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Synthesis and Characterization of $[Cr(CO)_5\{S{=}CHCH{=}C(SEt)_2\}]$ and $[Cr(CO)_5\{S{=}C(SCH{=}CH_2)SEt\}]$ by Ring-opening of 1,3-Dithiolane-2-thione: Crystal and Molecular Structure of $[Cr(CO)_5\{S{=}CHCH{=}C(SEt)_2\}]$ †

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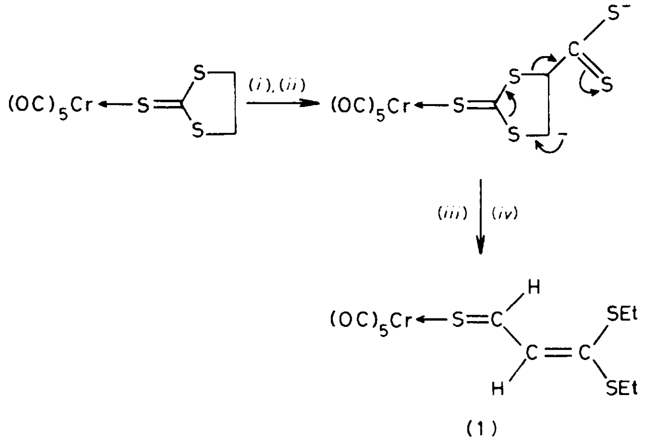
The compound $[Cr(CO)_5\{S{=}CS(CH_2)_2S\}]$ reacted with $Li(NPr^i_2)$, CS_2, and $[Et_3O][BF_4]$ to afford either $[Cr(CO)_5\{S{=}CHCH{=}C(SEt)_2\}]$ (1) or $[Cr(CO)_5\{S{=}C(SCH{=}CH_2)SEt\}]$ (2) depending upon the reaction conditions employed. The crystal structure of the co-ordinated thioaldehyde (1) was determined [orthorhombic, space group *Pbcm*, a = 11.530(5), b = 18.745(9), c = 7.889(4) Å, and Z = 4] and refined to R = 0.040 and R' = 0.038. All the atoms except those of four axial CO ligands and some hydrogens lie in one plane.

Very few stable thioaldehyde compounds are known; extensive electron delocalization seems to be a necessary condition for their existence.[1] We report here on the preparation and structure of an α,β-unsaturated thioaldehyde complex, $[Cr(CO)_5\{S{=}CHCH{=}C(SEt)_2\}]$, in which sulphur atoms contribute to the delocalization.

Vinyl sulphides have known synthetic applications and various methods for their synthesis exist.[2] None of these methods, however, makes use of saturated organosulphur functions as starting materials, and the preparation of the complex $[Cr(CO)_5\{S{=}C(SCH{=}CH_2)SEt\}]$ from $[Cr(CO)_5\{S{=}CS(CH_2)_2S\}]$ presents a novel procedure.

Results and Discussion

When $[Cr(CO)_5\{S{=}CS(CH_2)_2S\}]$, a co-ordination compound of 1,3-dithiolane-2-thione, was deprotonated at −78 °C with lithium di-isopropylamide, $Li(NPr^i_2)$, in tetrahydrofuran (thf), reacted with CS_2 and alkylated with $[Et_3O][BF_4]$ in CH_2Cl_2 at room temperature, allowing sufficient time intervals (see Experimental section) between consecutive additions, the thioaldehyde complex, $[Cr(CO)_5\{S{=}CHCH{=}C(SEt)_2\}]$ (1), was isolated in very low yield (0.8%). This intensely blue compound is stable in the solid state and in solution at room temperature and is soluble in both polar and non-polar solvents. Spectroscopic and analytical data alone could not unequivocally determine the structure of the compound, and an *X*-ray crystallographic study was undertaken. The formation of (1) does not take place in the absence of CS_2, but no net uptake of CS_2 occurs. A reaction utilizing ^{14}C-labelled CS_2 proved that added CS_2 was incorporated into the product. The reaction pathway in Scheme 1 rationalizes this result.



