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TRANSITION METAL COMPLEXES OF DIAZENES

XII *. SYNTHESIS AND DYNAMIC PROPERTIES OF (*cis*-DIAZENE)-$M_3(CO)_9$ CLUSTERS (M = Fe, Ru)

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Summary

The ability of the N=N group to coordinate to three metal atoms has been demonstrated by the synthesis of (*cis*-diazene)$M_3(CO)_9$ (M = Fe, Ru; *cis*-diazene = 2,3-diazanorbornene, 4-phenyl-3,3-bis(methoxycarbonyl)-1-pyrazoline). These new M_3 clusters are prepared thermally from the free diazene and $Fe(CO)_5$ or $Ru_3(CO)_{12}$, and photochemically from (*cis*-diazene)$Fe_2(CO)_6$ and -$Fe(CO)_5$. The complexes contain one seven-coordinated and two, equivalent, six-coordinated $M(CO)_3$ groups. Dynamic ^{13}C NMR spectroscopy over the range —130 to 40°C reveals that these two sets of carbonyl groups do not undergo internuclear carbonyl exchange. Localized scrambling at the 7-coordinated metal is rapid even at —130°, resulting in one sharp signal over the whole temperature range. Localized exchange at the 6-coordinated metals is frozen out between —130°C and about —40°C, giving rise to three signals of equal intensity which coalesce into one broad signal at room temperature. In addition to the carbonyl resonances, the ligand carbon and hydrogen signals exhibit temperature dependence. A possible rotation of the diazene ligand around the M_3-triangle is excluded because of the observation of chemically non equivalent $M(CO)_3$ groups in the room temperature ^{13}C NMR spectra and of two isomers for the mono- and di-substituted trimethylphosphite derivatives (^1H and ^{31}P NMR). The same type of dynamic behaviour is found with the binuclear (2,3-diazanorbornene)$Fe_2(CO)_6$; here again only localized CO exchange was observed from —110 to +40°C.

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[*] For part XI see ref. 18.

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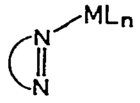
Introduction

The mechanism of the biological dinitrogen reduction is still a matter of considerable discussion [1]. Evidence for diimide (HN=NH, diazene) as the first intermediate comes from the observation that HD formation occurs only if enzymological [2,3] or inorganic model [4] reactions are performed under a D_2/N_2 atmosphere but not under an e.g. D_2/C_2H_2 or D_2/CO mixture. The known olefin-reducing capability of diimide was used to demonstrate its intermediate formation in the nitrogenase model systems [5]; fumarate is reduced to succinate only in the presence of N_2. It is still not known how the further reduction of HN=NH to NH_3 takes place in the biological process. One important feature, the interaction of diimide with iron and molybdenum, or any other transition metal, is essentially unknown. This lack of knowledge stems from the extreme instability of free diimide [6]. However, one type of complexes, L_nM(*trans*-N_2H_2)-ML_n (ML_n = $C_5H_5Mn(CO)_2$, $C_5H_5Re(CO)_2$; L_n = $(CO)_5$, M = Cr, Mo, W) can be prepared via oxidation of the corresponding hydrazine complex $L_nM(N_2H_4)$ [7]. In order to study the interaction of a diazene group (—N=N—) with a metal in a more direct way, we have used cyclic diazenes as models for *cis*-diimide [8]. The results obtained by us and others [9] reveal the powerful coordinating properties of diazenes towards low valent transition metals; complexes of type I—IX have so far been isolated.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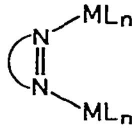
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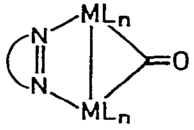
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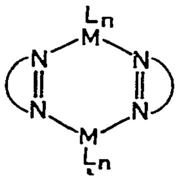
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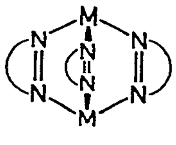
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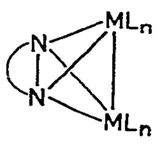
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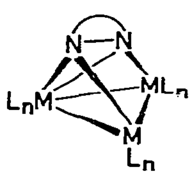
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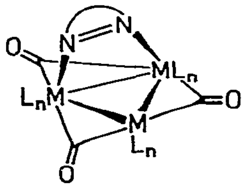
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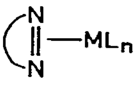
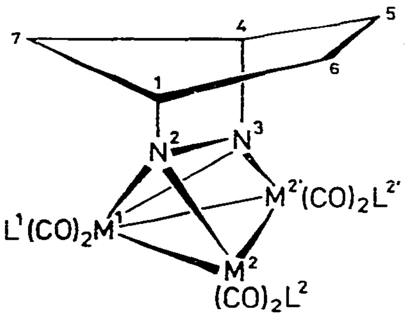

