Weak coordination of a telluroketone in an η^1-mode complex: synthesis and characterization of pentacarbonyl(1,1,3,3-tetramethylindantellone)tungsten

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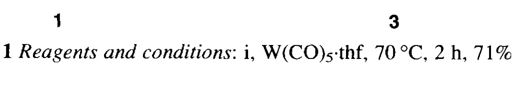
Treatment of a stable telluroketone with $W(CO)_5\cdot thf$ affords the title compound, the X-ray crystal structure of which shows η^1,σ-complexation and the *trans* influence of the weakly coordinated telluroketone; the regeneration of a 'free' telluroketone by ligand exchange of the complex under mild conditions is also reported.

Recently, much attention has been paid to the chemistry of double-bond compounds between carbon and heavier chalcogen atoms including that of their metal complexes.[1] Although a relatively large number of metal complexes with thio- and seleno-carbonyl compounds as ligands have been studied,[2] those with tellurocarbonyl compounds have been much less explored despite considerable interest that has been shown for tellurium containing complexes.[3] The paucity of telluroketone complexes is most likely due to the instability of C=Te compounds[4] and the lack of suitable synthetic methods. Although some telluroaldehyde or telluroketone metal complexes have recently been obtained,[5] all of them have been found to exist as η^2-π complexes except for $Ph_2CTe\cdot W(CO)_5$,[5a] the structure of which has not been crystallographically analysed. Very recently, we reported the successful synthesis of the first stable telluroketone, 1,1,3,3-tetramethylindantellone (**1**)[6] and its synthetic utility for novel organotellurium compounds.[7] We now report here (*i*) a new route to a telluroketone complex by the direct reaction of a stable telluroketone **1** with a tungsten pentacarbonyl complex, (*ii*) the first X-ray structure determination of an η^1-telluroketone complex having unique carbon–tellurium bonding character, and (*iii*) regeneration of 'free' telluroketone **1** by the decomplexation of **3** under mild conditions.

The telluroketone complex **3** was readily prepared by the reaction (70 °C, 2 h) of **1**, generated from telluradiazoline **2**,[8] with $W(CO)_5\cdot thf$. The purple reaction mixture was purified by preparative HPLC followed by chromatography on silica gel at ambient temperature to give **3** as dark purple crystals (71%) (Scheme 1).



Scheme 1 *Reagents and conditions*: i, $W(CO)_5\cdot thf$, 70 °C, 2 h, 71% yield

Interestingly, the isolated telluroketone complex **3**† was thermally very stable and not light sensitive unlike the telluroketone **1**.[6] The UV–VIS spectrum of **3** showed λ_{max} at 525 nm (ε 9460 $dm^3\ mol^{-1}\ cm^{-1}$) which is most likely assigned as an LMCT band.

The ^{13}C NMR spectrum of **3** shows that the signals due to the tellurocarbonyl carbon and its α-carbons are shifted to high field ($\delta_{C=Te}$ 285, $\delta_{C1,3}$ 74.7) relative to those of 'free' telluroketone **1** ($\delta_{C=Te}$ 301, $\delta_{C1,3}$ 79.9), but they are still much deshielded than those of usual carbonyl compounds. The ^{125}Te NMR resonance of **3** appears at δ 1783 which is highfield shifted relative to **1** (δ 2858) although the signal is much lowfield shifted relative to those of usual organotellurium compounds.[12] These observations indicate that the C=Te double bond in **3** still possesses substantial deshielding ability.

The *trans*-carbonyl carbon resonates at δ 200 with a large coupling constant[13] ($^1J_{CW}$ 161 Hz) and ^{17}O resonance of the carbonyl appears at a lower field by 16 ppm than those of the *cis* carbonyls. These differences between the *cis* and *trans* carbonyls is ascribable to the *trans* influence of the telluroketone **1** which coordinates to tungsten as a weak ligand.

