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Preparation, structure, and some reactions of the evasive azobenzene complex $[Fe_2(CO)_6(\mu\text{-}Ph_2N_2)]$ *

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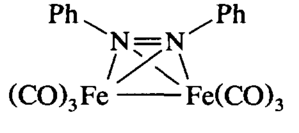
Abstract

The title compound $[Fe_2(CO)_6(\mu\text{-}Ph_2N_2)]$ (**1**) was obtained in a two-step sequence from $Fe_2(CO)_9$ and phenyl azide via the intermediate tetraazadiene complex $(CO)_3Fe \cdot Ph_2N_4$ (**2b**). Its N–N bond length (1.41 Å) is 0.04 Å longer than that in $[Fe_2(CO)_6(\mu\text{-}Et_2N_2)]$ corresponding to an enhanced reactivity. Accordingly, the reactions of **1** with CO and H_2 which lead to $[Fe_2(CO)_6(\mu\text{-}PhN\text{-}CO\text{-}NPh)]$ (**4**) and $[Fe_2(CO)_6(\mu\text{-}NHPh)_2]$ (**5**) respectively, involve cleavage of the N–N bond.

1. Introduction

Azoalkanes are a class of ligands well-established in the chemistry of polynuclear iron and ruthenium carbonyls [1], due to their ease of synthesis and versatile reactivity [2–5]. However, attempts to prepare the basic azoarene complexes $[M_2(CO)_6(\mu\text{-}Ph_2N_2)]$ and $[M_3(CO)_9(\mu_3\text{-}Ph_2N_2)]$ for M = Fe and Ru have invariably met with failure due to cleavage of the azobenzene N–N bond under the reaction conditions [6–10]. Only recently have the first azoarene complexes of the iron triad, $[Ru_4(CO)_{11}(PPh)(Ph_2N_2)]$ [11] and $[(\text{phenylazopyridine})Fe_2(CO)_8]$ [12] been described. And the simplest of all those complexes, **1**, has been reported twice in the literature [13,14] but without experimental details and without a characterization. We have now been able to prepare this compound without the use of azobenzene. This has enabled us experimentally to verify the high lability of its azobenzene ligand.



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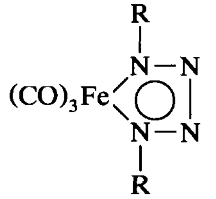

2a R = Me

2b R = Ph

2. Results and discussion

2.1. *Synthesis of 1*

Our preparation of **1** followed a procedure mentioned by Dekker and Knox [13] who claimed that the reaction between $Fe_2(CO)_9$ and phenyl azide leads to solutions of **1** which decompose with formation of **4** (see below). We found that a suspension of these reagents in hexane reacts to form the mononuclear tetrazadiene derivative **2b** in moderate yields. **2b** has been mentioned in the literature as well [15], again without spectra or elemental analyses. We have characterized **2b** by its EI-MS and by its IR bands (ν(CO) 2080s, 2020s, 2005vs, in hexane) which correspond to those of **2a** whose spectra [16] and crystal structure [17] have been reported.

Further reaction of **2b** with $Fe_2(CO)_9$ under UV irradiation produced the desired complex **1** with elimination of N_2. The identity of **1** was ascertained by the structure determination (see below). Its IR bands (ν(CO) 2072m, 2029vs, 1987vs, 1981s, 1970s, in hexane) are nearly superimposable on those of $[Fe_2(CO)_6(\mu\text{-}N_2Et_2)]$ [3]. Attempts to use this synthetic method for the preparation of $[Ru_2(CO)_6(\mu\text{-}N_2Ph_2)]$ or $[FeRu(CO)_6(\mu\text{-}N_2Ph_2)]$ starting from phenyl azide or **1** and various $Ru(CO)_3$ releasing reagents were unsuccessful.

2.2. *Structure determination of 1*

Details of the structure determination are given in the Experimental section. Table 1 lists some bond lengths and angles, Fig. 1 shows the molecular shape. **1**

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* Dedicated to Prof. E.O. Fischer on the occasion of his 75th birthday.