(1)

Scheme 1. (*i*) $Li(NPr^i_2)$, (*ii*) CS_2, (*iii*) $-CS_2$, (*iv*) $[Et_3O][BF_4]$

A reaction in which CS_2 has no part took place when $[Cr(CO)_5\{S{=}CS(CH_2)_2S\}]$, CS_2, and $[Et_3O][BF_4]$ were added immediately after one another to a thf solution of $Li(NPr^i_2)$ at −85 °C. The trithiocarbonate complex $[Cr(CO)_5\{S{=}C(SCH{=}CH_2)SEt\}]$ (2) is formed in relatively high yield (41%), even if CS_2 is omitted from the reaction mixture. The red crystalline complex is stable in the solid state and fairly stable in solution at room temperature; it is soluble in polar as well as non-polar solvents.

A possible mechanism for the reaction involves α,β-elimination (formerly called α-elimination[3]) of hydrogen upon deprotonation of the thioether alkylated cation (Scheme 2). The abstraction of the β hydrogen is most probably made possible only by the presence of the activating sulphur atom in the γ position.

The i.r. spectra are typical of pentacarbonylchromium complexes, although, by the presence of B_1 bands, the new complexes show a deviation from the idealized local C_{4v} carbonyl symmetry, which is not apparent in the starting compound, $[Cr(CO)_5\{S{=}CS(CH_2)_2S\}]$ (Table 1). Both compounds exhibit a shoulder, characteristic of sulphur-donor compounds, on the low-frequency side of the intense E band. Note (Table 1) that the Cotton–Kraihanzel force constant k_1, which refers to the *trans* carbonyl ligand, is smaller for the two trithiocarbonate ligands $S{=}C(SCH{=}CH_2)SEt$ (1 525 N m^{-1}) and $S{=}CS(CH_2)_2S$ (1 528 N m^{-1}) than for the other two thiones (1 546 N m^{-1}). The former values correspond well with an average k_1 of 1 530 N m^{-1} calculated for a series of pentacarbonyl-sulphide compounds.[4]

An alternative ylidic structure for (2), $[Cr(CO)_5\{S{=}\overset{-}{C}SCH_2CH\overset{+}{S}Et\}]$, was discarded on the basis of its ^{13}C and

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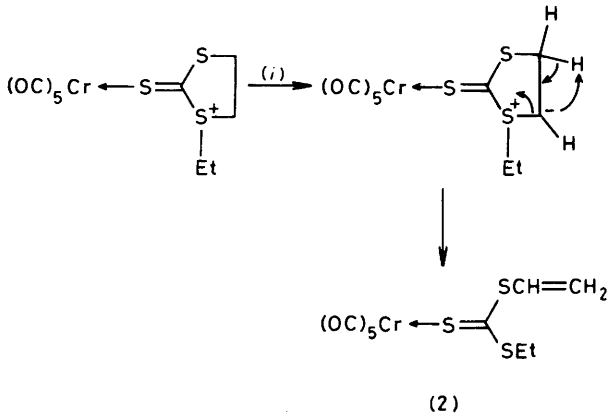
† [3,3-Bis(ethylthio)prop-2-enethial]pentacarbonylchromium(0).

Supplementary data available (No. SUP 56006, 8 pp.): observed and calculated structure factors, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Table 1. I.r. data [a] for pentacarbonyl–thione complexes of chromium(0)

Complex	ν(CO)/cm^{-1}				Cotton–Kraihanzel force constants [b]/N m^{-1}		
	$A_1^{(1)}$	B_1	E	$A_1^{(2)}$	k_1	k_2	k_i
(1) $[Cr(CO)_5\{S{=}CHCH{=}C(SEt)_2\}]$	2 060m	1 985vw	1 945s		1 546	1 584	28
(2) $[Cr(CO)_5\{S{=}C(SCH{=}CH_2)SEt\}]$	2 068w	1 985w	1 948s	1 932m	1 525	1 592	30
$[Cr(CO)_5\{S{=}\overline{CS(CH_2)_2S}\}]$ [c]	2 070		1 950	1 934	1 528	1 595	30
$[Cr(CO)_5(S{=}CMe_2)]$ [d]	2 062	1 980	1 953	1 946	1 546	1 594	27

[a] Hexane solutions. [b] k_1 and k_2 are the stretching parameters for CO *trans* to the thione ligand and to CO respectively; k_i is the approximate averaged *cis* interaction parameter. [c] ν(CO) from ref. 1. [d] ν(CO) from R. G. W. Gingerich and R. J. Angelici, *J. Organomet. Chem.*, 1977, **132**, 377.



