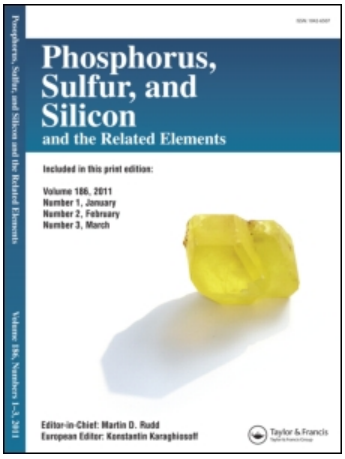


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# REACTIONS OF POLYDENTATE FUNCTIONALIZED TELLUROETHERS WITH DI-μ-CHLOROBIS-(TRICARBONYL DICHLORORUTHENIUM (II))

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# REACTIONS OF POLYDENTATE FUNCTIONALIZED TELLUROETHERS WITH DI-μ-CHLOROBIS- (TRICARBONYL DICHLORORUTHENIUM (II))

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The reactions of the $[Ru(CO)_3Cl_2]_2$ dimer with 2-(phenyltelluro)ethyl methylsulfide, (**1**), bis[2-(4-methoxyphenyltelluro)ethyl]amine, (**2**), 2-(2-{4-ethoxyphenyltelluro} ethyl)-1,3-dioxane, (**3**), bis(4-methoxyphenyltelluro)methane, (**4**), 2-(4-ethoxyphenyltelluromethyl)tetrahydro-2H-pyran, (**5**), N-[2-(4-methoxyphenyltelluro)ethyl]phthalimide, (**6**) in 1:2 molar ratio give complexes of the type $[Ru(CO)_2Cl_2.\mathbf{1}]_4$ (**7**), $[Ru(CO)_2Cl_2.\mathbf{2}]$ (**8**), $[Ru(CO)_2Cl_2.\mathbf{3}]_2$ (**9**), $[\{Cl_2(CO)_3Ru(\mu\text{-}\mathbf{4})\}_2Ru(CO)_2Cl_2]$ (**10**), $[Ru(CO)_2Cl_2.\mathbf{5}]_4$ (**11**) and $[\{\mathbf{6}.Cl_2(CO)_2Ru(\mu\text{-}\mathbf{6})\}_2Ru(CO)_2Cl_2]$ (**12**) which have been characterized by elemental analyses, $^1H$, $^{13}C\{^1H\}$ and $^{125}Te\{^1H\}$ NMR, FAB mass and IR spectra in conjunction with molecular weight and molar conductance measurement. Compound **10** on reaction with $AgClO_4$ gives $[Ru(CO)_3Cl.\mathbf{4}]ClO_4$ in ~66 % yield. All these complexes have terminal CO groups as in their IR spectra the ν(CO) bands do not appear below 1900 $cm^{-1}$. A molecular ion peak could not be observed in FAB spectra of most of the complexes but molecular associations are very well indicated. The deshielding of relevant signals on complexation indicates the binding modes of **1–6**.

*Keywords:* ruthenium; di-μ-chlorobis(tricarbonyldichlororuthenium(II)); tellurium; ligand; complex; telluroether

The reactions of $[RuX_2(CO)_3]_2$ (X = Cl or Br), $[RuCl_2(CO)_2]_n$, $[RuCl_4(CO)_2]^{2-}$ and $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(R)O\}_2(CO)_4]_n$ with phosphines (including functionalized one), arsines and nitrogen donors have resulted in a very rich and novel chemistry[1–6]. However, reactions of these ruthenium species with tellurium ligands[7–9] are either rarely attempted or little understood in spite of some current interest in them. The $Ph_2Te$ and

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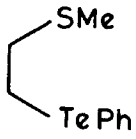
n-$Bu_2Te$ are known[10] to give the $Ru(CO)_2X_2L_2$ type of species on reacting with polymeric $[Ru(CO)_2X_2]_n$ (L = Te-ligand, X = Cl, Br, I). The reaction[11] of $Ru_3(CO)_{12}$ with $Ph_2Te$ results in polymeric $[Ru(CO)_2(TePh_2)]_n$ as a major product and $(CO)_3Ru(\mu\text{-}TePh)_2Ru(CO)_3$ as a minor product. The formation of these species suggests that the CO group may be substituted by Te-ligands. The reactions[12] of mixed metal clusters of ruthenium *viz.* $[HRuCo_3(CO)_{12}]$ and $[HRuRh_3(CO)_{12}]$ with $TeMe_2$ or $TePh_2$ also give products in which CO groups on one or both the types of metal atoms are substituted by the telluride ligand. It was therefore thought worthwhile to investigate the reactions of dimeric $[Ru(CO)_3Cl_2]_2$ with the polydentate telluroether ligands (**1–6**) which are designed and/or explored for their ligand chemistry in the recent past[13–17]. The results of these investigations are reported in the present paper.