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TABLE 1. Selected bond lengths (Å) and angles (deg.) in 1

Fe1–Fe2	2.493(1)	Fe1–N1–Fe2	81.6(1)
Fe1–N1	1.918(3)	Fe1–N2–Fe2	81.6(1)
Fe1–N2	1.893(3)	Fe1–N1–C16	137.9(2)
Fe2–N1	1.897(3)	Fe2–N1–C16	139.8(2)
Fe2–N2	1.922(3)	Fe1–N2–C26	143.3(2)
N1–N2	1.411(4)	Fe2–N2–C26	133.3(2)
N1–C16	1.411(4)	N1–N2–C26	128.3(3)
N2–C26	1.408(4)	N2–N1–C16	125.0(3)
Fe–C	1.796–1.812(4)	N1–Fe1–N2	43.1(1)
C–O	1.126–1.144(6)	N1–Fe2–N2	43.4(1)

belongs to the large class of compounds with a tetrahedral M_2E_2 core and an $M_2(CO)_6$ composition which all have a very similar arrangement of CO ligands and E substituents. Specifically the complexes $[Fe_2(CO)_6(\mu\text{-}N_2Me_2)]$ [18] and $[Fe_2(CO)_6(\mu\text{-}N_2Et_2)]$ [3] have core structures nearly identical to that of 1. The Fe–Fe bonds are in the very narrow range of 2.49–2.50 Å for all three compounds, as are the Fe–N bonds (1.89–1.92 Å). The major and significant difference lies in the N–N bond length which in 1 (1.41 Å) is considerably longer than that in $[Fe_2(CO)_6(\mu\text{-}N_2Et_2)]$ (1.37 Å) and still longer than that in $[Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}N_2\text{-}Et_2)]$ (1.39 Å) [3]. The chemical consequence of this N–N bond lengthening is the N–N bond lability of 1 which had previously prevented its isolation and which gives rise to the chemistry described below.

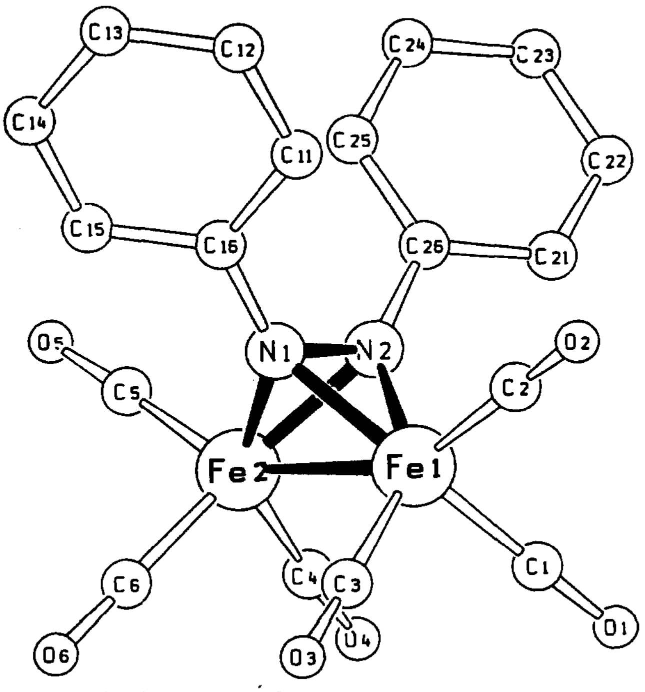
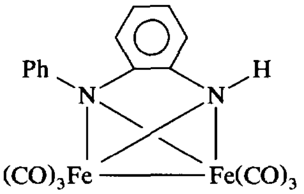


Fig. 1. Molecular structure of 1.

