Synthesis, Properties, and *X*-Ray Crystal and Molecular Structures of Homoleptic Alkenyls of Tin and Chromium †

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Reaction of Li(CPh=CMe$_2$) with SnCl$_4$ or CrCl$_3$·3thf (thf = tetrahydrofuran) affords the isoleptic compounds Sn(CPh=CMe$_2$)$_4$ or [Cr(CPh=CMe$_2$)$_4$] respectively. The mode of formation and chemical properties are reported for the chromium species, and the structures of the new compounds, both of which have been determined by single-crystal *X*-ray analysis, are described.

In the preceding paper we reported the discovery of a tin(IV) derivative obtained by intermolecular oxidative addition to an organotin(II) species.[1] In the present paper we give details of the synthesis of a tetra-alkenylchromium(IV) complex starting from a chromium(III) species, and of the analogous tin(IV) compound obtained from SnCl$_4$ by simple metathetical exchange. The *X*-ray data provide an unusual opportunity for detailed structural comparisons to be made between a transition metal organometallic and an exactly analogous main-group compound. Both compounds have been mentioned in preliminary publications.[2,3]

Results and Discussion

Reaction of tin(IV) chloride with Li(CPh=CMe$_2$) in ether at −78 °C affords, after work-up, colourless air-stable crystals of SnR$_4$ (R = CPh=CMe$_2$ throughout). Treatment of CrCl$_3$·3thf (thf = tetrahydrofuran) with the same lithium reagent (4 mol) affords the chromium analogue, [CrR$_4$]. The preparations must be carried out in ether rather than thf, in which the lithium reagent is known to rearrange to an allyl derivative.[4] The present derivatives are both produced in poor yield and this is believed to be a steric effect, at least for the tin compound, since the lithium reagent more readily organylates less bulky substrates: SnMe$_3$R, SnMe$_2$R$_2$, and SnR$_4$ were obtained in 95%, 65%, and 16% yields respectively.[2] The yields do not appear to be sensitive to slight changes in the stoicheiometry; as has been found with the homoleptic alkyls [M(CH$_2$SiMe$_3$)$_4$] (M = Zr or Hf).[5] Use of the Grignard reagent MgRBr did not afford an isolable chromium alkenyl, despite the generally lower reducing power of the magnesium compared with the lithium reagent.

The details of the oxidative step in the chromium synthesis are not known, but two paths appear reasonable. First, the initial formation of Li[CrR$_4$] which subsequently reacts with an oxidant such as oxygen, as has been suggested for the formation of [Ti(C$_6$H$_2$Me$_3$-2,4,6)$_4$] from TiCl$_3$ and mesityllithium[6] and found for homoleptic alkyls, *e.g.* [Cr(CH$_2$SiMe$_3$)$_4$].[7] The alternative route involves the formation of [CrR$_3$] which undergoes a radical transfer, either thermally or photochemically, giving [CrR$_4$] and reduced chromium species; such a pathway has been proposed for the formation of [CrPr$^i{}_4$].[8] Of the two possibilities, we believe the latter to be operative in this instance for the following reasons. Addition of the lithium reagent to CrCl$_3$·3thf in ether at −78 °C produces a colour change from purple to deep blue, and crystals of this colour separate from solution. On warming, the colour changes again between −60 and −50 °C to green, always accompanied by a brown material. Passage of oxygen through the blue solution causes instantaneous decomposition to intractable materials, whereas allowing the mixture to warm without any manipulation or additions gives the chromium(IV) compound. The blue material is extremely air- and moisture-sensitive, while the brown product is pyrophoric. We therefore believe that the initial chromium(III) product is [CrR$_3$] (blue crystals) which dissociates thermally to yield R$^\bullet$, and reduced chromium species (the brown material). Involatile oils, R$_2$, were obtained from the reaction mixtures, in agreement with the proposed reaction pathway. Further evidence comes from the isolation of [CrR$_3$(thf)] and [CrR$_3$(tmen)] from addition of thf and tmen (tetramethylethylenediamine) respectively to the blue solution at low temperature. U.v. photolysis of the reaction mixture did not materially affect the yield, but as the thermal reaction sets in at −60 °C this is perhaps not surprising.

The complex [CrR$_4$] forms dark green crystals which are not particularly sensitive to air, although they turn white on prolonged exposure. The compound is paramagnetic, and the ^{1}H n.m.r. shows broadened signals for the phenyl and methyl regions with satisfactory integration. The magnetic moment, determined by the Evans method in CDCl$_3$, is 2.81 B.M., in good agreement with the spin-only value (2.83 B.M.) predicted for a d^2 tetrahedral ion. The e.s.r. spectrum in hexane at 306 K shows only a broad signal near $g = 2$ which remains essentially unaltered on cooling. However, at 187 K a second, sharper signal also near $g = 2$ appears and sharpens further as the temperature is lowered. At 150 K a new signal at 1 250 G appears which we tentatively assign (in view of its relative weakness) to the 'forbidden' $\Delta M = 2$ transition of the triplet state.

On reaction with either chlorine or dry hydrogen chloride a transient red colour is seen, and this we believe to be the unstable chromium(IV) chloride observed transiently in similar decompositions of tetra-alkylchromium(IV) compounds.[7] Treatment of the tetra-alkenyl with HgCl$_2$ in diethyl ether affords the alkenylmercury(II) chloride as a white flaky solid. This was obtained in 49% yield after crystallisation from light petroleum and characterised by n.m.r. spectroscopy and elemental analysis. Some metallic mercury also appears to be formed in this reaction.

