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Reaction of α-Me$_2$TeJ$_2$ with Metal Carbonyl Compounds

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Organyltelluro (RTe–) and telluroether (R$_2$Te–) ligands have received much attention in transition metal chemistry and numerous examples are reported but at the present time only monodentate telluroether ligands are known [1–3]. Recently we reported the synthesis and molecular structure of [CpMo(CO)$_2$(μ-TePh)]$_2$ a double PhTe-bridged non planar heterocycle obtained by photolysis of [CpMo(CO)$_3$]$_2$ in the presence of Ph$_2$Te$_2$ or by addition of Ph$_2$Te$_2$ to the triply bonded [CpMo(CO)$_2$]$_2$ [4]. A remarkable feature of [CpMo(CO)$_2$(μ-TePh)]$_2$ is the short Te–Te distance (3.24 Å) consistent with the formulation of a partial bond.

We report here on reactions of M$_2$(CO)$_{10}$ (M = Mn, Re), Co$_2$(CO)$_8$, [CpMo(CO)$_3$]$_2$, MeCpMn(CO)$_3$ and the metalate anions Na[Co(CO)$_4$] or Na[Mn(CO)$_5$] with α-Me$_2$TeJ$_2$ in order to synthesize the corresponding bidentate telluroether compounds. Photoinduced reaction of the dimeric carbonyls M$_2$(CO)$_{10}$ with α-Me$_2$TeJ$_2$ produces in good yields *cis*-M(CO)$_4$(TeMe$_2$)J (M = Mn, Re). Both compounds were isolated by sublimation at 60 °C *in vacuo*. They were characterized by elemental analysis, cyclic voltammetry, infrared and mass spectra. No dimeric or tetrameric complexes were found after photolysis. The infrared spectra of the manganese and rhenium compound exhibit the ν(CO) pattern characteristic for a symmetric M(CO)$_4$ group. In the mass spectra (70 eV) molecular ion peaks are observed for both compounds confirming the calculated molecular weights of $M^+ = 454$(Mn) and 585(Re). The fragmentation of the molecular ions occurs by successive loss of the four carbonyls and then of the methyl groups. The observed isotopic distribution patterns for both compounds are as expected. The cyclic voltammograms of *cis*-Mn(CO)$_4$(TeMe$_2$)J exhibit two set of peaks. The first one electron oxidation wave at 690 mV (a$_1$) is followed by another one electron transfer at 1365 mV (a$_2$). The first redox couple shows reversible character but the second oxidation is not reversible. Re(CO)$_4$(TeMe$_2$)J shows only a irreversible one electron oxidation at 1545 mV (a$_1$). Metathetical reaction of the iodo-compounds M(CO)$_4$(TeMe$_2$)J with Na[Co(CO)$_4$] or Na[Mn(CO)$_5$] did not give the expected bimetallic complexes indicating a strong bonded not substitutable iodine ligand. Co$_2$(CO)$_8$ reacts vigorously with α-Me$_2$TeJ$_2$ under CO evolution and gives a nearly insoluble black polymeric compound which could best be formulated as [Co(CO)$_5$TeMe$_2$]$_n$. [CpMo(CO)$_3$]$_2$ showed no reaction with α-Me$_2$TeJ$_2$ even under forced conditions (UV or heat). MeCpMn(CO)$_2$thf obtained by photolysis of MeCpMn(CO)$_3$ in thf reacted with α-Me$_2$TeJ$_2$ under decomposition giving a dark brown coloured oil. The metalates Na[Co(CO)$_4$] or Na[Mn(CO)$_5$] showed formation of the respective red (Co(CO)$_4$)$_2$(TeMe$_2$) or purple (Mn(CO)$_5$)$_2$(TeMe$_2$) and precipitation of NaJ when α-Me$_2$TeJ$_2$ was added. These two new compounds which could be detected only by IR in benzene decomposed when the solvent was removed *in vacuo*. The IR (ν(CO)) spectra indicate a Co–Te–Co or Mn–Te–Mn arrangement.

Experimental

All manipulations were carried out under dry nitrogen. Solvents were dried and distilled under N$_2$. Infrared spectra were recorded on a Perkin-Elmer 180 and mass spectra on a Varian MAT CH7 (70 eV). All CV measurements were carried out under dry argon (oxisorb, Messer-Griesheim). Solvents were dried and distilled under N$_2$. Tetrabutylammonium hexafluorophosphate (TBAH) was purified by double recrystallization from purified methanol and dried under vacuum with P$_2$O$_5$.

Instrumentation

All electrochemical measurements were performed with a potentiostat (Bank-Wenking LT-78), a function generator (Bank Voltage Scan Generator VSG 72), a voltage integrator (Bank Wenking EVI 80) and a xy recorder (Hewlett-Packard 7015 B). The rotating disk electrode was a Metrohm RDE 628. We utilized a three electrode system. This consisted of a Pt-ring working electrode (Ingold), a glassy carbon counter electrode (Metrohm) and a Ag/AgCl (3 M KCl, Metrohm) reference electrode.

Synthesis of M(CO)$_4$(TeMe$_2$)J (M = Mn, Re)

Mn$_2$(CO)$_{10}$ (1.0 mmol, 390 mg; 652 mg Re$_2$(CO)$_{10}$) and α-Me$_2$TeJ$_2$ (1.0 mmol, 414.0 mg) were dissolved in thf/pentane 1:4 and irradiated with a mercury high-pressure lamp (Hanau 150 W) for one hour at 10 °C. During photoreaction the solution turned deep orange. Vacuum sublimation (10^{-2} mmHg, 45 °C) gave crystalline products (yield: >80%

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(Mn); >60% (Re)), with satisfactory elemental analyses (C,H,N).

IR ν(CO): 2080m, 2020s, 2005s, 1960s; CV: 200 mV/s; 0.1 M TBAH; $M(CO)_4(TeMe_2)J = 5{:}10^{-4}$ M, Mn(a_1): 690 mV(oxid.), (a_2): 1365 mV(oxid.), (c_1): 758 mV(red.). Re(a_2): 1545 mV(oxid.).

Reaction of α-Me_2TeJ_2 with $Na[Co(CO)_4]$

α-Me_2TeJ_2 (1.0 mmol, 414 mg) was dissolved in 180 ml benzene. After addition of 1.0 g $Na[Co(CO)_4]$ the solution changed colour to red and precipitation of NaJ occurred. The IR spectrum of the solution shows the following pattern: 2081m, 2060m, 2052m, 2038vs, 2036vs, 2027sh, 1972s (benzene), ν(CO). When the solvent is removed under vacuum the product decomposes immediately. Reaction of $Na[Mn(CO)_5]$ with α-Me_2TeJ_2 shows similar behaviour. Removal of the solvent benzene leads to decomposition. (IR ν(CO); 2060s, 2032m, 2011s, 1980m, 1978sh (benzene).

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