Fe/N complexes like 1 are isoelectronic with the Co/C complexes $[Co_2(CO)_6(\mu\text{-}RC{\equiv}CR)]$. Of these the structures for R = Ph and R = ^{t}Bu have been reported [19]. Their atomic arrangement is extremely similar to that in the complexes $[Fe_2(CO)_6(\mu\text{-}RN{=}NR)]$. This includes the Co–Co bond lengths (2.46–2.47 Å) as well as the acetylenic C–C bond lengths (1.33–1.37 Å). Furthermore the phenyl substituted alkyne has a longer (and weaker?) C–C bond (1.37 Å) than the alkyl substituted alkyne (1.33 Å). Another complex which offers itself for comparison is $[Fe_2(CO)_6(\mu\text{-}^tBuC{\equiv}C^tBu)]$ which has the same general structure as 1 but which has altogether two electrons fewer than 1 [19]. This difference is mainly reflected in the very short Fe–Fe bond (2.32 Å) and in a small shortening of the C–C bond (1.31 Å).

2.3. Reactivity of 1

The reported unsuccessful attempts to isolate 1 from reactions between azobenzene and iron carbonyls had produced, as the major isolable species, the *ortho*-semidine-Fe_2 complex 3 and the diphenylurea-derived Fe_2 complex 4 [6,7,10]. Assuming that 3 and 4 result from decomposition of 1, we tested the thermal behaviour of this compound. It turned out that solutions of 1 are stable at room temperature even in the presence of air. The complete decomposition of 1 required boiling in cyclohexane for a full day. After this time a 33% yield of 4 was obtained, but no 3 could be observed in the course of the decomposition. It can therefore be concluded that 1 is not part of the reaction sequence in the *ortho*-semidine rearrangement of azobenzene in the presence of iron carbonyls [20]. This corresponds to observations by Kisch [21] which show that *ortho*-metallated complexes are intermediates of this rearrangement.



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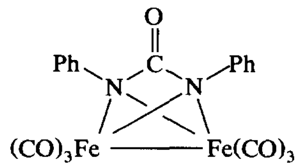
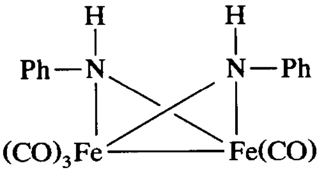


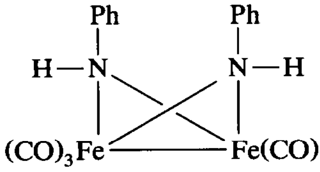
4

A more direct route from 1 to 4 was found in the reaction with CO under pressure. At 80°C and with 50 atm CO the conversion was essentially quantitative. This conversion was not possible starting from the azoethane analogue of 1. It is, however, completely analogous to the insertion of CO into the P–P bond of $[Fe_2(CO)_6(\mu\text{-}P_2{}^tBu_2)]$ [22]. Complex 4 is well known [13,23–25] and could be identified by its IR spectrum. But contrary to the straightforward synthesis described here the previous preparations were non-systematic and of low yields.

Another reagent known to affect cleavage of the P–P bond in $[Fe_2(CO)_6(\mu\text{-}P_2{}^tBu_2)]$ is hydrogen. As expected, this cleavage could also be performed in **1** with 50 atm H_2 at 80°C. However, yields were low and could be only slightly improved by the use of Pd/C catalyst. The resulting compound **5** shows an IR spectrum (ν(CO) 2068m, 2032vs, 1984vs, in hexane) which corresponds to that of the compound $[Fe_2(CO)_6(\mu\text{-}NHPh)_2]$ obtained by Alper from $Fe_3(CO)_{12}$ and nitrobenzene [26]. The ^{1}H-NMR spectrum which shows a single resonance for the NH protons at $\delta = 2.03$ in CD_2Cl_2 differs from that reported by Alper with two NH signals. We conclude from this that we have isolated a symmetrical isomer of **5** (**5a** or **5b**) while the two NH resonances correspond to the asymmetrical isomer. The sole formation of a symmetrical product must be related to the symmetrical *cis* arrangement of the phenyl groups in the starting compound **1**.