Treatment of the chromium(IV) alkenyl with methyl

† *Supplementary data available* (No. SUP 23479, 18 pp.): observed and calculated structure factors, isotropic and anisotropic thermal parameters. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Non-S.I. units employed: B.M. = 9.27 × 10^{-24} A m^2; G = 10^{-4} T.

Table 1. Bond lengths (Å) and angles (°) in $M(CPh{=}CMe_2)_4$ (M = Sn or Cr) *

(*a*) Bond lengths

	M = Sn	M = Cr
Round M		
M–C(1)	2.174(7)	2.049(12)
M–C(11)	2.173(7)	2.027(13)
M–C(21)	2.179(7)	2.032(13)
M–C(31)	2.173(6)	2.033(11)
$M \cdots C_\beta$ contact distances		
M ··· C(2)	3.11	2.97
M ··· C(12)	3.11	3.00
M ··· C(22)	3.11	2.96
M ··· C(32)	3.10	2.97
Ligand 1		
C(1)–C(2)	1.327(10)	1.331(16)
C(1)–C(5)	1.484(9)	1.501(16)
C(2)–C(3)	1.513(10)	1.511(17)
C(2)–C(4)	1.511(10)	1.521(19)
C(Ph)–C(Ph)	1.369(11)—1.396(10)	1.327(18)—1.421(17)
Ligand 2		
C(11)–C(12)	1.332(10)	1.353(17)
C(11)–C(15)	1.497(10)	1.445(16)
C(12)–C(13)	1.511(10)	1.523(18)
C(12)–C(14)	1.521(10)	1.507(17)
C(Ph)–C(Ph)	1.359(13)—1.390(11)	1.357(18)—1.415(16)
Ligand 3		
C(21)–C(22)	1.319(10)	1.339(16)
C(21)–C(25)	1.503(10)	1.476(17)
C(22)–C(23)	1.516(11)	1.498(18)
C(22)–C(24)	1.527(11)	1.537(18)
C(Ph)–C(Ph)	1.356(15)—1.408(11)	1.360(21)—1.421(22)
Ligand 4		
C(31)–C(32)	1.316(10)	1.338(15)
C(31)–C(35)	1.496(10)	1.470(15)
C(32)–C(33)	1.513(10)	1.494(17)
C(32)–C(34)	1.514(10)	1.523(16)
C(Ph)–C(Ph)	1.359(13)—1.390(10)	1.370(18)—1.411(17)

(*b*) Bond angles

	M = Sn	M = Cr
Round M		
C(11)–M–C(1)	106.5(3)	107.4(6)
C(21)–M–C(1)	116.4(3)	116.4(6)
C(21)–M–C(11)	105.5(3)	105.6(6)
C(31)–M–C(1)	106.3(3)	106.7(6)
C(31)–M–C(11)	115.3(3)	115.9(6)
C(31)–M–C(21)	107.3(3)	105.3(6)
Ligand 1		
M–C(1)–C(2)	123.3(5)	121.7(11)
M–C(1)–C(5)	114.4(5)	117.9(10)
C(1)–C(2)–C(3)	123.5(7)	124.2(14)
C(1)–C(2)–C(4)	123.8(7)	123.9(14)
C(3)–C(2)–C(4)	112.7(7)	111.9(14)
C(2)–C(1)–C(5)	122.2(6)	120.2(11)
Ligand 2		
M–C(11)–C(12)	123.4(5)	124.2(11)
M–C(11)–C(15)	114.3(5)	114.8(10)
C(11)–C(12)–C(13)	123.1(7)	124.6(14)
C(11)–C(12)–C(14)	124.0(7)	122.6(14)
C(13)–C(12)–C(14)	112.9(7)	112.8(13)
C(12)–C(11)–C(15)	122.2(7)	120.5(14)
Ligand 3		
M–C(21)–C(22)	123.3(6)	121.1(11)
M–C(21)–C(25)	114.2(5)	118.0(11)
C(21)–C(22)–C(23)	123.5(7)	125.7(14)
C(21)–C(22)–C(24)	123.8(8)	120.9(14)
C(23)–C(22)–C(24)	112.7(7)	113.4(13)
C(22)–C(21)–C(25)	122.2(7)	120.9(13)
Ligand 4		
M–C(31)–C(32)	122.9(5)	119.7(10)
M–C(31)–C(35)	115.9(5)	118.1(9)
C(31)–C(32)–C(33)	124.0(7)	124.5(13)
C(31)–C(32)–C(34)	123.8(7)	122.7(13)
C(33)–C(32)–C(34)	112.1(7)	112.9(13)
C(32)–C(31)–C(35)	121.1(6)	121.9(12)

* The crystals are not isostructural; the ligand numbering in the two molecules has simply been assigned to be as closely analogous as possible.

isocyanide in benzene resulted in insertion of only one mole of isocyanide, as shown by the relative areas of the appropriate n.m.r. peaks. In this respect the compound differs from the Zr analogue which is unusual in undergoing tetra-insertion.[9] Attempts to insert reagents with reactivity towards 1,2-dipolar systems were unsuccessful; for example, dimethylacetylenedicarboxylate was polymerised by $[CrR_4]$, though no chromium-containing products could be isolated.

