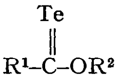
Telluroureas and Derived Transition Metal Complexes: the Crystal and Molecular Structure of $[Cr(CO)_5\{Te{=}CN(Et)CH_2CH_2NEt\}]$

By Michael F. Lappert* and Tony R. Martin
(*School of Molecular Sciences, University of Sussex, Brighton* BN1 9QJ)

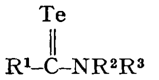
and George M. McLaughlin*
(*Research School of Chemistry, The Australian National University, P.O. Box* 4, *Canberra* A.C.T. 2600, *Australia*)

Summary Reaction of the electron-rich olefin $[EtN[CH_2]_2N(Et)C{=}]_2$ with tellurium affords the thermally or photochemically labile $EtN[CH_2]_2N(Et)C{=}Te$ which reacts with $[M(CO)_5(NCMe)]$ (M = Cr, Mo, or W) or $[NEt_4][MnBr_2(CO)_4]$ to yield $[M(CO)_5\{TeCN(Et)[CH_2]_2NEt\}]$ or *cis*-$[Mn(Br)(CO)_4\{TeCN(Et)[CH_2]_2NEt\}]$; the compound $[Cr(CO)_5\{TeCN(Et)[CH_2]_2NEt\}]$ is readily detellurated to yield the carbenemetal complex $[Cr(CO)_5\{CN(Et)[CH_2]_2NEt\}]$; the molecule of the title compound lies on a crystallographic mirror plane with the carbene ligand perpendicular to this plane and Te–Cr = 2·765(4), Te–C_{carb} = 2·12(2) Å, and ∠Cr–Te–C_{carb} = 96·1(5)°.

Barton and his co-workers[1] recently reported the first well documented account (but see ref. 2) of a class of compound containing the tellurocarbonyl group (>C=Te), the *O*-alkyl tellurocarboxylates (**1**), and Lerstrup and Henriksen[3] followed this with the disclosure of telluro-amides and -hydrazides (**2**). We now report on (a) a further class of C=Te compound,

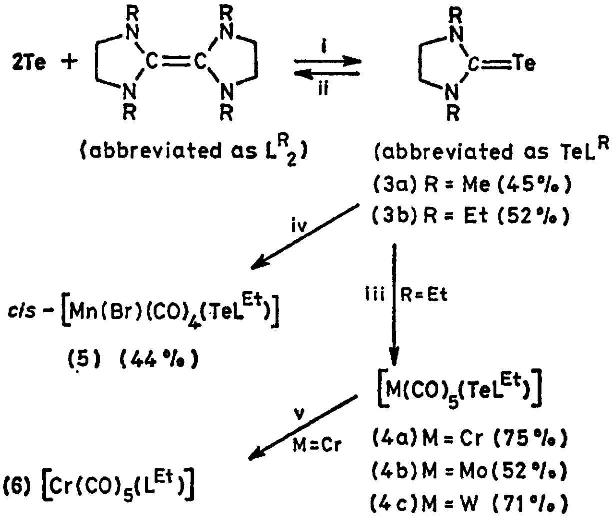

$R^1\text{–}\overset{\overset{\displaystyle Te}{\|}}{C}\text{–}OR^2$

(1)


$R^1\text{–}\overset{\overset{\displaystyle Te}{\|}}{C}\text{–}NR^2R^3$

(2)

the telluroureas (3) (see the Scheme and Table),[2]† (b) their conversion into the Te-ligated telluroureametal complexes (4) and (5), (c) the *X*-ray and molecular structure of one of these $[\mathrm{Cr(CO)_5\{Te{=}\overline{CN(Et)CH_2CH_2NEt}\}}]$, (4a) (the first C=Te compound to be so characterised), and (d) the facile detelluriation of compounds (3) or (4), *e.g.* to yield $[\mathrm{Cr(CO)_5\{\overline{CN(Et)CH_2CH_2NEt}\}}]$ from complex (4a). Feature (d) suggests that telluroureas may become useful as 'masked' nucleophilic carbenes, aminals, or acyl carbanions.



SCHEME. i, PhMe, reflux (unsuccessful for $R = C_6H_4Me\text{-}p$) ii, photolysis or thermolysis ($t_{\frac{1}{2}}$ *ca.* $\frac{1}{2}$ h at 110 °C in petroleum), iii, $[\mathrm{M(CO)_5(CNMe)}]$, PhMe, 20 °C, 24 h, iv, (a) $[\mathrm{NEt_4}][\mathrm{MnBr_2(CO)_4}]$, CH_2Cl_2, (b) $[\mathrm{OEt_3}][\mathrm{BF_4}]$, v (a) PhMe, 20 °C, slow, or (b) PhMe, 20 °C, *hν*, or (c) PhMe, Hg, 20 °C.

