[13,14] analogous to studies of similar transformations using alkyl halides.[3,15−19] This paper reports the reaction of PhSSPh with a paramagnetic, square-planar organometallic chromium(II) complex[20,21] to give an unusual five-coordinate chromium(III) complex via one-electron oxidative addition.

Results and Discussion

Addition of 0.5 equiv of PhSSPh to a brown solution of CrMe[N(SiMe$_2$CH$_2$PPh$_2$)$_2$] (**1**)[21] at 0 °C resulted in a rapid color change to purple; reaction at room temperature yielded a dark brown solution from which no product could be isolated. After workup, a solid with the empirical formula {CrMe(SPh)[N(SiMe$_2$CH$_2$PPh$_2$)$_2$]}$_x$ (**2**) was obtained (eq 1). The chromium(III) thiolate complex **2** was expected to be dinuclear, in part due to the overwhelming preference of chromium(III) to acquire an octahedral geometry[4] and also due to the high propensity of thiolates, in particular phenylthiolates, to bridge metal centers.[22] Examples of bridging chromium thiolates include [CpCr(CO)$_2$(SPh)]$_2$ and [CpCr(SPh)]$_2$S,[7] Cp$_2$Cr$_2$(μ-SPh)(μ_3-S)$_2$FeCp and CpCr(μ-SPh)$_3$Fe(μ-SPh)$_3$-CrCp,[23] and Cp$_2$W(μ-SPh)Cr(CO)$_4$.[24] However, the solution magnetic moment of **2** (Evans' method[25,26]) of 3.8



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(1) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

(2) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 2nd ed.; John Wiley & Sons: New York, 1994.

(3) Espenson, J. H. *Acc. Chem. Res.* **1992**, *25*, 222.

(4) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; John Wiley & Sons: New York, 1988.

(5) Kice, J. L. *Sulfur in Organic and Inorganic Chemistry*; Senning, A., Ed.; Marcel Dekker: New York, 1971; Vol. 1, pp 153.

(6) King, R. B. *J. Am. Chem. Soc.* **1963**, *85*, 1587.

(7) Goh, L. Y.; Tay, M. S.; Mak, T. C. W.; Wang, R.-J. *Organometallics* **1992**, *11*, 1711.

(8) Abrahamson, H. B.; Freeman, M. L. *Organometallics* **1983**, *2*, 679.

(9) Brandenburg, K. L.; Heeg, M. J.; Abrahamson, H. B. *Inorg. Chem.* **1987**, *26*, 1064.

(10) Ju, T. D.; Capps, K. B.; Lang, R. F.; Roper, G. C.; Hoff, C. D. *Inorg. Chem.* **1997**, *36*, 614.

(11) Lang, R. F.; Ju, T. D.; Kiss, G.; Hoff, C. D.; Bryan, J. C.; Kubas, G. *J. Am. Chem. Soc.* **1994**, *116*, 7917.

(12) Aubart, M. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1996**, *118*, 1793.

(13) Asher, L. E.; Deutsch, E. *Inorg. Chem.* **1973**, *12*, 1774.

(14) Asher, L. E.; Deutsch, E. *Inorg. Chem.* **1972**, *11*, 2927.

(15) Espenson, J. E. *Prog. Inorg. Chem.* **1983**, *30*, 189.

(16) Huber, T. A.; Macartney, D. H.; Baird, M. C. *Organometallics* **1993**, *12*, 4715−4717.

(17) Huber, T. A.; Macartney, D. H.; Baird, M. C. *Organometallics* **1995**, *14*, 592−602.

(18) Goulin, C. A.; Huber, T. A.; Nelson, J. M.; Macartney, D. H.; Baird, M. C. *J. Chem. Soc., Chem. Commun.* **1991**, 798−799.

(19) MacConnachie, C. A.; Nelson, J. M.; Baird, M. C. *Organometallics* **1992**, *11*, 2521−2528.

(20) Fryzuk, M. D.; Leznoff, D. B.; Rettig, S. J.; Thompson, R. C. *Inorg. Chem.* **1994**, *33*, 5528.

(21) Fryzuk, M. D.; Leznoff, D. B.; Rettig, S. J. *Organometallics* **1995**, *14*, 5193.

(22) Koschmieder, S. U.; Wilkinson, G. *Polyhedron* **1991**, *10*, 135.

