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# TRANSITION METAL COMPLEXES OF AZO COMPOUNDS

## V*. COMPLEXATION AND CLEAVAGE OF THE N=N BOND OF DIAZIRINES BY IRON CARBONYLS

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## Summary

3,3-Dimethyldiazirine and 3,3-pentamethylenediazirine, $R_2CN_2$, react with enneacarbonyldiiron initially via *N*-tetracarbonyl intermediates to give dark blue $\mu$-1,2-diazirine-bis(tetracarbonyliron) complexes and small amounts of an $Fe_3(CO)_9$-cluster of the diazirine. Depending upon the solvent, further reaction may take place by splitting of the N=N bond to yield orange $(R_2C{=}N)Fe_2(CO)_6(N{=}CR_2)$ and red $(R_2C{=}N)Fe_2(CO)_6(NCO)$, which contain bridging ketiminato and isocyanato groups. Formation of the latter complexes probably involves "nitrenic" intermediates. A general scheme is proposed for the reactions of the *cis*-azo group of cyclic azo compounds with iron carbonyls which permits estimation of the product ratio as a function of the ring size of the parent azo ligand. $(R_2C{=}N)Fe_2(CO)_6(NCO)$ adds methanol at room temperature to give $(R_2C{=}N)Fe_2(CO)_6(NHCO_2Me)$.

## Introduction

The N=N double bond of cyclic azo compounds has powerful coordinating properties towards transition metals, as was recently demonstrated by the synthesis of a series of iron and chromium carbonyl complexes in which the *cis*-azo group acts as a two-, four- or six-electron donor [1]. Diazirines, cyclic isomers of diazoalkanes, contain the azo link in a three membered ring and show a characteristic electron distribution different from other cyclic azo compounds. From MINDO/2 calculations of 3,3-dimethyldiazirine (Ia), it was concluded that the $\sigma$-C—N orbitals mix strongly with the $n_-$ and $n_+$ linear combina-

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* For parts III and IV see refs. 1d, 1e.

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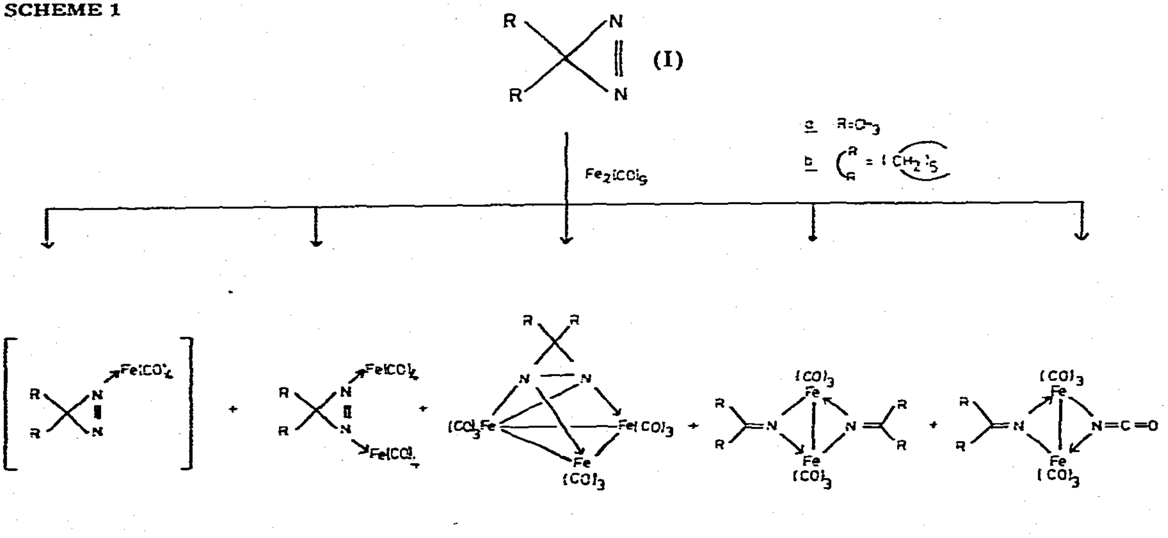
tions of the nitrogen lone pairs, so that "the concept of lone pairs largely loses its significance" [2] e.g. the electrons in the HOMO ($n_-$) are localised on the nitrogen atoms only to 56%. "The failure of diazirines to form complexes of any kind, quite distinct from for example azo compounds" was considered to prove the absence of "normal" lone pairs [3]. As part of our work on carbonyl complexes of the *cis*-azo group [1d] we have investigated the reactions of diazirines with metal carbonyls with reference to the formation of complexes of the diazirine or possibly dinitrogen, carbene or diazoalkane complexes. In the present paper we report the results of studies obtained with iron carbonyls.

