We recently found the usefulness of the Wittig-Horner reaction of 2-dimethylphosphono-1,3-benzodithiole 3a with conjugated 1,4-diketones for the preparation of 2,2'-bis(1,3-dithiole) donors. We have now used the Wittig-Horner reaction of 3b, which was synthesized by a similar method as that for 3a,[13] to prepare 1. In this case, a cyclopentadiene adduct of p-benzoquinone 4 was used as a diketone and after introduction of the 1,3-dithiole rings the cyclopentadiene was removed by a retro-Diels-Alder reaction, since the direct product of p-benzoquinone with 3b gave a complex mixture of products without formation of 1.

Thus, a solution of 3b in dry THF was treated with 1.1 equivalents of n-butyllithium at −78 °C under nitrogen, and after stirring for 5 min, 0.43 equivalent of 4 was added. The solution was then stirred at −78 °C for a further 10 min and allowed to warm to room temperature, whereupon the bis(1,3-dithiole) derivative 5 was obtained in 27% yield. Thermalysis of 5 at 200 °C under reduced pressure furnished, via a retro-Diels-Alder reaction, dark red crystals of 1 in 54% yield.[6] The benzo derivatives 6a, b were prepared analogously by reaction of the Diels-Alder adducts of 1,4-naphthoquinone and the corresponding methyl compound, respectively with cyclopentadiene. The dibenzo derivative 7 could be synthesized in 74% yield by direct Wittig-Horner reaction of 3b with 9,10-anthracenequinone. The dibenzothiadiazolefulvalene (TTF) analogue 2a could be prepared by a retro-Diels-Alder reaction of 8, which was obtained in 73% yield by reaction of 3a and 4. 9a, b and 10 were prepared similarly. The decomposition temperatures of the new donors are listed in Table 1. The TTF analogues 1 and 6a, b are air sensitive, whereas the dibenzo analogues 2a, 7, 9a, b, and 10 are stable towards air.

The oxidation potentials of the donors (Table 1) were measured by cyclic voltammetry. The values for the donors with quinoid structures are lower than those of TTF measured under the same conditions (0.28, 0.64 V vs. SCE); the parent compound 1, in particular, is an extremely strong electron donor. This may be due to the fact that the quinoid structures form a new aromatic sextet upon oxidation.

Other characteristic features are that the difference between the first and second oxidation potentials of 1 is very small and that two-electron oxidation waves are observed in the other new donors. Accordingly, the donors with quinoid structures form dications more readily upon oxidation, due to the decreased Coulombic repulsion. With tetracyanoquinodimethane (TCNQ), the donors 1, 6a, b, 2a, and 9a, b gave charge-transfer complexes which exhibit good conductivities (Table 2).

### Table 1. Decomposition temperatures and oxidation potentials [a] of the donors.

<table>
<thead>
<tr>
<th>Donor</th>
<th>$T_{\text{decomp}}$ [°C]</th>
<th>$E_{\text{anodic peak}}$ [V]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>230-245</td>
<td>-0.11, -0.04</td>
</tr>
<tr>
<td>6a</td>
<td>160-170</td>
<td>0.00</td>
</tr>
<tr>
<td>6b</td>
<td>190-194</td>
<td>-0.04</td>
</tr>
<tr>
<td>7</td>
<td>320-325</td>
<td>+0.25 [b]</td>
</tr>
<tr>
<td>9a</td>
<td>260-270</td>
<td>+0.18</td>
</tr>
<tr>
<td>9b</td>
<td>243-248</td>
<td>+0.15</td>
</tr>
<tr>
<td>10</td>
<td>314-317</td>
<td>+0.24</td>
</tr>
<tr>
<td>5</td>
<td>168-170</td>
<td>+0.17</td>
</tr>
<tr>
<td>8</td>
<td>260-275</td>
<td>+0.37</td>
</tr>
</tbody>
</table>

[a] 0.1 m $\text{EtNCICl}_2$ in MeCN, Pt electrode, scan rate: 100 mV s$^{-1}$; E vs. standard calomel electrode (SCE). [b] Irreversible. Calculated as $E_{\text{anodic peak potential}}$ = 0.03 V.