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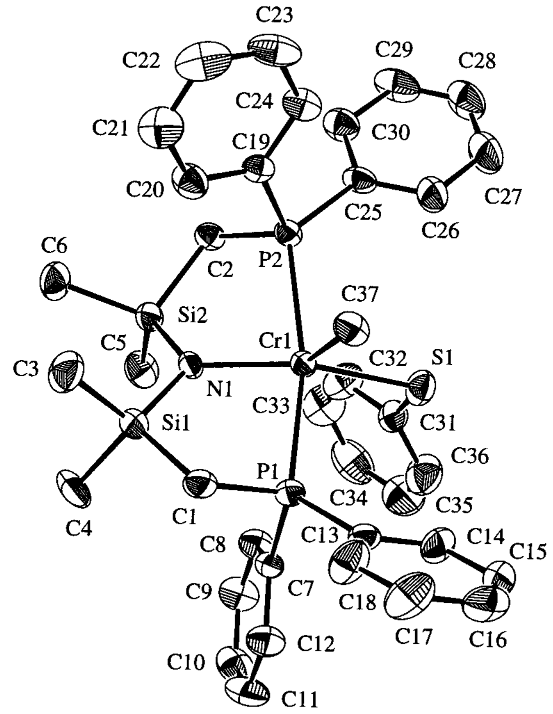

Figure 1. Molecular structure (ORTEP) and numbering scheme for $CrMe(SPh)[N(SiMe_2CH_2PPh_2)_2]$ (**2**), 33% probability ellipsoids.

Table 1. Crystallographic Data for $CrMe(SPh)[N(SiMe_2CH_2PPh_2)_2]$ (2)[a]

formula	$C_{37}H_{44}CrNP_2Si_2S$
fw	704.94
color, habit	purple, prism
cryst size, mm	0.20 × 0.25 × 0.35
cryst system	monoclinic
space group	$P2_1/c$ (No. 14)
a, Å	9.931(2)
b, Å	20.573(4)
c, Å	18.397(3)
β, deg	94.31(2)
V, Å^3	3748(1)
Z	4
ρ_{calcd}, g/cm^3	1.249
F(000)	1484
μ(Mo Kα), cm^{-1}	5.36
transmission factors	0.89−1.00
scan type	w-2q
scan range, deg in ω	1.26 + 0.35 tan θ
scan speed, deg/min	16 (up to 8 rescans)
data collected	$+h, +k, \pm l$
$2\theta_{max}$, deg	50
cryst decay, %	negligible
total no. of reflns	7221
no. of unique reflns	6789
R_{merge}	0.077
no. of reflns with $I \geq 3\sigma(I)$	2926
no. of variables	398
R	0.045
R_w	0.042
gof	1.98
max Δ/σ (last cycle)	0.001
residual density, e/Å^3	−0.28, +0.27

[a] Temperature 294 K, Rigaku AFC6S diffractometer, Mo $K\alpha$ radiation ($\lambda = 0.710\,69$ Å), graphite monochromator, takeoff angle 6.0°, aperture 6.0 × 6.0 mm at a distance of 285 mm from the crystal, stationary background counts at each end of the scan (scan/background time ratio 2:1), $\sigma^2(F^2) = [S^2(C + 4B)]/Lp^2$ (S = scan rate, C = scan count, B = normalized background count), function minimized $\sum w(|F_o| - |F_c|)^2$, where $w = 4F_o^2/\sigma^2(F_o^2)$, $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$, and gof $= [\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$. Values given for R, R_w, and gof are based on those reflections with $I \geq 3\sigma(I)$.

μ_B was consistent with a mononuclear high-spin Cr(III) complex; this value remained unchanged as the temperature was reduced to −78 °C. The mass spectrum indicated only a monomer fragment at m/e 689 ($M^+ - Me$), and the ^1H NMR spectrum consisted of a series of very broad, paramagnetically shifted resonances from which no structural information could be ascertained. An X-ray crystal structure of thiolate **2** was obtained in order to determine the nuclearity of the system.