## Results and discussion

Enneacarbonyldiiron reacts rapidly with 3,3-dimethyldiazirine (Ia) in tetrahydrofuran (THF), to give the relatively unstable complex IIIa in 40-60% yield. Compound IIIa crystallizes from n-hexane at $-70$°C in deep blue plates analysing as $C_3H_6N_2Fe_2(CO)_8$. The mass spectrum exhibits the stepwise loss of eight CO groups from the molecular ion. Both the $^1$H NMR spectrum and the IR spectrum below 1700 cm$^{-1}$ differ only slightly from that of the free ligand. In particular, the N=N stretching vibration of Ia seems to be unaltered upon complexation (1592 cm$^{-1}$ in Ia, 1594 in IIIa in $CCl_4$; 1603 cm$^{-1}$ reported for Ia in the gas phase [4]). Apparently the free ligand structure is conserved to a considerable extent in the complex. The most probable structure consistent with this evidence is one in which both Fe(CO)$_4$ groups are $\sigma$-bonded to the nitrogen atoms (Scheme 1). By analogy with the known *N*-tetracarbonyliron complexes of 1-pyrazolines [5], the ligand is expected to occupy an axial position of the trigonal bipyramidal Fe(CO)$_4$ moiety. The spatial requirement of the equatorial CO groups should fix the two tetracarbonyliron groups in non-equivalent positions. The appearance of six metal carbonyl absorptions

SCHEME 1



between 2100 and 1960 $cm^{-1}$ is in agreement with a low symmetry at the metal centres.

The proposed structure of IIIa is further supported by the fact that no stable complex is formed by reaction of 2-diazopropane with $Fe_2(CO)_9$, thus excluding the possibility that Ia isomerizes during complexation. Complexes of this type, in which a *cis*-azo group bridges two metal atoms which are not bonded to each other, have previously been postulated as intermediates in the corresponding reactions of other cyclic azo compounds [1d]. The only other known complexes of this type are the tungsten, manganese, and chromium carbonyls of diimide; by X-ray analysis, however, the chromium compounds have been shown to contain a *trans*-azo group [6]. Herberhold [1c] has prepared binuclear chromium carbonyls with two or three bridging azo groups but simple bridged complexes have not been reported so far. The deep violet color of n-hexane solutions of IIIa ($\lambda_{max}$ = 18300 $cm^{-1}$, $\epsilon$ = 3500) resembles the colours of the diimide complexes [7], and seems to be a general property of the $M{\leftarrow}(R)N{=}N(R){\rightarrow}M$ moiety. *N*-tetracarbonyliron complexes of a *cis*-azo group possess a characteristic electronic absorption band at 21000-23000 $cm^{-1}$ ($\epsilon$ = 1700), which probably originates from a metal-to-ligand charge-transfer transition [8]. The bathochromic shift observed by introduction of a second $Fe(CO)_4$ group is thus considerable.

3,3-Pentamethylenediazirine (Ib) affords the analogous complex IIIb, $C_6H_{10}N_2Fe_2(CO)_8$ (*m/e* = 446), which was obtained as a deep blue oil and characterized by comparison of its spectroscopic properties with those of IIIa.

Compounds of type III in solution slowly decompose into new complexes V and VI. These can be synthesized directly in good yields by conduct-

TABLE 1

PHYSICAL PROPERTIES OF COMPOUNDS I-VI AND IX

| Compound | M.p. (°C) | $\nu$(CO) ($cm^{-1}$)[a] | $^1H$ NMR ($\tau$) (ppm)[b] | UV[a] ($cm^{-1}$ × $10^{-3}$) (log $\epsilon$) |
|---|---|---|---|---|
| Ia | | | 9.18 s | 28.2 (~2) |
| Ib | | | 9.1 m, 8.65 | 28.5 (~2) |
| IIIa | 26-27[c] | 2083 s, 2045, 2014, 2005, 1985, 1961 all vs | 9.5 s | 18.3(3.54), 28.3 (sh) (3.5) |
| IIIb | oil | 2082 m, 2045, 2015 s, 1998, 1985, 1973 all vs | 9.3 m, 8.8 m | |
| IV | 110[d] | 2074 s, 2020 (sh), 2018 vs, 1989 s, 1972 m, 1967 m | 9.03 s, 8.59 s | 18.1(3.2), 23.9 (sh) (3.58) |
| Va | 122-123 | 2062, 2020, 1985, 1967 all vs, 1960 s | 8.25 s | 25.6 (sh) (3.52) 30.8(3.82) |
| Vb | 100-101 | 2060, 2020, 1985, 1970 all vs, 1960 s | 7.75 m, 8.75 m | 24.6(3.54), 30.8(3.82) |
| VIa | 65-67[d,e] | 2208 s ($\nu$ NCO); 2076, 2043, 2007, 1992 all vs | 8.44 s | 20.2(3.28), 28(3.85) 32.5(3.86) |
| VIb | 95-97[d,e] | 2210 s ($\nu$ NCO); 2076, 2043, 2007, 1993 all vs | 7.9 m, 8.85 m | 20.1(3.23), 27.8(3.88) 32.7(3.84) |
| IX | 92-93 | 3320 vw ($\nu$ NH); 2078 s, 2038 vs, 2005 vs, 1998 s, 1991 s, 1982 vs | 8.35, 6.65 s 9.25(br)[f] | 22.4 (sh) (3.23), 24.7 (sh) (3.43), 30(3.88) |