The ORTEP drawing of the crystallographically determined structure of **3**‡ clearly shows that it is an η^1,σ-complex and is consistent with the solution structure (Fig. 1). All the bond lengths of **3** indicate weak coordination at the telluroketone ligand. The tungsten–tellurium bond [2.8084(4) Å] is close to the upper limit observed for W–Te single-bond lengths (2.68–2.88 Å).[11] The W–CO_{trans} bond [1.971(6) Å] is shorter than the W–CO_{cis} bonds [2.027(6)–2.044(7) Å], whereas the *trans* C–O bond [1.162(7) Å] is longer than the *cis* C–O bond [1.135(6)–1.140(6) Å] in accord with the *trans* influence.

It is noteworthy that the C–Te bond length [1.987(5) Å] of the telluroketone ligand in **3** is the shortest ever reported for two-coordinate tellurium compounds, which are known to be in the range 2.025–2.298 Å[5j] with an average of 2.158 Å.[12] This bond length is rather close to a calculated value for the carbon–tellurium double bond of $Me_2C=Te$ (1.968 Å).[13] This suggests that the carbon–tellurium bond in **3** still has a substantial double bond character as for a 'free' telluroketone.

Although **3** was stable in benzene or chloroform as well as in the solid state, it gradually underwent decomplexation in acetonitrile *via* ligand exchange. Monitoring by UV–VIS spectroscopy indicated that this ligand exchange reaction proceeded best around 60 °C and was complete after 1 h leading to quantitative regeneration of telluroketone **1** along with $W(CO)_5\cdot MeCN$ **4** (Scheme 2 and Fig. 2). The absorptions of **3**

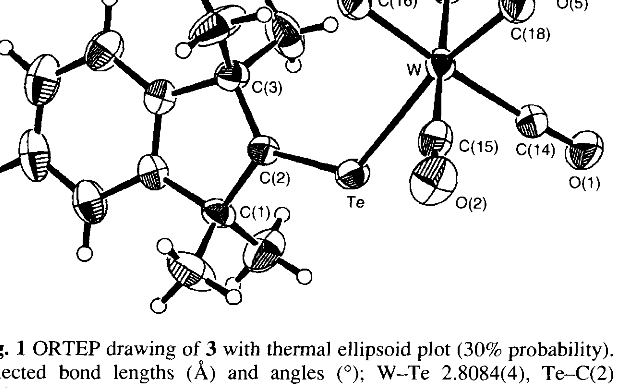


Fig. 1 ORTEP drawing of **3** with thermal ellipsoid plot (30% probability). Selected bond lengths (Å) and angles (°); W–Te 2.8084(4), Te–C(2) 1.987(5), W–C(14) 2.027(6), W–C(15) 2.038(7), W–C(16) 2.044(7), W–C(17) 2.028(6), W–C(18) 1.971(6), O(1)–C(14) 1.140(6), O(2)–C(15) 1.135(6), O(3)–C(16) 1.138(6), O(4)–C(17) 1.136(6), O(5)–C(18) 1.162(7), Te–W–C(18) 169.1(2), W–Te–C(2) 124.0(1), Te–C(2)–C(1) 119.5(3), Te–C(2)–C(3) 129.0(3), C(1)–C(2)–C(3) 111.4(4).

at λ_{max} 500 and 301 nm decreased with concomitant increase of the absorptions at λ_{max} 828 nm due to **1** and at λ_{max} 335 and 287 nm due to **4**. The regeneration of 'free' telluroketone **1** from the tungsten complex **3** was also confirmed by NMR spectroscopy and by a cycloaddition reaction. An acetonitrile solution of **3**, preheated at 60 °C for 1 h, was added to a solution of a diazo compound **5** to afford telluradiazoline **2** (76%) (Scheme 2). Thus **3** can be regarded as a useful and stable source of telluroketone **1**.

