44. ^{13}C- and ^{1}H-NMR. Studies on the Configuration of Tricarbonyliron Complexes of Oxa- and Aza[4.4.3]propellanes[1])

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Summary

The configurations of a series of *mono-* and *bis*-Fe(CO)$_3$ complexes of 12-oxa[4.4.3]-propella-2,4,7,9-tetraene (**1**) and of 11,13-dioxo-12-methyl-12-aza[4.4.3]propella-2,4,7,9-tetraene (**7**) as well as of a trienic aza-propellane complex have been studied in solution by ^{13}C- and ^{1}H-NMR. spectroscopy. Praseodymium-induced ^{13}C-shifts of the metalcarbonyl carbon atoms and of the central carbon atom of the complexed diene systems are particularly sensitive and useful to prove *exo-* or *endo*-configuration of the tricarbonyliron ligand. In addition, H,H- and C,H-coupling constants of the complexes and parent compounds are reported and discussed.

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1. Introduction. - In the course of our studies on electrocyclic reactions of tetraenic propellanes a number of stereoisomeric *mono*-Fe(CO)$_3$ and *bis*-Fe(CO$_3$) complexes of 12-oxa[4.4.3]propella-2,4,7,9-tetraene (**1**) and of 11,13-dioxo-12-methyl-12-aza-[4.4.3]propella-2,4,7,9-tetraene (**7**) were synthesized [3] [4] and investigated [4] [5]. In the oxa-series, the structures of the various constitutional isomers and stereoisomers were established by a combination of chemical correlation, X-ray structure analysis [6] and ^{1}H-NMR. data. In the aza-series, a structural reference point in form of an X-ray structure determination was not available when we started to investigate ^{13}C-NMR. spectra of Fe(CO)$_3$ complexed propellanes [7]. With the hope that the configuration and conformation of such complexes might also be obtained in solution by NMR. spectroscopy, we have undertaken a detailed study of carbon and proton chemical shifts, lanthanide-induced ^{13}C-shifts (LIS.) and of C,H- and H,H-spin coupling constants.

2. Tricarbonyliron complexes of tetraenic[4.4.3]propellanes. - The reaction of the tetraenic oxa-propellane **1** with diironnonacarbonyl in benzene solution was shown

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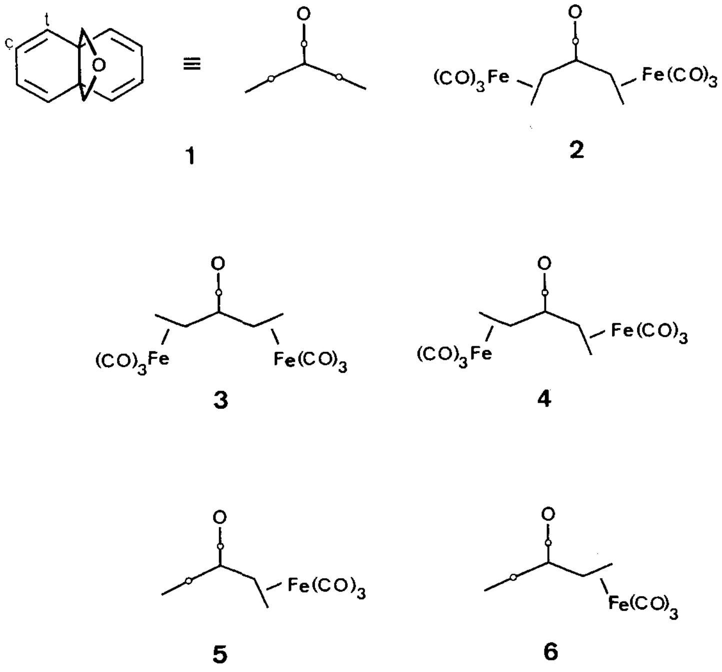
[1]) ^{13}C-NMR. Spectroscopy Part XV; for Part XIV see [1]; Propellanes, Part XL, for Part XXXIX see [2].

to afford five organometallic derivatives, whereby three compounds proved to be *bis*-$Fe(CO)_3$ complexes and the other two derivatives *mono*-$Fe(CO)_3$ complexes [3]. From the three *bis*-complexes one representative (m.p. 135–138°) exhibits an unsymmetrical proton spectrum indicating the *exo-endo* structure **4** as confirmed by X-ray analysis [6c]. The predominant isomer (m.p. 200–204°) among the *bis*-complexes was also shown by X-ray analysis to have structure **2** [6a] [6b]. The third *bis*-complex (m.p. 186–187°), formed in very small yield (~1%) and symmetrical by virtue of its proton spectrum, must therefore have structure **3**.

