

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

(1), IR (KBr): 3165, 3145 (furan), 3082 (=CH<sub>2</sub>), 3037 (=C—H), 1766, 1745 (ester carbonyl), 1688 (α,β-unsaturated six-membered ring ketone), 1504 (furan), 1247 (C—O), 881 and 874 cm<sup>-1</sup> (furan and =CH<sub>2</sub>)

(1), MS: *m/e* = 554 (3.8%, M<sup>+</sup>), 494 (7.6%), 476 (2.2%), 434 (9.2%), 346 (9.8%), 345 (8.7%, Ring-C-D fragment), 225 (39%), 209 (100%, Ring-A fragment), 208 (78%), 177 (40%), 121 (52%)

(2), IR: essentially the same as the spectrum of (1)

(2), MS: *m/e* = 612 (2%, M<sup>+</sup>), 552 (2.6%), 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%), 137 (34%), 121 (15%)

**Structure of 6-acetoxytoonacilin (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—O signal at δ = 5.31, and the simplification of the H<sup>5</sup> signal in the <sup>1</sup>H-NMR spectrum with hardly any other alteration in the pattern of the signals, it was concluded that (2) must be the acetoxy derivative of (1). The structure and stereochemistry of (2) were confirmed by X-ray structural analysis (Fig. 1).

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- [1] R. Steets, Dissertation, Universität Giessen 1976; and references cited therein.
- [2] P. R. Zanno, I. Miura, K. Nakanishi, J. Am. Chem. Soc. 97, 1975 (1975), and references cited therein.
- [3] D. Lavie, M. K. Jain, S. R. Shpan-Gabrielith, Chem. Commun. 1967, 910.
- [4] P. Grijpma, R. Ramalho, Turrialba 19, 531 (1969); P. Grijpma, *ibid.* 20, 85 (1970); P. Grijpma, S. C. Roberts, *ibid.* 25, 152 (1975); G. G. Allan, R. J. Gara, S. C. Roberts, *ibid.* 25, 255 (1975).
- [5] We are grateful to Prof. Dr. H. Schmutterer and his co-workers, Institut für Phytopathologie der Universität Giessen, and Prof. Dr. F. Mechelke, 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.
- [7] D. Lavie, E. C. Levy, R. Zelnik, Bioorg. Chem. 2, 59 (1972).
- [8] We thank Dr. W. E. Hull, Bruker, Karlsruhe, for recording the 360-MHz <sup>1</sup>H-NMR spectra.

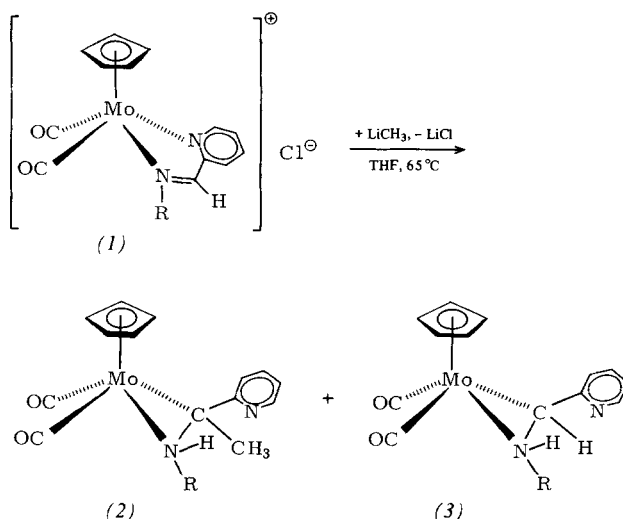
## Ring Contraction in the Reaction of Cationic C<sub>5</sub>H<sub>5</sub>Mo(CO)<sub>2</sub> Chelate Complexes with Methylithium

By Henri Brunner, Heinrich Schwägerl, Joachim Wachter, George M. Reisner, and Ivan Bernal<sup>[\*]</sup>

A stereospecific phenyl addition at the azomethine carbon has been proposed to occur in the reaction of C<sub>6</sub>H<sub>5</sub>Li with [C<sub>5</sub>H<sub>5</sub>Mo(CO)<sub>2</sub>NN']PF<sub>6</sub> (NN' = Schiff base derived from 2-pyridinecarbaldehyde and (*S*)-1-phenylethylamine)<sup>[1]</sup>. It has now been shown that reaction of CH<sub>3</sub>Li with [C<sub>5</sub>H<sub>5</sub>Mo(CO)<sub>2</sub>NN']PF<sub>6</sub> surprisingly results in a contraction of the five-membered chelate system present in the complex<sup>[2]</sup>. The rearrangement, which has been proved by IR, <sup>1</sup>H- and <sup>13</sup>C-NMR spectra as well as X-ray structure determination, involves several steps which can formally be considered as exchange of CH<sub>3</sub> for H at the azomethine carbon, addition of H to the imine nitrogen, cleavage of the Mo—N(pyridine)

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bond, and formation of a Mo—C bond to give a three-membered ring.



R = CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>, CH(CH<sub>3</sub>)<sub>2</sub>, CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>, CH(CH<sub>3</sub>)C<sub>6</sub>H<sub>5</sub>

The cationic pyridinecarbaldehyde complexes (1) react with excess CH<sub>3</sub>Li to give the neutral compounds (2) and (3). A strong N—H stretching vibration in the IR spectrum corresponds in the <sup>1</sup>H-NMR spectrum to a NH—CH coupling in the *N*-alkyl group of (2) and (3) and a NH—CH coupling within the three-membered ring of (3), both of which collapse on addition of D<sub>2</sub>O. In the complexes (2) the methyl substituent introduced gives a singlet. The structural relationship of both types of complexes (2) and (3) also is apparent from the similar <sup>13</sup>C-NMR spectra.

Compound (2) with R = CH(CH<sub>3</sub>)C<sub>6</sub>H<sub>5</sub> forms orange monoclinic crystals (space group P2<sub>1</sub>/a) with cell constants *a* = 17.053(9), *b* = 11.185(5), *c* = 11.011(3) Å, β = 104.48(3)°; *V* = 2033.5 Å<sup>3</sup>, *d*<sub>calc</sub> = 1.44 g·cm<sup>-3</sup>, *Z* = 4. From 6364 measured reflections (MoK<sub>α</sub> radiation, λ = 0.71069 Å) 3268 were used for the refinement of the structure (*R* value 5.4%). The dominant structural feature of the molecule is a η<sup>2</sup>-amino-methylene ligand with *trans* arrangement of the large pyridyl and 1-phenylethyl substituents. In accord with exclusive for-

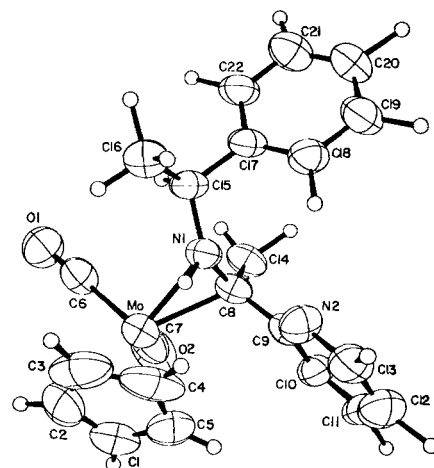


Fig. 1. ORTEP plot of (2), R = CH(CH<sub>3</sub>)C<sub>6</sub>H<sub>5</sub>. Bond lengths: Mo—N1 2.178(8), Mo—C8 2.223(12), C8—N1 1.418(16), Mo—C6 1.933(12), Mo—C7 1.932(13), Mo—Cp 2.348—2.407, C—C(phenyl and pyridyl ring) 1.381—1.415, C—N(pyridyl ring) 1.356(17), and 1.344(13) Å. Bond angles: N1—Mo—C8 37.6(4), N1—Mo—C6 92.3(4), C6—Mo—C7 78.4(6), C7—Mo—C8 78.9(5), Mo—N1—C8 72.9(6), Mo—C8—N1 69.5(6)°.

mation 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<sup>[3]</sup>; distances and angles in the three-membered ring of (2) are comparable with those in (CO)<sub>4</sub>MnCH<sub>2</sub>NR<sub>2</sub><sup>[4]</sup>.

#### Procedure

To a suspension of (1) (5.6 mmol) in THF (100 ml) is added dropwise at room temperature LiCH<sub>3</sub> (11.2 mmol) in diethyl ether. The reaction is completed by 30 minutes' heating under reflux. On chromatography over SiO<sub>2</sub> with benzene [C<sub>5</sub>H<sub>5</sub>(CO)<sub>3</sub>Mo]<sub>2</sub> is first 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 3–23%, depending on the substituents R.

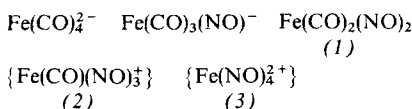
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- [1] H. Brunner, J. Wachter, J. Organomet. Chem. 113, C58 (1976).  
[2] S. J. LaPlaca, I. Bernal, H. Brunner, W. A. Herrmann, Angew. Chem. 87, 379 (1975); Angew. Chem. Int. Ed. Engl. 14, 353 (1975).  
[3] C. W. Fong, G. Wilkinson, J. Chem. Soc. Dalton Trans. 1975, 1100.  
[4] E. W. Abel, R. J. Rowley, R. Mason, K. M. Thomas, J. Chem. Soc. Chem. Commun. 1974, 72; E. W. Abel, R. J. Rowley, J. Chem. Soc. Dalton Trans. 1975, 1096.