The conversion of an electron-rich olefin into a tellurourea (3) [reaction (i) in the Scheme] has a parallel in the known olefin reactions with O_2 or S to afford oxygen or sulphur analogues.[4] The relatively modest yields of compounds (3) are attributed largely to their ready reversion to their factors [reaction (ii) in the Scheme]. The telluroureas (3) are crystalline (Table) and air-sensitive, both in solution and the solid state, depositing tellurium. The ease of conversion of compound (3b) into its group 6 metal derivative $[\mathrm{M(CO)_5(TeL^{Et})}]$ (4) falls off in the sequence M = Mo > Cr > W. The telluroureas (3) react slowly with $[\mathrm{OEt_3}][\mathrm{BF_4}]$; the use of the latter reagent with $[\mathrm{M(CO)_5(Hal)}]^-$ was thus not the method of choice for obtaining the complexes (4), although an analogous procedure was satisfactory for the synthesis of *cis*-$[\mathrm{Mn(Br)(CO)_4(TeL^{Et})}]$ (5), reaction (iv) in the Scheme.

TABLE. Melting point and spectroscopic data.[a]

	M.p./°C	Colour	$\nu(CN_2)$	$\delta(^{13}C)$
(3a)	150	Colourless	1510	187
(3b)	90	Colourless	1505	162
(4a)	85	Orange	1535	150
(4b)	75	Yellow	1525	152
(4c)	86	Yellow	1538	150
(5)	80	Red	1525	154
(6)	—	—	1492	220[b]

[a] $\nu(CN_2)$ in cm^{-1} (Nujol mull); $\delta(^{13}C)$ in p.p.m. rel. to $SiMe_4$.
[b] *Cf.* ref. 11.

Each of the telluroureametal complexes (4) and (5) is moderately air-stable especially in the solid state and indefinitely stable under an inert atmosphere in the dark at ambient temperature. However, they are light-sensitive, depositing tellurium.

A toluene solution of $[\mathrm{Cr(CO)_5(TeL^{Et})}]$ (4a) precipitated Te even at *ca.* 20 °C; this detelluriation to afford the carbene complex $[\mathrm{Cr(CO)_5(L^{Et})}]$ (6) was accelerated by heat, light, or reaction with mercury [reaction (v) in the Scheme]. A small quantity of the urea (3b) was a coproduct; it is unlikely that the olefin L^{Et}_2 is an intermediate in the conversion of (4a)→(3b), because of the mild reaction conditions.

Crystal Data: $C_{12}H_{14}CrN_2O_5Te$, $M = 445{\cdot}9$, orthorhombic, $a = 17{\cdot}994(4)$, $b = 7{\cdot}295(1)$, $c = 13{\cdot}035(3)$ Å, $U = 1711{\cdot}1$ Å^3, $Z = 4$, $D_m = 1{\cdot}72$, $D_c = 1{\cdot}73$ g cm^{-3}, $F(000) = 864$, space group *Pnam*, a non-standard setting of *Pnma* (D^{16}_{2h}), No. 62, Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å; μ(Mo-K_α) = 24·5 cm^{-1}. The structure was refined to $R = 0{\cdot}072$ for 109 variables and 836 data, obtained on a Picker FACS-1 diffractometer. The molecule $[\mathrm{Cr(CO)_5(TeL^{Et})}]$ has a crystallographic mirror plane on which lie the Te, Cr, C(1), O(1), C(2), O(2), C(3), O(3), and C(5) atoms (see the Figure). The organic ring is perpendicular to this plane, and its geometry is similar to that found in related carbenemetal complexes, as in *cis*-$[\mathrm{Mo(CO)_4(L^{Me})_2}]$.[5] The bond length C(5)–Te, 2·12(2) Å, is similar to that found previously for a tellurium–carbon single bond, *e.g.*, 2·17(3) Å in tellurocyclohexane-3,5-

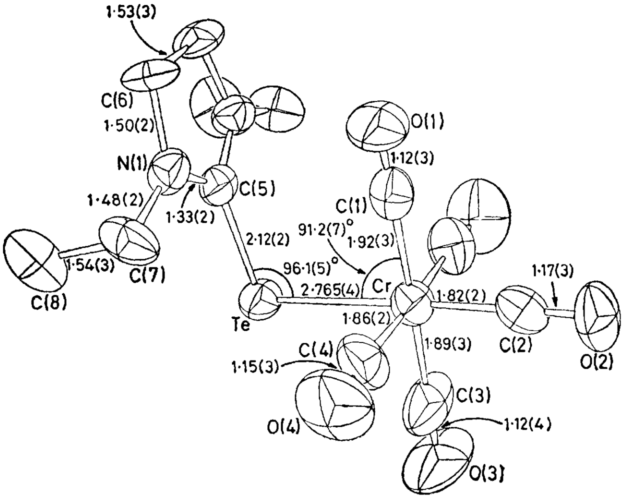


FIGURE. Molecular structure of $[\mathrm{Cr(CO)_5\{Te{=}\overline{CN(Et)CH_2CH_2NEt}\}}]$ (4a), showing atom numbering and important bond lengths and angles.