Scheme 2. (*i*) $Li(NPr^i_2)$

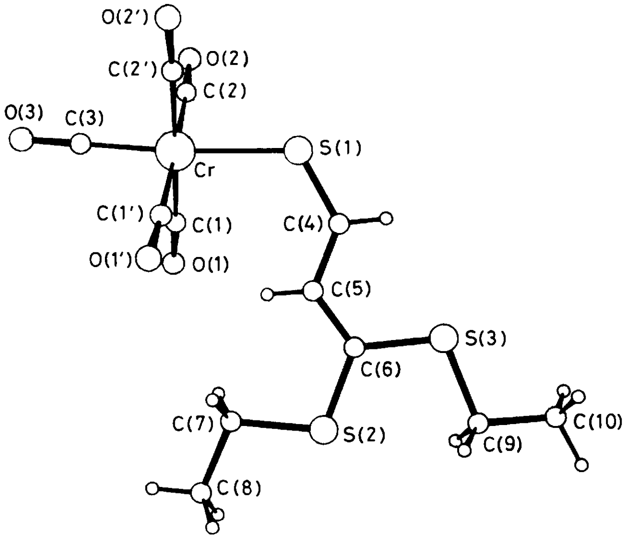


Figure 1. A perspective view of $[Cr(CO)_5\{S{=}CHCH{=}C(SEt)_2\}]$ (1) perpendicular to the mirror plane, illustrating the molecular structure and the labelling scheme; atoms are drawn as spheres of arbitrary radius

^{13}C-$\{^1H\}$ n.m.r. spectra, showing the presence of an sp^2 hybridized carbon atom for CH_2.

Structure of $[Cr(CO)_5\{S{=}CHCH{=}C(SEt)_2\}]$ (1).—The molecular structure of (1) is illustrated in Figure 1 with the crystallographic numbering scheme. Unit-cell contents of this complex are depicted in Figure 2. Final atomic co-ordinates are given in Table 2 and bond lengths and angles in Tables 3 and 4. The C–H bond distances are not tabulated but vary between 0.92 and 1.07 Å with e.s.d.s of less than 0.05 Å.

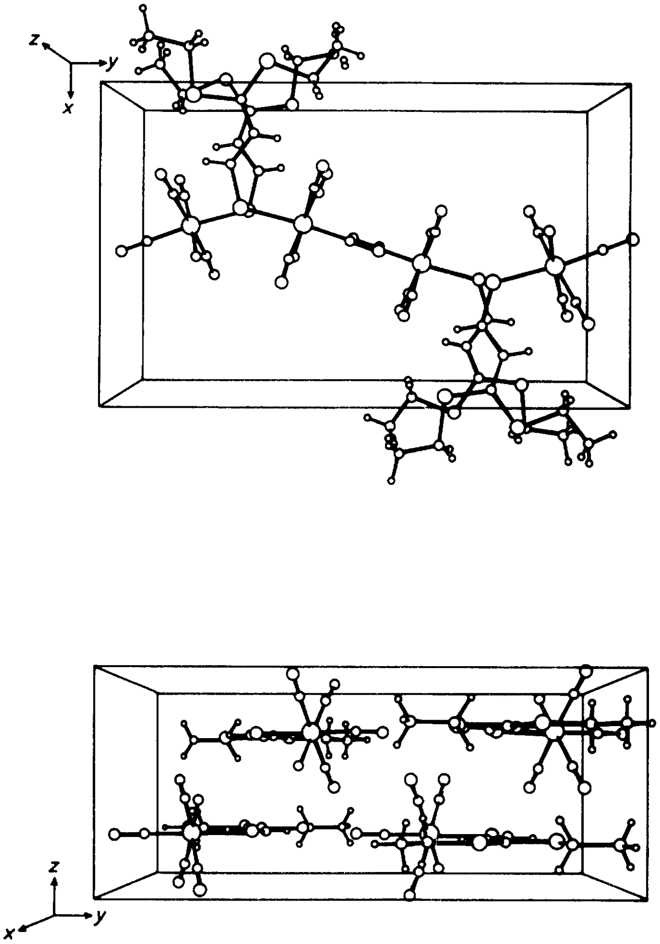


Figure 2. Perspective views of the unit cell and contents of (1) showing the mirror planes and crystal packing