5a



5b

In order to test another insertion reaction known for S–S [27] and P–P bonds [22] in $Fe_2(CO)_6(\mu\text{-}E_2)$ complexes, **1** was reacted with ethylene. However, even under ethylene pressure and at elevated temperatures, no reaction was observed. Similarly, neither phenyl acetylene nor propyl isonitrile could be made to react with **1**.

3. Conclusion

The reactions described in this paper show that complex **1** was probably previously unobtainable because conditions applied for its synthesis were too rigorous. Once isolated, **1** is of reasonable thermal and oxidative stability. Cleavage of the N–N bond can be performed by insertion of CO or H_2, but only under pressure and at elevated temperatures. The sequence of E–E bond labilities from this and related studies [3,22,27,28] seems to be $[Fe_2(CO)_6(\mu\text{-}N_2Et_2)] < [Fe_2(CO)_6(\mu\text{-}N_2Ph_2)] < [Fe_2(CO)_6(\mu\text{-}S_2)] < [Fe_2(CO)_6(\mu\text{-}P_2{}^tBu)_2]$.

4. Experimental details

The general experimental techniques were as described before [29]. All starting materials were obtained commercially.

4.1. Preparation of 1

A suspension of 1.0 g (2.8 mmol) $Fe_2(CO)_9$ in 50 ml of hexane was treated with 330 mg (2.8 mmol) of phenyl azide and stirred for 15 h. The solution was filtered over silica gel, the residue washed with CH_2Cl_2, and the combined filtrates evacuated to dryness. Chromatography of the residue over a 2 × 30 cm silica gel column yielded after a small orange fraction (eluted with hexane) a main red fraction (eluted with hexane/CH_2Cl_2, 1:1) containing **2b**. Recrystallization from hexane resulted in 173 mg (18%) of **2b**, red crystals, m.p. 104°C. Anal. Found: C, 50.90; H, 2.83; N, 15.74. $C_{15}H_{10}FeN_4O_3$ (350.1) calc.: C, 51.46; H, 2.88; N, 16.01%. Mol. wt. 350 (EI-MS).

100 mg (0.286 mmol) of **2b** and 1.0 g (2.8 mmol) $Fe_2(CO)_9$ in 100 ml of hexane were irradiated with a high pressure mercury UV lamp in a circulating apparatus for 3 h. The solution was filtered, evacuated to dryness, and the residue extracted with 50 ml of pentane. The resulting solution was reduced in volume until crystallization started, cooled for 1 day at 5°C and for another day at −25°C. 29 mg (22%) of **1** was obtained as red crystals, m.p. 123°C. Anal. Found: C, 46.72; H, 2.18; N, 6.02. $C_{18}H_{10}Fe_2N_2O_6$ (462.0) calc.: C, 46.80; H, 2.18; N, 6.06%.

4.2. Reactions of 1

(a) Thermal rearrangement: 20 mg (0.04 mmol) of **1** in 10 ml of cyclohexane was heated under reflux for 1 day. After filtration, evaporation to dryness and dissolution of the residue in a small amount of CH_2Cl_2, preparative t.l.c. with hexane/CH_2Cl_2 (3:2) yielded a trace of **1** in the first fraction (orange) and 7 mg (33%) of **4** in the second fraction (orange).

(b) Reaction with CO: 30 mg (0.07 mmol) of **1** in 15 ml of benzene in an autoclave was heated to 80°C for 22 h under a CO pressure of 50 atm. The solvent was removed *in vacuo* and the residue recrystallized from hexane/CH_2Cl_2 (7:3) yielding 30 mg (94%) of **4** as orange-red crystals.

