syn-Periplanar Bisazo Skeletons – Syntheses and Reactions with Carbonylmetal Complexes

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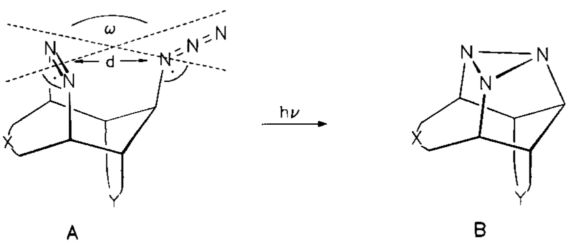
Preparatively useful syntheses for the novel, relatively mobile polycyclic *syn*-periplanar bisazo polycycles **4** and **5** are based on hydrazine condensation with readily available dienedione **6** and acid-catalyzed rearrangement of bisurazole **12**, respectively. In the preferred "closed" and "open" conformations of **4** and **5** the N = N bonds are 314 and 496 pm, respectively, apart (MMX). From the reactions of **4** and **5** with carbonyliron and -ruthenium compounds, complexes are derived which are typical of monoazo ligands [**4** · $Fe(CO)_4$ ≡ **20**, **4** · $Fe_2(CO)_7$ ≡ **21**, **4** · $Fe_3(CO)_9$ ≡ **22**, **4** · $[Fe_2(CO)_6]_2$ ≡ **23**, **4** · $Ru_3(CO)_9$ ≡ **24**, **5** · $[Fe_2(CO)_6]_2$ ≡ **25**, **5** · $Fe_2(CO)_6$ · $Fe_3(CO)_9$ ≡ **26**]. For **21**, **23** and **26** crystal structure analyses were performed, confirming i.a. in **26** the unique presence of a $Fe_2(CO)_6$ and a $Fe_3(CO)_9$ fragment attached to two azo units of the same molecule.

Introduction

The achievements detailed in this paper resulted from the combined efforts of two research groups which are interested in the chemistry of azo compounds. The investigation of the title compounds as ligands in coordination chemistry had looked promising with respect to a classical synthetic target and to structural and bonding modes in organometallic clusters.

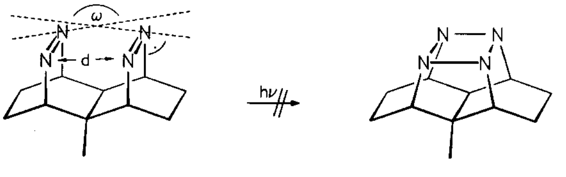
In search of the preparatively and theoretically interesting [π2 + π2] cycloaddition between two N = N bonds[1,2], the construction of adequate substrates, polycyclic skeletons featuring *syn*-periplanar bisazo chromophores as proximate as possible, is a longstanding topic in our research activities. There are good reasons why no azo/azo cycloaddition yielding a tetrazetidine – the missing member in the sequence of C_4, P_4, As_4 rings – has definitely been achieved until today[1–4]. The thermodynamic situation is relatively unfavorable, the steric and stereoelectronic prerequisites are unusually strict, and N_2 elimination is an omnipresent competition. Still, several intramolecular azo photocycloadditions (azo/ene[5,6]; azo/benzo[7,8]) and a N = N/N = N(O) photometathesis reaction in a structurally very special case (azoxide of **1**[1]) justified hope. Additional incentive came from the recent preparation of kinetically highly stable *cis,cis*-trialkyltriaziridines **B** via specifically designed *syn*-azo azides **A** (the potential nitrene nitrogen atom is forced into the N = N π plane at a very short distance[9,10]).



A B

d(calc.) = 270 – 293 pm
ω(calc.) = 152° – 162°

When bisazo substrates of seemingly favorable structural and stereoelectronic prerequisites, as e.g. **1**, resisted light-induced tetrazetidine formation to give **2**[1], the possibility was considered to further improve the situation on the side of the starting compound, as in ene/ene photocycloadditions[11], and possibly also on the product side, by metal complexation.

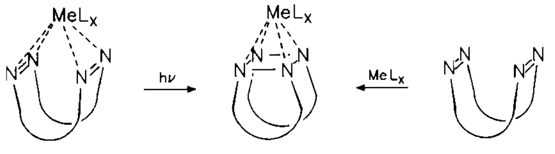


1 2

d(calc.) = 285.5 pm (av.)
d(exp.) = 285 pm (av.)
ω(calc.) = ω(exp.) = 169°

The hunt went for complexes of type **C**, in which bridging of the two N = N bonds by metal atoms would improve π,π distance and orientation; in respective products **D**, the n-electron repulsion should be diminished. In this context, the silver complex of cyclo-N_3H_3, embedded in a zeolith cavity, comes to mind[12].

The organometallic aspect of this investigation originated in isoelectronic considerations, exemplified for instance by



C D E

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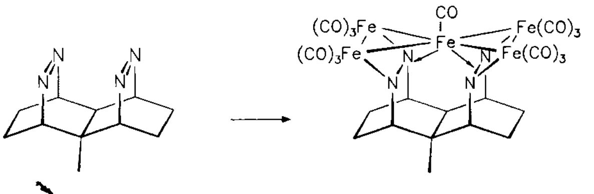
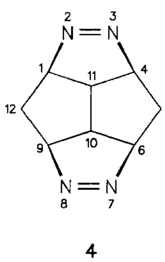
the very close similarity between the cluster compounds $FeCo_2(CO)_9(\mu\text{-}\eta^2\text{-}R_2C_2)$ and $Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}R_2N_2)$[13]. Isoelectronic considerations had allowed to develop reactivity patterns of cluster-bound azoalkane ligands[14] which closely resemble those of some cluster-bound alkyne ligands[15]. The most pertinent finding concerns the cleavage of an azoalkane to two cluster-bound nitrene units[16], analogous to the corresponding alkyne-to-alkylidyne cleavage[17]. It was therefore tempting to search for an analog of another well-known organometallic alkyne reaction, the dimerization yielding a cyclobutadiene ligand[18]. In the case of two azoalkane units, this would result in a metal-bound tetrazetidine (**E** → **D**).

It was with targets of type **C** in mind that we had studied the reaction of the highly rigid **1** with $Fe_2(CO)_9$. The by far major one of the two complexes formed was identified (X-ray diffraction analysis) as the unusual pentairon cluster **3**[19]. The bisazo ligand, acting as a 12-electron donor, preserves its overall geometry with the N=N distances being lengthened (137.1/139.1 pm), the transannular π-π distances being slightly shortened (273/281 pm). Cyclization to the tetraazetidine could not be achieved, yet[20].



Extending the study with **1**, *syn*-bisazo ligands became of interest featuring more mobile carbon skeletons and for that reason being better able to adjust to the geometrical needs of individual metal atoms in the complexation reaction. The ligand molecules of the present work are the novel bisazo compounds **4** (2,3,7,8-tetraazatetracyclo[7.2.1.$0^{4,11}$.$0^{6,10}$]dodeca-2,7-diene) and **5** (2,3,8,9-tetraazapentacyclo[8.3.2.$0^{4,13}$.$0^{7,11}$.$0^{11,13}$]pentadeca-2,8-diene). Carbonyl metal complexes of iron and ruthenium were chosen in line with the work of Kisch[21] and our studies[14,16,19,22].



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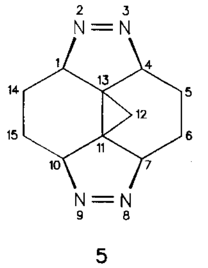
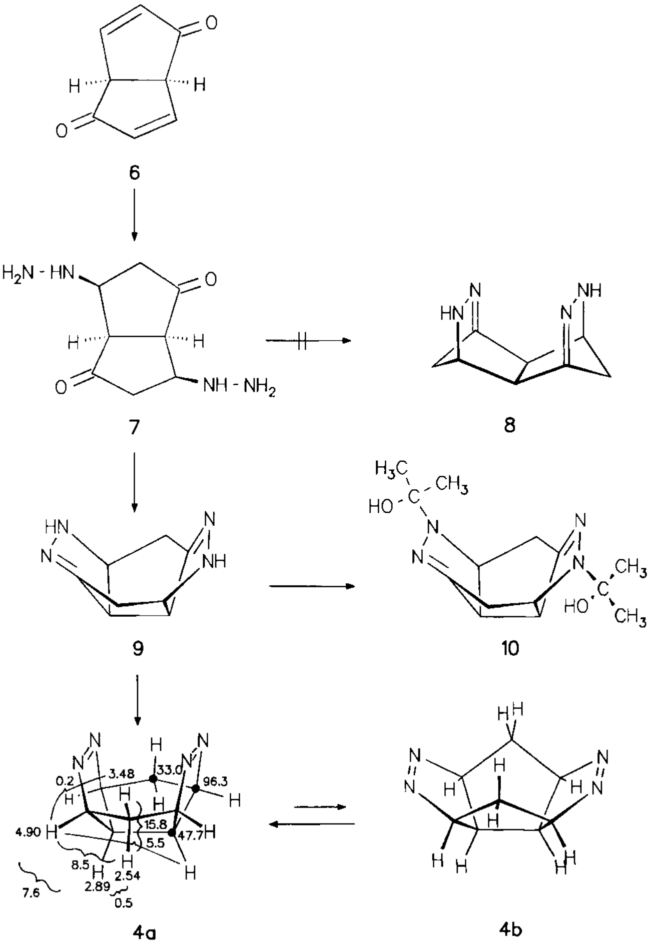