Octahedral symmetry is retained around the metal atom, with angles varying between 89.3 and 94.0° (Table 4). The *trans* Cr–CO bond [1.850(5) Å] is significantly shorter than the four *cis* Cr–CO bonds (average = 1.900 Å) (Table 3), which reflects the lower π acceptor–σ donor ratio of the thione function, as compared to co-ordinated CO. These bond lengths are, within experimental error, the same as those observed in the related complex $[Cr(CO)_5(S{=}CMe_2)]$.[5]

Table 2. Atomic co-ordinates (non-H atoms × 10^4; H atoms × 10^3) for $[Cr(CO)_5\{S{=}CHCH{=}C(SEt)_2\}$ (1)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Cr	4 341(1)	1 234(0)	2 500(0)
S(1)	3 807(1)	2 462(1)	2 500(0)
S(2)	−889(1)	1 949(1)	2 500(0)
S(3)	94(1)	3 401(1)	2 500(0)
C(1)	3 255(2)	982(2)	802(4)
O(1)	2 603(2)	800(1)	− 193(3)
C(2)	5 453(2)	1 467(2)	798(5)
O(2)	6 150(2)	1 583(2)	−189(4)
C(3)	4 881(4)	304(3)	2 500(0)
O(3)	5 212(4)	−273(2)	2 500(0)
C(4)	2 424(4)	2 670(2)	2 500(0)
C(5)	1 448(3)	2 224(2)	2 500(0)
C(6)	331(3)	2 484(2)	2 500(0)
C(7)	−341(4)	1 047(2)	2 500(0)
C(8)	−1 384(5)	554(3)	2 500(0)
C(9)	−1 459(4)	3 515(3)	2 500(0)
C(10)	−1 698(5)	4 307(3)	2 500(0)
H(4)	231	315	250
H(5)	158	175	250
H(7)	13	96	149
H(81)	−109	7	250
H(82)	−191	61	156
H(9)	−173	326	147
H(101)	−259	443	250
H(102)	−138	452	156

Table 3. Bond lengths (Å) for complex (1)

Cr–S(1)	2.383(1)	S(3)–C(9)	1.804(4)
Cr–C(1)	1.893(3)	C(4)–C(5)	1.401(5)
Cr–C(2)	1.908(4)	C(5)–C(6)	1.377(5)
Cr–C(3)	1.850(5)	C(7)–C(8)	1.518(7)
S(1)–C(4)	1.642(4)	C(9)–C(10)	1.510(7)
S(2)–C(6)	1.729(4)	C(1)–O(1)	1.140(3)
S(2)–C(7)	1.804(5)	C(2)–O(2)	1.140(4)
S(3)–C(6)	1.741(4)	C(3)–O(3)	1.150(5)

Table 4. Bond angles (°) for complex (1)

S(1)–Cr–C(1)	94.0(1)	C(6)–S(3)–C(9)	105.8(2)
S(1)–Cr–C(2)	87.3(1)	S(1)–C(4)–C(5)	129.7(3)
S(1)–Cr–C(3)	175.3(2)	C(4)–C(5)–C(6)	122.7(4)
C(1)–Cr–C(2)	90.2(1)	C(5)–C(6)–S(2)	123.8(3)
C(1)–Cr–C(3)	89.3(1)	C(5)–C(6)–S(3)	119.7(3)
C(2)–Cr–C(3)	89.4(1)	S(2)–C(6)–S(3)	116.4(2)
C(1)–Cr–C(1′)	90.1(1)	S(2)–C(7)–C(8)	107.0(4)
C(2)–Cr–C(1′)	178.7(1)	S(3)–C(9)–C(10)	107.3(4)
C(2)–Cr–C(2′)	89.5(1)	Cr–C(1)–O(1)	176.9(3)
Cr–S(1)–C(4)	118.7(2)	Cr–C(2)–O(2)	176.9(3)
C(6)–S(2)–C(7)	104.9(2)	Cr–C(3)–O(3)	179.7(2)

The planarity of the organic ligand is to be expected in view of the sp^2 hybridization of C(6), apparent from the bond angles approximating to 120° at this atom. Packing considerations most probably cause the confinement of the two SEt groups, in which the angles denote sp^3 hybridization, to the plane of the above mentioned atoms.