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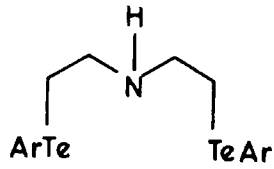


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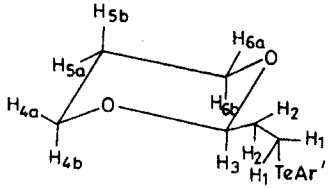


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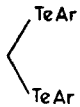


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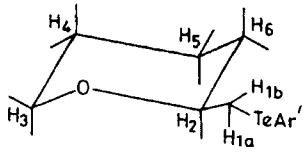


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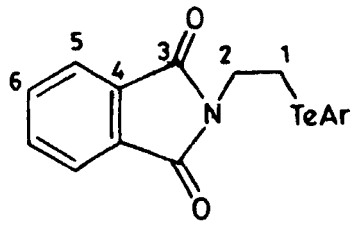


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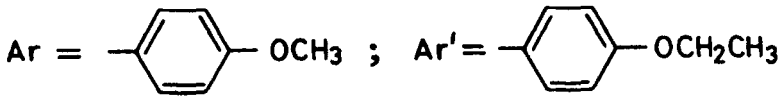





## EXPERIMENTAL

The $[Ru(CO)_3Cl_2]_2$ was used as received from Strem (USA). Published methods were used for the synthesis of 2-(phenyltelluro)ethyl methyl-sulfide, (**1**)[13], bis[2-(4-methoxyphenyltelluro)ethyl]amine, (**2**)[14], 2-(2-{4-ethoxyphenyltelluro}ethyl)-1,3-dioxane, (**3**)[15], bis(4-methoxy-phenyltelluro)methane, (**4**)[16], 2-(4-ethoxyphenyltellluromethyl)tetrahy-dro-2H-pyran, (**5**)[15], N-[2-(4-methoxyphenyltelluro)ethyl]phthalimide, (**6**)[17]. The C and H analyses were carried out with a Perkin Elmer ele-mental analyzer 240 C. Tellurium was estimated volumetrically[18]. The $^1H$ and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker Spectrospin DPX-300 NMR spectrometer at 300.1316507 and 25.4748884 MHz respectively. The $^{125}Te\{^1H\}$ NMR spectra were recorded at 126 MHz on a Bruker AMX 400 FT-NMR spectrometer, using $Me_2Te$ as an external standard. IR spectra were recorded in the range 200–4000 $cm^{-1}$ on a Nicolet 5DX FT-IR spectrometer using CsI pellets. FAB mass spectra were recorded on a JEOL SX-102/DA-6000 mass spectrometer using argon (6 kV, 10 mA) as FAB gas. Molecular weights were determined in chloro-form using a Knauer Vapour Pressure Osmometer model A028 at a con-centration ~1 mM and for conductance measurement an ORION conductivity meter model 162 was used.

### Synthesis of $[Ru(CO)_2Cl_2.\ \mathbf{1}]_4$ (7)

The dimer $Ru(CO)_3Cl_2$ (0.256 g; 0.5 mmol) was dissolved in ethanol (20 $cm^3$) and a solution of **1** (0.280 g; 1 mmol) made in 10 $cm^3$ of chloroform was added to it dropwise with stirring at room temperature under nitrogen atmosphere. The mixture was further stirred at room temperature for 2 h. The resulting orange yellow solution was filtered, concentrated to 5 $cm^3$ under reduced pressure and mixed with 10 $cm^3$ of n-hexane. The resulting precipitate was filtered, washed with n-hexane, recrystallized from a $CHCl_3$-n-hexane (1:3) mixture and dried in *vacuo*. Yield 55 %; m. p. 105–106 °C.

Analysis: Found: C, 26.76; H, 2.69; Te, 24.51 %; Calc for $[C_{11}H_{12}O_2STeRuCl_2]_4$: C, 26.00; H, 2.36; Te, 25.12%. Mol. wt.: 1818 (Calc. 2032). NMR ($^1H$, $CDCl_3$, 25 °C): δ, 2.69(s, 3H, $SCH_3$), 3.42–3.76(m, 4H, $CH_2$), 7.42–7.88(m, 5H, ArH); ($^{13}C\{^1H\}$, $CDCl_3$, 25 °C): δ, 14.7($CH_2Te$), 21.7($SCH_3$), 36.4($CH_2S$), 129.7(C-Te), 130.5(C *p* to Te), 134.7(C *m* to Te), 136.4(C *o* to Te), 185.3(CO); ($^{125}Te\{^1H\}$, $CDCl_3$, 25 °C): δ, 567, 589. IR ($cm^{-1}$): 2068, 2095, 2160(ν(CO)).

$FAB^+$ mass: m/z, 1151([$Ru(CO)_2Cl_2$.**1**]$_2$($SCH_2CH_2Ph$)), 843([Ru $(CO)_2Cl_2]_2$.**1**. (SPh)), 787 ($Ru(CO)_2Cl_2$.(**1**)$_2$) , 693($Ru(CO)_3Cl_2$.**1**. (Me $SCH_2CH_2Ph$)), 662 ($Ru(CO)_2Cl_2$.**1**. ($MeSCH_2CH_2Ph$)), 535(Ru $(CO)_3Cl_2$.**1**), 503($Ru(CO)_2Cl_2$.**1**), 475($Ru(CO)_2Cl_2$. ($MeCH_2CH_2TePh$)), 154 ($Ph_2$). Peaks have isotopic profile as expected.