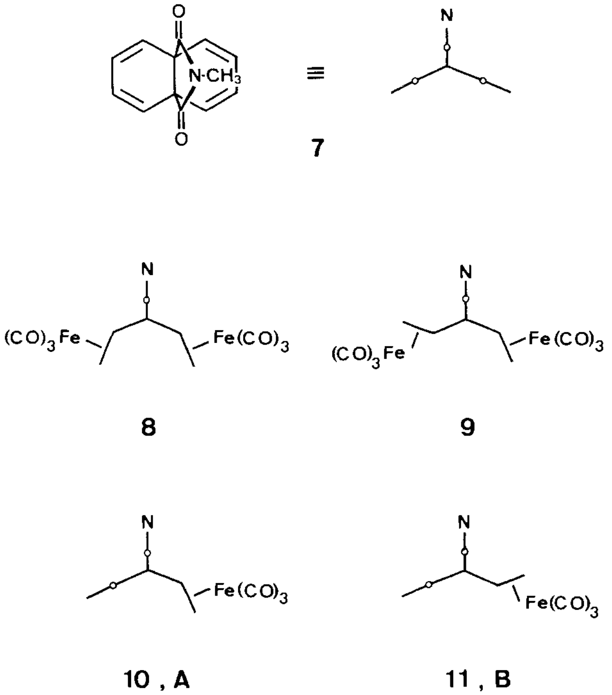
Scheme 1



Removal of one tricarbonyliron ligand from the symmetrical *bis*-complex **2** by means of ceric ammonium nitrate gave a *mono*-$Fe(CO)_3$ complex (m.p. 105–107°) which should be **5** since, under these conditions, a rearrangement of the $Fe(CO)_3$ group has never been observed. The same reaction carried out with the *exo-endo* *bis*-$Fe(CO)_3$ complex **4** also yields only one *mono*-$Fe(CO)_3$ complex (m.p. 115–130°) which differs from **5** and should, therefore, correspond to the *endo*-complex **6**. There is good steric reason for the selective removal of the $Fe(CO)_3$ group from the top face of **4** [6c]. In addition, the ceric ion, like praseodynium ion, may complex the oxygen atom of the ether or the imide carbonyl before it attacks the *exo*-$Fe(CO)_3$ group by neighbouring group participation.

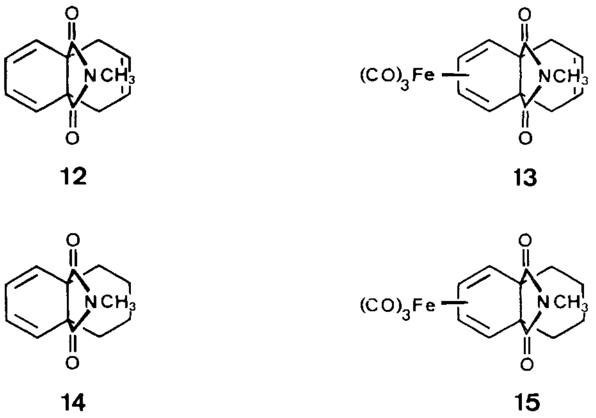
Reaction of the tetraenic aza-propellane **7** with $Fe(CO)_5$ or $Fe_2(CO)_9$ afforded only one of the two possible symmetrical *bis*-$Fe(CO)_3$ complexes (m.p. 221–222°) and an unsymmetrical *bis*-$Fe(CO)_3$ complex **9** (m.p. 179–180°). Treatment of **9** with ceric ion gave two *mono*-Fe(CO)$_3$ complexes A (m.p. 173–173.5°) and B (m.p. 199–200°) in the ratio of 1:9. The minor product A was also obtained from the symmetrical *bis*-Fe(CO)$_3$ complex.

Scheme 2



Provided that also in this series of propellane complexes top face attack of the ceric ion predominates because of steric and stereo-electronic reasons, the *mono*-Fe(CO)$_3$ complex B preferentially formed from the unsymmetrical *bis*-complex 9

Scheme 3



should correspond to structure **11**. Hence, the isomeric complex A should have structure **10**, with the consequence that the symmetrical *bis*-complex has structure **8**.

