1,5-Dihydropyrrol-2-ones from (1,4-Diaza-1,3-diene)tricarbonyliron, (DAD)Fe(CO)₃, and Alkyne. 5. Spectroscopic and X-ray Structural Characterization of a Bicyclo[2.2.1] Complex Resembling the Initial Cycloadduct. The C=N—Fe Fragment in (DAD)Fe(CO)₃ as an Isolobal Analogue of the Classical 1,3-Dipole Azomethine Ylide in 1,3-Dipolar Cycloaddition

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In solution, [biacetyl bis(4-methoxyanil)]Fe(CO)₃ (1a) reacts instantly with dimethyl acetylenedicarboxylate, even at -90 °C. Depending on the additional ligand offered, different products are isolated. Under 1 atm of CO, the expected 1,5-dihydropyrrol-2-one complex 3a is formed at room temperature from which the coordinated heterocycle can be displaced by using CO pressure (180 bar) at elevated temperature. When P(OMe)₃ is offered instead, a ferrabicyclo[2.2.1] complex, 4a, can be isolated which is spectroscopically characterized (IR, FD-MS, and ¹H, ¹³C, and ³¹P NMR). Above -20 °C, 4a transforms into 5a, C₂₈H₃₃N₂O₁₁PFe, of which the structure has been determined by single-crystal X-ray diffraction: space group P1̄, a = 11.833 (4) Å, b = 13.740 (2) Å, c = 11.607 (3) Å, α = 102.94 (2)°, β = 106.79 (2)°, γ = 76.54 (2)°, V = 1732.0 Å³, Z = 2, R = 0.048 (R_w = 0.075) for 5862 reflections with I > 2.5σ(I). In 5a the bicyclo[2.2.1] core of 4a is retained, while the phosphorus ligand has changed from a trivalent, 2e-donating phosphite in 4a to a covalently bound, pentavalent phosphonate in 5a. With the bicyclo[2.2.1] structure being established, the initial step in the reaction of (diazadiene)Fe(CO)₃ complexes with dipolarophilic acetylenes is formulated in terms of an oxidative 1,3-dipolar cycloaddition of the alkyne to the C=N—Fe fragment. The isolobal analogy between the latter and the classic Huisgen 1,3-dipole R₂C=N(R)—CR₂ is demonstrated.

Introduction

In previous papers in this series,[1-4] we have reported experimental data and preparative results along with mechanistic details about the later stages of the reaction sequence shown in Scheme I. The earliest intermediate that heretofore could be isolated and fully characterized was the bicyclo[2.2.2] complex 2.[2] The mechanism of its formation and hence of the initial reaction of 1 with the alkyne had to remain speculative.[3] Our working hypothesis for the initial step was a 1,3-dipolar cycloaddition reaction of the alkyne to the C=N—Fe fragment, resulting in the formation of a bicyclo[2.2.1] adduct, which then undergoes CO insertion.

Herein we report the X-ray molecular structure of a bicyclo[2.2.1] complex that is formed in the reaction of [biacetyl bis(p-methoxyanil)]Fe(CO)₃ (1a) with dimethyl acetylenedicarboxylate (DMAD) in the presence of 1 equiv of trimethyl phosphite and in its core structurally resembles the initial cycloadduct. On this basis we discuss the initial step of the title reaction in terms of the above-mentioned 1,3-dipolar cycloaddition, illustrating the isolobal analogy between the C=N—Fe unit and an azomethine ylide as a typical representative of a Huisgen 1,3-dipole.

Results and Discussion

Preparation and Properties of 4a and 5a. When at -78 °C under an atmosphere of argon 1 equiv of DMAD

Scheme I
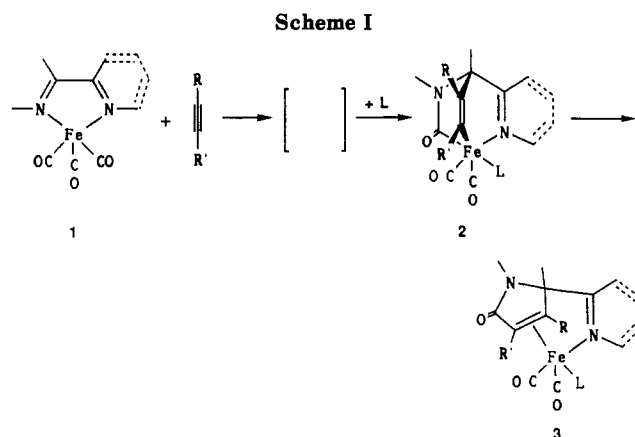
is added to a solution of [biacetyl bis(p-methoxyanil)]-Fe(CO)₃ (1a) in tetrahydrofuran (THF) or toluene, an immediate decoloration takes place. Depending on the kind of additional ligand offered to this solution, different products are obtained; cf. Scheme II.