(c) Reaction with H_2: 30 mg (0.07 mmol) of **1** was dissolved in 15 ml of ethyl acetate, treated with a few grains of Pd/C catalyst (10% Pd) and heated to 80°C for 3 h under a pressure of 50 atm of hydrogen in an autoclave. The solution was filtered over 2 cm of

Florosil and evacuated to dryness. The residue was chromatographed over a 2 × 20 cm Florosil column with hexane/benzene (3:2). After a small, orange fraction of **1** the main, orange fraction contained **5**. Evaporation to dryness and recrystallization from hexane/CH_2Cl_2 yielded 18 mg (56%) of **5** as an orange-red powder, m.p. 87°C (dec.). Anal. Found: C, 46.76; H, 2.19; N, 6.04. $C_{18}H_{12}N_2Fe_2O_6$ (464.0) calc.: C, 46.59; H, 2.61; N, 6.04%. Mol. wt. 464 (EI-MS).

4.3. Structure determination [30]*

Crystals of **1** (0.4 × 0.2 × 0.6 mm) were obtained from pentane. They belong to the space group $P2_1/n$: $a = 7.906(2)$, $b = 16.811(3)$, $c = 14.788(3)$ Å, $\beta = 99.56(3)°$, $Z = 4$, $V = 1938.1(7)$ Å^3, $d_{\text{calcd.}} = 1.58$ g cm^{-3}, $\mu = 15.3$ cm^{-1}. 2365 independent reflections were collected with a Nonius CAD 4 diffractometer using Mo Kα radiation and the $\omega/2\theta$ technique at $2\theta = 2$–$46°$ for the indices $\pm h$, $+h$, $+l$. 2123 reflections with $I \geq 6\sigma(I)$ were used for the structure solution with direct methods and the anisotropic least-squares refinement with the SHELX program system [31]. No absorption correction was applied, the phenyl rings were treated as rigid bodies, and all hydrogen atoms were included with a common isotropic temperature factor and a fixed C–H distance of 0.96 Å. The final unweighted R value was 0.024 for 229 variables. The difference electron density maxima were +0.3 and −0.2 e/Å^3. The drawing was produced with the SCHAKAL program [32]. Table 2 lists the atomic coordinates.

TABLE 2. Atomic coordinates (× 10^4) and equivalent isotropic thermal coefficients (pm^2 × 10^{-1}) for **1**

	x	y	z	U_{eq}
Fe(1)	2589(1)	3553(1)	4790(1)	48(1)
Fe(2)	4925(1)	2946(1)	5918(1)	47(1)
N(1)	2703(3)	2567(2)	5447(2)	44(1)
N(2)	3747(3)	2571(2)	4762(2)	44(1)
C(1)	3691(5)	4241(2)	4171(3)	68(2)
O(1)	4417(5)	4660(2)	3769(2)	109(2)
C(2)	626(5)	3498(2)	3972(3)	69(2)
O(2)	−628(4)	3485(2)	3472(2)	108(1)
C(3)	1877(4)	4287(2)	5517(2)	54(1)
O(3)	1449(4)	4745(2)	6000(2)	75(1)
C(4)	6743(5)	3466(3)	5652(3)	68(2)
O(4)	7879(4)	3803(2)	5447(2)	107(2)
C(5)	6024(4)	2095(2)	6471(3)	60(1)
O(5)	6690(4)	1559(2)	6848(2)	90(1)
C(6)	4792(4)	3498(2)	6940(3)	58(1)
O(6)	4683(4)	3848(2)	7585(2)	91(1)
C(11)	274(3)	1682(2)	4903(1)	65(1)
C(12)	−770	1048	5070	88(2)
C(13)	−512	678	5927	99(2)
C(14)	790	943	6616	88(2)
C(15)	1833	1577	6448	64(1)
C(16)	1575	1947	5592	48(1)
C(21)	4476(3)	2168(1)	3332(2)	64(1)
C(22)	4890	1589	2729	82(2)
C(23)	4878	787	2969	79(2)
C(24)	4451	563	3811	71(2)
C(25)	4036	1142	4414	59(1)
C(26)	4049	1944	4174	44(1)

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30 Further details of the structure determination may be obtained upon request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, giving reference to the depository number CSD-400115 and citing the authors and this paper.

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