At this stage, it appeared highly desirable to have an independent method to check the assigned configurations, in particular, to prove in a direct way the configuration of the Fe(CO)$_3$ moiety in the tetraenic *mono*-complexes **5** and **6**, and **10** and **11**, as well as in such cases where chemical correlations with *bis*-Fe(CO)$_3$ complexes are not possible, *e.g.*, the *mono*-Fe(CO)$_3$ complex **13** of the trienic propellane **12** and the Fe(CO)$_3$ complex **15** of the dienic propellane **14** [4].

3. Analysis of spectra. – Since accurate ^{1}H-NMR. data were not available from the literature, we have also analysed the ^{1}H-NMR. spectra of 12-oxa[4.4.3]propella-tetraene (**1**), its two *mono*-Fe(CO)$_3$ complexes **5** and **6** and the three *bis*-Fe(CO)$_3$ complexes **2**, **3** and **4**, as well as the two *mono*-Fe(CO)$_3$ complexes **10** and **11** of 11,13-dioxo-12-methyl-12-aza[4.4.3]propella-tetraene (**7**) and the trienic complex **13**. The spin systems of the olefinic protons in the tetraenic propellanes are of the type *AA'BB'* (non-complexed dienes) or *AA'XX'* (complexed dienes) and were analysed by standard subspectral methods. Assignment of the terminal protons (H$_t$) to the low-frequency multiplet of the complexed diene is based upon selective line-broadening observed due to inter-ring spin coupling. This assignment is in agreement with the general observation that in diene-Fe(CO)$_3$ complexes H$_t$ is always more shielded than H$_c$ [8]. The chemical shifts and H, H-coupling constants are given in Table 1.

Table 1. *^{1}H-NMR. chemical shifts*[a] [δ_H, ppm] *and H, H-coupling constants* [*J*, *Hz*]

	1	**2**	**3**	**4**	**5**	**6**	**10**	**11**	**13**
δ(H$_c$)[b]	5.60	–	–	–	5.47	5.63	5.81	5.69	5.75
δ(H$_t$)[b]	5.25	–	–	–	5.26	5.16		5.96	1.73 (ax) 2.81 (eq)
δ(H$_c$)[c]	–	4.52	4.52	4.74[e] 4.51[d]	4.27	4.69	5.18	5.37	5.39
δ(H$_t$)[c]	–	2.28	2.14	2.29[e] 2.52[d]	2.82	2.36	3.71	3.09	3.31
δ(CH$_2$)	4.01	3.72	3.10	3.55 3.45	3.70 3.23	3.52 3.00	–	–	–
δ(N–CH$_3$)	–	–	–	–	–	–	2.94	2.89	2.94
^3J(H$_c$,H$_t$)[b]	9.5	–	–	–	9.6			9.7	
^3J(H$_c$,H$_c$)[b]	5.5	–	–	–	5.2			5.5	
^5J(H$_t$,H$_t$)[b]	0.8	–	–	–	0.7			1.0	
^3J(H$_c$,H$_t$)[c]	–	6.4	6.3	6.4[e] 6.3[d]	6.2	6.3	6.3	6.3	6.3
^3J(H$_c$,H$_c$)[c]	–	4.0	3.9	4.0[e] 3.9[d]	4.1	4.2	4.1	4.3	4.1
^4J(H$_c$,H$_t$)[c]	–	1.4	1.7	1.4[e] 1.6[d]	1.3	1.5	1.4	1.6	1.4

[a] **1**–**6** in C$_6$D$_6$; **10**, **11**, **13** in CDCl$_3$.

[b] Non-complexed part.

[c] Complexed part.

[d] *endo*-Configuration.

[e] *exo*-Configuration.

