Journal of Organometallic Chemistry, 320 (1987) 283–288
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

PREPARATIVE AND SPECTRAL INVESTIGATIONS ON C_3 BONDED ACETYLACETONATES OF TELLURIUM(IV)

B.L. KHANDELWAL, A.K. SINGH and N.S. BHANDARI

Department of Chemistry, Indian Institute of Technology New Delhi 110 016 (India)

(Received September 2nd, 1986)

Summary

In the reaction of 3,3-bis(chloromercury)-2,4-pentanedione with $TeCl_4$, Ph_2TeCl_2, or Ph_3TeCl, the replacement of one HgCl group by a tellurium moiety gives $Cl_3Te(C_5H_6O_2)HgCl \cdot 2C_4H_8O_2$ (I), $Ph_2Te(Cl)(C_5H_6O_2)HgCl$ (II) and $Ph_3Te(C_5H_6O_2)HgCl$ (III), respectively. The IR and ^1H NMR data indicate that the Te is bonded to the C_3 carbon of acetylacetone. In solution the compounds appear to ionize into Cl^- and an organometallic cation in which Hg seems to be involved in secondary interaction with the carbonyl groups; far IR and mass spectral data suggest that Hg–O interaction is significant even in solid state.

Introduction

Compounds having tellurium moiety linked to terminal carbon [1–3] or oxygen [4] atoms of a β-diketone are known, but no C_3 bonded β-diketonates of tellurium(IV) have been reported previously. In an attempt to prepare such compounds through HgCl exchange reactions of 3,3-bis(chloromercury)-2,4-pentanedione with tellurium tetrachloride and organotellurium(IV) chlorides, we have been able to prepare only mixed derivatives of the type $Ph_nTeCl_{3-n}(C_5H_6O_2)HgCl$, where $n = 0$, 2 or 3, exhibiting for the first time the formation of C_3–Te bond. Attempts to make $PhTeCl_2(C_5H_6O_2)HgCl$ by a similar reaction failed. The preparation and spectral data of the derivatives are discussed below.

Experimental

3,3-Bis(chloromercury)-2,4-pentanedione was synthesized by the method of Bonati and Minghetti [5]. IR (KBr/CsI pellets; cm^{-1}): 1685s (ν(CO)), 1430b, 1360m, 568m, 524m (ν(Hg–C)), 458b, 419b (ν(Hg–O)), 338m (ν(Hg–Cl)), NMR (^1H, DMSO-d_6, 25°C): $-\delta$ 2.285 (s, 6H, CH_3); ($^{13}C\{^1H\}$, DMSO-d_6, 25°C): δ 30.622 (s, CH_3), 31.21 (s, CH_3), 70.92 (s, C_3 of acac), 201.929 (s, CO), 204.127 (s, CO): ($^{199}Hg\{H\}$, DMSO-d_6, 25°C): δ 743.789, 870.99.

0022-328X/87/$03.50

(a) Synthesis of $TeCl_3(C_5H_6O_2)HgCl \cdot 2C_4H_8O_2$ *(I)*

A solution of tellurium tetrachloride (0.80 g, 2.9 mmol) and $Hg_2(C_5H_6O_2)Cl_2$ (1.618 g, 2.8 mmol) in 20 cm^3 of dioxane was refluxed for 6.5 h. The $HgCl_2$-dioxane complex was filtered off, and the filtrate evaporated to dryness under vacuum. The residual brown solid was washed with petroleum ether, dried under vacuum, and recrystallized from ether. Yield: 37%; m.p. 91–92°C, Analysis: Found: C, 18.90; H, 2.90; Te, 20.59; Hg, 28.36; Cl, 21.18. $C_{13}H_{22}Cl_4HgO_6Te$ calc: C, 20.95; H, 2.82, Te, 17.40; Hg, 26.94; Cl, 19.08%. IR (KBr/CsI pellets, cm^{-1}): 1615s (ν(CO)); 1440m, 1395m; 1260; 565w, 525w, 516w (ν(Hg–C)); 474w (ν(Te–C_3)); 459b, 421b, (ν(Hg–O)); 343m (ν(HgCl) + ν(TeCl)). NMR (^{1}H, DMSO-d_6, 25°C); δ 3.598 (s, 6H, CH_3), 5.010 (s, 8H, CH_2 of dioxane); ($^{13}C\{^1H\}$, DMSO-d_6, 25°C): δ 29.163 (s, CH_3), 66.52 (s, C_3 of acac), 67.20 (s, CH_2 of dioxane); ($^{199}Hg\{^1H\}$, DMSO-d_6, 25°C), δ 1049.489. MS: m/e = 280 ($CH_3COHgCl^+$), 100 ($C_5H_8O_2^+$), 88 ($C_4H_8O_2^+$), 85 ($C_4H_5O_2^+$), 72 ($C_4H_8O^+$), 58 ($C_3H_6O^+$), 57 ($C_3H_5O^+$), 45 ($C_2H_5O^+$), 43 (CH_3CO^+), 31 (CH_3O^+).