IX

Owing to the similar electronic structures of *cis*-diimide and *cis*-diazenes [9,10] the observed modes of coordination may be possible ways for the interaction of *cis*-diimide with the iron and molybdenum site of nitrogenase. In this connection we describe below the synthesis and dynamic properties of iron and ruthenium clusters of type VII [11].

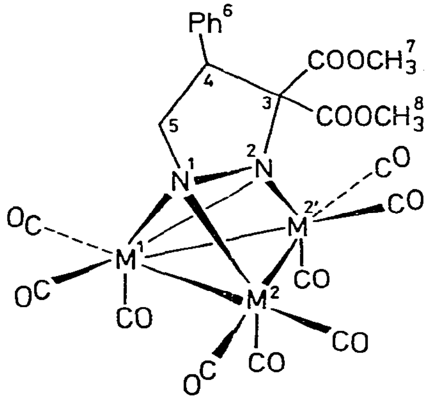
Results and discussion

Complex 1, (2,3-diazanorbornene)$Fe_3(CO)_9$, is prepared from the free ligand and $Fe(CO)_5$ at 150°C as described for the synthesis [12] of (2,3-diazanorbornene)$Fe_2(CO)_6$ (Type VI). Chromatographic work-up gives first the latter complex (n-hexane/benzene), and further elution (benzene) gives complex 1 in 20% yield. The new compound crystallizes from acetone/n-hexane in shiny black prisms which can be sublimed at 60°C/0.04 Torr. Elemental analysis and mass spectrum (highest peak at 516, loss of ten groups of *m/e* 28) lead to the molecular formula $(C_5H_8N_2)Fe_3(CO)_9$. The symmetrical coordination of the diazene ligand to an $Fe_3(CO)_9$ unit is strongly supported by the NMR data (Table 1). The bridgehead protons H(1,4) appear as one singlet at δ 3.0 ppm and only one signal is observed in the ^{13}C spectrum for the carbon pairs C(1,4) and C(5,6) at 76.6 and 31.5 ppm, respectively. The presence of an N—N bond is clearly suggested by the similarity of these data to those of (2,3-diazanorbornene)$Fe_2(CO)_6$ [13], the corresponding values are δ 2.7, 62.7, and 30.3 ppm, respectively. The conversion of 1 into the latter complex by treatment with dilute nitric acid also supports such formulation. (For comparison the values of free 2,3-diazanorbornene are δ 4.7, H(1,4); 76.7, C(1,4); 20.8 ppm, C(5,6). The appearance of five strong IR absorptions of terminal CO groups indicates a local C_{3v}-symmetry for the $Fe_3(CO)_9$ unit (Table 2). On the basis of these properties the novel structure 1 was proposed [11] which now has been confirmed by X-ray analysis and Mössbauer spectroscopy [14]. In agreement with the NMR and IR data the ligand-Fe_3-skeleton has mirror symmetry. The complexed diazene group is considered as a six-electron donor giving rise to a coordinatively saturated cluster molecule. The new compound resembles the (*ortho*-semidine) $Fe_3(CO)_9$ structure tentatively proposed [15] for the reaction product of *trans*-4,4′-dimethylazobenzene and $Fe_2(CO)_9$; the important difference between the two structures is the absence of an N—N bond in the *o*-semidine complex.