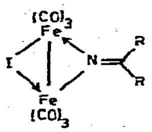
[a] In n-hexane. [b] In benzene-$d_6$; TMS external standard; s = singlet, m = multiplet. [c] In closed capillary. [d] Approximate subl. pt. in closed capillary. [e] With dec. and gas evolution. [f] Disappears on treatment with $D_2O$.

ing the reaction of $Fe_2(CO)_9$ and the diazirine in inert hydrocarbon solvents, such as n-hexane or toluene; the reaction is much slower than in THF and gives only traces of III. Complexes V and VI are also major products of the photochemical reaction of $Fe(CO)_5$ with diazirines.

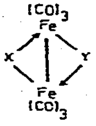
Complex Va is very stable compared to III and forms orange needles of composition $(C_3H_6N)_2Fe_2(CO)_6$ as shown by mass spectroscopy and elemental analysis. Thus, two molecules of the diazirine have reacted, accompanied by loss of two nitrogen atoms. The $^1H$ NMR spectrum exhibits only one singlet at $\tau$8.25, shifted downfield by 1 ppm from that of the free ligand, indicating a symmetric structure and excluding a diazirine carbene formulation $(R_2CN_2)Fe_2(CO)_6(CR_2)$ of Va. IR analysis reveals five absorption bands due to terminal metal carbonyls and the absence of bridging carbonyl groups (Table 1). From the above evidence we concluded that complex Va contains two dimethylketiminato groups, bridging the $Fe(CO)_3$ groups, which are connected by a metal—metal bond. This structure was shown to be correct by X-ray analysis of the pentamethyleneketiminato derivative Vb [9]. During the last phase of this work, King and Douglas [10] published a different route to Va, from $Na_2Fe(CO)_4$ and 2-bromo-2-nitrosopropane (3% yield). Iron carbonyl complexes of this type have been prepared recently by Bagga et al. [11] from an azine and $Fe_2(CO)_9$, and by Kilner and Midcalf [12a], from $Fe(CO)_4I_2$ and $R_2C{=}NLi$ (2-9% yields). In the diazirine-$Fe_2(CO)_9$ system, however, the corresponding complexes can be synthesized in yields up to 44%.

Complexes of type VI are the second major products of the reaction in inert solvents. VIa crystallizes from ether/n-hexane in beautiful red plates of stoichiometry $C_{10}H_6Fe_2N_2O_7$. The mass spectrum confirms the molecular formula but shows loss of only six CO groups from the molecular ion. The four IR absorption bands of terminal CO groups closely resemble those of Va, with all bands shifted to slightly higher wave numbers (Table 1); in addition, VIa absorbs very strongly at 2208 $cm^{-1}$. As in Va, the $^1H$ NMR spectrum shows only one singlet at about the same chemical shift ($\tau$8.44). On the basis of these spectroscopic properties and the failure of VIa to lose nitrogen on heating or treatment with phosphine, the structure with a dinitrogen ligand was excluded. The new complex VIa was therefore assumed to have a structure analogous to Va, but with a bridging isocyanate ligand instead of one dimethylketiminato group. This structure has been verified recently by X-ray analysis of VIb [9]. Isocyanate bridged iron carbonyls have not been described yet, but some compounds of the type $[(CO)_4M]_2(NCO)_2$, M = Re, Rh, Mn, with two bridging isocyanates are known [13]. The NCO absorption of VIa at 2208 $cm^{-1}$ is in accord with the values found in those complexes, whereas terminal NCO groups absorb at frequencies [13] 30-40 $cm^{-1}$ higher. Complexes of type VI can be derived formally from the halogeno bridged derivatives VII by substitution of iodine through the pseudohalide $NCO^-$. The physical properties of VI are indeed very similar to those of VII [12,14]. Both V and VI are further complexes of type VIII, in which X and Y are three electron donors, e.g. $NR_2$, $PR_2$, $AsR_2$, SR, Br, and I [12].