5

The *syn*-Bisazo Ligands

The synthesis of the tetraazatetraquinane **4** starts from the readily available bicyclic dienedione **6**[23]. Patterned after the work of Mellor et al.[3], this route is only seemingly trivial. (i) The addition of hydrazine (N_2H_4) must occur to both Michael units of **6** regio- and stereospecifically from the *endo* side to the enone β-carbon atoms; (ii) the intercyclic addition in the hydrazine bisadduct **7** must outrun the intracyclic one (to give e.g. **8**, rather improbable in view of the increase in strain), and (iii) a normally more stable bishydrazone (**9**) has to isomerize to a bisdiazene (**4**). After extensive optimization of the experimental conditions (solvent, reagent, temperature, reaction time, pressure), a one-pot protocol emerged which provides a 40–45% yield of **4** (besides polymers) – a preparatively useful result given the availability of **6** in hectogram quantities. To this end, the methanolic solution of **6** is added dropwise to a large excess of $N_2H_4 \cdot H_2O$ in methanol at ambient temperature within 4 h (N_2 atmosphere). After heating to 80°C in an autoclave for 10 d and simple workup, **4** crystallized from toluene. The reversed procedure, addition of N_2H_4 to **6** under otherwise identical conditions, only led to polymeric material[24]. The slow rate for the double tautomerization **9** → **4** obviously necessitates the long reaction time. In equilibration experiments with **4** in methanol, no **9** was observed; **4** {CI MS (NH_3): *m/z* = 180 [M^+ + 18], 163 [M^+ + 1]} melts at 175°C with decomposition, but can be sublimed at 110°C/0.01 Torr; it slowly decomposes at room temperature and

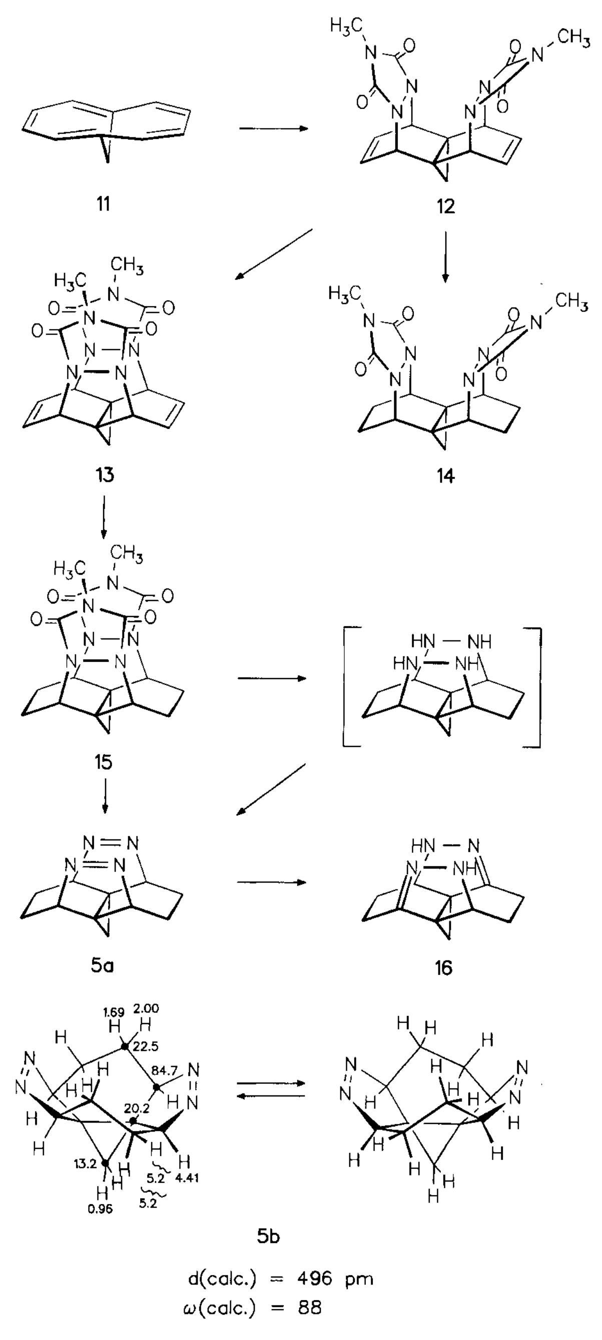


d(calc.) = 314 pm
ω(calc.) = 153

d(calc.) = 468 pm
ω(calc.) = 82

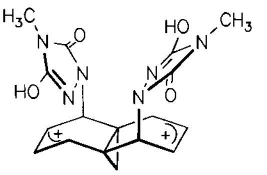
The data given in the formula generally are ^1H-, ^{13}C-chemical shifts (δ values) and H,H coupling constants [Hz] in daylight, but can be stored in the dark under nitrogen at −30 °C for months. Some insight into the reaction course was sought from experiments performed in boiling ethanol; with limited result, though. From originally very complex mixtures consisting of highly polar components and simplifying in composition with reaction time, the bishydrazone **9** could be intercepted as the bissemiaminal **10** in low (27%) yield. Competing *exo* addition of N_2H_4 to **6** is most probably responsible for the polymer formation.

The ^{1}H- and ^{13}C-NMR spectra of **4** with four and three signals, respectively, establish C_{2v} symmetry and a "closed" conformation. Typical for the latter are i.a. $J_{1,12s} = 0.2$ and $J_{1,12a} = 8.5$ Hz. From MMX force-field calculations[20], dihedral angles H−C1−C12−H_s/H−C1−C12−H_a of 79/40° and of 57/28° have been derived for the "closed" (**4a**) and "open" form (**4b**). The n,π* absorption of λ_{max} (ε) = 339 nm (650) in acetonitrile is typical of 1,2-pyrazolines and excludes a significant π,π interaction between the N=N bonds with calculated d = 314 pm and ω = 153° (MMX). The N=N stretching frequency is $\tilde{\nu}$ = 1541 cm^{-1}.



The synthetic route to *syn*-bisazo compound **5** uses methanocyclodecapentaene **11**[26] as starting material. Ginsburg et al.[27] had reported the *endo*-specific double addition of *N*-methyltriazoline-3,5-dione to give **12**. Via **14** we had earlier prepared the *syn*-bisazo compound **1**. In the course of experiments directed at the twofold hydration of **12**, its acid-catalyzed isomerization to **13** was discovered[28]. A nearly quantitative yield for this transformation was achieved when **12** was treated with 50% aqueous H_2SO_4 in a two-phase system with $CHCl_3$; **13** [m.p. 270 °C (dec.)] is distinguished from **12** (m.p. 253−254 °C) by NOE experiments: In the not characteristically different ^{1}H-NMR spectra, irradiation of the olefinic ^{1}H signal induces a significant effect on the cyclopropane signal of **12** but not of **13**; irradiation of the bridgehead ^{1}H signal has a strong (weak) effect on the cyclopropane signal of **13** (**12**), in line with an open conformation for **13**. The catalytic hydrogenation **13** → **15** (Pd/C, ethyl acetate, ambient temperature) is straightforward and somewhat faster than **12** → **14**.

The rearrangement **12** → **13**, even though profiting from a strong thermodynamic push, is astonishing indeed given the number of bond-breaking/bond-forming steps involved. Since no intermediates could be identified with certainty in NMR control experiments, there can only be a speculation about the mechanism involved. The simplest view invokes cationic intermediates of type **17**. The failure to induce an analogous transformation after saturation of the C=C bonds (**14**) could be an argument in this direction. It seems, however, improbable that the cyclopropane ring in cyclopropylcarbinyl ions like **17** would stay intact[29]. Sequences of N−N bond-breaking/bond-forming steps as suggested with **18** and **19** are judged more realistic.



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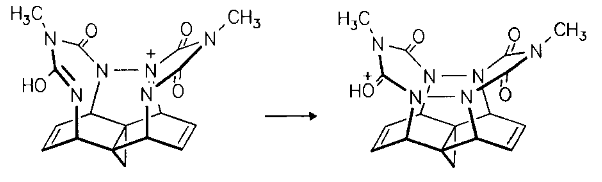


18 19

Degradation of the urazole rings in **15** was first attempted by alkaline hydrolysis, the proven procedure on the way from **14** to **1**. After heating **15** with NaOH in 2-propanol and oxidation with $CuCl_2$, the isolated product, however, was not **5**, but a mixture of semicarbazones[30]. Neat degradation **15** → **5** was effected by heating with hydrazine to 90°C in an inert atmosphere and oxidation ($CuCl_2$) of the intermediate bishydrazine; **5** was liberated from a brownish Cu complex of unknown composition with the help of ammonia and isolated after flash-chromatographic purification in 83% yield. Under more forcing basic conditions (CH_3ONa/CH_3OH), as well as in the presence of an excess of CF_3CO_2H[32], **5** was isomerized to the bishydrazone **16**.

The colorless needles of **5** (crystallized from diethyl ether) (MS: m/z = 203 [M^+ + 1]) melt at 170°C with decomposition, but survive sublimation at 120°C (0.01 Torr), and can be stored for months at -30°C. Four ^{1}H-NMR and ^{13}C-NMR signals confirm the time-averaged C_{2v} symmetry which results from the equilibration of the lowest energy, "open" conformations **5b** with nearly ecliptically positioned hydrogen atoms in the two ethano bridges. According to calculations (MMX[20]), the shortest transannular N/N distance between the nearly parallel N=N bonds (IR: $\tilde{\nu}$ = 1535 cm^{-1}) amounts to 496 pm. Consequently, no interaction between the chromophores shows up in the UV spectrum [λ_{max} (ε) = 331 (560)].

The photochemistry of **4** and **5** will be detailed in another context; it suffices here to comment that [π2 + π2] cycloaddition was not observed under various sets of conditions for direct and sensitized excitation in solution; **4** was thus at variance with its carbocyclic analogs[33]. Access to diene systems analogous to **5** is being explored[34].