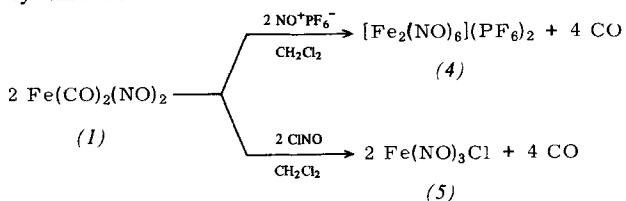
### [Fe<sub>2</sub>(NO)<sub>6</sub>]<sup>2+</sup>, A Binary Nitrosyliron Cation<sup>[\*\*]</sup>

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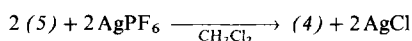
In the isoelectronic series of tetrahedral carbonyl(nitrosyl)-iron complexes [Fe(CO)<sub>4-n</sub>(NO)<sub>n</sub>]<sup>n-2</sup> (n = 0–4), the cationic members (2) and (3) have so far not been reported:



We attempted the preparation of (2) by reaction of the neutral complex (1) with NO<sup>+</sup>PF<sub>6</sub><sup>-</sup> 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 [Fe<sub>2</sub>(NO)<sub>6</sub>](PF<sub>6</sub>)<sub>2</sub> (4). This oxidation of (1) corresponds formally to the known<sup>[4]</sup> formation of the mononuclear complex Fe(NO)<sub>3</sub>Cl (5) from (1) and nitrosyl chloride.



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

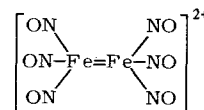


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Particularly noteworthy, however, is the reaction of iron powder with NO<sup>+</sup>PF<sub>6</sub><sup>-</sup> in nitromethane, which also leads to (4) without passage of NO gas.

We assume that the cation of the green salt (4) has a binuclear structure in which the iron atom achieves a noble gas configuration:



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

- The <sup>1</sup>H-NMR spectrum reveals diamagnetism.
- The equivalent conductivity ( $\Lambda_e = 148 \pm 2 \text{ cm}^2/\Omega \cdot \text{mol}$  of a 10<sup>-3</sup> M solution at -25.5°C) lies within the range (150–180 cm<sup>2</sup>/Ω · mol) typical for 2:1 electrolytes<sup>[2]</sup>.
- The Mössbauer spectrum<sup>[3]</sup> of a frozen solution ( $\delta = 0.33 \text{ mm/s}$ ,  $\Delta E_Q = 0.49 \text{ mm/s}$  rel. to Fe metal; -196°C) is reconcilable with only one sort of iron atoms.
- 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 [Fe(NO)<sub>3</sub>]-cation halves have D<sub>3d</sub> (staggered) or D<sub>3h</sub> (eclipsed) symmetry.

The salt (4) is stable only below -20°C. It can be handled in polar solvents not having coordinating properties (CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>); it is readily soluble in nitromethane. On addition of tetraalkylammonium halides, NR<sub>4</sub><sup>+</sup>X<sup>-</sup>, characteristic ν(NO) bands<sup>[4]</sup> of Fe(NO<sub>3</sub>)X (X = Cl, Br, I) appear in the IR spectrum. Phosphanes react with (4) to give adducts of the type [Fe(NO<sub>3</sub>)L]PF<sub>6</sub> which behave like 1:1 electrolytes (e.g. (6), L = PPh<sub>3</sub>;  $\Lambda_e = 82 \text{ cm}^2/\Omega \cdot \text{mol}$  in CH<sub>3</sub>NO<sub>2</sub> at -25.5°C).

Table 1. IR spectra in nitromethane solution (in cm<sup>-1</sup>).

Fe(CO) <sub>2</sub> (NO) <sub>2</sub> (1)	ν(NO) 1805 s, 1765 s;	ν(CO) 2095 s, 2043 s
[Fe <sub>2</sub> (NO) <sub>6</sub> ](PF <sub>6</sub> ) <sub>2</sub> (4)	1937 w, 1828 s	
Fe(NO) <sub>3</sub> Cl (5)	1898 w, 1790 s	
[Fe(NO) <sub>3</sub> PPh <sub>3</sub> ](PF <sub>6</sub> ) (6)	1919 m, 1828 s	
[Fe(NO) <sub>3</sub> PMe <sub>3</sub> ](PF <sub>6</sub> ) (7)	1917 m, 1824 s	

Cationic nitrosylmetal complexes are of interest for investigations of catalysis<sup>[5]</sup>. Hexanitrosyldiiron(2+) is the first example of a binary nitrosylmetal cation.

#### Experimental<sup>[6]</sup>

(4): NO<sup>+</sup>PF<sub>6</sub><sup>-</sup> (0.77 g, 4.4 mmol) is added to a solution of Fe(CO)<sub>2</sub>(NO)<sub>2</sub> (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<sub>2</sub> pressure through a cold (-30°C) frit. The dark-green residue consisting of (4) and unchanged NO<sup>+</sup>PF<sub>6</sub><sup>-</sup> is washed with CH<sub>2</sub>Cl<sub>2</sub> (2 × 30 ml) 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<sup>-2</sup> torr. Yield 0.08–0.10 g (ca. 10%).

(6): NO<sup>+</sup>PF<sub>6</sub><sup>-</sup> (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. 5 min), a cold (-30°C) solution of triphenylphosphane (0.54 g, 2 mmol) in nitromethane is added dropwise to the mixture. On subsequent addition of cold toluene lustrous green leaflets of (6) crystallize out which are then washed at -30°C with