As described above, the synthesis is believed to proceed *via* blue crystals of the highly air- and moisture-sensitive $[CrR_3]$. All attempts to isolate this species, which starts to decompose thermally at temperatures above −60 °C, were unsuccessful. However, low-temperature addition of donor species to solutions believed to contain the chromium(III) alkenyl led to the formation of highly sensitive but isolable adducts. Thus addition of thf to the ether solution caused a change of colour from blue to green and crystals which analysed satisfactorily for $[CrR_3(thf)]$ were obtained. Similar addition of tmen led to the isolation of green crystals which analysed satisfactorily for $[CrR_3(tmen)]$. The isolation of a mono-thf adduct is perhaps surprising, and it is quite possible that the species is associated. It was, unfortunately, too sensitive for isopiestic molecular weight determination. Reaction of the supposed $[CrR_3]$ species with bipyridyl did not lead to characterisable products, although solid adducts of variable elemental composition were precipitated from solution.

X-*Ray Structures*.—In a brief preliminary report on the structure of $[Cr(CPh{=}CMe_2)_4]$,[3] the structural feature of note was the regularity of the ligand geometry and absence of marked differences from the preliminary structural information available for $Sn(CPh{=}CMe_2)_4$ at that time.

Both compounds have now been studied under the same experimental conditions, refined using the same procedure (save that isotropic thermal parameters only are used for all carbon atoms in the refinement of the chromium structure), and compared in detail. Although both compounds crystallise in space group $P2_1/c$, they are not isomorphous, having different cell constants, and, as expected for the slightly smaller chromium atom, the Cr compound has a smaller cell volume. However, the numbering scheme adopted for the two sets of atoms has been chosen to emphasise the similarities in molecular geometry, since the four ligands cannot be uniquely identified, or compared individually.

To our knowledge, a structural comparison of analogous tin and chromium MR_4 compounds has not previously been

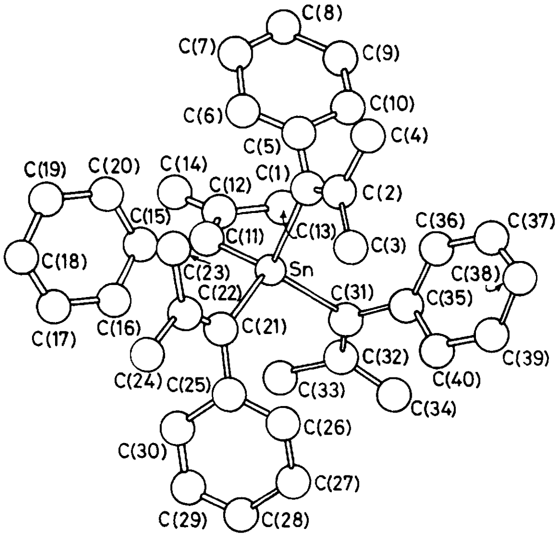

Figure 1. The molecular geometry of $Sn(CPh{=}CMe_2)_4$

possible. The most similar comparison is probably that made for the tetrabenzyl structures $M(CH_2Ph)_4$ [10] (M = Sn, Ti, Zr, or Hf) in which the irregular bond angles around the Ti, Zr, and Hf atoms were in contrast to the tetrahedral geometry around the tin. This difference has been ascribed to an interaction between the phenyl rings and the empty metal *d* orbitals in the transition-metal species. In the present case, it is hard to see any effect of the *d* electrons or orbitals on molecular geometry (but see discussion below) and it is possible that the small differences between the structures are entirely due to the different radii of the metal atoms.

The closely similar nature of the molecular geometries is seen in Table 1, in which individual bond lengths and angles are available for comparison. Both molecules have four equal M–C bond lengths, mean value 2.175(7) (M = Sn) and 2.036(13) Å (M = Cr). The bond angles around the metal show, in both cases, approximate $\bar{4}$ (S_4) symmetry, which is borne out by the overall ligand geometries (Figures 1 and 2). The striking feature is the remarkably close correspondence between the sets of angles in the two structures.

The four alkenyl ligands are closely similar in each compound (Table 1). When the ligands in the two compounds are compared, there are consistent but small * differences between the two sets of ligand geometries. Noteworthy among these differences are the (consistently) longer C(1)–C(2) distances of the four ligands in the chromium structure. This is in harmony with a small but significant interaction between the C(1)–$p(\pi)$ orbital and appropriate metal *d* orbitals, resulting in decreased $p(\pi)$–$p(\pi)$ bonding in the ligand. Unfortunately, the Cr–C bond lengths in the homoleptic alkyl $[Cr(CH_2CMe_2Ph)_4]$ [11] are not known with sufficient accuracy to draw conclusions about concomitant shortening of the metal–carbon bond lengths. Curiously, it is the tin compound which shows the greater deviation from regular sp^2 ligand geometry; there does not appear to be any obvious reason for this. However, in neither case do we find the large deviations observed for the same ligand in the $[M(\eta\text{-}C_5H_5)_2Cl(CPh{=}CMe_2)]$ (M = Ti, Zr, or Hf)

* Analysis of these differences shows that they are not statistically significant ($Z = -0.81$, regarding the individual bond lengths within each molecule as strongly interdependent). However, we feel that the lower value for the corresponding bonds in the tin compound in *all four cases* suggests that there is a real difference.