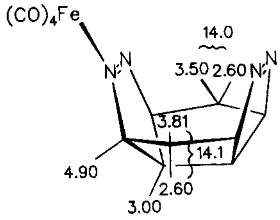
Reactions with Carbonylmetal Complexes

When oxygen-free solutions of **4** in CH_2Cl_2 were treated with a very large excess of $Fe_2(CO)_9$ at ambient temperature, a sequence of events was manifested by sequential changes in color from red to blue, then to green and finally to yellow.

$$\mathbf{4} \xrightarrow{Fe_2(CO)_9} \text{red} \longrightarrow \text{blue} \longrightarrow \text{green} \longrightarrow \text{yellow}$$

The red component was solely produced in the reaction of an excess of **4** with $Fe_2(CO)_9$ below 10°C, but could not cleanly be separated from the mixture (ca. 1:10) with unreacted **4**; in air or in contact with silica gel (aluminum oxide, etc.) it rapidly decomposed with liberation of **4**. For that reason, the limited amount of spectral data had to be secured from such mixtures. The structural assignment as the unsymmetrical **20** [**4** · $Fe(CO)_4$] rests on the IR spectrum with four typical CO frequencies[21] and on the partially assigned ^{1}H-NMR spectrum.

The blue component was shown to be derived from **20** by short-time exposure to an excess of reagent in benzene at room temperature. It was generated by treating **4** with 10 equiv. of $Fe_2(CO)_9$ in benzene (better enrichment than in CH_2Cl_2) at ambient temperature for 1 h. After isolation from the heterogeneous reaction mixture by preparative TLC in an inert atmosphere, the deeply blue and highly oxygen-sensitive solid was recrystallized from toluene (7%); the fine needles melt with decomposition at 150°C. C_s-symmetrical structure **21** {**4** · $Fe_2(CO)_7$; MS: m/z = 470 [M^+]} was derived from spectral data and was analyzed by X-ray structural determination (Figure 1). The IR spectrum provides the CO bands which are typical of an azoalkane-bound $Fe_2(CO)_7$ unit[35]. Remarkable in the NMR spectra are the diamagnetic (paramagnetic) shifts for the α-(β-)^{1}H and -^{13}C signals on the complexed side of the ligand; the H,H coupling constants are in line with a "closed" conformation.



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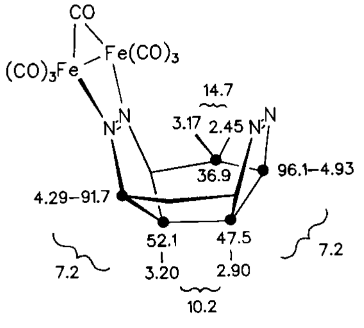

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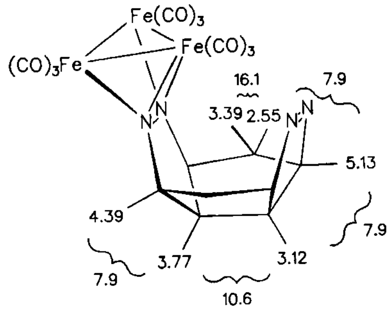

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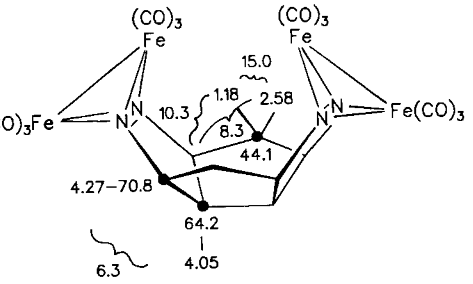
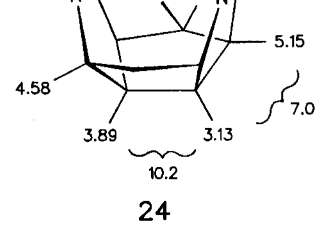


23

The green component was the most fleeting one. Though generally present in only small amounts, its isolation was greatly facilitated by its stability in air. It was isolated (3%) from the short-time reaction of **4** with 1.0 equiv. of $Fe_3(CO)_{12}$ in benzene at 60°C after TLC separation from mostly decomposed material and trace amounts of **4**, **21** and **23**. Crystallization from toluene yielded green needles which melt with decomposition at 140°C. C_s-symmetrical structure **22** [**4** · $Fe_3(CO)_9$] is firmly established. The IR spectrum (KBr) contains eight clearly separated CO bands and was found to be in this part superimposable to that of Et_2N_2 · $Fe_3(CO)_9$[16]. Shifts and coupling constants in the ^{1}H-NMR spectrum are very close to those in **21**.

The yellow component, as the last and most stable one in the sequence, was produced by analogy with **21** by extending the reaction time to 6 h. Its isolation from the crude residue was aided by its stability in air and was accomplished by column chromatography (50%). Crystallization from toluene/CH_2Cl_2 (1:5) afforded yellow-red crystals which melt with decomposition at 151°C. C_{2v}-symmetrical structure **23** {**4** · $[Fe_2(CO)_6]_2$; MS: m/z = 666 [M^+ − 2 CO]} was derived from IR, ^{1}H- and ^{13}C-NMR data and confirmed by crystal structure analysis (Figure 2). A remarkable IR feature is the appearance of CO bands as e.g. noted for R_2N_2 · $Fe_2(CO)_6$[16] and their doubling as typical of complexes with similar intramolecular interaction of two carbonylmetal units[36]. In comparison with **21**, the two-fold σ/π complexation of the azo units induces a much stronger dia(para)magnetic shift of the α-(β-)carbon signals. The large upfield shift by ca. 2 ppm for the 5*s*-(12*s*-)H signal should partly be due to the conformational change of the ligand **4**.

In the reactions of **4** with carbonylruthenium complexes [$Ru_3(CO)_{12}$, $Ru(CO)_{10}(CH_3CN)_2$, $Ru(CO)_5$] under the varied conditions exercised with the carbonyliron complexes, except for higher reaction temperatures [refluxing petroleum ether (boiling range 60−70°C), benzene], generally only one, deeply red, complex was observable (TLC). It was isolated in 85% yield from the reaction with 1.0 equiv. of $Ru_3(CO)_{12}$ in refluxing benzene by column chromatography with the exclusion of air and crystallized from toluene in the form of red needles (m.p. 148°C with decomposition). Structure **24** [**4** · $Ru_3(CO)_9$, elemental analysis] is consistent with the similarities to **22** as expressed in the IR- and ^{1}H-NMR spectra. No transformation of **24** analogous to **22** → **23** could be brought about; under forcing conditions only decomposition with partial reformation of **4** occurred.



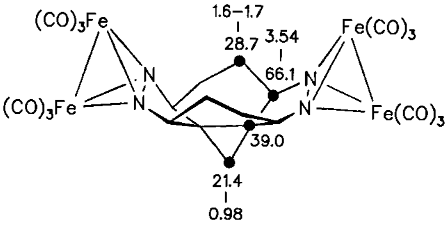
24

With **23** and **24** as the best manageable representatives, attempts were made to bring about bridging complexation by irradiation. In various experiments (varied light sources, solvents, temperature) with **23** in the presence of $Fe_2(CO)_9$, besides **21**/**22** and decomposed material, no novel complex was observed. When **24** was irradiated in a CO atmosphere (350-nm light), **4** and $Ru_3(CO)_{12}$ were the exclusive products.

The study with **5** as ligand was limited to its behavior towards $Fe_2(CO)_9$. In preliminary experiments, closely patterned after that with **4**, the observed color changes indicated a very similar sequence of events.

$$\mathbf{5} \xrightarrow{Fe_2(CO)_9} \text{red} \rightarrow \text{blue} \rightarrow \text{yellow/green (brown)}$$

However, only the last two complexes were generally present in amounts large enough to allow isolation; they proved also to be stable in air. From the reaction of **5** with ca. 10 equiv. of $Fe_2(CO)_9$ at ambient temperature (CH_2Cl_2), 42% of yellow **25** (m.p. 160°C, dec.) and 14% of green **26** (m.p. 171°C, dec.) were obtained after chromatographic separation; 33% of the latter originated from the reaction in refluxing benzene besides traces of **25**. For C_{2v}-symmetrical (time-averaged, ^{1}H, ^{13}C NMR) **25** {**5** · $[Fe_2(CO)_6]_2$, MS: m/z = 762 (100) [M^+]} the IR comparison with **23** marks a notable discrepancy in that the carbonyl bands are not doubled, in line with the much larger transannular distances.



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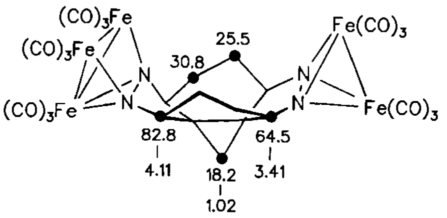

26

Structure **26** [**5** · $Fe_2(CO)_6$ · $Fe_3(CO)_9$, elemental analysis] was first proposed on the basis of the incompletely assigned NMR spectra – the very complex IR spectrum pointed to the presence of a $Fe_3(CO)_9$ fragment – and was unequivocally elucidated by the X-ray structural analysis (Figure 3).

Structure Determinations

The main purpose of the structure determinations, apart from product identification, was to find out the effects of metal atom coordination on the mutual orientation of the azo groups. Crystals of **21**, **23** and **26** proved of satisfactory quality for an X-ray structural analysis. For **21** the accuracy of the results suffered somewhat from decomposition of the crystal in the X-ray beam, but this does not affect the discussion here. Figures 1, 2 and 3 present views of the molecular frameworks and selected bond lengths and nonbonding distances.