### Synthesis of $[Ru(CO)_2Cl_2.2]$ (8)

To a solution of $[Ru(CO)_3Cl_2]_2$(0.256 g; 0.5 mmol) made in ethanol (20 $cm^3$) was added **2** (0.54 g; 1 mmol) dissolved in 10 $cm^3$ of chloroform, dropwise with stirring at room temperature under nitrogen atmosphere. The mixture was refluxed for 2 h. The resulting orange yellow solution was cooled to room temperature and filtered. The filtrate was concentrated to 5 $cm^3$ under reduced pressure and mixed with 10 $cm^3$ of n-hexane. The resulting precipitate was filtered, washed with n-hexane, recrystallized from a $CHCl_3$-n-hexane (1:4) mixture and dried in *vacuo*. Yield 75 %; m. p. 139–140 °C.

Analysis: Found: C, 31.69; H, 3.04; N, 2.02; Te, 32.89 %; Calc. for $[C_{20}H_{23}O_4NTe_2RuCl_2]$: C, 31.21; H, 2.99 ; N, 1.82; Te, 33.28 %. Mol. wt.: 1069 (Calc. 769). NMR($^1H$, $CDCl_3$, 25 °C): δ, 3.15–3.56(bm, 4H,

$CH_2$), 3.80(t, 3H, $OCH_3$), 4.34 (bs, 1H, NH); 6.96–6.99(d, 2H, ArH *m* to Te), 7.90–7.93(d, 2H, ArH *o* to Te): ($^{13}C\{^1H\}$, $CDCl_3$, 25 °C): δ, 14.5–17.0($CH_2Te$, 4 signals), 49.3–50.5($CH_2N$, 3 signals), 53.4–58.3($OCH_3$, 3 signals), 101.5–101.7(C-Te, 2 signals), 114.7–117.1(C *m* to Te, 8 signals), 134.6–140.9(C *o* to Te, 9 signals), 161.5–161.9(C *p* to Te, 2 signals), 193.0–193.6(CO, 2 signals). IR ($cm^{-1}$): 2046, 1994(ν(CO)).

$FAB^+$mass: m/z, 734($Ru(CO)_2Cl.$**2**), 706(Ru(CO)Cl.**2**), 571(**2**.HCl). 534(**2**-2H), 465 ($Ru(CO)_2Cl_2$.TeAr), 406($RuCl_2$.TeAr), 342(RuClTePh), 279($RuCl_2Ar$), 165(Ru(CO)Cl), 154($Ph_2$), 135(RuCl). Peaks have isotopic profiles as expected. The solubility was inadequate for recording $^{125}Te$ NMR spectrum.

## Synthesis of $[Ru(CO)_2Cl_2.3]_2$ (9)

To a solution of **3** (0.36 g; 1 mmol) made in 20 $cm^3$ of chloroform was added dropwise $[Ru(CO)_3Cl_2]_2$ (0.256 g; 0.5 mmol) dissolved in ethanol (20 $cm^3$) with stirring at room temperature under nitrogen atmosphere. Thereafter the mixture was refluxed for 2 h. The resulting orange yellow solution was cooled to room temperature and filtered. The filtrate was concentrated to 5 $cm^3$under reduced pressure and mixed with 10 $cm^3$ of petroleum ether (40–60 °C), the resulting precipitate was filtered, washed with n-hexane, recrystallized from a $CHCl_3$-petroleum ether (1:4) mixture and dried in *vacuo*. Yield 80%; m. p. 60–61 °C.

Analysis: Found: C, 32.97; H, 3.40 ; Te, 21.03 %; Calc. for $[C_{16}H_{20}O_5TeRuCl_2]_2$: C, 32.43; H, 3.37; Te, 21.62 %. Mol. wt.: 1223 (Calc. 1184). NMR($^1H$, $CDCl_3$, 25 °C): δ, 1.27(m, 1H, $H_{5b}$), 1.40(t, 3H, $CH_3$), 2.02 (m, 3H, $H_2 + H_{5a}$), 3.41(m, 2H, $H_1$), 3.66(m, 5H, $H_{4b} + H_{6b} + CH_2$ of OEt), 4.03(m, 2H, $H_{4a} + H_{6a}$), 4.55(t, 1H, $H_3$), 6.85–6.91(d, 2H, ArH *m* to Te), 7.69(d, 2H, ArH *o* to Te); ($^{13}C\{^1H\}$, $CDCl_3$, 25 °C) δ, 14.1($C_1$), 14.6($CH_3$ of OEt), 25.3, 25.6($C_5$), 32.4–33.9($C_2$, 4 signals), 63.6–63.7($OCH_2$), 66.68, 66.73($C_4$, $C_6$), 99.8–101.3(C-Te, 7 signals), 103.3($C_3$), 115.8–116.7(C *m* to Te, 6 signals), 136.7–137.1(C *o* to Te, 5 signals), 160.7(C-OEt), 189.8–194.1(CO) ; ($^{125}Te\{^1H\}$, $CDCl_3$, 25 °C): δ, 470, 580, 596, 607, 630. IR ($cm^{-1}$): 2053, 1986(ν(CO)).