1: M = Fe
2: M = Ru } $L^1 = L^2 = L^{2'} = CO$

3a: $L^1 = P(OMe)_3$, $L^2 = L^{2'} = CO$
3b: $L^{2'} = P(OMe)_3$, $L^1 = L^2 = CO$
4a: $L^1 = L^2 = P(OMe)_3$, $L^{2'} = CO$
4b: $L^{2'} = L^2 = P(OMe)_3$, $L^1 = CO$ } M = Fe



5: M = Fe
6: M = Ru

TABLE 1

^{1}H, ^{13}C AND ^{31}P NMR DATA FOR COMPLEXES 1–7

^{1}H NMR [a]				^{13}C NMR [a]			
Complex	Temperature	H(1,4)	H(5,6,7)	C(1,4)	C(7)	C(5,6)	CO
1	+77	—	—	76.6	41.1	31.5	209.8, 212.6
1	r.t.	3.0s	2.0d (J = 11) 0.65–1.0m	76.6	41.1	31.5	208.8 broad, 212.8
1	−80	2.5s	1.8d (J = 11) 0.4–0.7m	76.6	40.8	31.6	200.5, 212.7, 213, 0, 216.7
2	r.t.	3.15s	1.25s, 1.15m, 0.78d (J = 10)	74.2	38.8	32.9	196.6
2	−80	2.78s	1.1–0.9m, 0.85m 0.45d (J = 10)	73.3	38.4	32.7	186.2, 194.1, 196.4, 203

	H(1,4)	δ(P(OMe)$_3$) (ppm)	^{31}P NMR [b]
3a, b	4.35m, 4.05m 4.0m	3.70d (J 11 Hz) 3.65d (J 11 Hz)	3a: 170.6s; 3b: 160.1s
4a, b	4.40m, 4.0m	3.70d (J 11 Hz) 3.65d (J 11 Hz)	4a: 171.6d, 162.8d, J(P(1)P(2)) 5.9 Hz; 4b: 163.0s

	H(4)	H(5)	H(6)	H(7)	H(8)
5	4.0t	4.5q 2.8q	7.0m	3.3s	3.0s
6	3.85t	4.4q 3.1q	7.0m	3.31s	2.95s

[a] Measured in C_7D_8 on a Bruker WH-270 instrument except 3, 4 ($CDCl_3$, Varian A60A), Chemical shifts (δ, ppm) are relative to TMS as internal standard, coupling constants in Hz. ^{13}C spectra were recorded in CH_2Cl_2/C_7D_8 5/1 by volume containing 5 mg of tris(acetylacetonate)chromium. [b] $CDCl_3$, Bruker WP 80, δ-values (ppm) are relative to H_3PO_4 as external standard. ^{13}C and ^{31}P spectra are all proton noise decoupled.

TABLE 2

PHYSICAL DATA FOR COMPOUNDS 1—7

	ν(CO) (cm^{-1}) [a]	M.p. (dec.) (°C) [b]	M^+ [c]
1	2072s, 2021vs, 2012vs, 1993s, 1976s	130 [d]	516
2	2078s, 2038vs, 2033vs, 2003s, 1988(sh), 1983s, 1976s	180	651
3a, b	2056m, 2050m, 2008s, 1982s, 1976, 1956(sh)	112—115	
4a, b	2029s, 1990m, 1970s, 1957s, 1933(sh)	118—121	
5	2078s, 2027vs, 2021vs, 2001s, 1978m, 1972m	107—112	682
6	2087s, 2046vs, 2009vs, 1991s	109—111	789

[a] In n-hexane except 3, 4 (n-hexane/CH_2Cl_2 3/1 by volume). [b] In closed capillary tube. [c] Highest peak in the mass spectrum, corresponds to molecular ion except for 6 (M^+ — CO), MAT-CH5 instrument, I_V 70 eV, [d] Sublimes.