Apart from complexes of type V and VI another diazirine complex, type IV, was isolated from the reaction in n-hexane in very low yield (0.8%). Compound IVa forms dark brown crystals of composition $C_3H_6Fe_3N_2(CO)_9$ (mass



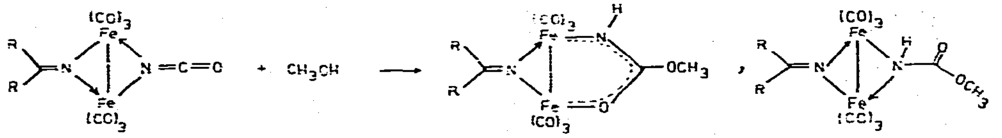
(VII)



(VIII)

spectrum); the molecular formula and the very striking similarity of UV and IR spectra of IVa with those of a previously reported $Fe_3(CO)_9$ complex of 2,3-diazanorbornene [1d], obviously point to the same structure, offering a second example of this interesting type of cluster compound.

From the reaction of Ia with $Fe_2(CO)_9$ an additional complex, IX, of stoichiometry $C_5H_{10}Fe_2N_2O(CO)_6$ was isolated in very low yield. Mass spectral analysis indicates the loss of six CO groups from the molecular ion, as well as a fragment arising from the release of $C_3H_5^+$, a typical fragmentation pattern observed with complexes containing the $(CH_3)_2C{=}N$ group (V and VI). In the $^1H$ NMR spectrum the corresponding singlet appears at $\tau$8.47 ($\tau$8.44 in VI a) and a second singlet at $\tau$6.8. A broad absorption signal at $\tau$9.25 is identified as an N—H proton by exchange experiments with $D_2O$. The CO stretching frequencies are very similar to those of VIa, except that the splitting of two bands indicates a lower symmetry than that of VIa; the medium but very sharp absorption at 3320 $cm^{-1}$ is tentatively assigned to an N—H stretching vibration. Complex IX was assumed to be a methoxycarbonylamido complex, formed by nucleophilic attack of traces of methanol on the isocyanate group of VIa (vide Experimental). This assumption was confirmed by synthesis of IX from VIa and methanol at room temperature.



(VI) (IX) (IX′)

The same type of reaction also occurs with the terminal NCO groups of $(Ph_3P)_2Pt(NCO)_2$ and $HBF_4$/EtOH, yielding the ethoxycarbonylamido complex $[(Ph_3P)_2Pt(NHCO_2Et)_2Pt(Ph_3P)_2]BF_4$ [15]. The above evidence makes most likely structure IX in which the bridging methoxycarbonylamido ligand is coordinated via nitrogen and oxygen. From the appearance of a weak absorption at 1710-1740 $cm^{-1}$, however, the alternative structure IX′ cannot be ruled out completely.

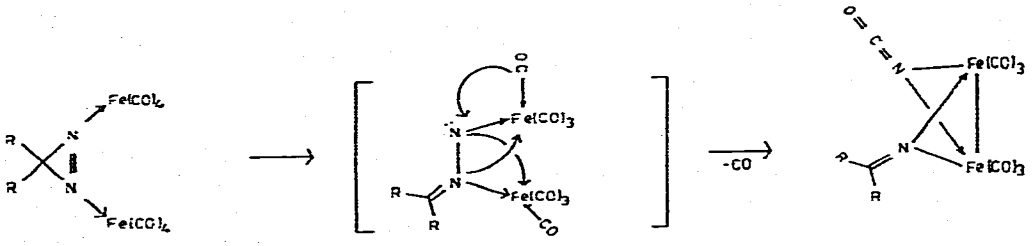
IR spectroscopic analysis of the reaction of Ib with enneacarbonyldiiron in n-hexane, indicated the initial formation of a labile tetracarbonyl complex, IIb, as shown by the appearance of a four band system (2066, 1988, 1974 and 1965 $cm^{-1}$) very similar to that of the known *cis*-azo-$Fe(CO)_4$ complexes [1d]. These bands disappear gradually and eventually give rise to a spectrum corresponding to a mixture of Vb and VIb. The intermediate formation of III, not observed by IR spectroscopy, is, however, well established by isolation and

