Table 2. IR- and MS data of compounds (1) and (2).

<table>
<thead>
<tr>
<th>Compound</th>
<th>IR (KBr): ν (cm⁻¹)</th>
<th>MS: m/e (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>3165, 3145 (furan), 3082 (=CH₂), 3037 (=C-H), 1766, 1745 (ester carbonyl), 1688 (ν(N=O), 1504 (ν(C=O))</td>
<td>554 (3.8%), 494 (7.6%), 476 (2.2%), 434 (9.2%), 346 (9.8%), 345 (8.7%), 225 (39%), 209 (100%, Ring-A fragment), 208 (78%), 177 (40%), 121 (52%)</td>
</tr>
<tr>
<td>(2)</td>
<td>3165, 3145 (furan), 3082 (=CH₂), 3037 (=C-H), 1766, 1745 (ester carbonyl), 1688 (ν(N=O), 1504 (ν(C=O))</td>
<td>612 (2% M⁺), 552 (26.6%), 492 (2.5%), 432 (1.5%), 345 (5.9%, Ring-C-D fragment), 267 (74%, Ring-A fragment), 225 (32%), 207 (100%, Ring-A fragment - 60%), 175 (18%), 157 (34%), 121 (15%)</td>
</tr>
</tbody>
</table>

Structure of 6-acetoxytocadocillin (2): From the greater mass of (2) compared to that of (1) (a difference of m/e = 58), an additional acetoxy signal at δ = 2.21, a --CH-e signal at δ = 5.31, and the simplification of the H₅ signal in the structure and stereochemistry of (2) were confirmed by X-ray structural analysis (Fig. 1).

Fig. 1. ORTEP plot of (2). R = CH₃(CH₂)₂CH₂CH₂C₆H₅. Bond lengths: Mo—N₁ 1.933(12), Mo—C₈ 2.223(12), C₈—N₁ 1.418(16), Mo—C₆ 1.937(12), Mo—C₇ 1.932(13), Mo—C₈ 2.348—2.407, C—(phenyl) and pyridyl ring) 1.381—1.415, C—(pyridyl) 1.355(17), and 1.344(13)Å. Bond angles: N₁—Mo—C₈ 92.6(4), N₁—Mo—C₆ 92.6(4), C₆—Mo—C₇ 78.6(6), C₇—Mo—C₈ 78.6(5), Mo—N₁—C₈ 72.9(6), Mo—C₈—N₁ 69.5(6).

[5] We are grateful to Prof. Dr. H. Schmutzer and his co-workers, Institut für Physiopathologie der Universität Giessen, and Prof. Dr. F. Meulicke, Institut für Genetik der Universität Hohenheim, for valuable discussions and support in carrying out the biological tests.
[6] We thank the Department of Forestry, Brisbane, Queensland (Australia) for the supply of materials.
[8] We thank Dr. W. E. Hull, Bruker, Karlsruhe, for recording the 360-MHz 1H-NMR spectra.

Ring Contraction in the Reaction of Cationic C₆H₅Mo(CO)₂ Chelate Complexes with Methyllithium

By Henri Brunner, Heinrich Schwägerl, Joachim Wachter, George M. Reisner, and Ivan Bernal

A stereospecific phenyl addition at the azomethine carbon has been proposed to occur in the reaction of CH₃Li with [C₆H₅Mo(CO)₂NN]PF₆ (NN' = Schiff base derived from 2-pyridinecarbaidehyde and (S)-1-phenylethylamine)⁴. It has now been shown that reaction of CH₃Li with [C₆H₅Mo(CO)₂(NN)]PF₆ surprisingly results in a contraction of the five-membered chelate system present in the complex². The rearrangement, which has been proved by IR, 1H- and 13C-NMR spectra as well as X-ray structure determination, involves several steps which can formally be considered as exchange of CH₃ for H at the azomethine carbon, addition of H to the imine nitrogen, cleavage of the Mo—N(pyridine) bond, and formation of a Mo—C bond to give a three-membered ring.
formation of the trans structure, the NMR spectra of (2) and (3) each exhibit only one set of signals.