The ^{13}C-spectra were obtained with proton noise-modulated decoupling and under single resonance conditions (fully proton coupled). Assignments of the central (C_c) and terminal carbons (C_t) within a diene system can be achieved either by inspection of the characteristic difference in multiplet pattern of C_c and C_t in non-decoupled spectra or from off-resonance decoupled spectra utilizing the known proton chemical shifts. In addition, C_c and C_t in metal complexed dienes can be distinguished by their very different coordination shifts. In the proton coupled spectrum C_c exhibits a double doublet fine structure which can be analysed according to first-order splitting rules [9] to yield the vicinal coupling constant $^3J(C_c, H_t)$ and the geminal $^2J(C_c, H_c)$. In contrast to C_c, the signal of the terminal carbon C_t consists of a complex multiplet due to a non-first-order splitting pattern and additional long-range coupling with neighbouring protons in the two other rings. Whereas complexed and non-complexed diene systems can be differentiated on the basis of the large low-frequency coordination shifts [$\Delta\delta(C_t)$: 60 ± 2 ppm; $\Delta\delta(C_c)$: 38 ± 2 ppm], it is not easy to distinguish complexed diene systems with different configuration of the tricarbonyliron moiety. Assignments in the unsymmetrical *bis*-$Fe(CO)_3$ complexes and determination of the configuration of the *mono*-$Fe(CO)_3$ complexes was achieved from lanthanide-induced

Table 2. *Carbon chemical shifts*a) [δ_C, ppm] *and C,H-coupling constants* [J, Hz) *in the oxa-propellane series*

	1	**2**	**3**	**4**	**5**	**6**
$\delta(C_c)$ b)	121.2	–	–	–	116.5	120.9
$\delta(C_t)$ b)	130.1	–	–	–	132.9	129.0
$\delta(C_c)$ c)	–	83.5	82.3	85.2 e) 84.0 d)	82.6	84.3
$\delta(C_t)$ c)	–	70.5	70.6	69.3 e) 78.6 d)	71.1	69.7
$\delta(C_q)$	48.3	58.7		58.4	49.2	55.6
$\delta(OCH_2)$	83.8	82.5	86.5	83.9	81.9	84.5
$\delta(Fe\text{-}CO)$	–	211.9		212.4 e) 213.0 d)	211.9	212.2
$^1J(C_c,H_c)$ b)	161.8	–	–	–	160.7	162.3
$^1J(C_t,H_t)$ b)	159.9	–	–	–	159.9	162.2
$^1J(C_c,H_c)$ c)	–	172.2	f)	173.9 e) 172.3 d)	172.7	172.3
$^1J(C_t,H_t)$ c)	–	159.4		156.8 e) 158.7 d)	157.7	160.0
$^1J(CH_2,H)$	148.7	144.7		145.4	146.4	146.4
$^3J(C_c,H_t)$ c)	–	7.2		7.4 e) 7.4 d)	6.8	7.9
$^2J(C_c,H_c)$ c)	–	2.2		2.4 e) 2.0 d)	2.3	2.0

a) In C_6D_6.
b) Non-complexed part.
c) Complexed part.
d) *endo*-Configuration.
e) *exo*-Configuration.
f) Proton-coupled spectrum could not be obtained.

Table 3. *Carbon chemical shifts*a) [δ_C, ppm] *and C,H-coupling constants* (J, Hz] *in the aza-propellane series*

	7	8	9	10	11	12	13	14	15
$\delta(C_c)$b)	121.5	–	–	119.7	123.7	122.0	–	124.0	–
$\delta(C_t)$b)	124.6	–	–	128.1	124.9	127.0	–	128.3	–
$\delta(CH_2)$	–	–	–	–	–	32.1	37.3	31.1 19.8	33.3 17.1
$\delta(C_{en})$	–	–	–	–	–	128.5	129.0	–	–
$\delta(C_c)$c)	–	83.9	84.8d) 84.6e)	83.6	84.8	–	83.7	–	83.2
$\delta(C_t)$c)	–	62.6	68.3d) 61.9e)	66.4	63.0	–	63.3	–	64.3
$\delta(CO)$	179.3	178.6	178.0	178.8	178.5	180.9	179.9	181.1	180.6
$\delta(C_q)$	51.1	58.6	57.2	50.6	55.3	50.4	53.7	49.1	51.1
$\delta(NCH_3)$	25.6	24.3	24.5	24.7	25.0	25.3	24.7	25.2	24.5
δ(Fe–CO)	–	209.7	210.4 209.8	209.6	209.6	–	209.4	–	209.8
$^1J(C_c,H_c)$b)		–	–	163.3	164.0		–	163.9	–
$^1J(C_t,H_t)$b)		–	–	165.8	165.0		–	165.3	–
$^1J(C_c,H_c)$c)	–	173.9		174.8	174.2	–		–	
$^1J(C_t,H_t)$c)	–	164.0		165.5	161.8	–		–	
$^3J(C_c,H_t)$c)	–	7.1		6.7	7.5	–		–	
$^2J(C_c,H_c)$c)	–	2.6		2.5	2.3	–		–	

a) In $CDCl_3$.
b) Non-complexed part.
c) Complexed part.
d) *endo*-Configuration.
e) *exo*-Configuration.

shift studies (LIS.) as described in section 4. The resultant carbon chemical shifts and C,H-coupling constants are summarized in Tables 2 and 3.