TABLE 2

ANALYTICAL VALUES OF COMPOUNDS III-VI AND IX

| | Crystal appearance (Recryst. Solvent) | Analysis found (calcd.)(%) | | | | Mol. wt. | |
|---|---|---|---|---|---|---|---|
| | | C | H | N | Fe | Vap. pressure lowering | Mass spectrum |
| IIIa | deep blue plates<br>(n-hexane) | 32.55<br>(32.55) | 1.65<br>(1.48) | 6.95<br>(6.9) | 27.70<br>(27.6) | | 406 |
| IIIb | deep blue oil | | | | | | 446 |
| IVa | dark brown plates<br>(n-hexane) | | | | | | 490 |
| Va | orange-yellow needles<br>(n-hexane) | 36.84<br>(36.7) | 3.06<br>(3.06) | 7.11<br>(7.15) | 28.61<br>(28.6) | | 392 |
| Vb | orange-yellow needles<br>(n-hexane) | 45.83<br>(45.8) | 4.32<br>(4.24) | 6.00<br>(5.94) | 23.71<br>(23.7) | 450 | 472 |
| VIa | deep red plates<br>(ether-hexane) | 32.45<br>(31.8) | 2.02<br>(1.6) | 7.25<br>(7.42) | 28.40<br>(29.62) | | 378 |
| VIb | deep red plates<br>(toluol) | 37.15<br>(37.3) | 3.25<br>(2.4) | 6.58<br>(6.7) | 26.72<br>(26.7) | 423 | 418 |
| IX | orange needles<br>(ether-hexane) | 33.39<br>(32.2) | 2.55<br>(2.44) | 7.05<br>(6.84) | 28.3<br>(27.35) | | 410 |

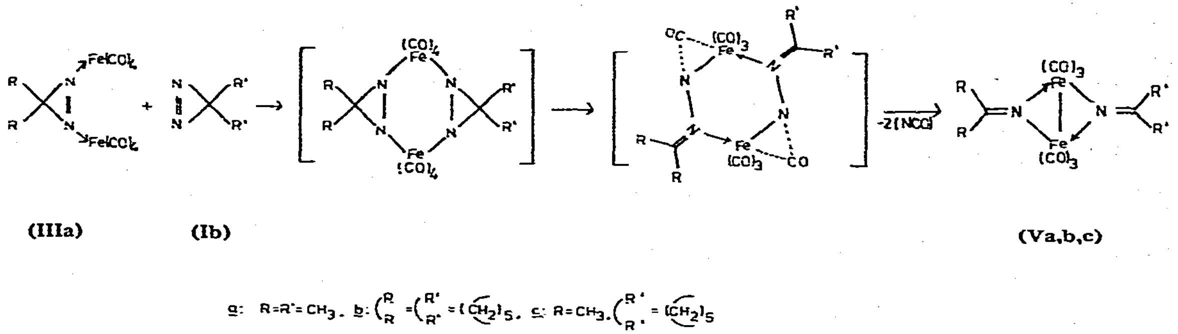
conversion of III into V and VI by dissolution in n-hexane. Formation of VI from III requires splitting of the C—N and N=N bond, and insertion of a nitrogen atom into an Fe—CO bond. The latter process is well known from the production of isocyanate complexes by reaction of azides with metal carbonyls and probably involves an intermediate nitrene complex [16,17]. By analogy, the first step of the conversion of III into VI should consist of ring opening of the diazirine to form a "nitrenic" intermediate in which the N—N bond is considerably weakened. Attack of the "nitrenic" nitrogen at a metal carbonyl, cleavage of the N—N bond, and further rearrangement gives the stable, doubly-bridged, complex VI. Without further experimental evidence, however, the proposed mechanism remains speculative.



(III)

(VI)