$FAB^+$ mass: m/z, 1149($Ru_2(CO)_4Cl_3.$(**3**)$_2$), 922($Ru_2(CO)_3Cl_4$(TeAr)2), 894 ($Ru_2(CO)_2Cl_4(TeAr)_2$), 866($Ru_2(CO)_2Cl_3(TeAr)_2$), 662($Ru_2$ $(CO)_2ClTeAr_2$), 600 ($Ru_2(CO)_2Cl_4$(TeAr)), 559(Ru(CO)$_2$Cl.**3**), 518(Ru

$(CO)_2$.**3**), 501($Ru(CO)_3Cl_2$(TeAr)), 482($Ru(CO)_2Cl_2$(TeAr)), 365(**3**.$H^+$), 154 ($Ph_2$). Isotopic profiles in the peaks were evident.

$^{13}C\{^1H\}$ NMR of **3** ($CDCl_3$, 25 °C): δ, 1.46($C_1$), 14.8($CH_3$ of OEt), 25.8($C_5$), 37.1($C_2$), 63.3($OCH_2$), 66.8($C_4$, $C_6$), 100.8(C-Te), 102.6($C_3$), 115.7(C *m* to Te), 140.9(C *o* to Te), 159. 1(C-OEt).

## Synthsesis of [{$Cl_2(CO)_3Ru(\mu$-4)}$_2$$Ru(CO)_2Cl_2$](10)

The dimer $[Ru(CO)_3Cl_2]_2$(0.256 g; 0.5 mmol) and **4** (0.48 g, 1 mmol) were reacted by the procedure given for **7**. The resulting precipitate of **10** was filtered, washed with n-hexane, recrystallized from a $CHCl_3$ – n-hexane (1:5) mixture and dried in *vacuo*. Yield 65 %; m. p. 190 – 192 °C (d).

Analysis: Found: C, 25.98; H, 2.04; Te, 30.52 %; Calc. for $[C_{38}H_{32}O_{12}Te_4Ru_3Cl_6]$: C, 26.75; H, 1.87; Te, 29.91 %. Mol. wt.: 1969 (Calc 1706). NMR($^1H$, $CDCl_3$, 25 °C): δ, 3.78(s, 2H, $CH_2$), 3.84(s, 3H, $OCH_3$), 6.87–6.93(d, 4H, ArH *m* to Te), 7.68–7.83(d, 4H, ArH *o* to Te); ($^{13}C\{^1H\}$, $CDCl_3$, 25 °C): δ, 55.5($OCH_3$), 106.0(C-Te), 115.8(C *m* to Te), 137.5(C *o* to Te), 162.0(C-OMe), 192.0(CO) ); ($^{125}Te\{^1H\}$, $CDCl_3$, 25 °C): δ, 638, 647. IR ($cm^{-1}$): 2040, 1900(ν(CO)).

$FAB^+$ mass: m/z, 739($Ru(CO)_3Cl_2$.**4**), 702($Ru(CO)_2Cl_2(TeAr)_2$), 502($Ru(CO)_4Cl(CH_2TeAr)$), 486(**4**), 385(Ru(Cl)($CH_2$TeAr)), 367(Ru (CO)($CH_2$TeAr)), 350(Ru($CH_2$TeAr)), 307($ArTeCl_2$), 289($Ru(CO)_3Cl_3$), 256($Ru(CO)_3Cl_2$), 228($Ru(CO)_2Cl_2$), 165(Ru(CO)Cl). The expected isotopic profile was observed.

Ligand **4**: NMR($^1H$, $CDCl_3$, 25 °C): δ, 3.77($CH_2$), 3.83($OCH_3$), 6.77–6.80(ArH *m* to Te), 7.68–7.72(ArH *o* to Te); ($^{13}C\{^1H\}$, $CDCl_3$, 25 °C): δ, –35.8($CH_2$), 55.0($OCH_3$), 100.2(C-Te), 115.5(C *m* to Te), 137.9(C *o* to Te), 161.1(C-OMe).

## Synthesis of [$Ru(CO)_3$Cl.4]$ClO_4$ (10a)

A solution of complex **10** (0.2 g) made in 15 $cm^3$ of $CHCl_3$ was mixed with $AgClO_4$(0.052 g) dissolved in methanol (5 $cm^3$) in a nitrogen atmosphere. The AgCl formed was filtered off and the filtrate was stirred for 3 h. The resulting pale yellow solid was filtered. washed with $CHCl_3$ and dried in *vacuo*. Yield 66 %; m. p. 160°C(d)

Analysis: Found: C, 26.37; H, 1.91; Te, 31.34 %; Calc. for $[C_{18}H_{16}O_5Te_2RuCl]ClO_4$: C, 26.91; H, 1.99; Te, 31.76 %. NMR($^1H$,

DMSO-$d_6$, 25 °C): δ, 3.78(s, 3H, $OCH_3$), 3.84(s, 2H, $CH_2$), 6.81–7.21(d, 4H, ArH *m* to Te), 7.64–7.92(d, 4H, ArH *o* to Te). IR ($cm^{-1}$) 2040, 1990(ν(CO)).