The solid state molecular structure, shown in Figure 1, revealed that thiolate **2** was a five-coordinate chromium(III) complex with a terminal phenylthiolate ligand. The geometry of the complex could be considered as a distorted square pyramid, in which the methyl group, C(37), occupies the apical position. The trans angles of the square base are then described by P(1)−Cr−P(2) and S(1)−Cr−N(1), which are 166.30(6)° and 150.0(1)°, respectively (Table 2). Although less satisfactory, a distorted trigonal-bipyramidal geometry can be considered, in which the phosphines are axial and the equatorial angles are defined by S(1)−Cr−C(37), S(1)−Cr−N(1), and C(37)−Cr−N(1). These angles are 92.8(2)°, 150.0(1)°, and 117.2(2)°, respectively, two of which are obviously substantially distorted from the ideal 120° for trigonal-bipyramidal coordination.

The few structurally characterized examples of five-coordinate chromium(III) complexes are trigonal-bipyramidal $CrCl_3(NMe_3)_2$,[27,28] distorted trigonal-bipyramidal $Na_2CrPh_5{\cdot}3Et_2O{\cdot}THF$,[29] square-pyramidal Cr(tmtaa)Cl (tmtaa = tetramethyl-dibenzotetraaza[14]-annulene), and recently, two-legged piano-stool $[\eta^5\text{-}Me_4C_5SiMe_2\text{-}\eta^1\text{-}N^tBu]CrCH_2SiMe_3$.[30] Other non-octahedral complexes of chromium(III) include trigonal $Cr(N^iPr_2)_3$[31] and $Cr[N(SiMe_3)_2]_3$[32] and trigonal-monopyramidal $Cr[(^tBuMe_2Si)NCH_2CH_2]_3N]$.[33]

The Cr−P bond lengths of 2.449(2) and 2.479(2) Å (Table 2) are typical of high-spin Cr(III)−P bonds. Other examples include Cr−P bonds ranging from 2.429(1) to 2.444(1) Å in $[CrCl\{N(CH_2CH_2PMe_2)_2\}_2]$,[34] 2.414(2) Å in $[CpCrCl_2](dppe)$[35] (dppe = $Ph_2PCH_2CH_2PPh_2$), and 2.426(2) Å in $Cp^*CrMe_2(PMe_3)$.[36] The Cr−N bond length of 2.017(4) Å in thiolate **2** is relatively long compared to other Cr(III)−amide bond lengths, examples including 1.996(2) and 2.017(2) Å in $[CrCl\{N(CH_2CH_2PMe_2)_2\}_2]$,[34] 1.932(3) and 1.931(3) Å in Cp*Cr-

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(23) Nefedov, S. E.; Pasynskii, A. A.; Eremenko, I. L.; Gasanov, G. S.; Ellert, O. G.; Novotortsev, V. M.; Yanovsky, A. I.; Struchkov, Y. T. *J. Organomet. Chem.* **1993**, *443*, 101.

(24) Prout, K.; Rees, G. V. *Acta. Crystallogr., Sect. B* **1974**, *B30*, 2717.

(25) Evans, D. F. *J. Chem. Soc.* **1959**, 2003.

(26) Sur, S. K. *J. Magn. Reson.* **1989**, *82*, 169.

(27) Fowles, G. W. A.; Greene, P. T. *Chem. Commun.* **1966**, 784.

(28) Greene, P. T.; Russ, B. J.; Wood, J. S. *J. Chem. Soc. A* **1971**, 3636.

(29) Müller, E.; Krause, J.; Schmiedeknecht, K. *J. Organomet. Chem.* **1972**, *44*, 127.

(30) Liang, Y.; Yap, G. P. A.; Rheingold, A. L.; Theopold, K. H. *Organometallics* **1996**, *15*, 5284.

(31) Bradley, D. C.; Hursthouse, M. B.; Newing, C. W. *Chem. Commun.* **1971**, 411.

(32) Bradley, D. C.; Hursthouse, M. B.; Rodesiler, D. F. *Chem. Commun.* **1969**, 14.

(33) Cummins, C. C.; Lee, J.; Schrock, R. R.; Davis, W. D. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1501.

(34) Al-Soudani, A. R. H.; Batsanov, A. S.; Edwards, P. G.; Howard, J. A. K. *J. Chem. Soc., Dalton Trans.* **1994**, 987.

(35) Fettinger, J. C.; Mattamana, S. P.; Poli, R.; Rogers, R. D. *Organometallics* **1996**, *15*, 4211.