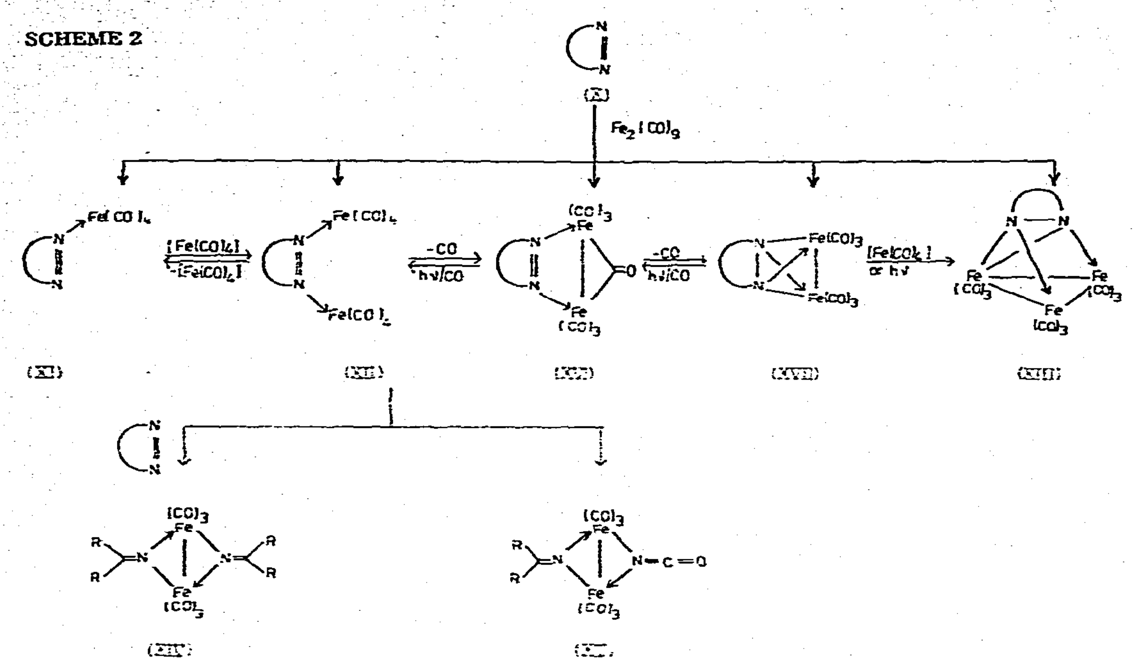
The formation of V would require the reaction of a second molecule of the diazirine with the assumed intermediate III. This assumption, was tested by reacting IIIa with Ib. In addition to Va and Vb, the excepted mixed complex Vc was indeed obtained. The same result is obtained from reaction of a mixture of Ia and Ib with $Fe_2(CO)_9$. In any case the formation of complexes of type V is accompanied by evolution of only very small amounts of gaseous nitrogen, far from the expected stoichiometric value. A considerable quantity of material which is insoluble in organic solvents, is always formed in these reactions. It contains C, H, N, O, and Fe, and a very strong IR absorption at 2200 cm$^{-1}$, which indicates the presence of NCO [18]. Complexes of type V are formed in trace quantities only by thermal reaction of $Fe_2(CO)_9$ or photolysis of $Fe(CO)_5$ with corresponding azines $(R_2C{=}N{-})_2$, although an analogous complex has been prepared from $[(p\text{-}CH_3C_6H_4)_2C{=}N{-}]_2$ [11]. This excludes the possibility that azines, initially formed from diazirine and the corresponding carbene, are the reacting species. It therefore seems reasonable to assume that attack of I on III generates an unstable "nitrenic" intermediate, which can lead to V by N—N bond scission, insertion of nitrogen into the Fe—CO bond, and elimination of inorganic isocyanate.



(IIIa) (Ib) (Va,b,c)

Scheme 2 summarizes the results obtained with cyclic azo compounds. In the case of diazirines the product of the first reaction step, XI, is too unstable to be isolated. The relative high ionisation potential of diazirines (9.7 eV in Ia [19]), and the weak lone pair character of the HOMO ($n_-$) [2], may explain their weaker interaction with the metal. The second step gives *N,N'*-bis(tetracarbonyliron) complexes XII, which were postulated as intermediates in the reaction of the five-membered 1-pyrazolines, where they are very easily decarbonylated to complexes of types XVI and XVII [1d]. This reaction path is very unfavorable in the case of diazirines as demonstrated by the absence of the complexes of types XVI and XVII and the formation of only very small amounts of the cluster of type XIII. The different stability and reactivity of complexes of type XII is obviously a function of the ring size of the cyclic azo ligand. Simple geometric considerations indicate that the distance of the centres of charge of both nitrogen lone pairs should increase considerably in going from six- to three-membered rings; assuming an idealized planar $Fe\leftarrow\overset{\frown}{N{=}N}\rightarrow Fe$ arrangement ($\angle$ NNFe = 180 — $\alpha/2$, $\alpha$ = $\angle$ NNC [19]) for complexes of type XII, the corresponding Fe—Fe distances should be 3.2, 3.5, 4.0, and 4.7 Å for the six, five, four, and three membered azo ligands, respectively. Thus, diazirines offer optimal steric conditions for the accomodation of one $Fe(CO)_4$ group at each nitrogen but pose difficulties for the decarbonylation reactions to XVI and XVII, which require bond formation between the two widely separated metal carbonyl groups. In this case therefore complexes of type XII prefer a new reaction path, involving initial C—N bond scission and formation of the more stable doubly-bridged complexes XIV and XV, probably via a "nitrenic" intermediate. The reaction of 1,2-diazetines is expected to proceed in a comparable extent through both pathways.

SCHEME 2



The cleavage of the N=N double bond is new in the chemistry of diazirines and furnishes an interesting example of this uncommon reaction type; it may be compared with the azobenzene-*o*-semidine rearrangement, occuring in the reaction of iron carbonyls with azobenzene [20], the reaction of hexafluorazomethane and *trans*-chlorocarbonylbis(methyldiphenylphosphine)iridium to yield the stable nitrene complexes *cis*- and *trans*-$(Ph_2PMe)_2Ir(CO)(Cl)(NCF_3)$, [21], and with the formation of the ketimine complex $(\pi\text{-}C_5H_5)Mn(CO)_2(HN{=}CMePh)$ from the reaction of $(\pi\text{-}C_5H_5)Mn(CO)_2(THF)$ with 1-diazo-1-phenylethane [22]. Preliminary results reveal that chromium carbonyls react with diazirines to give as the main product complexes of type XII and no compounds resulting from splitting of the azo group.