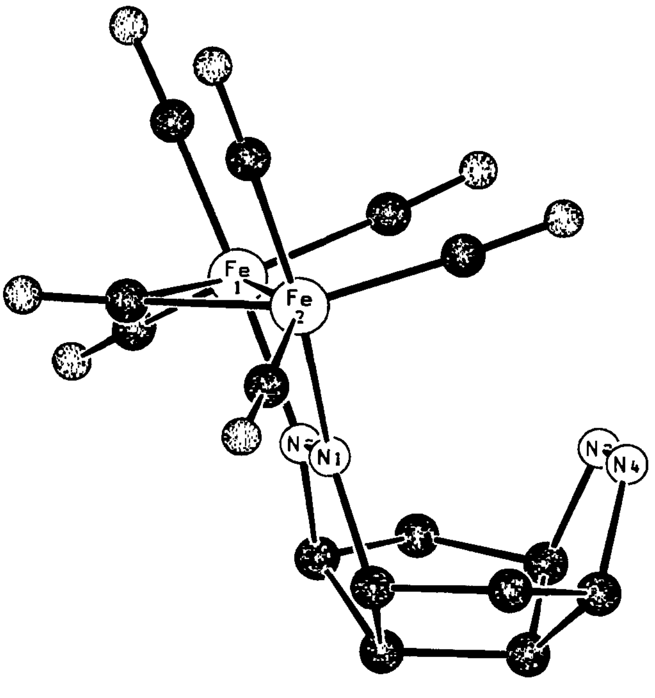

Figure 1. Molecular framework of **21**; selected distances [pm]: N1–N2 127(1), N3–N4 124(1), N1···N4 318(1), N2···N3 319(1), Fe1–Fe2 259.3(2)

The mode of attachment of the Fe_nL_x units to the azo groups generally corresponds to that observed earlier for monoazo ligands such as in the reference complexes (1,2-diazetidine)$Fe_2(CO)_7$[35] for **21**, (azoethane)$Fe_2(CO)_6$[16] for **23**, and (azoethane)$Fe_3(CO)_9$[16] for **26**. All details of the metal-atom and carbonyl-ligand arrangement including the size and distribution of the Fe–Fe, Fe–N, and N–C bond lengths are very similar to those of the reference compounds. Minor deviations are noted for the N–N bond lengths, that in **21** being slightly (1 pm) shorter and those in **23** being somewhat (av. 4.5 pm) longer than observed in the reference complexes. Distortions of the metallic parts of the molecules result from the close distance of two carbonylmetal units given in **23** and **26**, which push each other apart. As a consequence of the transannular steric compression, the $Fe_2N_2C_2$ arrangement of the Fe_3N_2 unit in **26** is nearly planar, and for all Fe_2N_2 units the Fe–N–C angles on the inside of the molecule (av. 145 pm) are noticeably larger than those on the outside (av. 131 pm).

It is interesting to see how the bisazo ligands **4** and **5** have responded differently to coordination. In complex **21**, the coordinated N=N bond (127 pm) is only slightly lengthened, with its uncoordinated N=N bond (124 pm) nicely reproducing the standard length of 125 pm[37]. The nonbonding N···N distances are extended by only 4–5 pm compared to those in free **4**.

In complex **23**, the N–N bonds are lengthened by 16 (17) pm, the nonbonding N···N distances are extended by 161 pm. The ligand is forced into its "open" conformation, in which 5*s*-H and 12*s*-H approach one another within van der Waals contact. Thus, while the shape of **4** changes grossly, its overall symmetry is maintained.

In complex **26**, the N–N bonds are similarly lengthened [by 13 (14) pm], the nonbonding N···N distances, however, increase by 21 (22) pm[38]. The change in molecular symmetry from C_2 in free **5** to C_s in **26**, due to a change of the twisting mode of the two cyclohexane rings, obviously re-

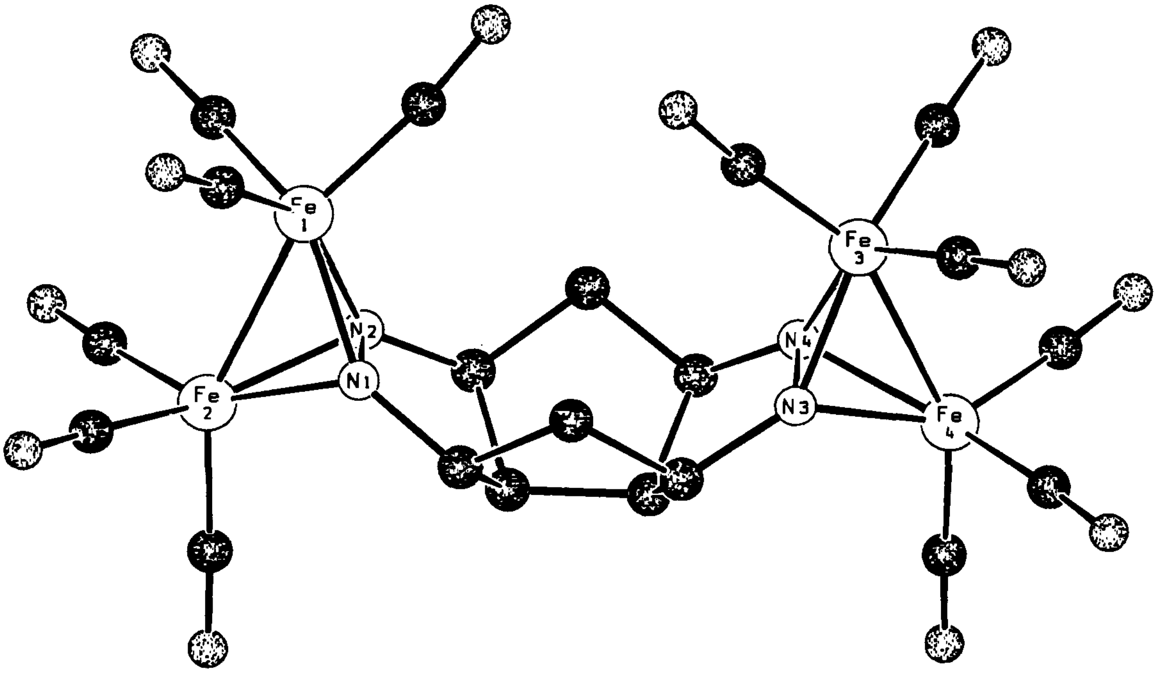

Figure 2. Molecular framework of **23**; selected distances [pm]: N1–N2 141.2(5), N3–N4 142.2(5), N1···N3 475(1), N2···N4 475(1), Fe1–Fe2 250.0(1), Fe3–Fe4 250.4(1)

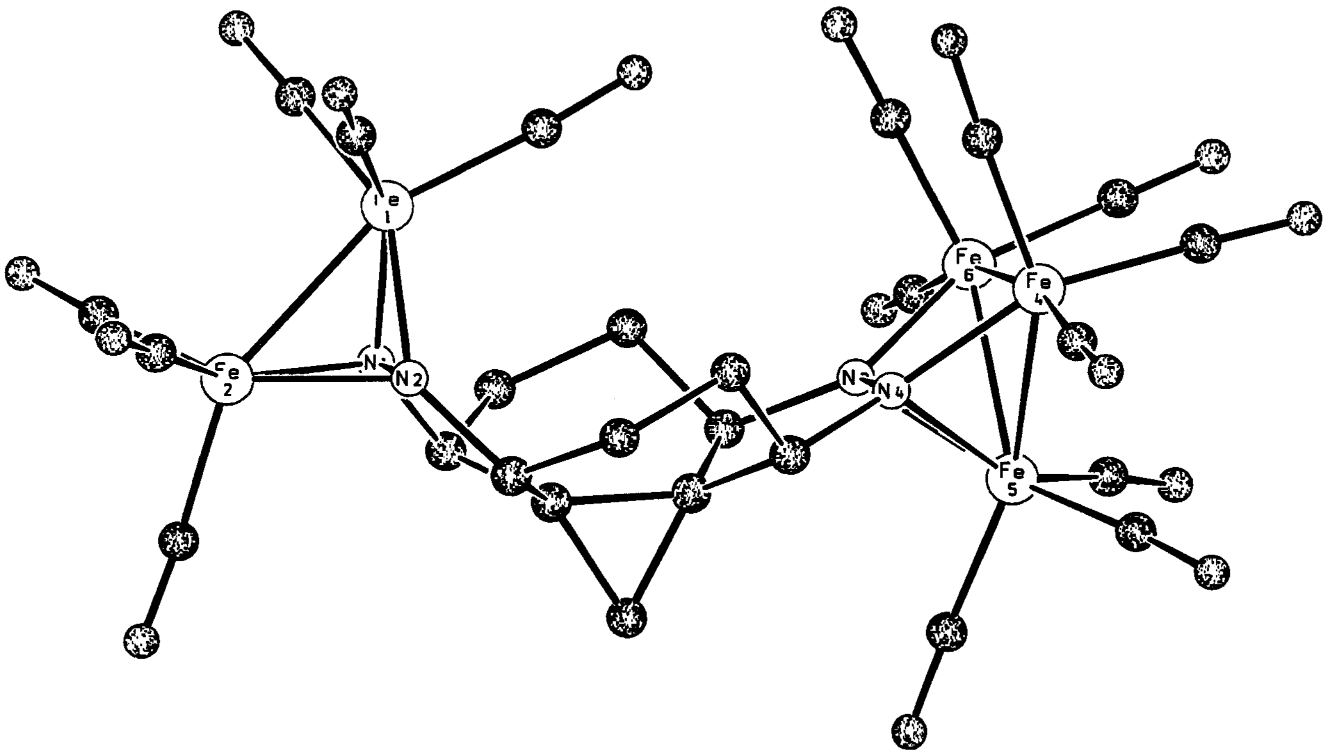

Figure 3. Molecular framework of **26**; selected distances [pm]: N1–N2 139.0(3), N3–N4 138.7(3), N1···N4 517(1), N2···N3 519(1), Fe1–Fe2 250.5(1), Fe5–Fe4 253.7(1), Fe4–Fe6 260.7(1), Fe5–Fe6 255.6(1)

sults from the geometrical restrictions imposed by the two carbonyliron units, which impose upon structure **26** a non-crystallographic mirror symmetry.

Result and Outlook

The availability of *syn*-periplanar N=N bonds in the conformationally mobile ligands **4** and **5**, with the carbonyliron and -ruthenium units used in this study, does not induce the bridging complexation formulated in **C**; **4** and **5** behave as azo ligands with independent N=N units. Attempts to transform photochemically unbridged complexes **23**, **24** into bridged ones (**C**, **D**) failed. Bridging complexation is pursued in an extension of the present study with carbonyl complexes of other metals (Cr, Mo, W, Mn, Co) as well as with structurally modified *syn*-bisazo ligands[31].

