

Synthesis and X-Ray Crystal and Molecular Structure of Tetrakis(2,2-dimethyl-1-phenylethenyl)chromium(IV), the First Structurally-characterised Homoleptic Alkenyl Compound of a Transition Metal

By CHRISTINE J. CARDIN, DAVID J. CARDIN*, and ABHIJIT ROY

(Department of Chemistry, Trinity College, Dublin University, Dublin, Ireland)

Summary The title compound, the first homoleptic Group 6A metal alkenyl, has been prepared from $\text{CrCl}_3 \cdot 3(\text{thf})$, and its properties, including X-ray crystal structure determination, are reported.

TREATMENT of $\text{CrCl}_3 \cdot 3(\text{thf})$ (thf = tetrahydrofuran) with 4 mol of $\text{LiCPh}=\text{CMe}_2$ in ether at -78°C affords, among other products, green crystals of $\text{Cr}(\text{CPh}=\text{CMe}_2)_4$. This compound is thermally stable at room temperature in the absence of air and moisture, and the pure solid reacts only slowly with oxygen. It has been characterised by elemental analysis, i.r., n.m.r., and e.s.r. spectroscopy, and by a single crystal X-ray structure determination.

Although water does not rapidly decompose the compound at ambient temperature, the Cr-C bonds are cleaved by dilute mineral acids, and undergo insertion reactions with methyl isonitrile, as do our previously reported homoleptic

alkenyls† of the early transition metals.¹ The initial product on reaction with HCl is an unstable, red material which we believe may be the unstable chromium(IV) chloride.² The ^1H n.m.r. spectrum shows peaks at δ ca. 1.36 (CMe_2) and ca. 7.18 (Ph), which are substantially broadened owing to the paramagnetism of the molecule. The magnetic moment, measured 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 tetrahedral d^2 ion. The e.s.r. spectrum in hexane shows only a broad signal centred near $g = 2$ at 33°C which remains essentially unaltered at lower temperatures. At -86°C a sharper signal also near $g = 2$ appears and sharpens further as the temperature is lowered. At -123°C a new signal at 1250 G appears which we tentatively assign (in view of its relative weakness) to the 'forbidden' $\Delta m = 2$ transition of the triplet state. The structure of the compound was determined by X-ray crystallography.

† In ref. 1, this compound was formulated as $\text{Cr}(\text{CPh}=\text{CMe}_2)_3$, a stoichiometry based on commercially obtained elemental analysis now admitted to be in error.

Crystal data: $C_{40}H_{44}Cr$, M 576.3, monoclinic, $a = 15.432(2)$, $b = 16.338(3)$, $c = 13.153(3)$ Å, $\beta = 93.22^\circ$, $U = 3311.5$ Å³; $Z = 4$, $D_c = 1.16$ g cm⁻³, space group $P2_1/c$,

$\mu(Mo-K\alpha) = 3.23$ cm⁻¹.[‡] Data were collected to $\theta_{max} = 15^\circ$ on a crystal mounted in a capillary under argon using a Hilger and Watts Y290 four-circle diffractometer with graphite monochromator. The structure was solved by heavy atom methods using 1407 observed unique reflections and refined, using anisotropic temperature factors for the chromium atom only, to $R = 0.078$. The SHELX series of programs was used for all calculations.[§]

The molecule (Figure) consists of four $-CPh=CMe_2$ ligands arranged tetrahedrally about the central chromium atom without obvious distortions. The Cr-C bond lengths are equal within experimental error, and average $2.03(2)$ Å. This is within the range $2.01-2.07(3)$ Å reported for $Cr(CH_2CPhMe_2)_4$,³ the only other Cr^{IV} homoleptic hydrocarbyl for which structural data are available. There is thus no significant multiple bond character in the metal-carbon bond, in accord with our previous findings on transition metal alkenyl compounds.^{4,5} All four ligands adopt a similar conformation, in which the phenyl plane is nearly orthogonal to the double bond plane. The phenyl rings appear not to interact with the metal.⁶ Overall, the molecular geometry parallels that of the tin analogue $Sn(CPh=CMe_2)_4$,⁷ the presence of the d^2 transition metal atom causing little distortion.

We are extremely grateful to Professor T. J. King (University of Nottingham) for his invaluable help with data collection and processing, and for diffractometer facilities, and to Professor B. J. Hathaway (University College, Cork) for generous assistance with computer facilities and programs. We thank Dr. R. C. Barklie (T.C.D.) for running the low temperature e.s.r. spectra, and the N.S.C. (Ireland) for support.

(Received, 10th July 1978; Com. 731.)

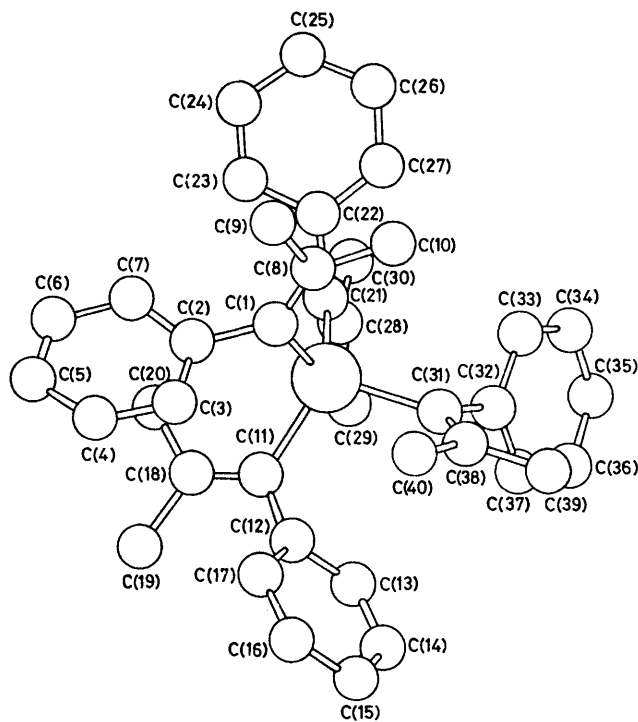


FIGURE. The molecular geometry of $Cr(CPh=CMe_2)_4$. Mean Cr-C bond length $2.03(2)$ Å. Mean bond angles around Cr atom: (a) mean of $C(1)-Cr-C(31)$ and $C(11)-Cr-C(21)$, $116.2(6)^\circ$; (b) mean of four remaining C-Cr-C bond angles, $106.2(6)^\circ$.

[‡] The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

[§] We are grateful to Dr. G. M. Sheldrick for supplying us with this program.

¹ C. J. Cardin, D. J. Cardin, J. M. Kelly, R. J. Norton, and A. Roy, *J. Organometallic Chem.*, 1977, **132**, C23.

² W. Mowat, A. Shortland, G. Yagupsky, N. J. Hill, M. Yagupsky, and G. Wilkinson, *J.C.S. Dalton*, 1972, 533.

³ V. Gramlich and K. Pfeifferkorn, *J. Organometallic Chem.*, 1973, **61**, 247.

⁴ C. J. Cardin and K. W. Muir, *J.C.S. Dalton*, 1977, 1593.

⁵ C. J. Cardin, D. J. Cardin, M. F. Lappert, and K. W. Muir, *J.C.S. Dalton*, 1978, 46.

⁶ G. R. Davies, J. A. J. Jarvis, and B. T. Kilbourn, *Chem. Comm.*, 1971, 1511.

⁷ C. J. Cardin and B. J. Hathaway, unpublished results.