## Experimental

Microanalyses and molecular weight determinations were performed by Dornis und Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr. Melting points are uncorrected and determined on a Kofler melting point apparatus. Spectra were taken as follows: NMR: Varian A 56/60 and A 60 A, Bruker WH 90; IR: Perkin—Elmer 621; UV: SEM Brückl HRS 4001 C; mass spectra: MAT CH 5. Diazirines and enneacarbonyldiiron were prepared according to literature methods [23,24].

*Caution.* Diazirines were distilled and handled according to recommended precautionary procedures. Although no difficulties were encountered during this work, it must be recalled that this class of compounds is highly explosive.

Opening ampoules containing 3-chloro-3-trichloromethyldiazirine or 3-chloro-3-methyldiazirine with a file has been reported to result in several explosions [25].

All reactions and manipulations with organometallic compounds were carried out in an argon atmosphere. Solvents were dried over alumina before use. Silica gel Merck (0.063-0.2 mm) was used in chromatographic separations.

*Preparation of IIIa, IIIb.* 3.6 g (10 mmol) of $Fe_2(CO)_9$ are stirred at room temperature with 80 ml of THF containing 0.7 g (10 mmol) of Ia. A violet color develops rapidly. After 2 h the solution is filtered, evaporated and the residue is crystallized from *n*-hexane at —78°C, yielding 0.8-1.2 g (40-60% based on: $2\ Fe_2(CO)_9 + R_2CN_2 = R_2CN_2Fe_2(CO)_8 + 2\ Fe(CO)_5$) of deep blue, very air sensitive crystals of IIIa. The complex can also be chromatographed at —20°C with some decomposition, but room temperature chromatography yields only Va and VIa, with traces of IVa. IIIb is obtained analogously as a deep blue oil.

*Preparation of Va, Vb.* 3.6 g (10 mmol) of $Fe_2(CO)_9$ are stirred at room temperature with 100 ml of n-hexane or toluene, containing 1.4 g (20 mmol) of Ia. A slow reaction occurs, taking 40 h for completion. The dark red oil obtained after evaporation of the filtered reaction mixture is chromatographed at —20°C, eluting with hexane/toluene mixture (4/1). This yields traces of IIIa, 0.8 g (40%) of Va, 0.2 g (12%) of VIa, 0.01 g (0.8%) of IVa, and a small variable amount of IX. Analogous reaction of Ib yields 1 g (44%) of Vb, 0.25 g (10%) of VIb and a small amount of an impure oil identifiable as IVb.

*Preparation of VIa and VIb.* If the reaction described above is conducted with only 0.7 g (10 mmol) of Ia, the formation of VIa is favored over that of Va. 0.3 g (15%) of Va and 1.09 g (56%) of VIa together with traces of IVa was obtained. The reaction of Ib gives 0.5 g of Vb and 1.25 g of VIb in 21 and 60% yield respectively; if n-hexane is used as solvent, the sparingly soluble VIb precipitates to a large extent during the reaction and can be directly purified by crystallisation from toluene.

*Photochemical reaction of $Fe(CO)_5$ with Ia and Ib.* 0.7 g (10 mmol) of Ia and 4 g (20 mmol) of $Fe(CO)_5$ in 190 ml of n-hexane are irradiated (Philips HPK 125 W) through a solidex filter ($\lambda \geqslant 270$ mm). After 8 h the solution is filtered from precipipated $Fe_2(CO)_9$, evaporated and chromatographed to give 0.1 g (2.9%) of Va and 0.3 g (6.5%) of VIa. Similar low yields are obtained from the reaction of Ib.

*Reaction of IIIa with Ib.* 0.6 g (1.5 mmol) of IIIa and 0.5 g (4 mmol) of Ib are stirred for 12 h in 40 ml of n-hexane. Chromatographic work up as decribed in the preparation of Va gives 0.3 g of a yellow oil; its IR spectrum is identical with that of complexes of type V, and mass spectrometric analysis reveals the presence of Va, Vb, and the mixed complex Vc (mol. wt. 432). The same result is obtained from the reaction of $Fe_2(CO)_9$ with an equimolar mixture of Ia and Ib in n-hexane.

*Preparation of IX.* 0.15 g (0.4 mmol) of Va are dissolved in 10 ml of MeOH. The red color of the solution quickly fades. After 1 h the yellow solution is evaporated and chromatographed. Elution with benzene gives a yellow fraction, which affords 0.02 g (12% yield) of IX after subsequent recrystallisation from ether/n-hexane. The physical properties of this complex are identical with the one obtained in low yield from Ia and $Fe_2(CO)_9$. The latter is assumed to contain traces of MeOH originating from its preparation, which involves methanol washing.