$FAB^+$mass: m/z, 991([$Ru_2(CO)_6Cl_4$].**4**), 809(M-H), 755($Ru(CO)_4Cl_2(TeAr)_2$), 697 ($Ru(CO)_2Cl_2(TeAr)_2$), 661($Ru(CO)_2Cl(TeAr)_2$), 623($Ru(CO)_2(TeAr)_2$), 601($Ru(CO)(TeAr)_2$), 572($Ru(TeAr)_2$), 502($Ru(CO)_2Cl_3$(TeAr)), 385($RuCl(CH_2TeAr)$), 344($ArCH_2TeAr$), 307($ArTeCl_2$), 238(ArTe), 154($Ph_2$). Correct isotopic profile was present.

## Synthesis of $[Ru(CO)_2Cl_2.\ 5]_4$ (11)

[$Ru(CO)_3Cl_2$]$_2$(0.256 g; 0.5 mmol)) was reacted with **5** (0.35 g; 1 mmol) using the method described for **7**. The yellow solid **11** thus obtained, was washed with $CHCl_3$-hexane (1:5 mixture). It was recrystallized from $CHCl_3$-n-hexane (1:1) mixture and dried in *vacuo*.

Yield 60 %; m. p. 142 °C.

Analysis: Found: C, 32.86; H, 2.93; Te, 21.78 %; Calc. for [$C_{16}H_{20}O_4TeRuCl_2$]$_4$: C, 33.35; H, 3.47; Te, 22.26 %. Mol. wt.: 2147 (Calc. 2303). NMR($^1$H, $CDCl_3$, 25 °C): δ, 1.41(t, 3H, $CH_3$), 1.60(m, 6H, $H_4 + H_5 + H_6$), 3.29 (t, 1H, $H_{1a}$), 3.46(t, 1H, $H_{1b}$), 3.59(m, 2H, $H_3$), 3.95(bs, 1H, $H_2$), 4.03(q, 2H, $OCH_2$), 6.83–6.86(d, 2H, ArH *m* to Te), 7.73–7.76(d, 2H, ArH *o* to Te); ($^{13}C\{^1H\}$, $CDCl_3$, 25 °C): δ, 14.6($CH_3$), 23.0($C_5$), 25.1($C_6$), 32.1($C_1$), 60.5($C_4$), 63.8($OCH_2$), 69.5($C_2$), 72.3($C_3$), 115.9(Te-C(aryl)), 120.9(C *m* to Te), 135.4(C *o* to Te), 161.4(C-OEt), 189.8(CO) ($^{125}Te\{^1H\}$, $CDCl_3$, 25 °C): δ, 578, 594. IR ($cm^{-1}$): 2240, 1940(ν(CO)).

$FAB^+$ mass: m/z 891($Ru(CO)_2Cl.(\mathbf{5})_2$), 851($Ru(CO)_2.(\mathbf{5})_2$), 807($Ru_2(CO)_4Cl_4.\mathbf{5}$), 733($Ru(CO)_2Cl_2(TeAr)_2$), 616($Ru(CO)_2Cl_3.\mathbf{5}$), 580($Ru(CO)_2Cl_2.\mathbf{5}$), 502($Ru(CO)_3Cl_2(TeAr)$), 449($RuCl_2(CO)(TeAr)$), 385(RuCl(TeAr)), 350(**5** or RuTeAr), 286($Ru(CO)_4Cl_2$), 154($Ph_2$), 99 ($OCH(CH_2)_3CHCH_2$). Isotopic profile was evident.

## Synthesis of $[\{\mathbf{6}.Cl_2(CO)_2Ru(\mu\text{-}\mathbf{6})\}_2Ru(CO)_2Cl_2]$ (12)

Complex **12** a yellow solid was synthesized by reacting [$Ru(CO)_3Cl_2$]$_2$ (0.256 g; 0.5 mmol) with **6** (0.41 g; 1 mmol) in the manner described for **11**. Yield 55%; m.p. 120 °C.

Analysis: Found: C. 39.08; H, 3.01; N, 3.01, Te, 21.41 %: Calc. for $[C_{74}H_{60}O_{18}N_4Te_4Cl_6Ru_3]$: C, 38.32; H, 2.58 ; N, 2.58; Te, 22.00 %. Mol. wt.: 2353 (Calc 2319). NMR($^1$H, $CDCl_3$, 25 °C): δ, 3.76–3.84(m, 5H, $OCH_3 + CH_2Te$), 4.06(m, 2H, $CH_2N$), 6.98–7.03(m. 2H, ArH *m* to Te), 7.66(m, 4H, phthalimide ring protons), 7.99–8.02(d, 2H, ArH *o* to Te); ($^{13}C\{^1H\}$, $CDCl_3$, 25 °C): δ, 20.0($C_1$), 38.3($C_2$), 55.3($OCH_3$), 85.0,102.4(C-Te), 115.7(C *m* to Te), 123.6($C_5$), 129.7($C_6$), 132.3,137.3($C_4$), 143.7(C *o* to Te), 161.4(C-OMe), 167.5($C_3$), 192.5(CO). IR ($cm^{-1}$): 2004, 1920(ν(CO)). The solubility was inadequate for recording $^{125}$Te NMR spectrum.