Compounds (2) and (3) correspond to a previously described complex type\(^1\); distances and angles in the three-membered ring of (2) are comparable with those in \((\text{CO})_6\text{MnCH}_2\text{NR}\)^\(^2\).

**Procedure**

To a suspension of (1) (5.6 mmol) in THF (100 ml) is added dropwise at room temperature LiCH\(_3\) (11.2 mmol) in diethyl ether. The reaction is completed by 30 minutes' heating under reflux. On chromatography over SiO\(_2\) with benzene/ether/pentane at -35°C. Yields of (2) and (3) have been found to be 50%.

We attempted the preparation of the deep-green salt \([\text{Fe}_2(\text{NO})_6]\)(PF\(_6\)) by reaction of the neutral complex \([\text{Fe}(\text{CO})_4(\text{NO})]^+\) with NO'PF\(_6\) and found that even less than 1 mol% NO'PF\(_6\) is eluted, then (2), and on addition of some ether also (3). The products were recrystallized from ether/pentane at -35°C. Yields of (2) and (3) are comparable with those in \((\text{CO})_6\text{MnCH}_2\text{NR}\)^\(^2\).

**[Fe\(_2\)(NO)\(_6\)]^2+**, A Binary Nitrosyliron Cation**\(^{[*]}\)**

By Max Herberhold and Reinhard Klein\(^{[*]}\)

In the isoelectronic series of tetrahedral carbonyl(nitrosyl)iron complexes \([\text{Fe}(\text{CO})_4(n\text{NO})_2]^-\)\(^{(-n=0-4)}\), the cationic members (2) and (3) have so far not been reported:

\[
\begin{align*}
\text{FeCoO}^+ & : \text{FeCoO}_2(\text{NO})^- & \text{FeCoO}_2(\text{NO})_2^- \\
\{\text{FeCO}(\text{NO})\}_2^+ & \{\text{FeNO}^2^+\} & \{\text{FeNO}^3\} \\
\end{align*}
\]

We attempted the preparation of (2) by reaction of the neutral complex (1) with NO'PF\(_6\) and found that even less than an equimolar amount of the nitrosyl salt effects cleavage of both CO ligands from the complex, leading to formation of the deep-green salt \([\text{Fe}_2(\text{NO})_6]\)(PF\(_6\)) (4). This oxidation of (1) corresponds formally to the known\(^{[11]}\) formation of the mononuclear complex \([\text{Fe}(\text{NO})_3\text{Cl}]\) (5) from (1) and nitrosyl chloride.

The new compound (4) is also obtainable by removal of halide from (5):

\[
2 \text{Fe}(\text{CO})_3(\text{NO})_2 \rightarrow 2 \text{NO}^+\text{PF}_6^- + 4 \text{CO}
\]

The compound (4) is also obtained by removal of halide from (5):

\[
2 \text{Fe}(\text{CO})_3(\text{NO})_2 \rightarrow 2 \text{NO}^+\text{PF}_6^- + 4 \text{CO}
\]

The reaction is completed by 30 minutes' heating under reflux. On chromatography over SiO\(_2\) with benzene/ether/pentane at -35°C. Yields of (2) and (3) are comparable with those in \((\text{CO})_6\text{MnCH}_2\text{NR}\)^\(^2\).