### Table 2. Properties of charge-transfer complexes with TCNQ.

<table>
<thead>
<tr>
<th>Donor (D)</th>
<th>$T_{\text{d}}$ [°C]</th>
<th>Molar ratio [D:A]</th>
<th>$\sigma$ [S cm$^{-1}$] [b]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>&gt; 400</td>
<td>3:4</td>
<td>$5.3 \times 10^{-4}$</td>
</tr>
<tr>
<td>6a</td>
<td>&gt; 380</td>
<td>2:3</td>
<td>2.9 x 10^{-2}</td>
</tr>
<tr>
<td>6b</td>
<td>&gt; 400</td>
<td>2:3</td>
<td>1.9 x 10^{-2}</td>
</tr>
<tr>
<td>2a</td>
<td>250-253</td>
<td>1:1</td>
<td>4.1 x 10^{-3}</td>
</tr>
<tr>
<td>9a</td>
<td>245-249</td>
<td>3.5:3 H$_2$O</td>
<td>1.9 x 10^{-2}</td>
</tr>
<tr>
<td>9b</td>
<td>220-225</td>
<td>1:1:8 H$_2$O</td>
<td>2.2 x 10^{-2}</td>
</tr>
</tbody>
</table>

[a] Based on elemental analyses. [b] Electrical conductivities measured on compressed pellets by two-probe technique at room temperature.

2-Isocyanato-2-alkenoates—Synthesis and Reactions

By Franz Effgenberger,* Christian Baumgartner, and Jürgen Kühlein

Dedicated to Professor Christoph Rüchardt on the occasion of his 60th birthday

Very few data have been quoted in the literature about 2-isocyanato-2-alkenoates; they have been detected spectroscopically as reaction intermediates [a, b] and in two cases have even been isolated [12] α-isocyanatoacrylic acid esters have on one occasion been presumed as intermediates in the thermolysis of ethyl 1-isocyanato-cyclobutane-2-carboxylate,[12a] and on another their formation and their spectroscopic detection—likewise in thermolysis reactions—have been reported in a patent.[12b]

In the perrenate-catalyzed decomposition of α-azido-carboxylic acid derivatives such as 1 we could successfully replace acetic anhydride by other acylating reagents, thereby providing easy access to a series of interesting N-substituted α,β-didehydroamino acid esters.[14a]

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[b] This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

The results which we have now found with phosgene and diphosgene as "acylating reagent" in this decomposition reaction, although hoped for, are still surprising; as reaction products, the 2-isocyanato-2-alkenoates 2 were obtained in very good yields (Table 1).[4]

![Chemical structure](image)

Table 1. R and R' in 1 and 2 and yields of 2.

<table>
<thead>
<tr>
<th>R</th>
<th>R'</th>
<th>Yield of 2 [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>H</td>
<td>69</td>
</tr>
<tr>
<td>b</td>
<td>H</td>
<td>88</td>
</tr>
<tr>
<td>c</td>
<td>Me</td>
<td>82</td>
</tr>
<tr>
<td>d</td>
<td>H</td>
<td>80</td>
</tr>
<tr>
<td>e</td>
<td>H</td>
<td>53</td>
</tr>
</tbody>
</table>

Whereas the substituted esters 2b–e could be isolated and worked-up by distillation without any problem, the synthesis of pure α-isocyanatoacrylate 2a at first presented great difficulties, because it was always formed in a mixture with its—distillatively—inseparable HCl-adduct 3, and because it is exceptionally reactive, and easily polymerizes. However, the addition product 3 could be completely converted into the acrylate 2a by careful extrusion of HCl with triethylamine in diethyl ether, so that 2a was obtained in 69% yield—referred to 1a—in this way.

As expected, all usual addition reactions to the isocyanato group of the compounds 2 could be carried out, which, e.g., upon using appropriate alcohols (tert-butyl alcohol, benzyl alcohol) yield directly the urethane-protected dehydroamino acids 4, which are of special interest in peptide chemistry.

```
2 + R²OH -> R²C=CC(OMe)NCO₂R²
```

R² = tBu, PhCH₃

The acrylic ester 2a, which, besides the isocyanato group, has an activated and sterically unhindered C=C double bond, provides access to further, versatile reactions. In the presence of azoisobutyronitrile (AIBN) radical polymerization leads to the polymers 5; with methanol these yield the polymeric urethanes 6, which can be hydrolyzed to the poly(α-aminoacyclic acid) 7. We have no explanation for the astonishingly low degree of polymerization of 5 (n = 14–15).[5] The properties of 7 are almost identical with the properties of the poly(α-aminoacyclic acid) obtained by hydrolysis of the N-acetyldehydroalanine polymers.[6]