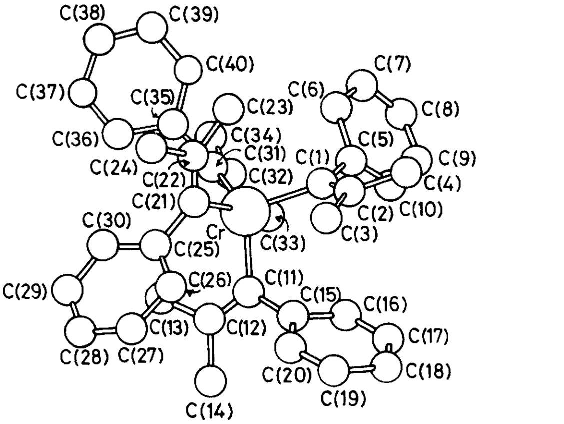

Figure 2. The molecular geometry of $[Cr(CPh{=}CMe_2)_4]$

compounds,[12] in which M–C(sp^2)–C(Ph) angles as small as 100° are observed. The angle contractions in these cases therefore are approximately 20°, as large as those found in the tetrabenzyls of Ti, Zr, or Hf, and probably also due to interaction of the phenyl ring with empty metal *d* orbitals.

In both the present compounds the alkenyl planes are more truly planar than in the sterically crowded $Sn(CPh{=}CPh_2)_3Bu^n$,[1] and the dihedral angles between alkenyl planes show close agreement in the two cases, with five of the six possible angles close to 110°, and the sixth smaller. Inter- and intra-ligand interactions clearly dominate the geometry. The intraligand phenyl/alkenyl plane dihedral angles (Table 2) are larger in the chromium compound, approaching orthogonality for ligand 3. The lower limit to this dihedral angle is presumably set by the metal–*o*-carbon atom contact distance; thus it is geometrically impossible for the phenyl to be conjugated with the alkenyl double bond (dihedral angle 0°) when σ-bonded to metal atoms of this size. Table 3 shows the metal–*o*-carbon contact distances in the two structures, and here the greater regularity of the tin structure finally becomes apparent: in each ligand there is a short contact (of 3.65 Å) and a longer contact (of 4.1 Å) which is not seen in the chromium structure. In ligand 3 of the latter, the two distances are the same, as expected when the phenyl/alkenyl dihedral angle is 90°. However, since the Cr–C(21)–C(25) angle is 118.0(11)°, there is no evidence that this ligand is distorted due to an interaction of the phenyl ring with the metal.

Experimental

All manipulations involving air-sensitive materials were carried out under an atmosphere of pure, dry nitrogen or argon with rigorous exclusion of air and moisture unless otherwise stated. Solvents were distilled from appropriate drying agents and stored under inert atmosphere. N.m.r. spectra were recorded on Bruker WP 60 or WP 80 pulsed Fourier-transform machines, and shifts are quoted in p.p.m. downfield (positive) from internal $SiMe_4$. I.r. spectra were recorded on Perkin-Elmer 298 or 599 spectrophotometers. E.s.r. spectra were obtained on a Bruker model 420 equipped with 11-inch magnet operating in the *X*-band region (*ca.* 9.2 GHz). Molecular weights were measured isopiestically using a Mechrolab model 301A vapour pressure osmometer. Analyses were performed initially by Butterworths Laboratories, Teddington, Middlesex, and recently by Canadian Analytical Services, University Boulevard, Vancouver, British Columbia.

Tetrakis(2,2-*dimethyl*-1-*phenylethenyl*)*tin*(IV).—To 1-bromo-2-methyl-1-phenylpropene (52.588 g, 249 mmol) in ether (450

Table 2. Geometry of mean planes in $M(CPh=CMe_2)_4$ (M = Sn or Cr)

(*a*) Planarity of mean planes

Plane	Defining atoms	r.m.s.d.[a] M = Sn	r.m.s.d.[a] M = Cr
Alkenyl 1	M, C(1), C(2), C(3), C(4), C(5)	0.017	0.021
Alkenyl 2	M, C(11), C(12), C(13), C(14), C(15)	0.017	0.044
Alkenyl 3	M, C(21), C(22), C(23), C(24), C(25)	0.019	0.036
Alkenyl 4	M, C(31), C(32), C(33), C(34), C(35)	0.013	0.045
Phenyl 1	C(5), C(6), C(7), C(8), C(9), C(10)	0.007	0.007
Phenyl 2	C(15), C(16), C(17), C(18), C(19), C(20)	0.011	0.014
Phenyl 3	C(25), C(26), C(27), C(28), C(29), C(30)	0.008	0.014
Phenyl 4	C(35), C(36), C(37), C(38), C(39), C(40)	0.003	0.015

(*b*) Dihedral angles (°) between mean planes[b]

Planes	M = Sn	M = Cr
Phenyl 1–alkenyl 1	71.2	69.7
Phenyl 2–alkenyl 2	70.8	75.5
Phenyl 3–alkenyl 3	64.3	86.1
Phenyl 4–alkenyl 4	68.4	78.7
Alkenyl 1–alkenyl 2	109.7	110.3
Alkenyl 1–alkenyl 3	109.4	111.5
Alkenyl 1–alkenyl 4	110.7	111.3
Alkenyl 2–alkenyl 3	104.7	102.7
Alkenyl 2–alkenyl 4	110.1	110.7
Alkenyl 3–alkenyl 4	111.3	110.2

[a] Root mean square deviation of the atoms from the least-squares plane. [b] Alkenyl–alkenyl angles expressed as the larger of the two possible values to emphasise the relationship to tetrahedral geometry.