(b) Synthesis of $Ph_2TeCl(C_5H_6O_2)HgCl$ *(II)*

A solution of diphenyltellurium dichloride (1.76 g, 4.9 mmol) and $Hg_2(C_5H_6O_2)Cl_2$ (2.69 g, 4.7 mmol) in 30 cm^3 dioxane was stirred for 8 h at 40–50°C then cooled to 10°C and filtered. The volume of the filtrate was reduced to 10 cm^3 under vacuum, then petroleum ether (60–80°C) was added and the mixture kept overnight in the refrigerator. The white precipitate was recrystallized from ethanol, to give crystals, with m.p. 105–106°C. Yield 30%. Analyses: Found: C, 31.80; H, 2.30; Te, 19.34; Hg, 30.78; Cl, 10.56. $C_{17}H_{16}Cl_2HgO_2Te$ calc: C, 31.33; H, 2.45; Te, 19.59; Hg, 30.79; Cl, 10.90%. IR (KBr/CaI pellets, cm^{-1}): 1625s (ν(CO)): 1450m; 1440w; 1115–1260ms; 615–915s 570w, 529w, 506w (ν(Hg–C)); 466s (ν(Te–C_3)); 456m, 418m (ν(Hg–O)); 338m (ν(Hg–Cl) + ν(Te–Cl)); 236m (ν(Te–C)). NMR (^{1}H, DMSO-d_6, 25°C): δ 3.588 (s, 6H, CH_3), 7.488–8.034 (m, 10H, C_6H_5): ($^{13}C\{H\}$, DMSO-d_6, 25°C): δ 27.16 (s, CH_3), 66.375 (C_3 of acac), 128.87 (C_6H_5, *m* to Te), 130.637 (C_6H_5, *p* to Te), 133.127 (C_6H_5, *o* to Te), 139.355 (C_6H_5, C–Te) ($^{199}Hg\{H\}$, DMSO-d_6, 25°C): δ 1026.459. MS: m/e = 284 (Ph_2Te^+), 280 ($CH_3COHgCl^+$), 207 ($PhTe^+$), 202 (Hg^+), 154 (Ph_2^+), 130 (Te^+), 77 (Ph^+), 56 ($CH_2COCH_2^+$), 42 (CH_2CO^+).