*Reactions of 2-diazopropane and azines*

3.6 g (10 mmol) of $Fe_2(CO)_9$ and 70 ml of a freshly prepared ethereal solution of 2-diazopropane [26] are stirred for 8 h at room temperature. A brown precipitate is formed but no soluble complex is found by thin layer chromatography or IR analysis.

3.6 g (10 mmol) of $Fe_2(CO)_9$ are stirred at room temperature in 200 ml of toluene containing 1.9 g (10 mmol) cyclohexanone azine. After 24 h the reaction is worked up by column chromatography affording traces of a yellow oil consisting of impure Vb as evidenced by mass and IR spectroscopy. The photochemical reaction of cyclohexanone azine, or the thermal or photochemical reaction of acetone azine does not afford better yields.

## Acknowledgements

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## References

1 (a) M. Herberhold and K. Leonhard, J. Organometal. Chem. 78 (1974) 253.
  (b) H. Kisch, J. Organometal. Chem., 38 (1972) C19.
  (c) M. Herberhold, W. Golla and K. Leonhard, Chem. Ber., 107 (1974) 3209 and refs. therein.
  (d) A. Albini and H. Kisch, Angew. Chem., 1975, in press.
  (e) C. Krüger and H. Kisch, J. Chem. Soc. Chem. Commun., 1975 in press.
2 E. Haselbach, E. Heilbronner, A. Mannschreck and W. Seitz, Angew. Chem., 82 (1970) 879; Angew. Chem. Int. Ed. Engl., 9 (1970) 901.
3 H.M. Frey, Adv. Photochem., 4 (1966) 255.
4 R.W. Mitchell and J.A. Merrit, J. Mol. Spectros., 27 (1968) 197.
5 C. Krüger, Chem. Ber., 106 (1973) 3230.
6 G. Huttner, W. Gartzke and K. Allinger, Angew. Chem., 86 (1974) 860.
7 D. Sellmann, A. Brandl and R. Endell, Angew. Chem., 85 (1973) 1121; Angew. Chem. Int. Ed. Engl., 12 (1973) 1019.
8 H. Weigel, H. Kisch and F. Mark, to be published.
9 C. Krüger, private communication.
10 R.B. King and W.M. Douglas, Inorg. Chem., 13 (1974) 1339.
11 (a) M.M. Bagga, P.L. Pauson, F.J. Preston and W.I. Reed, Chem. Commun., 1965, 543.
  (b) D. Bright and O.S. Mills, Chem. Commun., 1967, 245.
12 (a) M. Kilner and C. Midcalf, J. Chem. Soc. Dalton, (1974) 1620.
  (b) E. Koerner von Gustorf, J.C. Hogan and R. Wagner Z. Naturforsch. B, 27 (1972) 140.
13 (a) R.B. Saillant, J. Organometal. Chem., 39 (1973) C71.
  (b) R.J. Angelici and G.C. Faber, Inorg. Chem., 10 (1971) 514.
  (c) L. Busetto, A. Palazzi and R. Ross, Inorg. Chem., 9 (1970) 2792.
  (d) R. Mason, G.A. Rusheline, W. Beck, H. Engelmann, K. Jos, B. Lindenberg and M.S. Smedal, Chem. Commun., (1971) 2196.
14 M. Kilner and C. Midcalf, Chem. Commun., (1971) 944.
15 K. von Werner and W. Beck, Chem. Ber., 105 (1972) 3947.

16 (a) W. Beck, H. Werner, H. Engelmann and H.S. Smedal, Chem. Ber., 101 (1968) 2143.
(b) A.T. McPhail, G.R. Knox, C.G. Robertson and G.A. Sim, J. Chem. Soc. A, (1971) 205.
17 G. La Monica, S. Cenini and M. Freni, J. Organometal. Chem., 76 (1974) 355.
18 F.A. Miller and L.H. Wilkins, Anal. Chem., 24 (1952) 1253.
19 F. Brogli, W. Eberbach, E. Haselbach, E. Heilbronner, V. Hornung and D.M. Lemal, Helv. Chim. Acta., 56 (1973) 1933.
20 M.M. Bagga, W.T. Flannigan, G.R. Knox and P.L. Pauson, J. Chem. Soc. C, (1969) 1334.
21 J. Ashley-Smith, M. Green, N. Mayne and F.G.A. Stone, Chem. Commun., (1969) 409.
22 W.A. Herrmann, Chem. Ber., 107 (1974) 2899.
23 E. Schmitz and R. Ohme, Chem. Ber., 94 (1961) 2166.
24 R.B. King, Organometallic Chemistry, Vol. 1, Academic Press, New York, 1 ed., 1965, p. 93.
25 M.T.H. Liu, Chem. Eng. News, 52 (1974) 3.
26 S.D. Andrews, A.C. Day, P. Raymond and M.C. Whiting, Org. Synth., 50 (1970) 27.