4. Discussion of the results. – An inspection of the ^{13}C-chemical shifts (Tables 2 and 3) of the *mono*- and *bis*-$Fe(CO)_3$ complexes and of the corresponding parent compound leads to the following conclusions with regard to structural isomerism:

(1) The observed changes in chemical shift ($\Delta\delta$) of the olefinic carbon atoms upon complexation are essentially coordination shifts, 60 ± 2 ppm for the terminal carbon C_t and 38 ± 2 ppm for the central carbon atom C_c. They are not a sensitive probe to reflect the different configuration of the $Fe(CO)_3$ group, with the exception that an *exo*-$Fe(CO)_3$ group exerts a significant deshielding effect of 7–9 ppm on C_t of the neighbouring complexed diene system, *cf.* **4** and **9**;

(2) The chemical shifts of the $Fe(CO)_3$ groups (averaged CO resonances in the fast exchange limit) are remarkably constant within the oxa- and aza-propellane series, respectively. The range of shifts in the oxa-series is 212.4 ± 0.6 ppm in C_6D_6 and 211.5 ± 0.5 ppm in $CDCl_3$ solutions. They closely correspond to the respective data of $Fe(CO)_3$ complexed model dienes, *e.g.*, 1,3-butadieneiron tricarbonyl (212.1 ppm, C_6D_6; 211.9 ppm, $CDCl_3$) and 1,3-cyclohexadieneiron tricarbonyl (212.5 ppm, C_6D_6). In the aza-series the Fe–CO shifts have only been obtained in $CDCl_3$ solution (209.9 ± 0.5 ppm) and when compared with those of the oxa-series in the same

solvent reveal a low-frequency shifts of about 2 ppm. Thus, the $Fe(CO)_3$ shifts appear to depend upon the nature of the 5-membered bridge in the propellane but they are not a sensitive probe for configurational differences in either series.

The chemical shift of the olefinic protons upon complexation exhibit essentially parallel shift trends as described for the carbon nuclei and do not provide information about the configuration of the $Fe(CO)_3$ moiety.

H,H- and C,H-coupling constants in butadieneiron tricarbonyl [9] and H,H-coupling constants in cyclohexadieneiron tricarbonyl [10] have already been studied in detail. The corresponding data in the present study (Tables 1–3) of $Fe(CO)_3$ complexed *bis*-dienic propellanes show in general close agreement with the reported parameters. It appears, therefore, that coupling constants are mainly determined by the local geometry of the complexed diene system and to a lesser extent by secondary factors such as the nature of the heterocyclic bridge or the presence of a second diene or complexed diene system.

From the discussion of the spectral parameters it is evident that they are as such not suitable to clearly differentiate *mono-exo* and *mono-endo* $Fe(CO)_3$ complexes in both propellane series. For this reason, we have studied lanthanide-induced ^{13}C-chemical shifts (LIS.). The ether oxygen and the imide function can be expected to be the dominant sites for complexation by the lanthanide ion (see below). The iron carbonyl cannot compete with the heterocyclic function in the complexation by the lanthanide ion, as shown by the following model studies. Under the same experimental conditions the LIS. effects on all carbon atoms of butadieneiron tricarbonyl are negligible, whereas the effects on the uncomplexed tetraenic oxa-propellane **1** are comparable with those on the two *mono*-$Fe(CO)_3$ complexes. Because of the relatively small contact term contribution of the praseodymium ion as compared with the europium ion [11] we have used $Pr(fod)_3$ as the reagent throughout the following studies. As models for the LIS. studies in the propellane series we shall first discuss the effects on the ^{13}C-chemical shifts of the two stereoisomeric *mono*-$Fe(CO)_3$ oxa-propellane complexes **5** and **6**. The methylene carbon atoms exhibit the largest induced shifts. For each isomer the induced CH_2 shift serves as an internal reference (100%) and the effects on the other carbon atoms are expressed as relative numbers (Table 4). As expected from molecular models of the *mono-exo* and *mono-endo*-$Fe(CO)_3$