(36) Grohmann, A.; Köhler, F. H.; Müller, G.; Zeh, H. *Chem. Ber.* **1989**, *122*, 897.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for CrMe(SPh)[N(SiMe$_2$CH$_2$PPh$_2$)$_2$] (2)

Cr(1)−S(1)	2.371(2)	Cr(1)−P(1)	2.449(2)
Cr(1)−P(2)	2.479(2)	Cr(1)−N(1)	2.017(4)
Cr(1)−C(37)	2.054(5)	S(1)−C(31)	1.771(7)
P(1)−C(1)	1.826(6)	P(1)−C(7)	1.818(6)
P(1)−C(13)	1.829(6)	P(2)−C(2)	1.829(5)
P(2)−C(19)	1.826(6)	P(2)−C(25)	1.834(6)
Si(1)−N(1)	1.732(4)	Si(1)−C(1)	1.862(6)
Si(1)−C(3)	1.876(7)	Si(1)−C(4)	1.880(6)
Si(2)−N(1)	1.731(4)	Si(2)−C(2)	1.897(5)
Si(2)−C(5)	1.860(6)	Si(2)−C(6)	1.864(7)
S(1)−Cr(1)−P(1)	93.90(7)	S(1)−Cr(1)−P(2)	99.76(6)
S(1)−Cr(1)−N(1)	150.0(1)	S(1)−Cr(1)−C(37)	92.8(2)
P(1)−Cr(1)−P(2)	166.30(6)	P(1)−Cr(1)−N(1)	85.6(1)
P(1)−Cr(1)−C(37)	88.4(2)	P(2)−Cr(1)−N(1)	83.1(1)
P(2)−Cr(1)−C(37)	89.9(2)	N(1)−Cr(1)−C(37)	117.2(2)
Cr(1)−S(1)−C(31)	101.9(2)	Cr(1)−P(1)−C(1)	100.4(2)
Cr(1)−P(1)−C(7)	117.0(2)	Cr(1)−P(1)−C(13)	121.5(2)
C(1)−P(1)−C(7)	104.6(2)	C(1)−P(1)−C(13)	107.6(3)
C(7)−P(1)−C(13)	104.2(3)	Cr(1)−P(2)−C(2)	104.5(2)
Cr(1)−P(2)−C(19)	112.6(2)	Cr(1)−P(2)−C(25)	124.6(2)
C(2)−P(2)−C(19)	103.9(3)	C(2)−P(2)−C(25)	107.4(3)
C(19)−P(2)−C(25)	102.2(3)	N(1)−Si(1)−C(1)	107.0(2)
N(1)−Si(1)−C(3)	115.0(3)	N(1)−Si(1)−C(4)	113.5(3)
C(1)−Si(1)−C(3)	105.7(3)	C(1)−Si(1)−C(4)	108.4(3)
C(3)−Si(1)−C(4)	106.8(3)	N(1)−Si(2)−C(2)	106.8(2)
N(1)−Si(2)−C(5)	113.6(3)	N(1)−Si(2)−C(6)	114.0(2)
C(2)−Si(2)−C(5)	107.7(3)	C(2)−Si(2)−C(6)	107.5(3)
C(5)−Si(2)−C(6)	106.8(3)	Cr(1)−N(1)−Si(1)	120.7(2)
Cr(1)−N(1)−Si(2)	120.5(2)	Si(1)−N(1)−Si(2)	118.6(2)
P(1)−C(1)−Si(1)	108.0(3)	P(2)−C(2)−Si(2)	109.3(3)
S(1)−C(31)−C(32)	122.6(6)	S(1)−C(31)−C(36)	119.3(6)