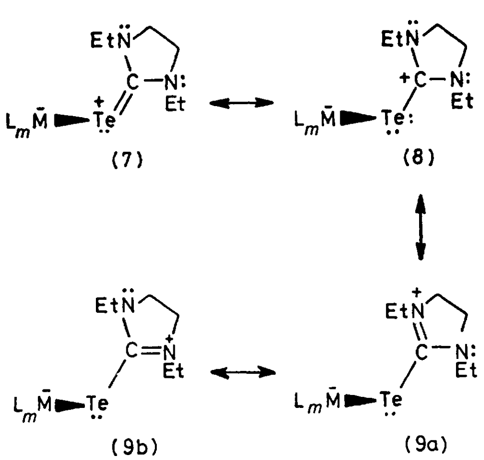
---

† The new compounds (3)—(5) have been characterised by analytical and spectral data.

dione.[6] The C(5)–Te–Cr angle of 96·1° can be compared with that for two other two-co-ordinate tellurium species: di-*p*-tolyl telluride, 101°,[7] and benzisotellurazole 80°.[8] There appears to be only two previous reports of tellurium bound to a metal, in $[Hg(TePh)_3]^-$ [9] and *trans*-$[Pd(SCN)_2\{Te(CH_2CH_2CH_2SiMe_3)_2\}_2]$.[10] The Cr–C distances to *cis*-carbonyls have a mean value of 1·88(2) Å so that they are longer than the 1·82(2) Å for the *trans* carbonyl.‡

Insight into the electronic distribution in the telluroureas (**3**) and their complexes, (**4**), is provided also by spectroscopic data. The $\nu(CN_2)$ values indicate that the $C\overset{..}{-}N$ double bond character is higher than in $[M(CO)_5L^R]$ complexes, such as (**6**). The tellurium atom appears to be more electronegative than the $M(CO)_5$ group, as indicated also by the ^{13}C n.m.r. spectra; there is an upfield shift of the unique carbon (*C* in the Scheme) atom compared with C_{carb} in carbenemetal complexes.

Telluroureametal complexes may be described in terms of the resonance hybrids (**7**)—(**9**), but *X*-ray and spectroscopic data suggest that (**9**) predominates; C(5)–N(1) [1·33(2) Å] is significantly shorter than a single bond.



We thank the S.R.C. for the award of a studentship to T.R.M. and Dr. P. L. Pye for discussions.

(*Received*, 23*rd April* 1980; *Com.* 417.)

‡ The atomic co-ordinates 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.

[1] A. G. M. Barrett, D. H. R. Barton, and R. W. Read, *J. Chem. Soc., Chem. Commun.*, 1979, 645.

[2] M. Z. Girshovich and A. V. El'tsov, *Zh. Obshch. Khim.*, 1969, **39**, 941, briefly refer to o-$C_6\overline{H_4N(Me)C(:Te)N}Me$ prepared in 8·8% yield from tellurium and o-$C_6\overline{H_4N(Me)CH_2N}Me$; identification rested on analysis for nitrogen and interpretation of u.v. spectrum.

[3] K. A. Lerstrup and L. Henriksen, *J. Chem. Soc., Chem. Commun.*, 1979, 1102.

[4] H. E. Winberg, J. E. Carnahan, D. D. Coffman, and M. Brown, *J. Am. Chem. Soc.*, 1965, **87**, 2055.

[5] M. F. Lappert, P. L. Pye, and G. M. McLaughlin, *J. Chem. Soc., Dalton Trans.*, 1977, 1272.

[6] C. L. Raston, R. J. Secomb, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1976, 2307.

[7] W. R. Blackmore and S. C. Abrahams, *Acta Crystallogr.*, 1955, **8**, 317.

[8] H. Campsteyne, L. Dupont, J. Lamotta-Brassear, and M. Vermeire, *J. Heterocycl. Chem.*, 1978, **15**, 745.

[9] U. Behrens, K. Hoffmann, and G. Klar, *Chem. Ber.*, 1977, **110**, 3672.

[10] H. J. Gysling, H. R. Luss, and D. L. Smith, *Inorg. Chem.*, 1979, **18**, 2696.

[11] P. B. Hitchcock, M. F. Lappert, and P. L. Pye, *J. Chem. Soc., Dalton Trans.*, 1977, 2160.