![Chemical reaction](image)

That the acrylic ester 2a is also suitable as dienophile for Diels-Alder reactions is demonstrated by the reactions with cyclopentadiene to give 8 and with 9-methylantracene to give 9, whereby 2a proves to be distinctly more reactive than N-acetyldehydroalanine.[7] The cycloadducts 8a, b can be further converted by alcohol addition into urethane-protected cyclic α-amino acids and by acid hydrolysis into the corresponding free cyclic α-amino acids.[8]

The previously reported reactivity sequence for Diels-Alder reactions with anthracenes is confirmed in the reactions of 2a with anthracenes: no cycloadducts were obtained at temperatures up to 115 °C, neither with anthracene nor with 9-methoxyanthracenes. Higher reaction temperatures are not possible because of the thermolability of 2a.

**Experimental**

2a: Phosgene was passed into a cold mixture of sodium perrhenate (1.0 g, 3.66 mmol) and methanesulfonic acid (0.2 g) in ethyl acetate (500 mL). After addition of 64.5 g (0.5 mmol) of 1a and of 330 mg of hydroquinoline, phosgene was condensed into the mixture such that it was always present in excess. The mixture was then heated at 70–80 °C until completion of evolution of gas. After evaporation of the ethyl acetate, distillation at 50°C/12 torr furnished 69 g of a mixture of 2a and 3 in the ratio 1:2. At 0°C, 125 mL of diethyl ether were added, which, e.g., upon using appropriate alcohols (tert-butyl alcohol, benzyl alcohol) yield directly the urethane-protected dehydroamino acids 4, which are of special interest in peptide chemistry.

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A Polymeric Technetium Compound of the Composition \([\text{Te}_2\text{O}_3(\text{C}_5\text{Me}_5)]_n\)

By Basil Kanellakopoulos, Bernd Nuber, Konstantinos Raptis, and Manfred L. Ziegler*

Dedicated to Professor Margot Becke on the occasion of her 75th birthday

The tricarboxylrhenium complex 1 reacts with \(\text{H}_2\text{O}_2\) to give the trixo-complex 2, which has proved to be an interesting and versatile starting compound for exploring the remarkable chemistry of rhenium in high oxidation states. So far it has not been possible to carry out an X-ray structure analysis of 2 itself; however, the structure of one of its derivatives is already known, namely that of 3, which forms discrete molecules. This might also be assumed in the case of 2.

\[
\begin{align*}
\{\text{[\text{C}_5\text{Me}_5\text{Re}(\text{CO})_3]}\} \quad & \{\text{[\text{C}_5\text{Me}_5\text{Ir}(\text{CO})_3]}\} \\
\{\text{[\text{C}_5\text{Me}_5\text{Ir}(\text{CO})_3]}\} & \{\text{[\text{C}_5\text{Me}_5\text{Ir}(\text{CO})_3]}\} \\
\{\text{[\text{C}_5\text{Me}_5\text{Ir}(\text{CO})_3]}\} & \{\text{[\text{C}_5\text{Me}_5\text{Ir}(\text{CO})_3]}\}
\end{align*}
\]

In the reaction of the tricarboxytechnetium complex 4 with perhydrol it has now been shown that the technetium species 5 behaves differently than its rhenium homologue 1. Elemental analysis, mass spectra, and, above all, an X-ray structure analysis yielded the empirical formula \(\text{C}_5\text{H}_{15}\text{Te}_2\text{O}_3\) for the product 5 in a polymeric structure. It is clear from Figure 1 that, in 5, two Te atoms are bridged by three \(\mu\)-oxo ligands and the coordination of the Te atoms is in each case completed by a \(\text{C}_5\text{Me}_5\) ring (= \(\text{Cp}^*\)). These \(\text{Cp}^*\) rings are, however, concomitantly a component of the neighboring units, so that the above mentioned empirical formula results. The planes of the \(\text{Cp}^*\) rings and of the \(\mu\)-oxo-bridge ligands are, crystallographically exactly parallel to one another, i.e. a kind of polydecker structure is formed (distances: \(\text{Cp}^*\)-O, planes 93.4(3), Te-0, plane 186.7(4) pm). A striking feature is the unusually short distance (186.7(4) pm) between the two Te atoms coupled by the three \(\mu\)-oxo ligands (distance between the \(\text{Cp}^*\)-bridged Te atoms 407.7(4) pm); the shortest Te–Te distance recorded so far is 213(1) pm. Shorter metal–metal distances are found only in binuclear chromium complexes with a minimum of 182.8(2) pm in \([\text{Cr}_2(\text{2-MeO-5-MeC}_6\text{H}_3)_2]\). Formally, the two technetium centers must be assigned on oxidation number of +5.3. This would mean that the ground state has the relatively rare \(\sigma^2\pi^6\delta^1\) configuration and thus a bond order of 3.5. This bond order together with the three \(\mu\)-oxo ligands makes the extremely short Te–Te distance understandable.