When the inert atmosphere is replaced by CO and the mixture is allowed to warm to room temperature, the expected 1,5-dihydropyrrol-2-one complex 3a can be isolated

(1) Frühauf, H.-W.; Seils, F.; Romão, M. J.; Goddard, R. J. *Angew. Chem.* 1983, 95, 1014; *Angew. Chem., Int. Ed. Engl.* 1983, 22, 992; *Angew. Chem. Suppl.* 1983, 1435.
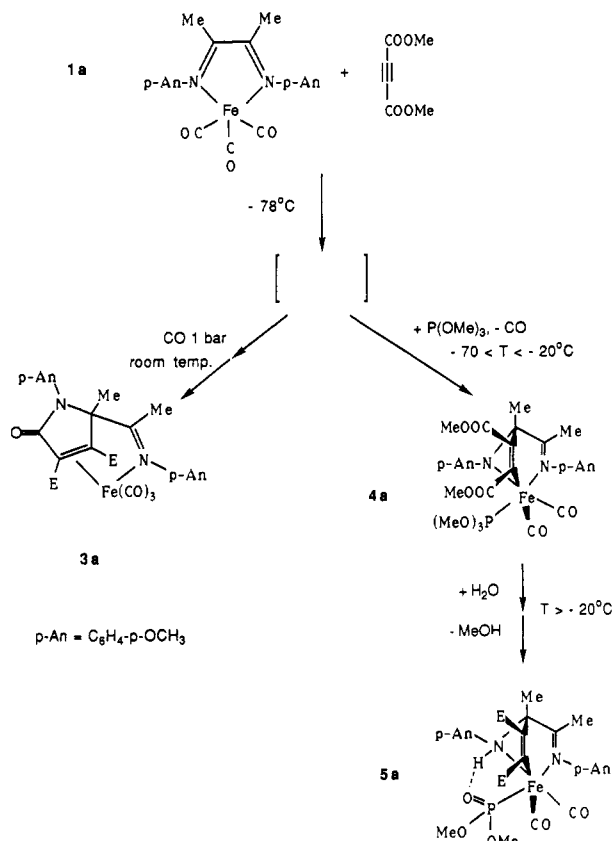(2) Frühauf, H.-W.; Seils, F.; Goddard, R. J.; Romão, M. J. *Organometallics* 1985, 4, 948.
(3) Frühauf, H.-W.; Seils, F. *J. Organomet. Chem.* 1986, 302, 59.
(4) Frühauf, H.-W.; Seils, F. *J. Organomet. Chem.* 1987, 323, 67.

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Scheme II

Table I. Spectroscopic Properties of Complex 4a

IR (THF): ν(CO) 2033.0, 1976.0 cm^{-1} [a]
MS (FD mode): m/e = 674 (M$^+$)
^{31}P NMR:[b,c] 16.4 ppm (^3J(P,H) = 10.2 Hz)

	^{13}C NMR[b,d]			
nucleus[e]	δ, ppm	^1J(C,H), Hz	$^{(n)}J$(C,P), Hz	^{1}H NMR[b,d] δ, ppm (mult)
1, 2, 3	224.6		(2) 52.7	
	221.0		(2) 37.2	
	217.1		(2) 35.9	
4	131.8		(3) 3.8	
5	77.8		(3) 5.2	
6	183.7		(3) 1.9	
7	178.5			
8/10	51.6/51.2	147/147		3.91/3.72 (s/s)
9	161.4		(4) 5.0	
11	18.1	129		1.83 (br)
12	18.8	130		2.04 (d, 1.2 Hz)
13	137.6		(3) 4.2	
14/18	124.4/121.1	163/157		
15/17	113.3/112.1	155/160		aryl-H
21/25	122.1/122.3	162/162		6.6–7.0 (m)
22/24	113.0/113.0	158/158		
16/23	156.5/156.7			
19/26	55.2/55.3	144/144		3.81/3.82 (s/s)
20	143.7			
P(OMe)$_3$	51.5	147	(2) 8.5	3.24 (d, 10.2 Hz)

[a] ±0.5 cm^{-1}; calibrated against DCl gas rotational bands.[12] [b] All NMR spectra measured in CDCl$_3$ at 248 K. [c] Chemical shift downward from external P(OMe)$_3$ in CDCl$_3$ at 248 K. [d] TMS internal standard. [e] Tentative assignments referring to the numbering scheme of complex 5a (cf. Figure 1).

in good yields (see Experimental Section). When, instead, 1 equiv of trimethyl phosphite is added, complex **4a** is formed at temperatures below –20 °C. It could be isolated in the form of a bright yellow microcrystalline powder from acetone/methanol at –78 °C.