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Experimental

Melting points (m.p.): Bock Monoscop M. – Anal. TLC: Merck silicagel plates with F_{254} indicator. – Flash chromatography: 0.04–0.06 *mm silica* gel, Macherey-Nagel. – Anal. GC: Varian 3700, glass capillary column 25 m, OV 17, FID; integrator Varian CDS 111. – IR: Perkin-Elmer 457, Philips PU 9706. – UV: Perkin-Elmer Lambda 15. – NMR: ^{1}H: Bruker AC 250, AM 400; ^{13}C: Bruker AC 250, AM 400; chemical shifts relative to TMS (δ = 0), coupling constants in Hz; if not specified differently the 250-MHz spectra are given; assignments of signals with * may be interchanged; in the atom numbering *a* and *s* denote *anti* and *syn* positions; in the complexes **20**, **21**, **22** and **24** the metal atoms have been attached to the nitrogen atoms of lowest numbering. – Elemental analyses:

Table 1. Elemental analyses of the new compounds[a]

No.	Formula (Mol. mass)	Analysis C	H	N
4	$C_8H_{10}N_4$ (162.2)	59.24 58.86	6.21 6.18	34.55 34.07
5	$C_{11}H_{14}N_4$ (202.3)	65.32 65.12	6.98 6.97	27.70 26.99
15	$C_{17}H_{20}N_6O_4$ (372.4)	54.82 54.60	5.42 5.30	22.57 22.31
21	$C_{15}H_{10}Fe_2N_4O_7$ (470.0)	38.33 37.36	2.14 2.17	11.92 11.02
22	$C_{17}H_{10}Fe_3N_4O_9$ (581.9)	35.09 34.11	1.73 2.01	9.63 8.70
23	$C_{20}H_{10}Fe_4N_4O_{12}$ (721.7)	32.96 33.28	1.43 1.39	7.65 7.76
24	$C_{11}H_{10}N_4O_9Ru_3$ (717.5)	28.47 28.52	1.41 1.41	7.81 7.63
25	$C_{23}H_{14}Fe_4N_4O_{12}$[b] (761.8)	– –	– –	– –
26	$C_{26}H_{14}Fe_5N_4O_{15}$ (901.7)	34.63 34.18	1.57 1.56	6.21 6.08

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[a] **10** and **13** were characterized by their mass spectra (see text). – [b] Calcd. 761.81; found 762 (EI MS), 761.84 (HR EI MS).

Table 1. – MS: Finnigan MAT 44S. – General techniques and instruments for the X-ray determinations were those described in ref.[39,40]. For force-field calculations, the commercial program PC Model[41] was used with an extended set of parameters for azo compounds[9,20].

(1R,4S*,6R*,9S*,10S*,11R*)-2,3,7,8-Tetraazatetracyclo[7.2.1.0^{4,11}.0^{6,10}]dodeca-2,7-diene* (**4**): A solution of **6** (2.00 g, 14.9 mmol) in methanol (100 ml) was added dropwise at ambient temp. within 4 h to a solution of $N_2H_4 \cdot H_2O$ (20.6 g, 411 mmol) in methanol (50 ml). The solution was transferred under nitrogen to a 500-ml autoclave and heated to 80°C for 10 d. After removal of all volatile components in vacuo, the residue was subjected to flash chromatography on silica gel [R_f = 0.23, CH_2Cl_2/acetone (5:1)] and then crystallized from toluene at 4°C, **4** (ca. 1 g, 40–45%) was obtained as colorless needles, m.p. 175°C (dec.), sublimable at 110°C/0.01 Torr. – IR (KBr): $\tilde{\nu}$ = 2968 cm^{-1}, 2920, 1541 (N=N), 1421. – UV (CH_3CN): λ_{max} (ε) = 339 nm (650). – ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 4.90 (dddd, 1-, 4-, 6-, 9-H), 3.48 (dt, 5*s*-, 12*s*-H), 2.89 (ttt, 10-, 11-H), 2.54 (dtt, 5*a*-, 12*a*-H); $J_{1,10} = 5.5$, $J_{1,11} = 7.6$, $J_{1,12s} = 0.2$, $J_{1,12a} = 8.5$, $J_{5s,5a} = 15.8$, $J_{5a,10} = 0.5$. – ^{13}C NMR (CD_2Cl_2): δ = 96.3 (C-1, -4, -6, -9, $J_{C,H} = 148$), 47.7 (C-10, -11, $J_{C,H} = 144$), 33.0 (C-5, -12, $J_{C,H} = 132$); $J_{1,12(4,5;5,6;9,12)} = 36.6$, $J_{1,11(4,11;6,10;9,10)} = 32.6$. – CI MS ($NH_3$, 70 eV): *m/z* (%) = 180 (100) [$M^+ + 18$], 163 (19) [$M^+ + 1$].

(1R,4S*,6R*,9S*,10S*,11R*)-3,8-Bis(dimethylhydroxymethyl)-2,3,7,8-tetraazatetracyclo[7.2.1.0^{4,11}.0^{6,10}]dodeca-2,7-diene* (**10**): A solution of **3** (200 mg, 1.50 mmol) in ethanol (10 ml) was added dropwise within 3 h to a solution of $N_2H_4 \cdot H_2O$ (2.00 g, 41.1 mmol) in ethanol (5 ml). Then the mixture was heated to reflux under nitrogen for 12 h. After removal of all volatile components in vacuo, the residue was dissolved in acetone and the solution stirred with a catalytic amount of SiO_2 for 7 d. The solvent was evaporated in vacuo, and the residue was subjected to flash chromatography on silica gel [R_f = 0.18, CH_2Cl_2/acetone (5:1)] to give 115 mg (27%) of **10** as colorless crystals, m.p. 110°C. – IR (KBr): $\tilde{\nu}$ = 3434 cm^{-1} (OH), 3234 (OH), 1641 (C=N). – ^{1}H NMR ($CDCl_3$): δ = 5.75 (br. m, 2H, OH), 5.12 (ddd, 4-, 9-H), 3.43 (d, 5*s*-, 12*s*-H), 3.06 (dd, 10-, 11-H), 2.63 (dd, 5*a*-, 12*a*-H), 1.76 (s, 6H, CH_3), 1.74 (s, 6H, CH_3); $J_{4,5a(9,12a)} = 9.0$, $J_{4,10(9,11)} = 2.5$, $J_{4,11(9,10)} = 4.5$, $J_{5s,5a(12s,12a)} = 15.0$. – ^{13}C NMR ($CDCl_3$): δ = 149.1 (C-1, -6), 117.4 (2 C, OCN), 96.3 (C-4, -9), 50.0 (C-10, -11), 35.4 (C-5, -12), 25.4 (2 C, CH_3), 15.8 (2 C, CH_3). – EI MS (70 eV): *m/z* (%) = 279 (2) [$M^+ + 1$], 92 (52), 56 (100).

(1R,4S*,7R*,10S*,11S*,13R*)-2,3,8,9-Tetraazapentacyclo[8.3.2.0^{4,13}.0^{7,11}.0^{11,13}]pentadeca-5,14-diene-2,3:8,9-bis(methyldicarboximide)* (**13**): To a solution of **12** (4.00 g, 10.9 mmol) in $CHCl_3$ (400 ml), half-concd. H_2SO_4 (150 ml) was added in one portion. The mixture was stirred vigorously for 24 h and then poured on ice (500 g). The aqueous layer was repeatedly extracted with $CHCl_3$, the combined organic layers were washed with a $NaHCO_3$ solution, dried ($MgSO_4$), and concentrated in vacuo. After crystallization (methanol) of the residue, 3.80 g (95%) of **12** was obtained as colorless crystals, m.p. 270°C (dec.). – IR (KBr): $\tilde{\nu}$ = 2994 cm^{-1}, 1762 (CO), 1694 (N–CO–N), 1461. – ^{1}H NMR ($CDCl_3$): δ = 6.24 (d, *J* = 2.8, 4H, HC=C), 4.50 (d, *J* = 2.8, 4H, HCN), 3.07 (s, 6H, NCH_3), 1.14 (s, 2H, CH_2). – ^{13}C NMR ($CDCl_3$): δ = 155.6 (CO), 123.9 (C=C), 53.5 (CHN), 26.5 (C-11, -13), 25.5 (NCH_3), 9.8 (C-12). – EI MS (70 eV): *m/z* (%) = 369 (11) [$M^+ + 1$], 368 (53) [M^+], 141 (100).

(1R,4S*,7R*,10S*,11S*,13R*)-2,3,8,9-Tetraazapentacyclo[8.3.2.0^{4,13}.0^{7,11}.0^{11,13}]pentadecane-2,3:8,9-bis(methyldicarboximide)* (**15**): **13** (500 mg, 1.4 mmol), dissolved in ethyl acetate (50 ml), was hydrogenated (H_2, 1 Torr) over Pd/C (50 mg, 10%). The catalyst was removed by suction filtration and the solvent evaporated in vacuo to give 490 mg (98%) of colorless, crystalline **15**, m.p. 177°C. – IR (KBr): $\tilde{\nu}$ = 2942 cm^{-1}, 1761 (CO), 1694 (N–CO–N), 1464. – ^{1}H NMR ($CDCl_3$): δ = 3.96 (dd, *J* = 3.9, *J* = 7, 1-, 4-, 7-, 10-H), 3.08 (s, 6H, NCH_3), 2.11 (m_c, 5-, 6-, 14-, 15-H), 1.72 (m_c, 5′-, 6′-, 14′-, 15′-H), 1.09 (s, 12-H).