The fact that extensive delocalization of the double bonds occurs, emerges from the equivalent lengths [1.401(5) Å and 1.377(5) Å respectively] of the C(4)–C(5) and C(5)=C(6) bonds and the relatively small difference between S(1)=C(4) [1.642(4) Å], S(2)–C(6) [1.729(4) Å], and S(3)–C(6) [1.741(4) Å].

Experimental

General.—All solvents were dried and saturated with nitrogen before use. Manipulations were carried out under nitrogen. Di-isopropylamine (BDH) was used without further purification and LiBu,[6] $[Cr(CO)_5\{S{=}\overline{CS(CH_2)_2S}\}]$,[7] and $[Et_3O][BF_4]$ [8] were prepared according to published methods. Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 297, ^1H n.m.r. spectra on a Bruker WP-80, and ^{13}C n.m.r. spectra on a Bruker WP-20. Molecular-ion (M^+) determinations were carried out on a Hitachi–Perkin-Elmer RMU-6H (70 eV) instrument and analyses were performed by the Microanalytisches Laboratory of Bonn.

Preparation of $[Cr(CO)_5\{S{=}CHCH{=}C(SEt)_2\}]$ (1).—A solution of $Li(NPr^i{}_2)$ was prepared by slowly adding LiBu (5 mmol, 1.6 mol dm^{-3} in hexane) to di-isopropylamine (0.5 cm^3, 5 mmol) in thf (10 cm^3) at −78 °C. After 10 min, $[Cr(CO)_5\{S{=}\overline{CS(CH_2)_2S}\}]$ (1.64 g, 5 mmol) was added. The reaction mixture was allowed to warm up, and was stirred at room temperature for 4 h before an excess of CS_2 (1.2 cm^3, 20 mmol) was added. After 6 h, the solvent was removed under vacuum and the residue redissolved and alkylated with a small excess of $[Et_3O][BF_4]$ in dichloromethane at −10 °C. Repeated chromatography on SiO_2 (−20 °C) with hexane–diethyl ether (100 : 1) as eluant yielded the pure compound which crystallized as blue needles at −80 °C from hexane (15 mg, 0.8%), m.p. 50—52 °C, M^+ = 384 (Found: C, 37.75; H, 3.25; Cr, 13.5; S, 24.6. $C_{12}H_{12}CrO_5S_3$ requires C, 37.50; H, 3.15; Cr, 13.50; S, 25.00%). ^1H N.m.r. ($CDCl_3$, 80 MHz): δ 10.70 (d, *J* = 11, 1 H, S=C*H*CH), 7.13 (d, *J* = 11, 1 H, S=CHC*H*), 3.13 (q, *J* = 7, 2 H, C*H*$_2$CH$_3$), 3.10 (q, *J* = 7, 2 H, C*H*$_2$CH$_3$), 1.45 (t, *J* = 7, 3 H, CH$_2$C*H*$_3$), and 1.40 p.p.m. (t, *J* = 7 Hz, 3 H, CH$_2$C*H*$_3$).

Preparation of $[Cr(CO)_5\{S{=}C(SCH{=}CH_2)SEt\}]$ (2).—A solution of $Li(NPr^i{}_2)$ (2 mmol) was prepared as above and $[Cr(CO)_5\{S{=}\overline{CS(CH_2)_2S}\}]$ (0.328 g, 1 mmol) and $[Et_3O][BF_4]$ (2 mmol) added at −85 °C. The mixture was stirred at −85 °C for 1 h and allowed to warm up to room temperature. Chromatography on SiO_2 (−20 °C) with CH_2Cl_2–hexane (1 : 1) as eluant yielded a red product which crystallized as red prisms (142 mg, 41%) from hexane, m.p. 41—42 °C, M^+ = 356 (Found: C, 33.40; H, 2.40; Cr, 14.2; S, 25.9. $C_{10}H_8CrO_5S_3$ requires C, 33.70; H, 2.25; Cr, 14.60; S, 27.00%). ^1H N.m.r. ($CDCl_3$, 80 MHz): δ 687.—7.28 (m, 1 H, C*H*=CH$_2$), 5.65—6.23 (m, 2 H, CH=C*H*$_2$), 3.48 (q, *J* = 7, 2 H, C*H*$_2$CH$_3$), and 1.48 p.p.m. (t, *J* = 7 Hz, 3 H, CH$_2$C*H*$_3$). ^{13}C-{^1H} N.m.r. ($CDCl_3$, 90 MHz): δ 223.3 (C=S), 222.4 (*trans* CO), 214.6 (*cis* CO), 126.9 (*C*H=CH$_2$), 126.0 (CH=*C*H$_2$), 32.2 (*C*H$_2$CH$_3$), and 12.4 p.p.m. (CH$_2$*C*H$_3$).