The pyrazoline cluster 5 cannot be prepared in a manner analogous to 1 because of the thermal instability of the free pyrazoline [16] which decomposes above 80°C. However, irradiation of a 10/1 mixture of $Fe(CO)_5$ and (4-phenyl-3,3-bis(methoxycarbonyl)-1-pyrazoline)$Fe_2(CO)_6$ [17] in toluene affords the dark green complex 6 in 20% yield. The structural assignment is based on comparison with the data of 1. The mass spectrum exhibits M^+ (682) and succssive loss of eleven groups * of m/e 28, the pattern of the ν(CO) bands is very similar to that of 1 and the ^{1}H NMR spectrum shows, inter alia, the typical absorptions of the pyrazoline ring protons as known from the $Fe(CO)_4$ [19,20] and $Fe_2(CO)_6$ complexes of this ligand (Tab. 1, 2). The $Ru_3(CO)_9$ clusters 2 and 6 are prepared in ~60% yield by heating equimolar amounts of the free ligand and $Ru_3(CO)_{12}$ in n-hexane to 70°C. Both complexes are obtained as red crystals on crystallization from Et_2O/n-hexane. The structural assignment is again based on the comparison with complex 1. Tables 1 and 2 summarize the relevant spectroscopic data.

Dynamic properties

The ^{13}C NMR spectra of 1 and 2 are very similar and show the same type of temperature dependence (Tab. 1). Because of the better solubility the ruthenium cluster 2 has been studied in more detail than the iron derivative. At room temperature 1 and 2 exhibit three sharp resonances for the diazene ligand carbons. The spectra are presented in Fig. 1. In the carbonyl region one sharp and one broad signal is observed for 1 at 212.8 and 208.8 ppm, respectively. Complex 2 shows only one sharp resonance at 196.6 ppm.

The carbonyl region of the spectrum of complex 2 exhibits from —130 to —60°C four sharp resonances A, B, C, D, (see Fig. 1) of approximate intensities 2/3/2/2 at 203.2, 196.4, 194.1 and 186.2, respectively. If we assume that 2 has the same solid state structure [14] as 1, it should have three pairs of symmetrical carbonyl groups at Ru(2) and Ru(2′). We therefore assign the three resonances of equal intensity to the six carbonyls at these metal atoms. The

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* Due to the presence of ester groups in the ligand.

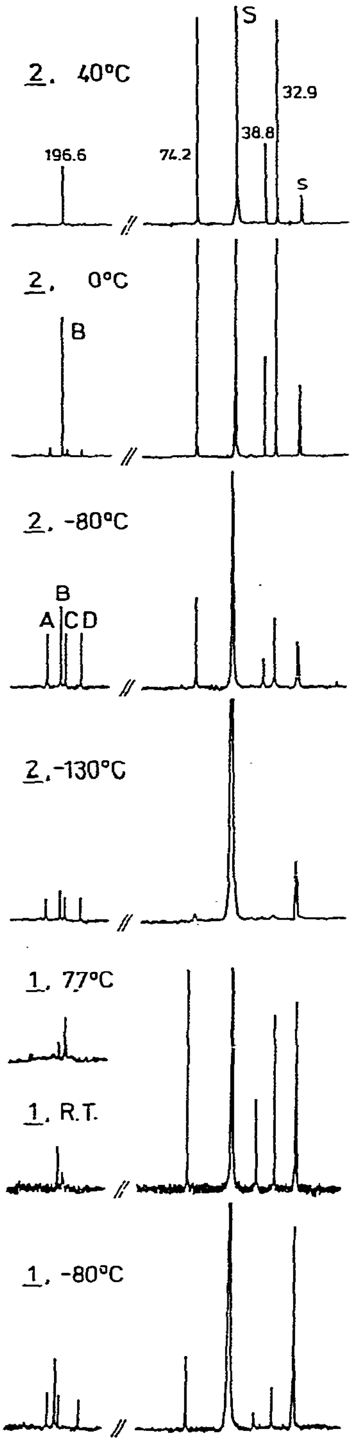


Fig. 1. Dynamic ^{13}C NMR spectra of 1 and 2; for experimental details see Tab. 1; spectra at —130°C were recorded in the solvent mixture CH_2Cl_2/Freon 22/C_7D_8 ~ 3/1/1 by volume; the spectrum at 77°C is in C_7D_8. Due to the large sweep width (18 000 Hz) line shape changes for the fast exchange limit are manifested mainly in peak hight changes.

fourth resonance of relative intensity three, located at 196.4 ppm, remains then to arise from the carbonyls at the unique metal atom Ru(1). The fact that only one signal is observed for these three carbonyls may be due to a fast localized scrambling even at —130°C or to an accidental coincidence of the two expected resonances of relative intensity 2/1.