Table 3. Metal–*o*-C contact distances (Å) for phenyl rings

	M = Sn	M = Cr
M–C(6)	3.67	3.62
M–C(10)	4.04	3.99
M–C(16)	3.67	3.65
M–C(20)	4.07	3.88
M–C(26)	3.61	3.77
M–C(30)	4.13	3.78
M–C(36)	3.69	3.73
M–C(40)	4.10	3.90

cm³) cooled in an ethanol–dry-ice bath was added dropwise with stirring, n-butyl-lithium (145.5 cm³ of 1.695 mol dm⁻³ solution, 247 mmol). When addition was complete, the cloudy pale yellow mixture was stirred at low temperature for a further 30 min. On warming slowly to room temperature the reaction mixture became a clear yellow solution. The solution was recooled to −78 °C and tin(IV) chloride (6.6 cm³, 57 mmol) was added dropwise with stirring. After addition, the mixture was allowed to warm to room temperature and stirred overnight. The solvent was removed under vacuum to leave a gummy yellow residue, which was refluxed (30 min) with benzene (180 cm³) and filtered to remove lithium chloride. Solvent was removed from the filtrate under vacuum, diethyl ether (50 cm³) was added to the residue, and the resulting mixture filtered to obtain the precipitated compound. Recrystallisation from benzene–hexane afforded pale yellow crystals. Soxhlet extraction with hexane gave pure white crystals of $Sn(CPh=CMe_2)_4$ (5.65 g, 16%), m.p. 194—195 °C (Found: C, 75.0; H, 6.8; *M*, 641. $C_{40}H_{44}Sn$ requires C, 74.65; H, 6.9%; *M*, 643). ¹H N.m.r. ($CDCl_3$): δ 1.325 (s, 3 H), 1.372 (s, 3 H), 6.95—7.28 p.p.m. (m). ¹H N.m.r. (C_6D_6): δ 1.516 (s), 7.0—7.3 p.p.m. (m). ¹³C N.m.r. ($CDCl_3$): δ 21.927, 27.028, 124.830, 127.405, 129.057, 140.475, 145.090, 145.965 p.p.m. ¹³C N.m.r. (C_6D_6): δ 22.146, 27.397, 125.389, 127.01, 141.143, 145.435, 146.394 p.p.m. I.r. (Nujol mull): 1 624vs, 1 618 (sh), 1 600s, 1 575w, 1 235m, 1 080s, 1 040s, 920s, 765vs, 715vs cm⁻¹.

Tetrakis(2,2-*dimethyl*-1-*phenylethenyl*)*chromium*(IV).—1-Lithio-2,2-dimethyl-1-phenylethene was prepared as described above, using $BrPhC=CMe_2$ (7.286 g, 34.5 mmol) and n-butyl-lithium (17.417 cm³ of 1.98 mol dm⁻³ solution, 34.48 mmol) in diethyl ether (70 cm³). This reagent was added to a vigorously stirred suspension of $CrCl_3$·3thf (3.007 g, 8.025 mmol) in diethyl ether (100 cm³) during 30 min at −70 °C, after which the colour changed to deep blue. The mixture was warmed to room temperature and stirred (2 h) while the solution became deep green; solvent was removed under vacuum, the residue was taken up in hexane (70 cm³), and filtered rapidly. (Pentane is unsuitable for this step owing to rapid evaporation at a glass frit under reduced pressure.) The residue was brown and pyrophoric. The filtrate was reduced to 10 cm³ under vacuum and on standing afforded the product as dark green crystals (100 mg, 2.16%), m.p. 116—118 °C (decomp.) (Found: C, 83.5; H, 7.7. $C_{40}H_{44}Cr$ requires C, 83.3; H, 7.8%). ¹H N.m.r. (C_6D_6): δ 1.40 (s), 1.73 (s), 7.15 p.p.m. (br). I.r. (Nujol mull): 1 590m (sh), 1 568m, 1 475s, 1 433s, 1 355m (sh) (on Nujol bands), 1 263w, 1 075m, 1 063w, 1 037m, 807w br, 755s, 710s (sh), 703vs (sh) cm⁻¹.

Attempted oxidation to chromium(IV) *with oxygen*. A similar experiment with $CrCl_3$·3thf, (2.33 g, 6.22 mmol) and lithium reagent (122 cm³ of 0.204 mol dm⁻³ solution, 24.88 mmol) was carried out as far as the filtration. At this point oxygen (dried successively by passage through anhydrous calcium chloride and phosphorus pentoxide) was bubbled through the solution for 1 min. The solution darkened to an opaque brown or black, and a white precipitate was formed. No alkenylchromium(IV) species could be detected.

Magnetic moment. [CrR_4] (0.0224 g, 0.086 mmol) was dissolved in $CDCl_3$ (concentration 0.027 12 g cm⁻³) and sealed in a 5-mm n.m.r. tube containing both internal and external (capillary) $SiMe_4$ reference, giving $\Delta\nu(SiMe_4)$ 19.9 Hz, corresponding to $\mu_{obs.}$ = 2.81 ± 0.03 B.M. [$\mu_{calc.}$ (d^2 tetrahedral) = 2.83 B.M.]. Ligand corrections were made using standard values of Pascal's constants.