(1R,4S*,7R*,10S*,11S*,13R*)-2,3,8,9-Tetraazapentacyclo[8.3.2.0^{4,13}.0^{7,11}.0^{11,13}]pentadeca-2,8-diene* (**5**): A solution of **15** (100 mg, 0.50 mmol) in anhydrous N_2H_4 (1.00 g, 31.0 mmol) was heated under nitrogen to 90°C for 18 h. After removal of excess N_2H_4 in vacuo, a solution of $CuCl_2$ (1.50 g, 11.0 mmol) in water (40 ml) was added to the residue. The solution (pH ≈ 5) was stirred at room temp. for 4 h. After decomplexation with concd. NH_3, extraction with CH_2Cl_2, drying (Na_2SO_4), and solvent evaporation, the residue was subjected to flash chromatography on silica gel (R_f = 0.28, ethyl acetate) to yield 45 mg (83%) of **5** as colorless crystals, m.p. 170°C (dec.); sublimable at 120°C (0.1 Torr). – IR (KBr): $\tilde{\nu}$ = 2908 cm^{-1}, 2856, 1535 (N=N), 1525 (N=N), 1451, 1440. – UV (CH_3CN): λ_{max} (ε) = 331 (560). – ^{1}H NMR (CD_2Cl_2): δ = 4.41 (t, *J* = 5.2 Hz, 1-, 4-, 7-, 10-H), 2.00 (br. m, 5-, 6-, 14-, 15-H), 1.69 (br. m, 5′-, 6′-, 14′-, 15′-H), 0.96 (s, 12-H). – ^{13}C NMR (CD_2Cl_2): δ = 84.7 (C-1, -4, -7, -10), 22.5 (C-5, -6, -14, -15), 20.2 (C-11, -13), 13.2 (C-12). – CI MS (isobutane, 70 eV): *m/z* (%) = 203 (100) [$M^+ + 1$].

Complex **20**: **4** (30 mg, 0.19 mmol) and $Fe_2(CO)_9$ (54 mg, 0.15 mmol) in CH_2Cl_2 (25 ml) were stirred in an ice bath for ca. 15 min until the solution had turned red. After filtration, preparative TLC with CH_2Cl_2 on silica gel separated a trace of blue **21** (R_f = 0.23) from 20 mg of a red material (R_f = 0.21) which, according to NMR, consisted of a mixture of **4** and **20**. Attempted crystallization resulted in decomposition of **20**. – IR (KBr): $\tilde{\nu}$ = 2050 cm^{-1} m, 1960 s, 1945 s, 1930 s (CO). – ^{1}H NMR (CD_2Cl_2): δ = 4.90 (m, 1-, 4-, 6-, 9-H), 3.81 (d, 12*s*-H, *J* = 14.1), 3.50 (d, 5*s*-H, *J* = 14.0), 3.00 (m, 10-, 11-H), 2.60 (m, 5*a*-, 12*a*-H).

Complex **21**: **4** (40 mg, 0.23 mmol) and $Fe_2(CO)_9$ (900 mg, 2.50 mmol) in benzene (40 ml) were stirred at ambient temp. for ca. 1 h until the solution had turned blue. After filtration of the solution and evaporation of the solvent in vacuo, preparative TLC of the residue with CH_2Cl_2 on silica gel separated 8 mg (7%) of **21** (R_f = 0.23). Crystallization from toluene at −18°C yielded blue, air-sensitive needles of **21**, m.p. 150°C (dec.). Single crystals were obtained from benzene/heptane at 4°C. – IR (KBr): $\tilde{\nu}$ = 2050 cm^{-1} m, 2000 s, 1962 m, 1951 m, 1726 m (CO). – ^{1}H NMR (CD_2Cl_2): δ = 4.93 (t, 6-, 9-H), 4.29 (t, 1-, 4-H), 3.20 (dt, 11-H), 3.17 (d, 5*s*-, 12*s*-H), 2.90 (dt, 10-H), 2.45 (dt, 5*a*-, 12*a*-H); $J_{1,11(4,11)} = J_{6,10(9,10)} = J_{1,12a(4,5a)} = J_{6,5a(9,12a)} = 7.2$, $J_{5s,5a(12s,12a)} = 14.7$, $J_{10,11} = 10.2$. – ^{13}C NMR (CD_2Cl_2): δ = 219.0 (CO), 96.1 (C-6, -9), 91.7 (C-1,-4), 52.1 (C-11), 47.5 (C-10), 36.9 (C-5, -12). – EI MS (70 eV): *m/z* (%) = 470 (1) [M^+], 442 (1) [$M^+ - CO$], 414 (3), 386 (10), 358 (3), 330 (8), 302 (27), 274 (57) [$M^+ - 7\,CO$], 162 (5) [$C_8H_{10}N_4^+$], 112 (99) [Fe_2^+].

Complex **22**: **4** (35 mg, 0.22 mmol) and $Fe_3(CO)_{12}$ (109 mg, 0.22 mmol) in benzene (30 ml) were heated to 60°C for 30 min. After filtration of the solution and evaporation of the solvent in vacuo, preparative TLC of the residue with CH_2Cl_2 on silica gel separated 3.5 mg (3%) of **22** (R_f = 0.44) from 1.5 mg (2%) of **21** (R_f = 0.23) and a trace of yellow **23** (R_f = 0.81). Crystallization from toluene at −18°C yielded **22** as green, air-stable needles, m.p. 140°C (dec.). – IR (KBr): $\tilde{\nu}$ = 2070 cm^{-1} w, 2026 sh, 1998 s, 1973 m, 1963 m, 1957 m, 1949 m, 1937 m (CO). – ^{1}H NMR (CD_2Cl_2): δ = 5.13 (t, 6-, 9-H), 4.39 (t, 1-, 4-H), 3.77 (dt, 11-H), 3.39 (d, 5*s*-, 12*s*-H), 3.12

(dt, 10-H), 2.55 (dt, 5*a*-, 12*a*-H); $J_{1,11(4,11)} = J_{6,10(9,10)} = J_{1,12a(4,5a)} = J_{6,5a(9,12a)} = 7.9$, $J_{5s,5a(12s,12a)} = 16.1$, $J_{10,11} = 10.6$.

Complex **23**: **4** (50 mg, 0.31 mmol) and $Fe_2(CO)_9$ (1.12 g, 3.10 mmol) in benzene (50 ml) were stirred at room temp. for 6 h. The color of the solution changed over red, blue, green to finally yellow. After filtration of the solution and evaporation of the solvent in vacuo, the residue was subjected to column chromatography on silica gel [$R_f = 0.49$, hexane/CH_2Cl_2 (1:1)] to give 110 mg (50%) of **23**. Crystallization from toluene/CH_2Cl_2 (1:5) at −18 °C afforded yellow-red, air-stable crystals of **23**, m.p. 151 °C (dec.), one of which was used for the X-ray structural analysis. — IR (KBr): $\tilde{\nu} = 2073$ cm^{-1} sh, 2066 s, 2034 sh, 2022 s, 2002 s, 1991 s, 1974 s, 1967 s, 1953 s, 1946 s (CO). — ^1H NMR (400 MHz, CD_2Cl_2): δ = 4.27 (dddd, 1-, 4-, 6-, 9-H), 4.05 (tt, 10-, 11-H), 2.58 (dt, 5*a*-, 12*a*-H), 1.18 (dt, 5*s*-, 12*s*-H); $J_{1,12a(4,5a;6,5a;9,12a)} = 8.3$, $J_{1,12s(4,5s;6,5s;9,12s)} = 10.3$, $J_{1,11(4,11;6,10;9,10)} = 9.0$, $J_{1,10(4,10;6,11;9,11)} = 6.3$, $J_{5s,5a(12s,12a)} = 15.0$. — ^{13}C NMR (CD_2Cl_2): δ = 210.2 (CO), 70.8 (C-1, -4, -6, -9), 64.2 (C-10, -11), 44.1 (C-5, -12). — ^{13}C NMR: δ = 214.9 (CO), 211.8 (CO), 208.7 (CO), 70.9 (C-1, -4, -6, -9), 65.7 (C-10, -11), 44.9 (C-5, -12). — EI MS (70 eV): *m/z* (%) = 666 (16) [$M^+ - 2$ CO], 638 (5), 610 (4), 582 (11), 554 (18), 526 (18), 498 (100) [$M^+ - 8$ CO], 470 (23), 442 (24), 414 (27), 386 (60) [$M^+ - 12$ CO], 112 (23) [Fe_2^+].

Table 2. Crystallographic details

	21	**23**	**26**
Formula	$C_{15}H_{10}Fe_2N_4O_7 \cdot \frac{1}{2} C_6H_6$	$C_{20}H_{10}Fe_4N_4O_{12}$	$C_{26}H_{14}N_4O_{15}Fe_5$
Mol. mass	511.0	721.7	901.7
Cryst. from	C_6H_6/heptane	toluene/CH_2Cl_2	C_6H_6/CH_2Cl_2/ hexane
Size [mm]	0.6 × 0.2 × 0.2	0.5 × 0.2 × 0.1	0.8 × 0.2 × 0.2
Color	blue	yellow-red	green
Space group	*C*2/*c*	*P*2₁/*n*	*P*2₁/*a*
Z	8	4	4
a [pm]	2376.5(5)	890.36(6)	1506.4(2)
b [pm]	1249.2(1)	1196.57(7)	1474.9(2)
c [pm]	1595.1(3)	2455.07(11)	1676.5(2)
α [°]	90	90	90
β [°]	118.17	97.136(5)	116.29(1)
γ [°]	90	90	90
V [nm^3]	4.174	2.616	3.339
$d_{calcd.}$ [g cm^{-3}]	1.62	1.83	1.79
d_{found} [g cm^{-3}]	–	1.83	–
μ [cm^{-1}]	14.35	21.6	21.94
2Θ range [°]	2−54	2−44	2−63
hkl range	±*h*, +*k*, +*l*	±*h*, +*k*, +*l*	±*h*, +*k*, +*l*
Obsd. reflections	2041	3092	6509
Variables	265	362	507
R (unit weights)	0.049	0.033	0.026
Res. elec. dens.	+0.8	+0.5	+0.4
[10^{-6} e/pm^3]	–	−0.4	–