(c) Synthesis of $Ph_3Te(C_5H_6O_2)HgCl$ *(III)*

A solution of triphenyltellurium chloride (3.94 g, 9.92 mmol) and $Hg_2(C_5H_6O_2)Cl_2$ (5.38 g, 9.4 mmol) in 30 cm^3 methanol was refluxed for 8–10 h with stirring. The solution was filtered, and then kept in the refrigerator overnight. The white precipitate was rejected and the mother liquor was evaporated to dryness under vacuum. The residual solid was washed 3–4 times with hexane then recrystallized from methanol. (Yield 25%; m.p. 104–105°C). Analyses: Found: C, 39.01; H, 2.90; Te, 17.59; Hg, 28.19; Cl, 4.91. $C_{23}H_{21}ClHgO_2Te$ calc: C, 39.84; H, 3.03; Te, 18.47; Hg, 28.93; Cl, 5.1%. IR (KBr/CsI pellets; cm^{-1}): 1690s (ν(CO)), 1490m; 1440w; 1165–1335m; 615–915ms; 565w; 530w (ν(Hg–C)), 455s (ν(Te–C_3)); 446b, 418b (ν(Hg–O)); 342m (ν(Hg–Cl) + ν(Te–Cl)), 232w (ν(Te–C)). NMR (^{1}H, DMSO-d_6, 25°C): δ 2.337 (s, 6H, CH_3), 7.629 (s, 15H, C_6H_5); ($^{13}C\{H\}$, DMSO-d_6, 25°C): δ 30.695 (s, CH_3), 79.126 (C_3 of acac), 127.546 (C_6H_5, *m* to Te), 131.356 (C_6H_5, *p* to Te), 132.601 (C_6H_5, *o* to Te), 135.386 (C_6H_5, C–Te); ($^{199}Hg\{H\}$, DMSO-d_6, 25°C):

δ 1013.82. MS: $m/e = 361$ (Ph_3Te^+), 312 ($PhHgCl^+$), 284 (Ph_2Te^+), 280 (CH_3CO-$HgCl^+$), 100 ($C_5H_8O_2^+$), 85 ($C_4H_5O_2^+$), 72 ($C_4H_8O^+$), 57 ($C_3H_5O^+$), 56 ($C_3H_4O^+$), 43 (CH_4CO^+).

Mercury, chloride and tellurium were determined by standard volumetric methods [6,7]. The C and H analyses were carried out in the microanalytical laboratory of Aston University, (Great Britain). The ^1H, ^{13}C NMR and ^{199}Hg spectra were recorded on a JEOL FX-100 FT-NMR spectrometer at 99.55, 25, and 17.75 MHz, respectively. The IR spectra were recorded on a Pye Unicam SP-1200 and Nicolet 5 DX FT infrared spectrometer. For mass spectra (70 eV) a Varian AE1 MS9 mass spectrometer of Aston University was used. For TGA/DTA (under a self generated atmosphere) a DuPont 1090 thermal analyzer was used. Conductivities of 0.18 to 1.5 mM solutions in DMF were measured with a Pye conductivity bridge.

Results and discussion

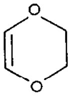
3,3-Bis(chloromercury)-2,4-pentanedione and tellurium derivatives react according to eq. 1.

$$Hg_2(C_5H_6O_2)Cl_2 + Ph_nTeCl_{4-n} \rightarrow HgCl_2 + Ph_nTeCl_{3-n}(C_5H_6O_2)HgCl \qquad (1)$$

Complex I crystallizes with dioxane (~ 2 mol/mol) which is given off slowly on storage and seems to be responsible for the unsatisfactory analyses for the various elements. The TGA curve of I shows two well defined steps, which can be accounted for in terms of the following reactions, which reflect the weak bonding of dioxane in it.

$$Cl_3Te(C_5H_6O_2)HgCl \cdot 2C_4H_8O_2 \xrightarrow{86-108°C} Cl_3Te(C_5H_6O_2)HgCl + 2C_4H_8O_2 \qquad (2)$$

(weight loss: Observed 20.19%; Calc 23.65%).