(quinolinediamide),[37] and a very short 1.87 Å in Cr(N^{i}Pr$_2$)$_3$.[31] Note that the change in coordination number and geometry does not affect these bond lengths to any great extent. The Cr−S bond length of 2.371(2) Å is unremarkable and can be compared with terminal Cr(III)−S bonds of 2.389(5) Å in [(en)Cr(SCH$_2$CH$_2$NH$_2$)$_2$]ClO$_4$,[38] 2.364(5) Å (average) in (PPh$_4$)Na[Cr$_3$(SCH$_2$CH$_2$O)$_6$],[39] and 2.396(2) Å (average) in Cr(CS$_2$NEt$_2$)$_3$.[40] Interestingly, the Cr(III)−S bond lengths in bridging phenylthiolates are not that different. The Cr−S bond lengths in Cp$_2$Cr$_2$(μ-SPh)(μ_3-S)$_2$FeCp and CpCr(μ-SPh)$_3$Fe(μ-SPh)$_3$CrCp[23] range from 2.336(3) to 2.383(8) Å, and in [CpCr(μ-SPh)]$_2$S the range is from 2.365(1) to 2.383(1) Å.[7] Note that the Cr−S(1)−C(31) bond angle of 101.9(2)° in **2** implies that the second lone pair on the thiolate is not interacting with the metal; a bond angle of closer to 180° would be expected in that situation. A Cr(II) phosphine thiolate, namely *trans*-Cr(SH)$_2$(dmpe)$_2$, has been reported.[41]

The Cr(III)−C(37) bond length of 2.054(5) Å in **2** is quite short and can be compared to Cr(III)−Me bond lengths of 2.09(2) and 2.14(2) Å in octahedral, neutral CrMe$_3$[^{t}BuSi(CH$_2$PMe$_2$)$_3$],[42] 2.067(5) Å in Cp*CrMe$_2$(PMe$_3$),[36] 2.073(3) Å in [CpCrMe]$_2$(μ-Cl)$_2$,[43] and 2.087(2) Å in [Cp*CrMe]$_2$(μ-Cl)$_2$.[44] A very long Cr−C bond length of 2.300(15) Å in Li$_3$CrMe$_6$·3C$_4$H$_8$O$_2$ can be attributed to the trianionic nature of the complex.[45] The only other comparable Cr(III)−C bond length can be found in the cationic complex [Cp*CrMe(THF)$_2$]BPh$_4$, with a Cr−C bond length of 2.056(8) Å;[46] it was noted that this was the shortest Cr−C$_{\mathrm{Me}}$ bond length observed in a series of complexes prepared in the Theopold laboratory.[47] The pentacoordinate nature of thiolate **2** could be a factor in rationalizing this short bond length, although how is not clear.

Experimental Section

All manipulations were performed under an atmosphere of dry, oxygen-free dinitrogen or argon by means of standard Schlenk or glovebox techniques. The glovebox used was a Vacuum Atmospheres HE-553-2 workstation equipped with a MO-40-2H purification system and a −40 °C freezer. ^{1}H NMR spectroscopy was performed on a Varian XL-300 or a Bruker AC-200 instrument operating at 300 and 200 MHz, respectively, and were referenced to internal C$_6$D$_5$H (7.15 ppm). Magnetic moments were measured by a modification of Evans' method[25,26] (C$_6$D$_5$H or Cp$_2$Fe as a reference peak) on the NMR spectrometers listed above at room temperature and down to −78 °C. Microanalyses (C, H, N) were performed by Mr. P. Borda of this department.

The chromium(II) complex CrMe[N(SiMe$_2$CH$_2$PPh$_2$)$_2$] was prepared as previously described.[20] Diphenyl disulfide was sublimed prior to use. All other reagents were obtained from commercial sources and used as received. Hexanes, toluene, and THF were heated to reflux over CaH$_2$ prior to a final distillation from either sodium metal or sodium benzophenone ketyl under an Ar atmosphere. Deuterated solvents were dried by activated 3 Å molecular sieves; oxygen was removed by trap-to-trap distillation and three freeze−pump−thaw cycles.

Synthesis of CrMe(SPh)[N(SiMe$_2$CH$_2$PPh$_2$)$_2$] (2). To a red-brown solution of CrMe[N(SiMe$_2$CH$_2$PPh$_2$)$_2$] (**1**) (0.16 g, 0.27 mmol) in toluene (10 mL) cooled to 0 °C was added a solution of PhSSPh (0.03 g, 0.14 mmol) in toluene (5 mL). Immediately, the solution changed to a dark purple color. After the mixture was stirred for 1 h at 0 °C, the solution was warmed to room temperature and the solvent removed almost to dryness. The residue was quickly dissolved in 1 mL of hexanes and filtered through Celite, and the solvent was removed *in vacuo*. Recrystallization from hexanes/toluene (1 mL: 3 drops) in a −40 °C freezer yielded a thick oil, which upon agitation gave CrMe(SPh)[N(SiMe$_2$CH$_2$PPh$_2$)$_2$] (**2**) as purple crystals. Yield: 0.12 g (66%). Anal. Calcd for C$_{37}$H$_{44}$CrNP$_2$SSi$_2$·C$_7$H$_8$: C, 63.04; H, 6.29; N, 1.99. Found: C, 62.95; H, 6.36; N, 2.13. ^{1}H NMR (C$_6$D$_6$): δ 13.0, 10.6, 10.0, 6.0, 4.7, all very broad. MS: m/e 689 (M$^+$ − Me), 580 (M$^+$ − Me − SPh). $\mu_{\mathrm{eff}} = 3.8\ \mu_{\mathrm{B}}$.