Tris(2,2-*dimethyl*-1-*phenylethenyl*)(*tetramethylethylenediamine*)*chromium*(III).—$BrPhC=CMe_2$ (8.097 g, 38.31 mmol) was lithiated in diethyl ether (60 cm³) at −70 °C under argon using n-butyl-lithium (20.07 cm³ of 1.91 mol dm⁻³ solution, 38.84 mmol) as described above. This reagent was added to $CrCl_3$·3thf (3.58 g, 11.07 mmol) in diethyl ether (90 cm³) at −70 °C during 30 min, the mixture becoming deep blue. The product was kept at −70 °C (to avoid thermal reaction of the blue product) while tetramethylethylenediamine (4.45 g, 38.3 mmol) in diethyl ether (10 cm³) was added during 30 min. The solution became green on allowing it to warm to room temperature. Solvent was removed under vacuum and hexane (70 cm³) added. The product was filtered giving a green filtrate from which solvent was removed under reduced pressure to *ca*. 30 cm³. After standing overnight under nitrogen a precipitate formed which was filtered off and dried under vacuum affording [Cr(CPh=CMe$_2$)$_3$(tmen)] (1.73 g, 27.8%) as an extremely air-sensitive green-brown powder (Found: C, 77.5; H, 7.7; N, 5.3. $C_{36}H_{49}CrN_2$ requires C, 77.0; H, 8.8; N, 5.0%).

Tris(2,2-dimethyl-1-phenylethenyl)(tetrahydrofuran)chromium(III).—The Grignard reagent was used in this reaction because of the known decomposition of the lithium reagent [4] in thf. 2,2-Dimethyl-1-phenylethenylmagnesium bromide was prepared from magnesium (0.703 g, 30.3 mmol) and BrPhC=CMe$_2$ (6.18 g, 29.3 mmol) in thf (50 cm^3). This solution was added (30 min) to CrCl$_3$·3thf (3.68 g, 11.3 mmol) in thf (100 cm^3) at −63 °C, and finally allowed to warm to room temperature. The volume was reduced to 50 cm^3 under vacuum, the mixture cooled to between −50 and −60 °C, and the blue crystalline precipitate filtered off. Further concentration of the filtrate under vacuum to 5 cm^3 and addition of hexane (40 cm^3) afforded a further crop of [Cr(CPh=CMe$_2$)$_3$(thf)] as blue crystals which are extremely sensitive to air and moisture (turning brown) (Found: C, 78.8; H, 7.0. $C_{34}H_{41}CrO$ requires C, 78.9; H, 8.0%).

Reaction with mercury(II) *chloride*. The chromium alkenyl was prepared as above using BrPhC=CMe$_2$ (2.45 g, 11.60 mmol), magnesium (0.294 g, 12.1 mmol), and CrCl$_3$·3thf (1.49 g, 4.58 mmol). After filtration of the product, mercury(II) chloride (3.17 g, 11.55 mmol) in thf (40 cm^3) was added slowly. The mixture was stirred overnight (−5 °C), stirred at ambient temperature (3 h), and solvent removed under vacuum. The product was extracted into benzene (50 cm^3) (2.90 g, 68% crude material) and recrystallised from the same solvent affording HgCl(CPh=CMe$_2$) (2.08 g, 48.8%) as colourless needles, m.p. 62—63 °C (Found: C, 31.8; H, 3.1; Cl, 8.8. $C_{10}H_{11}ClHg$ requires C, 32.65; H, 3.0; Cl, 9.65%). A mixed m.p. with an authentic sample gave no depression. Also produced in the reaction were small quantities of metallic mercury which could not be separated and a violet chromium species (CrCl$_3$·3thf) which turned green rapidly on contact with moisture.

Chloro(2,2-dimethyl-1-phenylethenyl)mercury(II).—1-Lithio-2,2-dimethyl-1-phenylethene was prepared as above using BrPhC=CMe$_2$ (2.49 g, 11.82 mmol) and n-butyllithium (6.79 cm^3 of 1.74 mol dm^{-3} solution, 11.81 mmol) in diethyl ether (70 cm^3). Mercury(II) chloride (3.19 g, 11.74 mmol) was suspended in diethyl ether (70 cm^3) and the lithium reagent added slowly at −35 to −45 °C. The mixture was stirred for 30 min and then allowed to warm to room temperature and stirred (2 h), and finally heated under reflux (30 min). Solvent was removed under vacuum, the product extracted into benzene, and recrystallised from light petroleum (b.p. 60—80 °C) affording the product (2.1 g, 48.7%) as flaky crystals, m.p. 63—65 °C (Found: C, 32.15; H, 3.1. $C_{10}H_{11}ClHg$ requires C, 32.65; H, 3.0%). ^1H N.m.r. (C_6D_6): δ 1.444 (s), 1.524 (s), 6.8—7.2 p.p.m. (broad multiplet). I.r. (Nujol mull): 3 080vw, 3 055vw, 1 640w, 1 598vw, 1 480 (sh), 1 365 (sh) (on Nujol bands), 1 203w, 1 075w (sh), 1 060w, 1 027w, 915w, 850w, 748s, 698vs, 561w, 518m, 393m, 329m, 300 (sh), 220 (sh) cm^{-1}.