The spectroscopic data are fully consistent with the results of the X-ray structure analysis. Thus, in the EI mass spectrum the molecular peak is clearly visible at \(m/z\) 381.6 (18%), and the Te–O stretching vibrations appear in the IR spectrum at 909 (symmetric) and 880 cm\(^{-1}\) (antisymmetric). In the \(^1\text{H NMR}\) spectrum the methyl protons are observed at \(\delta = 1.606\).

**Experimental**

A solution of 4 (180 mg, 0.57 mmol) in \(\text{C}_6\text{H}_6\) (15 mL) was treated with 5 mL of 30% \(\text{H}_2\text{O}_2\) and the mixture stirred at room temperature. The initial concentration of 4 first started to decrease after 24 h. After 3 days, 4 could no longer be detected. After separation of the phases the organic phase was dried with \(\text{Na}_2\text{SO}_4\) and freed of oily reaction products by chromatography (silica gel 60, 30 × 20 cm, \(\text{C}_6\text{H}_6\)). Subsequent elution with \(\text{C}_6\text{H}_6\)ethyl ether (1:1) gave a yellow zone. After slow evaporation of solvent from the eluate (ca. 12 h), 5 was recovered in the form of needle-shaped yellow crystals. Yield: 25.0 mg (16.0% \text{calcd.} 51.94%). El-MS fragmentation (relative intensity [YO] in parenthesis): \(\text{Cp}^*\) (100); \(\text{Cp}^*\text{Te}^3\) (36); \(\text{Cp}^*\text{Te}^1\text{OF}^1\) (18). The corresponding relative intensities for 2 under similar conditions are 100, 35, 100, and 0.0%.

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[3] Yellow column-shaped crystals (0.23 × 0.26 × 0.31 mm\(^3\)), \(a = 594.6(5), b = 869.7(4), c = 1063.0(7)\text{ pm}, V = 549.70 \times 10^4 \text{ pm}^3; Z = 4; space group D\(_{2d}\)-Pna\(_2\). Data collection with a Siemens-Stoe diffractometer (AED II), \(\theta\) scan 3° < \(\theta < 60°\); \(\Delta(\text{min}/\text{max}) 0.8 / 0.12, 0.15\), Mo\(_{\alpha}\) radiation (\(\lambda = 0.71069 \text{ Å}\)); 969 possible reflections in the measuring range, 381 (\(I > 2 \sigma(I)\)), 348 independent (\(I > 2.2 \sigma(I)\)); empirical absorption correction (\(\psi\) scans, 4 reflections 13° < \(\psi < 42°\), transmission factors (\text{min}/\text{max}) 0.74/1.00, \(\mu = 24.41 \text{ cm}^{-1}\), \(\theta\) scans, 10 cm\(^{-1}\)), solution of structure by Patterson and Difference Fourier syntheses, refinement by method of least squares (all non-hydrogen atoms anisotropic, H atoms fixed at ideal positions), \(R = 0.059, R_a = \frac{\sum \sqrt{\langle W(F)\rangle} - \langle F\rangle^2}{\sum \sqrt{\langle W(F)\rangle}} = 0.044, \text{Goof} = \frac{\sum \sqrt{W(F) - \langle F\rangle^2/\langle W(F)\rangle}}{\langle W(F)\rangle} = 2.19, \text{ residual electron density} 1.47 = -3.13 e\text{ Å}^3, \text{shifted (mean)/max} 0.18/1.8. All calculations based on the program system SHIELDXTL. Further details of the crystal investigation are available on request from the Fachinformation-Zentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Egggenstein-Leopoldshafen 2, quoting the depository number CSD-53780, the names of the authors, and the journal citation.