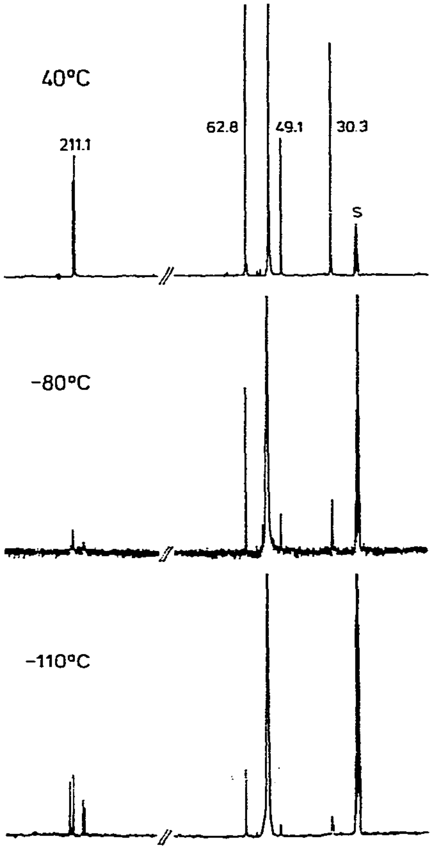
Above —40°C the three resonances, A, C, D, start broadening and by 0°C only very weak peaks slightly above the base line are observed. At room temperature only the resonance B is observable. Because of decomposition of complex 2 at higher temperatures, we could not observe the expected sharp average resonance of A, C, D. However, this was possible with the corresponding iron complex 1.

At —80°C the spectrum of complex 1 in the carbonyl region also consists of four signals A, B, C, D of the same relative intensities as observed for the ruthenium compound 2. These signals are shifted by 13—18 ppm to lower field compared to 2. Raising the temperature results in qualitatively similar the same changes as found for 2, except that in addition to the sharp resonance of B, a broad signal is also observed at the average shift of A, C, D at room temperature (integral ratio B/A, C, D = 1/2). By +77°C this latter signal is sharp, and about twice as intense as resonance B.

The signals of the diazene ligand are also broadened as the temperature is decreased. To see whether this effect is a unique property of the cluster, we investigated the dynamic ^{13}C NMR spectra of (2,3-diazanorbornene)$Fe_2(CO)_6$ in CH_2Cl_2/C_7D_8 5/1 solutions (Fig. 1). At —80°C the resonances of C(1,4), C(5,6) and C(7) appear at 62.3, 30.0 and 49.1 ppm, respectively, and are significantly broader than at room temperature, where they are located at 62.8, 30.3 and 49.1 ppm. At —110°C especially the resonances C(5,6) and C(7) are very broad, but the rest of the spectrum contains much sharper signals. At this temperature four carbonyl resonances of relative intensities 2/2/1/1 are observed at 216.0, 214.9, 210.9 and 210.3 ppm, respectively. This is in agreement with the solid state structure [13] of the complex (Fig. 3). The presence of two sharp signals at room temperature, 211.6 and 211.1 ppm, indicates that only localized scrambling of CO occurs at each $Fe(CO)_3$ moiety.

The ^{1}H NMR spectra of 1 and 2 show also some changes upon cooling. Compared to room temperature, all the ligand signals at —80°C are shifted by 0.2 tp 0.5 ppm to higher field. The largest shifts are found for H(1,4) and amount 0.5 and 0.3 ppm for 1 and 2, respectively. The same proton signal is shifted also by 0.45 ppm in (2,3-diazanorbornene)$Fe_2(CO)_6$ but remains unchanged in free 2,3-diazanorbornene. In the latter case H(5,6,7) show a small shift of 0.1—0.2 ppm.