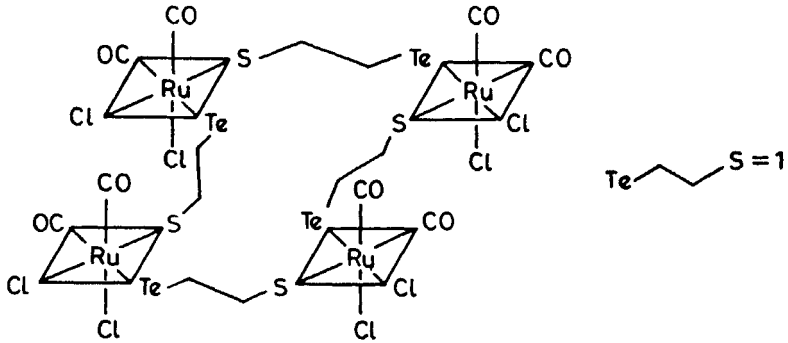
$FAB^+$ mass: m/z, 661($Ru(CO)_4Cl$.**6**), 639($Ru(CO)_2Cl_2$.**6**), 604($Ru(CO)_2Cl$.**6**), 568($Ru(CO)_2$.**6**), 540(Ru(CO).**6**), 512(Ru.**6**), 484($Ru(CO)_4Cl$(TeAr)), 461($Ru(CO)_3Cl$(TeAr)), 411($RuCl_2$(TeAr)), 391($Ru(CO)_2$(TeAr)), 307($ArTeCl_2$), 289($Ru(CO)_4Cl_2$), 154($Ph_2$). Isotopic profile was as expected.



## RESULTS AND DISCUSSION

The bi- and tridentate hybrid organotellurium ligands **1–6** react with the dimer $[Ru(CO)_3Cl_2]_2$ resulting in mono/polymetallic species. However, none of the products gives single crystals suitable for X-ray diffraction. The ligand **1** on reacting with $[Ru(CO)_3Cl_2]_2$ gives **7** by breaking chloro bridges of the dimer and substitution of CO ligand. The tetrameric nature of **7** is supported by its molecular weight and non-conducting nature ($\Lambda_M$= 21.1 $ohm^{-1}cm^2mol^{-1}$ in $CH_3CN$). The observed molecular weight is lowered (~ 15 %) when the concentration of **7** is changed from 1 mmol to 0. 1 mmol. The partial dissociation of **7** even at very low concentration level supports the bridging of four Ru atoms of tetrameric **7** by **1**. The deshielding of SMe, $CH_2$ and Ar signals (0.2 to 0.7 ppm) in $^1$H NMR spectrum of **7** with respect to those of the free ligand, supports the bonding of **1** through Te as well as S. This is further corroborated by significant downfield shift(~29 ppm)[8] of phenyl ring C linked to Te in the $^{13}C\{^1H\}$ NMR spectrum of **7** with respect to that of free **1**. In the IR spectrum of **7** three terminal ν(CO) bands appear at 2068, 2095 and 2160 $cm^{-1}$, in agreement with the proposed structure of **7**. The FAB mass of **7** does not exhibit a molecular ion peak but the presence of a peak at 1151 ($[Ru(CO)_2Cl_2.\mathbf{1}]_2SCH_2CH_2Ph$)

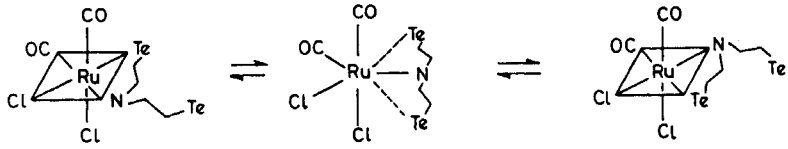
supports the formation of polymetallic species. This is also supported by fragmentation pattern observed with appropriate isotopic profile. The $^{125}$Te NMR spectrum of **7** exhibits two signals (nearly equal intensity) at 567 and 589 ppm (ligand signal at 503 ppm). Both of them are deshielded but consistent with the two types of Te expected on the basis of proposed structure of **7**.



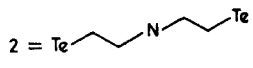

**7**

The reaction of **2** with the dimer $[Ru(CO)_3Cl_2]_2$ also occurs by breaking of chloro bridges and CO group substitution, resulting in **8** which is a non-electrolyte ($\Lambda_M$ = 51.4 ohm$^{-1}$cm$^2$mol$^{-1}$). The molecular weight of **8** at 1 mmol concentration level indicates some molecular association, probably through Te of pendent arm of **2**. On decreasing the concentration of **8** to 0.1 mmol, the molecular weight has been found to be 897, closer to the formula weight. This suggests that association of **8** in solution is not very strong and presumption about its monomeric nature is not unreasonable The $^1$H NMR spectrum of **8** exhibits deshielded[14] $CH_2NH$( ~ 2.6 ppm) and Ar signals (~0. 1 – 0.2 ppm) with respect to those of the free ligand, supporting the ligation of **2** in a tridentate mode (through N and both Te atoms). The $^{13}$C{$^1$H}NMR spectrum of **8** also has downfield Te-$CH_2$ and ArC-Te signals (2–5 ppm) with respect to those of free **2**. However the multiplicity of signals in $^1$H as well as $^{13}$C NMR spectra in conjunction with these downfield shifts suggests very strongly that **8** is a mixture of isomers and in solution there is an exchange between coordinated and free

ArTe group too, as shown below. The CO groups are terminal as two ν(CO) bands appear at 2046 and 1994 $cm^{-1}$ in IR spectrum of **8**. The FAB mass spectrum of **8** does not have a molecular ion peak but the fragmentation pattern is in agreement with the postulated stoichiometry of **8**.