Crystal Structure Determination of $[Cr(CO)_5\{S{=}CHCH{=}C(SEt)_2\}]$ (1).—A single crystal with dimensions 0.6 × 0.6 × 0.2 mm, cut off the tip of a larger flat needle, was used for data collection.

Crystal data. $C_{12}H_{12}CrO_5S_3$, *M* = 384.4, orthorhombic, *a* = 11.530(5), *b* = 18.745(9), *c* = 7.889(4) Å, *U* = 1 705 Å^3, D_m = 1.48, *Z* = 4, D_c = 1.50 g cm^{-3}, *F*(000) = 784, space group *Pbcm*, Mo-K_α radiation, λ = 0.710 7 Å, μ(Mo-K_α) = 9.8 cm^{-1}.

Data were collected with a Philips PW 1100 diffractometer to a maximum θ of 23°. A scan rate of 0.044° s^{-1} and a scan width of 1.1° θ was used; backgrounds were measured at each end of the scan for half the scan time. Three standard reflections were monitored regularly and showed no changes during the data collection. 1 299 Unique reflections were measured of which 1 148 were regarded as observed [$I/\sigma(I) > 1.65$]. All reflections with non-zero intensities (1 277) were corrected for Lorentz and polarization effects and were used in the refinement. No absorption corrections were applied.

The systematic absences $0kl$, k odd; $h0l$, l odd indicated space groups $Pbcm$ or $Pbc2_1$. The former was selected and shown to be correct by the successful refinement. All the atoms except those of four of the five carbonyl groups and some hydrogens lie in the mirror plane at $z = \frac{1}{4}$. The structure was determined by Patterson and Fourier techniques using the SHELX[9] program. The positions of the hydrogen atoms were found from difference maps and refined with a common isotropic thermal parameter. All other atoms were refined with anisotropic thermal parameters, Refinement converged to agreement indices of 0.040 for the conventional R and 0.038 for R', weighted using $1/\sigma^2$ weights. The R factors could be reduced to $R = 0.038$ and $R' = 0.035$ by removing the mirror plane and refining in space group $Pbc2_1$. The resulting model, however, showed only deviations of less than three standard deviations from the $z = \frac{1}{4}$ plane and the centrosymmetric $Pbcm$ was retained as the correct space group.

Acknowledgements

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References

1 I. Duus, in 'Comprehensive Organic Chemistry,' eds. D. Barton and W. D. Ollis, Pergamon Press, Oxford, 1979, vol. 3, p. 375.
2 G. C. Barret, in ref. 1, p. 78.
3 A. W. Johnson, 'Ylid Chemistry,' Academic Press, New York, 1966, p. 341.
4 H. G. Raubenheimer, S. Lotz, H. W. Viljoen, and A. A. Chalmers, *J. Organomet. Chem.*, 1978, **152**, 73.
5 B. A. Karcher and R. A. Jacobson, *J. Organomet. Chem.*, 1977, **132**, 387.
6 H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn, and L. S. Miller, *J. Am. Chem. Soc.*, 1949, **71**, 1499.
7 G. J. Kruger, L. Linford, H. G. Raubenheimer, and A. A. Chalmers, *J. Organomet. Chem.*, 1984, **262**, 69.
8 H. Meerwein, *Org. Synth.*, 1966, **46**, 113.
9 G. M. Sheldrick, in 'Computing in Crystallography,' eds. H. Schenk and R. Olthof-Hazelkamp, Delft University Press, 1978.

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