The temperature dependence of the ^{13}C diazene ligand signals in complexes 1 and 2 might suggest a rapid rotation of the diazene ligand relative to the $M_3(CO)_9$ skeleton (structures 3a, 3b and 4a, 4b, L = CO). The process should be fast compared on the NMR time scale since sharpening of the signals could not be observed at even —130°C. However, from the appearance of four ^{13}C-metal carbonyl resonances at —80 to 0°C, the temperature range in which the diazene signals are sharp, it follows that diazene ligand rotation does not occur. To provide a further, independent proof for the absence of this process we prepared mono- and bis-(trimethylphosphite) derivatives of complex 1 by photochemical



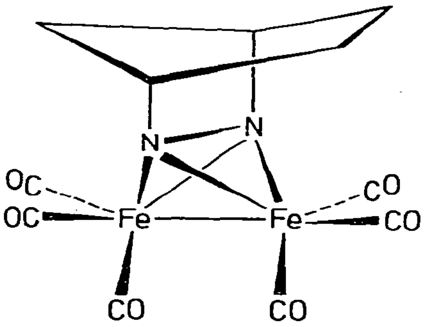


Fig. 2. Dynamic ^{13}C NMR spectra of (2,3-diazanorbornene)$Fe_2(CO)_6$ in CH_2Cl_2/C_7D_8 5/1.

Fig. 3. Solid state structure of compound (2,3-diazanorbornene)$Fe_2(CO)_6$.

CO substitution. The ^1H NMR spectrum of the monosubstituted complex shows doublets at δ 3.7 and 3.65 ppm, J(PH) 11 Hz * for the methyl groups of the phosphite; the intensity ratio of these signals to those of the bridgehead protons (δ 4.35, 4.05 and 4.0 ppm) is 4.7. In the ^{31}P NMR spectrum two singlets are observed, at 160.1 and 170.6 ppm, which are assigned to 3b and 3a, respectively, by comparison with the spectrum of 4a, 4b. From these data and from the relative intensities of the phosphorous signals it follows that the monosubstituted complex is a mixture of two isomers, 3a (~48%) and 3b (~52%), and that therefore no rotation of the diazene ligand takes place. The same conclusion is obtained for the disubstituted compound: the methyl groups give rise to two doublets, the bridgehead protons, to two broad signals; the corresponding intensity ratio is 8.5. The presence of two isomers, 4a and 4b, is further substantiated by the ^{31}P NMR spectrum. The two doublets at 171.6 and 162.8 ppm, J(PP) 5.9 Hz, are assigned to the unsymmetrical isomer 4a and the singlet

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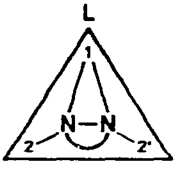
* This value was also found for a $P(OMe)_3$ group coordinated to an other Fe_3-cluster [21].

at 163 ppm to the symmetrical complex 4b. From the relative intensity of these signals, the composition is 80% 4a and 20% 4b.



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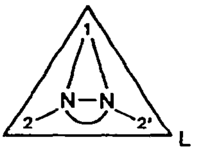
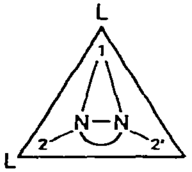
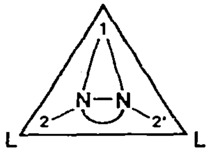


3b



4a



4b

L = P(OMe)$_3$

These results clearly rule out the possibility that diazene ligand rotation gives rise to the temperature dependent diazene ligand signals, and call for another explanation. From the fact that this temperature dependent behaviour is observed only for the cluster and the binuclear $Fe_2(CO)_6$ complex but not for the free ligand itself, it follows that the unknown process is made feasible by the "reduction" of the N=N double bond to a formal single bond upon coordination and/or by the presence of fluxional $M(CO)_3$ groups. Due to the very rigid bicyclic ligand sekleton it seems unlikely that a motion of this part of the complex is responsible for the phenomenon. We assume instead that it is brought about by the CO scrambling process. The resulting temperature-dependent anisotropy of the magnetic environment should influence the ligand protons much more than the more shielded carbon atoms, and so the observed temperature (proton) shifts may be rationalized. However, this assumption has to be tested by further investigations.