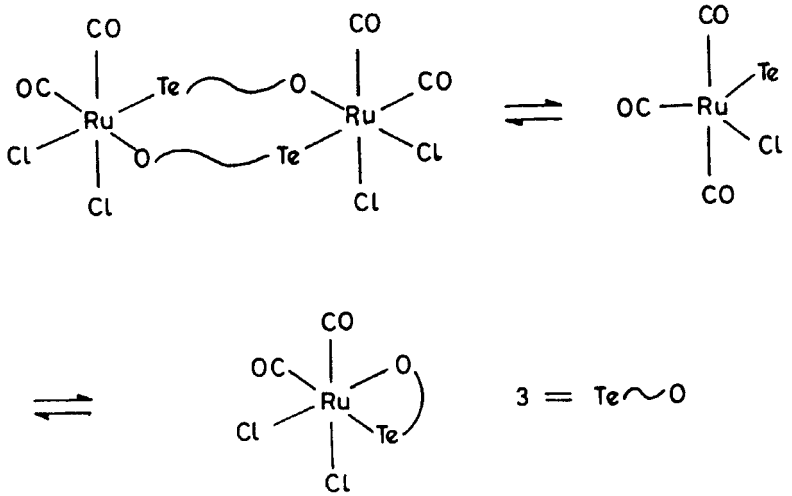



**8**




The reaction of **3** with the dimer $[Ru(CO)_3Cl_2]_2$ also takes place *via* substitution of a CO group and results in **9**, which is supported by its molecular weight and $\Lambda_M$ (15.6 $ohm^{-1}cm^2mol^{-1}$). At 0.1 mmol concentration level the value of molecular weight has been found to be 814. Most probably due to the weak nature of the Ru-O interaction, the dimer dissociates. With respect to free **3** the deshielding of the $H_1$ proton in the $^1H$ NMR spectrum of **9** is very significant (~0.55 ppm)[15]. This is not the case for $H_4$ or $H_6$. This suggests that bonding of **3** in **9** is through tellurium and oxygen but the latter bond is not strong and equilibria given below prevail in solutions. The coordination through Te is further supported by ~ 13 ppm deshielding of $C_1$ in $^{13}C$ NMR spectrum of **9** with respect to that of free ligand. Moreover in $^{13}C\{^1H\}$ NMR of **9** five CO signals appear, supporting the presence of equilibria along with isomeric forms. This is further supported by multiplicities of other signals in $^{13}C$ NMR spectra. The FAB mass spectrum of **9**, has a peak at 1149 which may be assigned to $[Ru_2(CO)_4Cl_3.(\mathbf{3})_2]$ and, a fragmentation pattern supporting the above formulation for **9**. The position of ν(CO) band in IR spectrum of **9** rules out presence of any bridging CO. The five signals at 470, 580, 596, 607 and 630 ppm appear in the $^{125}Te$ NMR spectrum of **9**. The first of these is weak and seems to arise from free ligand **3** ($^{125}Te$ NMR signal reported[15] at 467 ppm) present due to small dissociation of the complex **9**. Two sig-

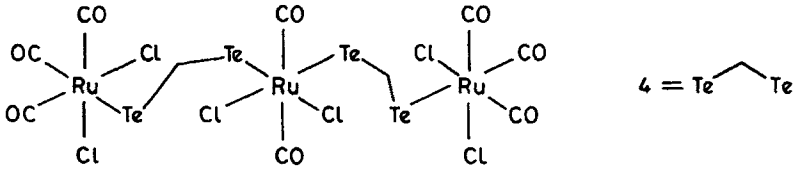
nals (at 596 and 630 ppm) out of these four are of equal intensity and stronger than the remaining two. They probably arise from the dimeric moiety and equilibrium is probably shifted towards this species. In view of the chelate shift reported in the complexes of tellurium ligand **3**, the signal at 580 seems to originate from the monomeric six coordinated species of Ru which has **3** in a bidentate coordination mode.