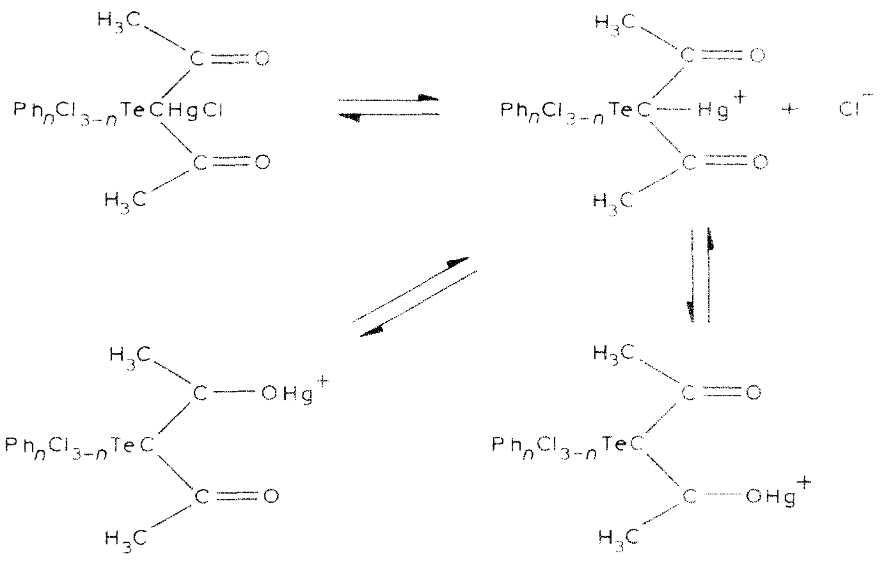
$$Cl_3Te(C_5H_6O_2)HgCl + C_4H_8O_2 \xrightarrow{168°C} TeCl_4 + C_5H_8O_2 + Hg +$$  (3)

(weight loss: Observed 63.66; Calc 64.73%).

Mass spectral data support the presence of dioxane. The other compounds are fairly stable and do not crystallize with solvent molecules, and the greater Lewis acid character of $TeCl_3$ is probably responsible for the unusual odd behaviour of I. The reactions of 3,3-bis(chloromercury)-2,4-pentanedione with tellurium compounds in 1/2 ratio do not give derivatives of the type $(Ph_nTeCl_{3-n})_2(C_5H_6O_2)$. For $n = 0$, tellurium metal separates out, and in other case some ill-defined products containing mercury are obtained.

NMR spectra

The chemical shifts for the methyl protons of $Hg_2(C_5H_6O_2)Cl_2$ agrees well with those reported previously [5]. After crystallization of this compound from methanol two peaks appear in the (δ 2.772 and 2.402 ppm) as reported earlier, and can be attributed to the intermolecular interaction [5] of Hg with oxygen of carbonyl group. The replacement of one HgCl by a $TeCl_3$ or Ph_2TeCl group deshields the methyl protons owing to the higher electronegativity of Te, and this effect is increased by the presence of electronegative chlorine. In III, in which the Te is not linked to



SCHEME 1

chlorine, the deshielding effect is significantly lower, as is obvious from the broad singlet for the phenyl protons.

Comparison of the signals for the C_3 carbon atom in ^{13}C NMR spectra of I, II and III suggests that the presence of a chlorine-containing Te moiety unexpectedly shields this carbon. This may be attributed to the existence the equilibria shown in Scheme 1, at least in DMSO, and is consistent with the shielding of C(1) and C(5) of the β-diketone moiety. In III the ionization of Cl is reduced as the HgCl bond is more covalent, and this in turn shifts the equilibrium to left, and so, C(3), C(1) and C(5) all are deshielded relative to I and II.

The larger deshielding of the ^{199}Hg signal on replacement of one HgCl group by a tellurium moiety also favours the presence of this ionization equilibria. The derivative containing the Ph_3Te group gives the most shielded ^{199}Hg signal since it is the least ionic. The conductivity measurements also show that the compounds are ionized in DMF as 1 : 1 electrolytes (Λ_M 67 to 78 ohm^{-1} cm^2 mol^{-1}), except for II, which being a telluronium salt type derivative, exhibits a higher association between the ions (Λ_M 24–27 ohm^{-1} cm^2 mol^{-1}).

IR spectra

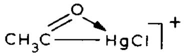
The ν(CO) band in the parent mercury compound and its triphenyltellurium derivative are very close, indicating the involvement of oxygen in a similar type of interaction in the two compounds [8]. For the other two compounds it is much lower, indicating a decrease in double bond character of CO, as suggested by the ^{13}C NMR data. Intermolecular [8] or intramolecular Hg–O interaction seems to be mainly responsible for this. The range of ν(CO) frequencies however, favours C_3–Te bond formation [9]. The ν(Hg–C) band is observed in all cases indicating that, at least in solid state, Hg is primarily linked to C_3, and interaction with the oxygen of $>$CO group is secondary. The IR spectrum of I has bands at 3590, 3530, 800 and

625 cm^{-1} which cannot be accounted for without assuming the presence of dioxane in this compound [10]. The far infrared spectra of I, II, III and the parent mercury compound show a number of unexpected bands, probably due to strong mercury–oxygen secondary interactions, and so unequivocal assignment in this region is difficult. However, bands indicating Te–C_3 [11], Hg–O, Hg–Cl, Te–Cl [11] and Te–C (phenyl) [11] interactions are present.