Table 4. *Relative praseodymium induced* ^{13}C*-shifts LIS.* [%] *for* **5** *and* **6**

	LIS. = $(\Delta\nu_C/\Delta\nu_{OCH_2}) \cdot 100$		Q = LIS.(**5**)/LIS.(**6**)
	5	**6**	
CH_2	100.0	100.0	1.0
C_q	39.1	41.0	0.95
C_c[a])	15.5	24.7	0.63
C_t[a])	27.3	28.9	0.95
C_c[b])	13.5	12.5	1.08
C_t[b])	21.2	20.0	1.06
$Fe(CO)_3$	24.3	8.3	2.93

[a]) Complexed part.

[b]) Non-complexed part.

complex pronounced differences in the induced shifts are observed for the tricarbonyliron group and for the central carbon C_c of the complexed diene, whereas the data for the remaining carbons are very similar in both isomers.

It is known that in the interpretation of LIS. data, particularly for carbon nuclei, both the pseudo contact and the contact term have in principle to be taken into account [11] [12]. In the present study, however, we compare LIS. data for the respective carbon atoms in stereoisomers which differ only in the configuration of the $Fe(CO)_3$ moiety and in the concomitant change in the geometry of the $Fe(CO)_3$-complexed ring. Since the contact contribution is transmitted from the site of complexation to the carbon atom in question *via* spin polarisation in the chemical bonds, it can be expected to be very similar for such stereoisomeric pairs so that in a discussion of the *relative* data for **5** and **6** this term will be effectively eliminated. Furthermore, the $Fe(CO)_3$ carbon atoms and C_c of the complexed diene are separated from the site of lanthanide complexation (ether oxygen) by a sufficient number of bonds to ensure a strong attentuation [13] of the contact term. For these reasons, the LIS. data given in Table 4 can be interpreted safely in terms of the pseudo contact mechanism, *i.e.*, the parameters R and θ. The induced low-frequency shifts in the two *mono*-$Fe(CO)_3$ complexes of the oxa series differ by a factor (Q) of 2.93 for the $Fe(CO)_3$ carbon atoms and by 0.63 for C_c of the complexed diene, whereas the induced shifts for the remaining carbon atoms are very similar and yield Q values of 1.0 ± 0.1. The isomer (m.p. 105–107°) with the larger LIS. value for the $Fe(CO)_3$ group combined with the smaller value for C_c must clearly be assigned to the *exo*-complex **5** as evident from an inspection of molecular models. An estimate for the ratios of the geometrical factors $(3\cos^2\theta\text{-}1)/R^3$ for the Fe–CO carbon atoms and for C_c of the complexed diene in the *exo*- and *endo*-isomers was obtained on the following basis: (1) it is known that the lanthanide ion complexes the lone pairs of the oxygen atom in oxa-propellanes at a distance of 2.4 Å [14]. The five-membered ether ring is assumed to be statistically planar, and in the case of the *mono-exo* complex **5** complexation of the oxygen by the praseodymium ion occurs only at the orbital *anti* to the $Fe(CO)_3$ moiety; (2) atomic coordinates for C_c of the complexed diene and for the three iron carbonyls were taken from the X-ray analysis of the *bis*-$Fe(CO)_3$ complex **4** [6b]. The numerical results for the calculated LIS. ratios Q $(= \text{LIS.}_{exo}/\text{LIS.}_{endo})$ are 0.62 for C_c and 1.89 for the $Fe(CO)_3$ group taking into account rotational averaging of the three CO positions. These data are in satisfactory agreement with the experimental ratios (Table 4).

Since the interpretation of the LIS. data of the oxa-propellane complexes have led to an assignment of the two *mono*-$Fe(CO)_3$ complexes consistent with the results obtained from the combination of X-ray analysis and chemical correlations (section 2), we have applied the same procedure to deduce the configuration of the tetraenic aza-propellane complexes. LIS. studies on amides and ureas have shown that the lanthanide ion complexes the carbonyl oxygen rather than the nitrogen atom [15], which was also demonstrated by calculations on imide propellanes [14]. Although in imides there are two potential sites for complexation by the praesodymium ion statistical averaging would lead to a situation in which the differences in the LIS. effects for the $Fe(CO)_3$ and C_c carbons in the *exo*- and *endo*-isomers can be expected to be similar to those in the ether series. The experimental data for the isomeric