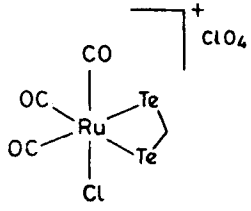

9

The reaction of **4** with the dimer $[Ru(CO)_3Cl_2]_2$ too occurs through the partial substitution of CO ligand, resulting in **10**. The formation of **10** is supported not only by molecular weight data and $\Lambda_M$ (6 $ohm^{-1}cm^2mol^{-1}$) but also by the reaction of **10** with $AgClO_4$ which results in **10a** in ~ 66 % yield. Such a product is not obtained from **7–9.** In **10a** $ClO_4$ is not coordinating as it gives characteristic band in its IR spectrum at 1090 $cm^{-1}$. Moreover, the molar conductance of **10a** is found to be 136 $ohm^{-1}cm^2mol^{-1}$, concurring with its 1:1 electrolytic nature. In the $^1H$ NMR spectrum of complex **10** signals are only marginally deshielded with respect to those of free **4**. However, most of the signals are somewhat broad indicating that probably a few isomeric forms of **10** coexist in solu-

tion. The involvement of Te in coordination is well reflected by deshielding of the Te-C(Ar) signal by ~6 ppm with respect to that of free **4**, in the $^{13}C$ NMR spectrum of **10**. The FAB mass spectrum of **10** does not have a molecular ion peak but the fragmentation pattern is quite characteristic of **10**. The $^{1}H$ NMR spectrum of **10a** also indicates the existence of isomeric forms as in the case of **10**. However, the positions of ν(CO) in the IR spectra of **10** and **10a** are characteristic of terminal CO group.




10



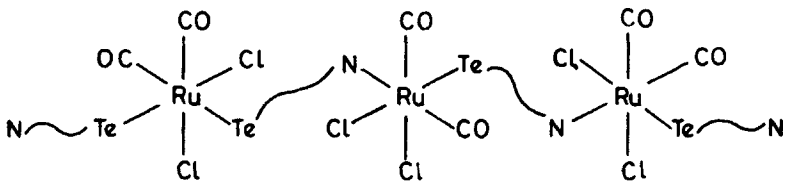

10a

In the $^{125}Te$ NMR spectrum of **10** two signal at 638 and 647 ppm were observed in comparison to the signal of free ligand **4** found at 571 ppm[16]. This rules out the chelating mode of bonding for **4**, as shielding of signal in $^{125}Te$ NMR occurs in such a situation but corroborates with the proposed structure of **10**.

The ligand **5** reacts with $[Ru(CO)_3Cl_2]_2$ resulting in a complex **11** which appears to be similar to that of **7**. This is supported by molecular data and conductance values ($\Lambda_M = 2.7$ ohm$^{-1}$cm$^2$mol$^{-1}$). Even at 0.1 mmol concentration the molecular association is indicated by the observed value of molecular weight (1051) which is higher than that of a monomer. The $H_{1a}$

signal in the $^1H$ NMR spectrum of **11** appears deshielded (0.2 ppm) with respect to that of free **5**. This suggests that Te is involved in coordination. However, due to weak interaction of pyran ring oxygen with Ru, the deshielding of $H_3/H_2$ signals with respect to those of the free ligand is not observed in the $^1H$ NMR spectrum of **11**. Similarly in the $^{13}C$ NMR spectrum of **11** deshielding of only Te-C(Ar) and $C_1$ signals (5 to 15 ppm) with respect to those of free ligand **5**[15], has been found significant. The $^{125}Te$ NMR spectrum of **11** exhibits two signals of nearly equal intensity at 578 and 594 ppm. With respect to the signal of free **5** (489 ppm)[15] both of these are deshielded and thus support the coordination of **5** through Te. This observation agrees with the proposal that the structure of **11** is analogous to that of **7**. The pyran oxygen appears to play a role in bridging the various Ru centres of the tetramer, as without this its formation is difficult to visualize. The FAB mass spectrum does not have molecular ion peak but the fragmentation pattern agrees well with the molecular association and formulation of **11**. The position of the ν(CO) band in the IR spectrum of **11** indicates the terminal nature of two the CO groups.

The complex **12** formed by loss of CO group and breaking of dimer $[Ru(CO)_3Cl_2]_2$ moiety, seems to be polymetallic as supported by its molecular weight and molar conductance ($\Lambda_M = 3.3$ ohm$^{-1}$cm$^2$mol$^{-1}$) values. The molecular weight of **12** has been found to be 1238 even at 0.1 mmol concentration level, thus supporting reasonable strength of its molecular association. The $^1H$ and $^{13}C$ NMR spectra indicate that Te and N both are involved in bonding as the relevant signals appear deshielded (0.2 to 0.7 ppm in $^1H$ NMR; 14 ppm in $^{13}C$ NMR). The two ligands at the two end of the chain have free uncomplexed N. Probably intramolecular Te....O interaction also exists in these two. This results in an additional deshielded signal for $C_4$ and a shielded one for $H_2C$-Te in $^{13}C$ NMR spectrum of **12**. The Te is *trans* to Cl as well as CO in **12**. This results in broadness or multiplicity in some signals of the $^1H$ and $^{13}C$ NMR spectra. On the basis of limited data available for **12** it is difficult to speculate any structure for **12** uneqivocally. The structure proposed for **12** is based on the presumption that a CO group and bridging Cl are substituted by the ligand **6** without any reorganization of ligands around Ru. The rearrangement of ligands around Ru would lead to other isomeric forms and their presence is not ruled out. The inadequate solubility of **12** restricted us from recording its $^{125}Te$ NMR and furnishing more evidence for the proposed structure. The formulation of **12** is not supported by a molecular ion peak in its FAB mass spectrum but the fragmentation pattern is characteristic. The terminal nature of CO is indicated by the position of $\nu$(CO) bands in the IR spectrum of **12**.




6 = Te~N

12

***Acknowledgements***

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