A single crystal X-ray diffraction study is desirable to throw light on the nature of the secondary interaction but none of these three compounds gave crystals suitable for this purpose.

Mass spectra

None of the three compounds give molecular ion peaks, decomposition taking place during the vaporization. The decomposition products exhibit to some extent characteristic fragmentation patterns. In the mass spectra of all three compounds there is a peak at $m/e = 280$ which can be attributed to



,

indicating a very significant Hg–O interaction in solid state. The mass spectrum of I is complex. It has ions characteristic of those formed from acetylacetone [12] and dioxane [13], confirming the presence of latter in I.

The results suggest that in the compounds of type $Ph_nCl_{3-n}Te(C_5H_8O_2)HgCl$, Te is linked to the C_3 carbon of acetylacetone and Hg–O secondary interaction is greater than that in $HgCl(C_5H_8O_2)HgCl$. On treatment of these compounds with HCl or CH_3I, the tellurium moiety rather than HgCl is replaced by H or CH_3 group, respectively. The higher C–Hg bond energy coupled with the Hg–O secondary interaction seems to be responsible for this. It would be unwise to infer too much from this qualitative data, but of the three compounds, II seems to show the most secondary interaction, as expected from its telluronium salt nature. In solution the secondary Hg–O interaction appears to be intramolecular, but in the solid state it may also be intermolecular, as reported for $Hg_2(C_5H_4O_2)Cl_2$ [8].

Acknowledgement

We thank Professor W.R. McWhinnie of The Aston University (Great Britain) for useful discussions.

References

1 G.T. Morgan and H.D.K. Drew, J. Chem. Soc., 121 (1922) 923.
2 G.T. Morgan and H.D.K. Drew, J. Chem. Soc., 117 (1920) 1456.
3 D.H. Dewar, J.E. Fergusson, P.R. Hentschel, C.J. Wilkins, and P.P. Williams, J. Chem. Soc., (2964) 688.
4 B.L. Khandelwal, A.K. Singh, H.B. Singh, K.M. Prasad, N.S. Bhandari and W.R. McWhinnie, J. Organomet. Chem., 291 (1985) 185.
5 F. Bonati and G. Minghetti, Angew. Chem. Int. Ed. Engl., 7 (1968) 629 and J. Organomet. Chem., 22 (1970) 5.
6 I.M. Kolthoff, P.J. Elving and E.B. Sandell, Treatise on Analytical Chemistry Part II, Vol. 3, Wiley, New York, 1965, p. 309.

7 A.I. Vogel, A Textbook of Quantitative Inorganic Analysis, 2nd Edn., Longmans, London, 1961, p. 266 and 324.

8 L.E. McCandlish and J.W. Macklin, J. Organomet. Chem., 99 (1975) 31.

9 R.C. Mehrotra, R. Bohra and D.P. Gaur, Metal-β-Diketonates and Allied Derivatives, Academic Press, New York, 1978, p. 109 and 195.

10 R.W. Silverstein, C.G. Basaler and T.C. Mornill, Spectrometric Identification of Organic Compounds, 3rd Edn., Wiley, New York, 1974, p. 132.

11 K.J. Irgolic, The Organic Chemistry of Tellurium, Gordon and Breach Science Publisher, New York, 1974, p. 325.

12 H. Budzilkiewicz, C. Djerassi and D.H. Williams, Mass Spectrometry of Organic Compounds, Holden Day INC. London, 1967, 134.

13 J.E. Collin, Bull. Soc. Chim. Belg., 69 (1960) 585.