Table 5. *Relative praseodymium induced* ^{13}*C-shifts LIS.* [%] *for* **10**, **11** *and* **13**

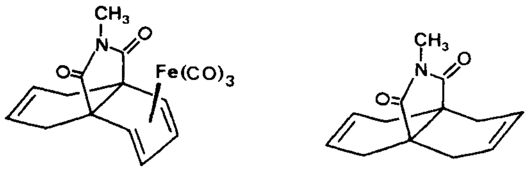
	LIS. = $(\Delta\nu_C/\Delta\nu_{C=O}) \cdot 100$			Q = LIS.(**10**)/LIS.(**11**)
	10(A)	**11**(B)	**13**	
C=O	100.0	100.0	100.0	1.0
C_q	85.0	85.0	93.1	0.99
N–CH_3	81.2	83.0	87.1	0.98
C_c[a]	26.1	38.5	30.0	0.68
C_t[a]	56.0	62.0	65.4	0.90
C_c[b]	27.5	30.5	–	0.90
C_t[b]	62.8	63.0	–	1.00
CH_2	–	–	70.5	–
C_{en}	–	–	44.7	–
$Fe(CO)_3$	26.6	13.0	31.3	2.05

[a] Complexed part.
[b] Non-complexed part.

mono-$Fe(CO)_3$ complexes A and B (Table 5) yield experimental ratios Q ($LIS._A/LIS._B$) of 2.05 for the $Fe(CO)_3$ carbon atoms and 0.68 for the C_c carbon atoms of the complexed diene. These values when compared with the corresponding ratios in the ether series (Table 4) clearly prove that A must have the *exo*-configuration **10** and B the *endo*-configuration **11**. Our assignment of the configurations for the two *mono*-$Fe(CO)_3$ complexes is in agreement with the chemical correlation (section 2) between the *exo*-complex **10** and the symmetrical *bis*-$Fe(CO)_3$ complex which meanwhile has been shown by X-ray analysis to correspond to structure **8** [16].

The $Fe(CO)_3$ complexes **13** and **15** of the trienic and dienic aza-propellanes respectively should have the same configuration of the $Fe(CO)_3$ group (*exo* or *endo*) since **13** was shown to give **15** upon catalytic hydrogenation [4]. Application to **13** of the LIS. method described for the tetraenic complexes leads to relative induced shifts which are listed in Table 5. A comparison of the data for the $Fe(CO)_3$ group (31.3%) and for C_c of the complexed diene (30.0%) with the corresponding numbers of the *mono-exo* tetraenic complex **10** proves that the trienic and dienic complexes **13** and **15** must both also have an *exo*-$Fe(CO)_3$ group. The olefinic carbons (C_{en}) of the non-complexed cyclohexene ring in **13** exhibit a very large induced shift (44.7%) which, when compared with the data of the complexed carbon C_c (38.5%) in the *mono-endo* complex **11**, suggests that the cyclohexene ring predominantly exists in an *exo*-boat conformation. The same conformation has been shown to apply for 11,13-

Scheme 4



13 **16**

dioxo-12-methyl-12-aza[4.4.3]propella-3,8-diene (**16**) in the solid state [17] as well as in solution by proton LIS. studies [14].

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5. Experimental part. – ^{1}H-NMR. spectra were measured on a *Varian* HA-100 spectrometer, ^{13}C-NMR. spectra on a *Varian* XL-100-12 spectrometer equipped with a pulse *Fourier* transform unit and a 620-L 16K computer. Proton coupled ^{13}C-spectra were measured with a spectral width of 2500 Hz and an aquisition time of 1.6 s, corresponding to 1.6 points per Hz in the transformed spectra. The reproducibility of C,H-coupling constants measured under these conditions and after averaging of several equivalent line separations is better than ± 0.2 Hz. Compounds **1–6** were measured in C_6D_6, **7–13** in $CDCl_3$. TMS as internal standard was used in all cases. The LIS. studies of both the oxa- and aza-propellane series were carried out in $CDCl_3$ using $Pr(fod)_3$ [*Merck*, Darmstadt] as shift reagent. The LIS. data (low-frequency shifts) were measured in each case for several reagent/substrate ratios in the range of 0.1–0.3 and extrapolated to a 1:1 ratio. In both series relative LIS. were then calculated using the OCH_2 groups in the oxa-series and the N-CO groups in the azaseries as internal reference (Tables 4 and 5).

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