Reaction between [Cr(CPh=CMe$_2$)$_4$] *and Methyl Isocyanide*.—A C_6D_6 solution of [Cr(CPh=CMe$_2$)$_4$] (4.4 mg, 7.6 μmol) was prepared in an n.m.r. tube sealed with a rubber cap. The n.m.r. spectrum was recorded and then methyl isocyanide (0.42 mm^3, 7.6 μmol) was injected into the sample. The spectrum was recorded again and showed that insertion had occurred. A second equivalent of methyl isocyanide injected into the tube failed to react. ^1H N.m.r. data (C_6D_6): [Cr(CPh=CMe$_2$)$_4$, δ 1.40 (s) and 1.73 (s) (CMe$_2$). [Cr(CPh=CMe$_2$)$_3${C(=NMe)CPh=CMe$_2$}], 0.945 (s) and 1.147 [s, C(=NMe)CPh=C*Me*$_2$]; 1.110 (s) and 1.436 (s, Cr–CPh=C*Me*$_2$); 3.153 p.p.m. (s, 3 H, N*Me*).

Crystal Data for Sn(CPh=CMe$_2$)$_4$.—$C_{40}H_{44}Sn$, M = 643.39, Monoclinic, a = 12.3530, b = 20.0911, c = 14.8009 Å, β = 113.23°, U = 3 375.46 Å^3, D_m = 1.29 g cm^{-3} (by flotation), Z = 4, D_c = 1.27 g cm^{-3}, F(000) = 1 336, space group $P2_1/c$, Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 7.04 cm^{-1}.

Measurements.—A suitable crystal was obtained by recrystallisation from acetone. A crystal of approximate dimensions 0.1 × 0.2 × 0.2 mm was mounted up the b axis. The space group and unit-cell dimensions were determined using Weissenberg photographs. Final values of the unit-cell dimensions and the intensities of 5 658 reflections in the range θ(Mo-K_α) ⩽ 25° were measured on a Hilger and Watts Y290 four-circle diffractometer equipped with graphite monochromator. Three intensity standards were remeasured every 100 reflections and found to show insignificant deviations. A symmetrical θ—2θ scan was used for all the intensity measurements; 1.2 s counts were taken at intervals of 0.03° over a range of 0.6° in θ.

Structure Analysis.—Processing of the measured data gave 3 886 independent reflections for which $I > 2.5\sigma(I)$. No correction was made for absorption (μ = 7.04 cm^{-1} for Mo-K_α). The structure was solved, and refined straightforwardly by Patterson, difference-Fourier, and least-squares methods. In the final unblocked full-matrix refinement, anisotropic thermal parameters were used for all non-hydrogen atoms, and all hydrogen atoms were placed geometrically (in fact at least 22 hydrogen atoms could be readily located by difference synthesis after isotropic refinement of the tin and carbon positions) with common thermal parameters for all the methyl and all the phenyl hydrogen atoms. Unit weights were used, as the weighting scheme did not refine satisfactorily. Refinement converged with R = 0.0477 and R' = 0.0541. A final difference-Fourier map showed a maximum peak height of 0.45 e Å^{-3} and a minimum of 0.55 e Å^{-3}. The minimum peak height of a carbon atom in the final Fourier map was 5.7 e Å^{-3}. The final maximum shift/least-squares deviation was <0.03.

Crystal Data for [Cr(CPh=CMe$_2$)$_4$].—$C_{40}H_{44}Cr$, M = 576.3, Monoclinic, a = 15.432(2), b = 16.338(9), c = 13.153(9) Å, β = 93.22°, U = 3 311.5 Å^3, D_m not measured, Z = 4, D_c = 1.16 g cm^{-3}, F(000) = 948, space group $P2_1/c$, Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 3.23 cm^{-1}.

Measurements.—A suitable crystal was difficult to obtain, but a specimen of moderate quality was prepared by recrystallisation from pentane. It was mounted in a capillary under argon, approximate dimensions 0.1 × 0.15 × 0.3 mm. The space group and preliminary cell constants were obtained from Weissenberg photographs. Final values of the cell constants and the intensities of 2 517 reflections for which θ(Mo-K_α) < 15° were measured on a Hilger and Watts Y290 four-circle diffractometer with graphite monochromator. Three intensity standards remeasured every 100 reflections showed insignificant deviations.

Structure Analysis.—Processing of the measured data gave 1 407 reflections for which $I > 2.5\sigma(I)$. The structure was solved by Patterson and difference-Fourier methods, and

Table 4. Atom co-ordinates ($\times 10^4$) for [Cr(CPh=CMe$_2$)$_4$] with estimated standard deviations in parentheses