The fluxional behaviour of the carbonyl groups is clearly divided into two stages: for 1 and 2 internal CO exchange at M(1) is rapid at even —130°C, whereas is it still slow at M(2,2') at —40°C; no internuclear scrambling between M(1) and M(2,2') could be observed up to 40°C. Thes results reveal a significant difference in the activation energies of localized CO scrambling between a six- and seven-coordinated $M(CO)_3$ group, as well as a large energy barrier to internuclear exchange between these groups of different coordination numbers. A similar difference in activation barriers for internal CO exchange at a 6- and 7-coordinated $Fe(CO)_3$ group has been very recently reported for $S_2Fe_3(CO)_9$ [22]. Our findings are important in view of the current discussion of the mechanism of CO scrambling in di- and poly-nuclear carbonyl complexes [23—25].

The major point of discussion is the question whether the Fe_3 triangle in $Fe_3(CO)_{12}$ rotates within a fixed arrangement of the CO groups [24] or some carbonyls move relative to others [25]. The second process has been shown [25] to occur in the triply CO-bridged 1,2-diazene compound (pyridazine)$Ru_3(CO)_{10}$ (type VIII). The same process was formulated also for the unsubstituted $M_3(CO)_{12}$ compound under the assumption that replacement of two CO groups by pyridazine does not invalidate the premises of the Fe_3-rotation mechanism [25]. Our results can only be explained by the second process, that is, different sets of carbonyl groups move relative to each other, and not by a rotation of the M_3 or M_3N_2 unit within a rigid ligand skeleton. Although the *cis*-diazene clusters studied in this work are formally trisubstituted $M_3(CO)_{12}$ derivatives, we cannot decide if the dynamic CO scrambling observed, does also occur in the unsubstituted $M_3(CO)_{12}$ molecules.

Experimental

For a general description of instruments and procedures see ref. 26. $Ru_3(CO)_{12}$ was purchased from Pressure Chemicals, $Fe(CO)_5$ was a gift from BASF; 2,3-diazanorbornene [27], 4-phenyl-3,3-dimethoxycarbonyl-1-pyrazoline [16] and (2,3-diazanorbornen)$Fe_2(CO)_6$ [12] were prepared according to literature. All manipulations with metal carbonyls were performed in an argon atmosphere. Irradiations were conducted in a water cooled solidex reaction vessel ($\lambda \geqslant 270$ nm) using a Philips HPk 125 W lamp.

Preparation of 1. Following the procedure given [12] for the synthesis of (2,3-diazanorbornene)$Fe_2(CO)_6$ 2,3 g (24 mmol) of 2,3-diazanorbornene and 9.6 g (48 mmol) of $Fe(CO)_5$ were heated in 90 ml of decaline for 2 h at 150°C. After removing excess $Fe(CO)_5$ at 0.01 Torr, the remaining residue was chromatographed on neutral Al_2O_3. Elution with n-hexane/benzene 1/1 affords 3.9 g (42%) of the binuclear complex, and further elution with benzene yields 3 g (23%) of 1. Crystallisation from acetone/n-hexane gives black-green crystals of 1; Fp: sublimes at 130°C in closed tube. Anal.: Found: C, 32.7; H, 1.69; Fe, 32.33; N, 5.49; Mol. wt. 516. $C_{14}H_8Fe_3N_2O_9$ calcd.: C, 32.56; H, 1.55; Fe, 32.56; N, 5.43%; Mol. wt. 529.