Table 3. Positional parameters for **21**; starred atoms were refined isotropically; parameters without errors were not refined; the anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)\,[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$

Atom	x	y	z	B (Å²)
FE1	0.61995(5)	0.1309(1)	0.72196(8)	2.82(3)
FE2	0.63580(5)	0.1211(1)	0.57207(8)	2.77(3)
O1	0.4807(2)	0.1244(7)	0.6352(4)	7.0(2)
O2	0.5025(3)	0.1108(6)	0.4256(5)	7.1(2)
O3	0.6487(3)	-0.1082(5)	0.5525(5)	8.4(3)
O4	0.6231(3)	-0.0983(5)	0.7658(5)	7.3(2)
O5	0.6339(3)	0.2630(6)	0.8845(4)	7.2(2)
O6	0.6747(3)	0.2370(6)	0.4491(4)	7.8(2)
O7	0.5762(2)	0.3196(4)	0.5941(4)	4.0(2)
N1	0.7159(2)	0.1431(5)	0.6832(4)	2.4(2)
N2	0.7086(2)	0.1473(5)	0.7571(4)	2.3(2)
N3	0.7747(3)	-0.0824(5)	0.8183(5)	3.6(2)
N4	0.7830(3)	-0.0847(5)	0.7470(5)	3.6(2)
C1	0.5338(4)	0.1243(8)	0.6690(5)	3.9(2)
C2	0.5540(4)	0.1134(7)	0.4802(6)	4.2(3)
C3	0.6456(4)	-0.0198(7)	0.5641(6)	5.0(3)
C4	0.6238(4)	-0.0109(7)	0.7506(6)	4.6(3)
C5	0.6282(4)	0.2135(7)	0.8229(6)	3.8(3)
C6	0.6600(4)	0.1904(8)	0.4963(6)	4.4(3)
C7	0.6017(3)	0.2401(6)	0.6202(6)	3.0(2)
C8	0.7833(4)	0.0728(7)	0.9186(5)	3.6(3)
C9	0.8200(4)	-0.0082(6)	0.8923(5)	3.1(2)
C10	0.8536(3)	0.0492(6)	0.8478(6)	3.3(2)
C11	0.8355(3)	-0.0126(6)	0.7566(6)	3.5(2)
C12	0.8110(3)	0.0646(7)	0.6739(6)	3.8(2)
C13	0.7842(3)	0.1609(6)	0.7073(5)	2.9(2)
C14	0.8208(3)	0.1628(6)	0.8157(6)	3.3(2)
C15	0.7686(3)	0.1674(6)	0.8469(5)	3.1(2)
C100	0.000	0.056(1)	0.250	7.3(4)*
C101	0.0155(5)	0.0053(9)	0.3342(7)	7.3(3)*
C102	0.0145(5)	-0.106(1)	0.3319(7)	8.2(4)*
C103	0.000	-0.169(1)	0.250	8.6(5)*

Table 4. Positional parameters for **23**; the equivalent isotropic displacement parameter U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

ATOM	X	Y	Z	U_{eq} (Å²)
Fe1	0.2676(1)	0.1417(1)	0.5840(0)	0.0349(4)
Fe2	0.1141(1)	0.2595(1)	0.5138(0)	0.0325(4)
N1	0.1489(4)	0.2745(3)	0.5919(1)	0.029(2)
N2	0.0582(4)	0.1806(3)	0.5755(1)	0.029(2)
C11	0.4568(7)	0.1909(5)	0.5811(3)	0.063(4)
O11	0.5729(5)	0.2271(5)	0.5793(3)	0.105(4)
C12	0.2855(6)	0.0293(5)	0.5368(2)	0.042(3)
O12	0.2957(5)	-0.0397(3)	0.5060(2)	0.066(3)
C13	0.3056(7)	0.0554(6)	0.6446(2)	0.060(4)
O13	0.3343(7)	-0.0070(5)	0.6792(2)	0.107(4)
C21	0.0694(5)	0.1666(5)	0.4561(2)	0.041(3)
O21	0.0362(5)	0.1079(4)	0.4205(2)	0.072(3)
C22	-0.0359(6)	0.3566(5)	0.4906(2)	0.046(3)
O22	-0.1295(5)	0.4155(4)	0.4736(2)	0.075(3)
C23	0.2679(7)	0.3371(6)	0.4891(2)	0.057(4)
O23	0.3663(5)	0.3841(5)	0.4754(2)	0.096(4)
C1	-0.0795(5)	0.1813(4)	0.6034(2)	0.031(2)
C2	-0.0962(5)	0.3060(4)	0.6195(2)	0.030(2)
C3	0.0702(5)	0.3484(4)	0.6281(2)	0.028(2)
C4	0.1226(5)	0.3375(4)	0.6895(2)	0.030(2)
Fe3	0.0653(1)	0.1693(1)	0.8106(0)	0.0349(4)
Fe4	-0.1876(1)	0.2606(1)	0.8109(0)	0.0333(4)
N3	-0.0299(4)	0.2876(3)	0.7664(1)	0.029(2)
N4	-0.1038(4)	0.1842(3)	0.7528(2)	0.031(2)
C31	0.0445(6)	0.0381(5)	0.8447(2)	0.053(3)
O31	0.0294(6)	-0.0440(4)	0.8662(2)	0.086(3)
C32	0.1503(7)	0.2350(5)	0.8719(3)	0.053(3)
O32	0.2028(6)	0.2786(4)	0.9110(2)	0.089(3)
C33	0.2460(7)	0.1396(4)	0.7862(2)	0.047(3)
O33	0.3656(5)	0.1264(4)	0.7768(2)	0.068(3)
C41	-0.3582(7)	0.3295(5)	0.7783(2)	0.047(3)
O41	-0.4654(5)	0.3712(4)	0.7596(2)	0.077(3)
C42	-0.1497(6)	0.3584(5)	0.8674(2)	0.048(3)
O42	-0.1199(5)	0.4209(4)	0.9018(2)	0.076(3)
C43	-0.2866(6)	0.1533(5)	0.8448(2)	0.045(3)
O43	-0.3472(5)	0.0840(4)	0.8642(2)	0.070(3)
C5	-0.0222(5)	0.3540(4)	0.7167(2)	0.029(2)
C6	-0.1515(5)	0.3067(4)	0.6756(2)	0.030(2)
C7	-0.1619(5)	0.1831(4)	0.6935(2)	0.032(2)
C8	-0.0675(5)	0.1152(4)	0.6574(2)	0.035(3)

Complex **24**: **4** (50 mg, 0.31 mmol) and $Ru_3(CO)_{12}$ (200 mg, 0.31 mmol) in benzene (90 ml) were heated to reflux for 1.5 h. After removal of the solvent in vacuo, the residue was subjected to column chromatography on silica gel (R_f = 0.47, CH_2Cl_2) to yield 189 mg (85%) of **24**. Crystallization from toluene at −78°C afforded red, air-sensitive needles of **24**, m.p. 148°C (dec.). – IR (KBr): $\tilde{\nu}$ = 2077 cm^{-1} w, 2037 sh, 2023 s, 2005 m, 1995 m, 1976 s, 1958 m, 1945 m (CO). – ^1H NMR (CD_2Cl_2): δ = 5.15 (t, 6-, 9-H), 4.58 (t, 1-, 4-H), 3.89 (dt, 11-H), 3.43 (d, 5*s*-, 12*s*-H), 3.13 (dt, 10-H), 2.56 (ddd, 5*a*-, 12*a*-H); $J_{6,5a(9,12a)} = J_{6,10(9,10)} = 7.0$, $J_{1,12a(4,5a)} = J_{1,11(4,11)} = 7.4$, $J_{10,11} = 10.2$, $J_{5s,5a(12s,12a)} = 15.8$.

Complex **25**: **5** (50 mg, 0.25 mmol) and $Fe_2(CO)_9$ (1.00 g, 2.80 mmol) were stirred in CH_2Cl_2 (50 ml) at ambient temp. for 12 h. After filtration of the solution and evaporation of the solvent in vacuo, preparative TLC of the residue with CH_2Cl_2/hexane (1:1) on silica gel separated 80 mg (42%) of **25** (R_f = 0.55) from 30 mg (14%) of **26** (R_f = 0.35). After crystallization from toluene at −40°C, yellow, air-stable crystals of **25**, m.p. 160°C (dec.) were obtained. – IR (KBr): $\tilde{\nu}$ = 2062 cm^{-1} m, 2022 s, 1980 sh, 1969 s, 1958 sh, 1947 s (CO). – ^1H NMR (CD_2Cl_2): δ = 3.54 (m_c, 1-, 4-, 7-, 10-H), 1.65 (m_c, 5-, 6-, 14-, 15-H), 0.98 (s, 12-H). – ^{13}C NMR (CD_2Cl_2): δ = 210.4 (CO), 66.1 (C-1, -4, -7, -10), 39.0 (C-11, -13), 28.7 (C-5, -6, -14, -15), 21.4 (C-12). – EI MS (70 eV): *m/z* (%) = 762 (7) [M^+], 734 (8) [M^+ − CO], 706 (24), 678 (8), 650 (4), 622 (14), 594 (27), 566 (58), 538 (100), 510 (35), 482 (18), 454 (22), 426 (85) [M^+ − 12 CO]; HR EI MS (70 eV): *m/z* (%) = 759.91 (22), 760.92 (2), 761.84 (100), 762.98 (38), 763.91 (8).