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Cr	2 417(1)	119(1)	6 721(2)	C(21)	3 442(8)	−463(8)	7 437(10)
C(1)	2 581(8)	1 336(7)	6 413(9)	C(22)	3 889(8)	−119(9)	8 228(10)
C(2)	3 324(9)	1 625(9)	6 092(10)	C(23)	3 762(9)	733(9)	8 616(11)
C(3)	4 113(9)	1 104(8)	5 923(11)	C(24)	4 626(10)	−584(10)	8 811(12)
C(4)	3 471(11)	2 517(10)	5 816(12)	C(25)	3 649(9)	−1 299(9)	7 099(11)
C(5)	1 814(8)	1 893(8)	6 490(10)	C(26)	4 205(10)	−1 427(9)	6 335(11)
C(6)	1 513(9)	2 084(8)	7 443(11)	C(27)	4 379(10)	−2 222(10)	6 040(13)
C(7)	785(9)	2 610(9)	7 503(12)	C(28)	4 033(10)	−2 887(11)	6 477(13)
C(8)	396(10)	2 900(9)	6 627(12)	C(29)	3 492(12)	−2 759(13)	7 243(15)
C(9)	675(10)	2 731(9)	5 714(13)	C(30)	3 304(11)	−1 960(11)	7 594(13)
C(10)	1 378(9)	2 212(9)	5 615(12)	C(31)	1 442(7)	43(8)	7 696(9)
C(11)	2 206(8)	−465(8)	5 371(10)	C(32)	627(8)	213(8)	7 362(10)
C(12)	1 796(9)	−1 194(9)	5 257(11)	C(33)	347(9)	370(8)	6 274(10)
C(13)	1 332(10)	−1 630(9)	6 094(11)	C(34)	−121(9)	254(9)	8 067(10)
C(14)	1 737(9)	−1 653(9)	4 262(11)	C(35)	1 676(7)	−109(8)	8 778(9)
C(15)	2 631(8)	−101(8)	4 530(9)	C(36)	1 834(9)	−911(9)	9 142(11)
C(16)	2 253(9)	588(8)	4 027(10)	C(37)	2 060(9)	−1 049(10)	10 150(12)
C(17)	2 651(10)	971(8)	3 239(12)	C(38)	2 163(10)	−418(10)	10 832(12)
C(18)	3 413(11)	691(10)	2 904(12)	C(39)	1 970(10)	369(10)	10 531(13)
C(19)	3 783(10)	7(10)	3 351(11)	C(40)	1 748(9)	501(10)	9 500(12)
C(20)	3 385(9)	−382(8)	4 137(10)				

Table 5. Atom co-ordinates ($\times 10^4$) for Sn(CPh=CMe$_2$)$_4$ with estimated standard deviations in parentheses

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Sn	2 330	1 291	2 621	C(21)	3 276(6)	1 973(4)	3 818(5)
C(1)	1 612(6)	401(3)	3 014(5)	C(22)	4 003(7)	1 773(4)	4 699(6)
C(2)	1 010(7)	410(4)	3 585(5)	C(23)	4 220(9)	1 048(4)	4 995(6)
C(3)	777(8)	1 036(4)	4 045(6)	C(24)	4 708(8)	2 247(5)	5 529(6)
C(4)	456(8)	−200(4)	3 822(6)	C(25)	3 121(7)	2 695(4)	3 532(5)
C(5)	1 795(6)	−220(3)	2 549(5)	C(26)	2 037(7)	2 999(4)	3 252(6)
C(6)	2 881(7)	−516(4)	2 837(6)	C(27)	1 874(10)	3 656(5)	2 956(7)
C(7)	3 045(8)	−1 078(4)	2 366(8)	C(28)	2 814(13)	4 023(5)	2 929(8)
C(8)	2 112(9)	−1 368(4)	1 608(7)	C(29)	3 888(11)	3 733(5)	3 204(8)
C(9)	1 014(8)	−1 082(4)	1 313(6)	C(30)	4 067(8)	3 081(4)	3 520(7)
C(10)	865(7)	−525(4)	1 786(6)	C(31)	837(6)	1 831(3)	1 576(5)
C(11)	3 620(6)	955(3)	2 061(5)	C(32)	947(6)	2 287(3)	979(5)
C(12)	3 330(6)	679(4)	1 177(6)	C(33)	2 109(7)	2 483(4)	937(6)
C(13)	2 071(7)	578(4)	463(6)	C(34)	−79(8)	2 671(4)	248(6)
C(14)	4 222(8)	449(5)	771(7)	C(35)	−333(6)	1 680(4)	1 607(5)
C(15)	4 873(6)	1 025(4)	2 774(6)	C(36)	−878(7)	1 068(4)	1 296(6)
C(16)	5 392(7)	1 643(4)	3 004(6)	C(37)	−1 965(8)	935(5)	1 330(7)
C(17)	6 526(8)	1 715(5)	3 694(8)	C(38)	−2 520(8)	1 399(6)	1 662(8)
C(18)	7 175(8)	1 175(6)	4 154(8)	C(39)	−1 988(8)	2 010(6)	1 980(9)
C(19)	6 688(9)	550(6)	3 914(9)	C(40)	−914(7)	2 146(4)	1 942(7)
C(20)	5 548(7)	471(5)	3 220(8)				

refined by full-matrix least squares. As the crystal used was only of moderate quality, limiting the quantity of data, anisotropic thermal parameters were used for the chromium atom only. Placing all hydrogen atoms in calculated positions and using unit weight, refinement converged at $R = 0.069$, $R' = 0.074$. Common thermal parameters were refined for all the methyl and phenyl hydrogen atoms. A final difference-Fourier synthesis showed a maximum peak height of 0.36 e Å^{-3} and a minimum of 0.29 e Å^{-3}. The minimum peak height of a carbon atom in the final Fourier map was 3.6 e Å^{-3}. The final maximum shift/least-squares deviation was 0.045 for the methyl hydrogen thermal parameter. Others were less than 0.013.

In both structures, the SHELX series of programs was used, together with the geometry program XANADU and the plotting program PLUTO. Data reduction was carried out on the University of Nottingham ICL 1906A computer, and subsequent calculations on the DEC-20 system in Trinity College, Dublin and the IBM 370/138 computer at University College, Cork. Literature values for atomic scattering factors were used.[13]

Atomic co-ordinates for the two structures are shown in Tables 4 and 5. (The atom numbering and final atomic co-ordinates for the chromium structure do not correspond to those in ref. 3.) Bond lengths and angles for the two structures are in Table 1, and dihedral angles between mean planes in Table 2. Table 3 lists important short contact distances.

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