The behaviour of the telluroketone complex **3** described above is explicable in terms of weak tellurium–metal bonding as well as the characteristic η^1,σ-mode of its complexation which is obviously different from that of η^2-coordination found in a metallatellurirane.[5]

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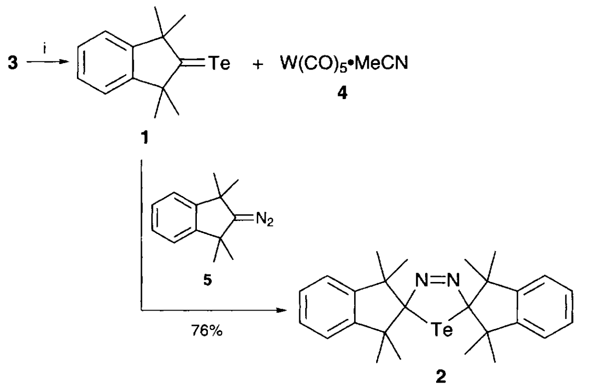

Scheme 2 *Reagents and conditions*: i, MeCN, 60 °C, 1 h, quantitative

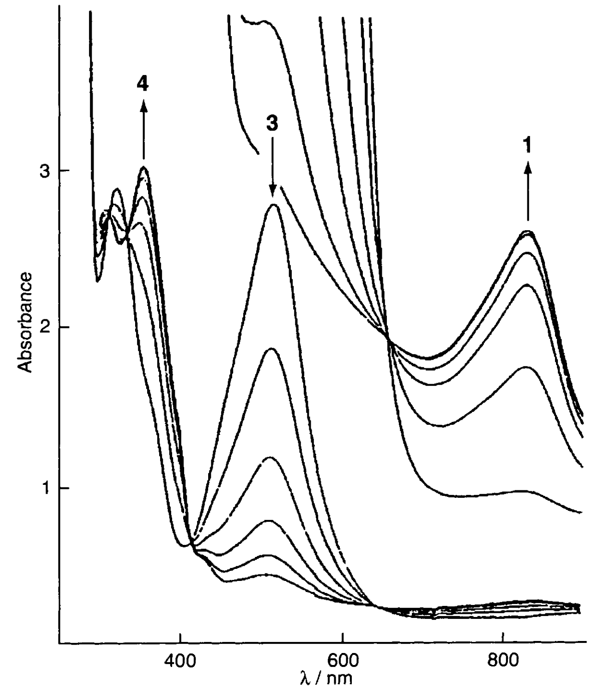

Fig. 2 Spectral changes of **3** in acetonitrile at 60 °C

Footnotes

† *Spectral data for* **3**; deep purple plates, mp 95–97 °C; ^{1}H NMR (CDCl$_3$, 500 MHz) δ 1.65 (br s, 6 H), 1.73 (br s, 6 H), 7.30 (m, 4 H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 25.9(q), 30.3(q), 74.7(s), 123.0(d), 123.1(d), 128.2(d), 128.3(d), 145.7(s), 147.9(s), 198.4 (s, J_{CW} 127.1 Hz) 200.4 (s, J_{CW} 161.1 Hz), 285.2(s); ^{125}Te NMR (CDCl$_3$, 158 MHz) δ 1783; ^{17}O NMR (CDCl$_3$, 68.7 MHz) δ 352, 368; UV–VIS λ_{max} (cyclohexane) 305 (log ε 3.90), 350 (sh, 3.57), 525(3.98) nm; IR (KBr) ν_{max}(CO) 2067(s), 1952(vs), 1913(vs) cm^{-1}.

‡ *Crystal data for* **3**: monoclinic, space group *C*2/*c*, a = 24.643(2), b = 6.603(8), c = 28.442(3) Å, β = 117.344(8)°, U = 4111(2) Å^3, Z = 8. The intensity data were collected on a Rigaku AFC7R diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71069 Å), and the structure was solved by direct methods and an absorption correction was applied. The final cycle of full-matrix least-squares refinement was based on 3957 observed reflections [$I > 2.00\sigma(I)$] and 226 variable parameters with $R(R_w)$ = 0.031(0.026). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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