Preparation of 2. 0.3 g (3 mmol) of 2,3-diazanorbornene and 2 g (3 mmol) of $Ru_3(CO)_{12}$ are heated for 6 h in 250 ml of n-hexane at 70°C. After evaporation at 0.01 Torr the residue is dissolved in n-hexane/ether 1/1 and chromatographed on SiO_2/n-hexane. Elution with ether yields a red fraction which is crystallized from ether/n-hexane affording 1.14 g (60%) of red crystals of 2; Fp. 108°C dec. Anal.: Found: C, 25.88; H, 1.25; N, 4.3; Ru, 46.43. $C_{14}H_8N_2O_9Ru_3$ calcd.: C, 25.8; H, 1.23; N, 4.3; Ru, 46.5%.

Preparation of 3 and 4. 0.675 g (0.131 mmol) of 1 and 1.2 g (9.68 mmol) of $P(OMe)_3$ are irradiated in 150 ml of toluene at room temperature. After 4 h all 1 is consumed (due to thin layer chromatography). Work-up is performed as described in the procedure for 2. Elution with benzene/n-hexane 1/1 and crystallisation from n-hexane/dichloromethane affords 0.1 g (10%) of crystalline 3. Anal.: Found: C, 31.55; H, 2.93; N, 4.76. $C_{16}H_{17}Fe_3N_2O_{11}P$ calcd.: C, 31.37; H, 2.78; N, 4.58%. Fp. 122—115°C (dec.). Further elution with n-hexane/dichloromethane 1/1 affords, after crystallisation from n-hexane/dichloromethane 0.35 g (37%) of black crystals of 4, Fp. 118—121°C (dec.). Anal.: Found: C, 30.16; H, 3.28; N, 3.88. $C_{18}H_{16}Fe_3N_2O_{13}P_2$ calcd.: C, 30.51; H, 3.67; N, 3.95%.

Preparation of 5. 0.623 g (1.15 mmol) (4-phenyl-3,3-bis(methoxycarbonyl)-1-pyrazoline)$Fe_2(CO)_6$ and 1.5 ml (11.5 mmol) $Fe(CO)_5$ are irradiated for 57 h in 150 ml of toluene. The colour change from orange to dark green is accompanied by formation of small amounts of $Fe_2(CO)_9$. After evaporation (0.01 Torr) to dryness the residue is dissolved in benzene, filtered and chromatographed on SiO_2. Elution with n-hexane/toluene 1/1 gives some $Fe_3(CO)_{12}$, and with ether/n-hexane a green oil which is crystallized from ether/n-hexane affording 0.157 g (20%) dark green crystals of 5; Fp. 107—112°C dec. Anal.:

Found: C, 38.55; H, 1.9; Fe, 24.9; N, 4.3. $C_{19}H_{15}Fe_3N_2O_{13}$ calcd.: C, 38.71; H, 2.05; Fe, 24.63; N, 4.10%.

Preparation of 6. 0.262 g (1 mmol) of 4-phenyl-3,3-bis(methoxycarbonyl)-1-pyrazoline and 0.639 g (1 mmol) of $Ru_3(CO)_{12}$ are heated for 4 h in 100 ml of n-hexane at 70°C. Chromatography at SiO_2/n-hexane is performed at −30°C. Elution with ether affords a red fraction which is crystallized from ether/n-hexane; 0.449 g (55%) red crystals of 6, Fp. 109—111°C, dec. Anal.: Found: C, 32.9; H, 2.0; N, 3.83; Ru, 37.16. $C_{19}H_{15}N_2O_{13}Ru_3$ calcd.: C, 32.3; H, 1.71; N, 3.42; Ru, 37.08%.

Conversion of 1 to (2,3-diazanorbornene)$Fe_2(CO)_6$. 2 ml of diluted HNO_3 (1/10), 2 ml of ether, and two drops of methanol are placed in a test tube. Upon addition of 20 mg of 1, the colour of the etheral layer turns from green to red within a few minutes. TLC-analysis (toluene/n-hexane 1/1, SiO_2) of this layer shows the presence of 1 and (2,3-diazanorbornene)$Fe_2(CO)_6$ identified by comparison with the authentic complexes.

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