Table 5. Positional parameters for **26**; the anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: (4/3) [$a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)$]

Atom	x	y	z	B(Å^2)
Fe1	0.62033(3)	-0.33307(3)	0.65224(2)	3.165(9)
Fe2	0.70016(3)	-0.35938(3)	0.55116(3)	3.411(9)
Fe4	0.73966(3)	0.01401(3)	0.95298(2)	2.795(8)
FE5	0.77025(3)	0.12506(2)	0.85227(2)	2.757(8)
Fe6	0.59140(3)	0.08558(3)	0.81686(2)	2.876(8)
O1	0.6787(2)	-0.5043(2)	0.7505(2)	9.4(1)
O2	0.5688(1)	-0.2486(2)	0.7846(1)	6.53(7)
O3	0.4163(1)	-0.3824(2)	0.5302(2)	6.19(7)
O4	0.5233(2)	-0.4089(2)	0.3888(1)	6.01(7)
O5	0.7892(2)	-0.5391(2)	0.6064(2)	9.06(9)
O6	0.8280(2)	-0.3135(2)	0.4665(2)	9.33(8)
O7	0.4496(2)	-0.0574(2)	0.7933(2)	7.71(8)
O8	0.5258(2)	0.2007(2)	0.9223(2)	9.26(8)
O9	0.4664(2)	0.1817(2)	0.6497(1)	5.65(7)
O10	0.6238(2)	-0.1356(2)	0.9714(2)	8.39(8)
O11	0.9321(2)	-0.0513(2)	1.0893(1)	6.28(7)
O12	0.7181(2)	0.1345(2)	1.0805(1)	8.42(8)
O13	0.9453(2)	0.1622(2)	1.0187(1)	6.70(7)
O14	0.6836(2)	0.3046(2)	0.8392(2)	9.3(1)
O15	0.8727(2)	0.1754(2)	0.7451(1)	8.52(8)
N1	0.6613(1)	-0.2498(1)	0.5868(1)	2.35(5)
N2	0.7419(1)	-0.2890(1)	0.6573(1)	2.52(5)
N3	0.6793(1)	0.0313(1)	0.7778(1)	2.22(4)
N4	0.7587(1)	-0.0075(1)	0.8493(1)	2.19(4)
C1	0.6540(2)	-0.4390(2)	0.7114(2)	5.6(1)
C2	0.5907(2)	-0.2784(2)	0.7330(2)	4.16(7)
C3	0.4957(2)	-0.3641(2)	0.5784(2)	4.20(7)
C4	0.5929(2)	-0.3916(2)	0.4511(2)	4.03(7)
C5	0.7527(2)	-0.4697(2)	0.5833(2)	5.6(1)
C6	0.7776(2)	-0.3280(2)	0.4998(2)	5.32(8)
C7	0.5066(2)	-0.0025(2)	0.8041(2)	4.41(8)
C8	0.5528(2)	0.1547(2)	0.8827(2)	5.19(9)
C9	0.5155(2)	0.1448(2)	0.7140(2)	3.53(7)
C10	0.6684(2)	-0.0772(2)	0.9625(2)	4.71(8)
C11	0.8587(2)	-0.0270(2)	1.0352(2)	3.73(7)
C12	0.7242(2)	0.0872(2)	1.0299(2)	4.82(8)
C13	0.8740(2)	0.1483(2)	0.9549(2)	3.98(7)
C14	0.7122(2)	0.2322(2)	0.8430(2)	5.3(1)
C15	0.8317(2)	0.1544(2)	0.7857(2)	4.72(8)
C16	0.6802(2)	-0.1529(2)	0.5758(1)	2.51(5)
C17	0.7720(2)	-0.1316(2)	0.6611(1)	2.27(5)
C18	0.8211(2)	-0.2210(2)	0.7030(1)	2.42(5)
C19	0.8643(2)	-0.2261(2)	0.8041(2)	2.77(6)
C20	0.8120(2)	-0.1665(2)	0.8440(1)	2.38(5)
C21	0.8168(2)	-0.0683(2)	0.8198(1)	2.15(5)
C22	0.7704(2)	-0.0544(2)	0.7199(1)	2.12(5)
C23	0.6752(2)	-0.0004(2)	0.6920(1)	2.42(5)
C24	0.5848(2)	-0.0595(2)	0.6399(2)	2.62(6)
C25	0.5901(2)	-0.0928(2)	0.5562(2)	3.06(6)
C26	0.8320(2)	-0.0476(2)	0.6702(2)	2.97(6)

Complex **26**: **5** (50 mg, 0.25 mmol) and $Fe_2(CO)_9$ (1.00 g, 2.80 mmol) in benzene (80 ml) were heated to reflux for 4 h. After filtration and evaporation of the solution in vacuo to dryness, the residue was subjected to preparative TLC on silica gel [R_f = 0.35, CH_2Cl_2/hexane (1:1)] to give 70 mg (33%) of **26** besides a trace of **25**. Crystallization from benzene/CH_2Cl_2/hexane at 4°C yielded green crystals of **26**, m.p. 171°C (dec.)., one of which was used for X-ray structural analysis. – IR (KBr): $\tilde{\nu}$ = 2064 cm^{-1} m, 2006 s, 1986 sh, 1972 s, 1962 sh, 1952 s (CO). – ^1H NMR (400 MHz, CD_2Cl_2): δ = 4.11 (d, *J* = 6.3, 1-, 4-H)*, 3.41 (dd, *J* = 4.5, 12.2, 7-, 10-H)*, 2.14 (m_c, 4H), 1.9–2.0 (m_c, 2H), 1.45–1.55 (m_c, 2H), 1.02 (s, 12-H). – ^{13}C-NMR (CD_2Cl_2): δ = 210.9 (CO), 210.5 (CO), 82.8 (C-1, -4), 64.5 (C-7, -10), 30.8 (C-5, -14)*, 25.1 (C-6, -15)*, 18.2 (C-12).

Structure Determinations[42]: Crystals of **21**, **23**, **26** were obtained as described above. Table 2 gives the crystallographic details. The data sets obtained with Mo-K_α radiation were subjected to an empirical absorption correction[43], the structures solved by means of direct methods. For **21** and **23** the H atoms were included in the calculations with fixed C–H distance (96 pm) and a common isotropic temperature factor. For **26** the H atoms were refined. The rapid decomposition of **21**, which crystallized with 0.5 equiv. of benzene, in the X-ray beam did not allow us to secure a data set of high quality, hence the relatively high *R* value and standard deviations. In Tables 3, 4 and 5 are compiled the atomic parameters. Drawings of the molecules with assignment of all atoms are deposited[42]. All computations were done with the MOLEN program package[44], the drawings of the complexes were made with the SCHAKAL program[45].

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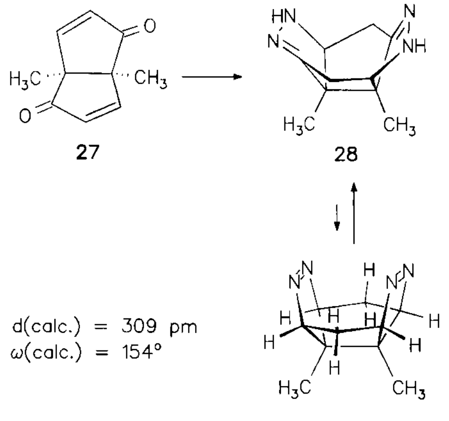
[24] From the analogously executed reaction of **27**[25] – *exo* attack is sterically prohibited – with $N_2H_4 \cdot H_2O/CH_3OH$, a practically quantitative yield of a ca. 9:1 mixture of easily separable tautomers **28** $\rightleftharpoons$ **29** was obtained[20]. The latter, like **4**, prefers the "closed" conformation [UV (CH_3CN): λ_{max} (ε) = 343 nm (770); ^{1}H NMR: $J_{1,12a}$ = 8.0 Hz].



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29

d(calc.) = 309 pm
ω(calc.) = 154°

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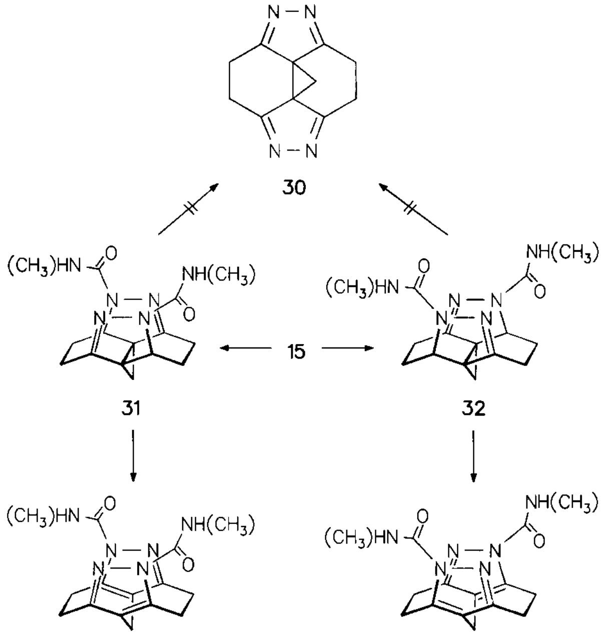

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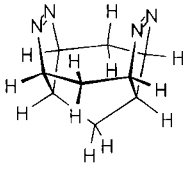

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ω(calc.) = 158°
d(exp.) = 304 pm (av.)
ω(exp.) = 160°

35

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CAS Registry Numbers

3: 100580-90-3 / **4**: 143775-45-5 / **5**: 143790-31-2 / **6**: 4945-71-5 / **10**: 143775-46-6 / **12**: 143839-29-6 / **13**: 143775-47-7 / **15**: 143775-48-8 / **20**: 143775-54-6 / **21**: 143775-52-4 / **21** · $^1/_2$ C_6H_6: 143775-53-5 / **22**: 143775-55-7 / **23**: 143775-56-8 / **24**: 143775-57-9 / **25**: 143775-58-0 / **26**: 143790-33-4 / **27**: 91221-25-9 / **28**: 143775-49-9 / **29**: 143790-32-3 / **33**: 143775-50-2 / $Fe_2(CO)_9$: 15321-51-4 / $Fe_3(CO)_{12}$: 17685-52-8 / $Ru_3(CO)_{12}$: 15243-33-1