The new compound \([\text{Fe}_2(\text{NO})_6]\)(PF\(_6\)) has a binuclear structure in which the iron atom achieves a noble gas configuration:

\[
\text{Fe}(\text{NO})^2^+ \text{Fe}(\text{NO})_2\text{PF}_6^-
\]

This structure is in agreement with the experimental findings on nitromethane solutions of (4):

1. The \(^{1}H\)-NMR spectrum reveals diamagnetism.
2. The equivalent conductivity (at 20°C) lies within the range (150-180 \text{ cm}^2/\text{mol} \cdot \text{cm}^2/\text{mol}) typical for 2:1 electrolytes\(^{[2]}\).
3. The Mössbauer spectrum\(^{[3]}\) of a frozen solution \((\delta=0.33 \text{ mm/s, } E_{0}=0.49 \text{ mm/s rel. to Fe metal})\) is reconcilable with only one sort of iron atoms.
4. The IR spectrum gives no indication of the presence of bridging nitrosyl ligands. The pattern of the two NO stretching absorptions corresponds to that expected for terminal nitrosyl groups (A + E). However, it remains unclear whether the NO ligands of both \([\text{Fe}(\text{NO})_3]\)-cation halves have \(D_{4d}\) (staggered) or \(D_{3h}\) (eclipsed) symmetry.

The salt (4) is stable only below -20°C. It can be handled in polar solvents not having coordinating properties (CH\(_2\)Cl\(_2\), CH\(_3\)Cl); it is readily soluble in nitromethane. On addition of tetraalkylammonium halides, NR\(_4\)X, characteristic (ν(NO) bands\(^{[4]}\) of Fe(NO\(_3\))X \((X=CI, Br, I)\) appear in the IR spectrum. Phosphanes react with (4) to give adducts of the type \([\text{Fe}(\text{NO})_3\text{L}]\)PF\(_6\) which behave like 1:1 electrolytes (e.g., \(6), \text{L=PP_3H}: \Lambda_e=82 \text{ cm}^2/\text{mol} \text{ in CH}_3\text{NO}_2 \text{ at } -25.5°C)\).

**Table 1. IR spectra in nitromethane solution (in cm\(^{-1}\))**

<table>
<thead>
<tr>
<th>Compound</th>
<th>ν(NO) (3-23%)</th>
<th>ν(CO) (150-180 cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(NO3)(PF6)_2</td>
<td>1805, 1765</td>
<td>2095, 2043</td>
</tr>
<tr>
<td>Fe(NO3)CI</td>
<td>1898, 1790</td>
<td></td>
</tr>
<tr>
<td>Fe(NO3)PP3PF6</td>
<td>1919, 1828</td>
<td></td>
</tr>
<tr>
<td>Fe(NO3)2Fe(NO3)Cl</td>
<td>1917, 1824</td>
<td></td>
</tr>
</tbody>
</table>

Cationic nitrosylmetal complexes are of interest for investigations of catalysis\(^{[9]}\). Hexanitrosyliron(2+) is the first example of a binary nitrosylmetal cation.

**Experimental**

(4) : \(\text{NO}^+\text{PF}_6^-\) (0.77 g, 4.4 mmol) is added to a solution of \(\text{Fe}(\text{CO})_3(\text{NO})_2\) (0.52 g, 3 mmol) in dichloromethane (20 ml) and the mixture stirred for 2 h (evolution of gas), cooled to -30°C, and filtered under N\(_2\) pressure through a cold (-30°C) frit. The dark-green residue consisting of (4) is purified by recrystallization from CH\(_2\)Cl\(_2\) and the combined washings and filtrate slowly cooled to -78°C. The dark-green fibrous needles which crystallize out are washed several times with pentane (-40°C) and dried for 3 h at -78°C/10\(^{-2}\) torr. Yield 0.08-0.10 g (ca. 10%).

(6) : \(\text{NO}^+\text{PF}_6^-\) (0.35 g, 2 mmol) is added portionwise to a stirred solution of (1) (0.34 g, 2 mmol) in nitromethane (20 ml) at -30°C. When evolution of CO has ceased (after ca. 3 min), a cold (-30°C) solution of triphenylphosphine (0.54 g, 2 mmol) in nitromethane is added dropwise to the mixture. On subsequent addition of cold toluein lustrous green leaflets of (6) crystallize out which are then washed at -30°C with