X-ray Crystallographic Analysis of CrMe(SPh)[N(SiMe$_2$CH$_2$PPh$_2$)$_2$] (2). Crystallographic data appear in Table 1. The final unit-cell parameters were obtained by least-squares on the setting angles for 25 reflections with $2\theta = 21.0-28.9°$. The intensities of three standard reflections, measured every 200 reflections throughout the data collection, showed only small random fluctuations. The data were processed[48] and corrected for Lorentz and polarization effects and absorption (empirical, based on azimuthal scans).

The structure was solved by direct methods. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were fixed in calculated positions with C−H = 0.99 Å and $B_{\mathrm{H}} = 1.2B_{\text{bonded atom}}$. A

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[37] Danopoulos, A. A.; Wilkinson, G.; Sweet, T. K. N.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1996**, 271.

[38] Stein, C.; Bouma, S.; Carlson, J.; Cornelius, C.; Maeda, J.; Weschler, C.; Deutsch, E.; Hodgson, K. O. *Inorg. Chem.* **1976**, *15*, 1183.

[39] Nicholson, J. R.; Christou, G.; Wang, R.-J.; Huffman, J. C.; Chang, H.-R.; Hendrickson, D. N. *Polyhedron* **1991**, *10*, 2255.

[40] Raston, C. L.; White, A. H. *Aust. J. Chem.* **1977**, *30*, 2091.

[41] Arif, A. M.; Hefner, J. G.; Jones, R. A.; Koschmieder, S. U. *J. Coord. Chem.* **1991**, *23*, 13.

[42] Gardner, T. G.; Girolami, G. S. *J. Chem. Soc., Chem. Commun.* **1987**, 1758.

[43] Richeson, D. S.; Hsu, S.-W.; Fredd, N. H.; duyne, G. v.; Theopold, K. H. *J. Am. Chem. Soc.* **1986**, *108*, 8273.

[44] Herrmann, W. A.; Thiel, W. R.; Herdtweck, E. *J. Organomet. Chem.* **1988**, *353*, 323.

[45] Krausse, J.; Marx, G. *J. Organomet. Chem.* **1974**, *65*, 215.

[46] Thomas, B. J.; Noh, S. K.; Schulte, G. K.; Sendlinger, S. C.; Theopold, K. H. *J. Am. Chem. Soc.* **1991**, *113*, 893.

[47] Theopold, K. H. *Acc. Chem. Res.* **1990**, *23*, 263.

[48] *teXsan, Structure Analysis Package*; Molecular Structure Corp.: The Woodlands, TX, 1995.

secondary extinction correction was applied (Zachariasen type, isotropic), and the final value of the extinction coefficient was $3.4(6) \times 10^{-7}$. Neutral-atom scattering factors and anomalous dispersion corrections were taken from the *International Tables for X-ray Crystallography*.[49]

Selected bond lengths and bond angles appear in Table 2. Tables of final atomic coordinates and equivalent isotropic thermal parameters, anisotropic thermal parameters, complete bond lengths and angles, torsion angles, intermolecular contacts, and least-squares planes are included as Supporting Information.

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Supporting Information Available: Tables of final atomic coordinates and equivalent isotropic thermal parameters, anisotropic thermal parameters, complete bond lengths and angles, torsion angles, intermolecular contacts, and least-squares planes (25 pages). Ordering information is given on any current masthead page.

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(49) (a) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K. (present distributor Kluwer Academic Publishers: Boston, MA), 1974; Vol. IV, pp 99−102. (b) *International Tables for Crystallography*; Kluwer Academic Publishers: Boston, MA, 1992; Vol. C, pp 200−206.