Attempts to prepare crystals of **4a** suitable for X-ray analysis failed so far, partially due to a consecutive reaction finally giving stable complex **5a** which crystallizes much more readily. Single crystals of **5a** suitable for X-ray diffraction could be grown from acetone solution (see below). The intimate steps of the formation of **5a** from **4a** are presently under investigation employing low-temperature IR and NMR spectroscopy.

The structure of **4a** in Scheme II has been tentatively assigned on basis of its MS, IR, and NMR (^{1}H, ^{13}C, ^{31}P) spectroscopic properties. Its molecular ion in the field-desorption mass spectrum of 674 mass units indicates a stoichiometry corresponding to a 1:1:1 adduct of **1a** with alkyne and phosphite minus one CO. The two equally intense IR stretching bands of the two remaining CO ligands, at 2033 and 1976 cm^{-1} in THF, indicate terminal coordination. The band positions do not differ significantly from those observed in the [2.2.2] bicyclic complexes **2** with L = P(OMe)$_3$ of N-alkyl-substituted diazadienes.[4] The ^{31}P NMR resonance of the phosphite ligand in **4a**, at 16.4 ppm downfield from external P(OMe)$_3$, again shows a chemical shift very similar to those in the related complexes **2**.[3,4] The stoichiometry that was indicated by mass spectrometry is confirmed in the ^{13}C NMR spectrum. Only three carbon atoms directly bonded to the iron are present, i.e., with chemical shifts exceeding 190 ppm and showing a two-bond coupling to phosphorus. Taken together, this clearly speaks in favor of a bicyclic structure without inserted CO, thus of the [2.2.1] type, resembling the arrangement of the proposed initial cycloadduct (vide infra) with one terminal CO being replaced by trimethyl phosphite.

When a solution of **4a** in THF was allowed to warm to ambient temperature in an IR cell, new CO stretching bands grew in at 2048 and 1995 cm^{-1}, which in turn were replaced by bands, close to the original positions in **4a**, at 2036 and 1983 cm^{-1} of a product stable at this temperature. In preparative runs, solutions of **4a** in THF were left standing at 0 °C for several days. Cooling to –30 °C gave varying yields of a pale yellow, air-stable precipitate of **5a**. Its spectroscopic properties are collected in Table II. Its FD mass spectrum (m/e = 660) suggested a loss of 14 mass units with respect to **4a**. A major chemical change had obviously taken place at the phosphorus ligand as its ^{31}P NMR resonance is shifted upfield by almost 40 ppm. An initial 80-MHz ^{1}H NMR spectrum showed eight signals in the methoxy region between 3.4 and 3.9 ppm, integrating for a total of 18 protons, thus one OCH$_3$ group less than in **4a**. A 250-MHz spectrum allowed the identification of the signal splittings due to P,H coupling and made clear that only two P–OCH$_3$ groups were present, both being magnetically inequivalent and giving rise to two doublets at 3.40 and 3.61 ppm, respectively (cf. Table II). The assignments given for the methoxy groups at the p-anisyl and ester moieties, as well in **4a** as in **5a**, are based on the consideration that the former, due to their remoteness from the coordination center, should be much more alike than the latter. This holds also for the respective ^{13}C resonances. Comparison of the ^{13}C NMR chemical shifts of **4a** and **5a** (Tables I and II) shows major changes only for the carbon atoms directly bonded to the iron. This restriction of changes in chemical shifts to those atoms most likely to be influenced by the altered phosphorus ligand suggested that the rest of the molecule was structurally unaffected. A single-crystal X-ray diffraction analysis of **5a** confirmed the integrity of the ferrabicyclo-[2.2.1] structure.

Crystal Structure of the Bicyclo[2.2.1] Complex 5a. The unit cell contains two molecules of the complex and two acetone molecules of crystallization. There are no close

Table II. Spectroscopic Properties of Complex 5a

IR (THF): ν(CO) 2036.0, 1983.0 cm^{-1} [a]
MS (FD mode): m/e = 660 (M$^+$)
^{31}P NMR:[b,c] -24.4 ppm

nucleus[f]	δ, ppm	^1J(C,H), Hz	$^{(n)}J$(C,P), Hz	^{1}H NMR[d,e] δ, ppm (mult)
1, 2, 3	210.7		(2) 31.3	
	209.9		(2) 40.1	
	206.8		(2) 28.9	
4	134.0			
5	80.8		(3) 2.6	
6	186.3		(3) 2.2	
7	176.8		(3) 2.2	
8/10	52.1/51.6	147/147		3.88/3.71 (s/s)
9	161.7		(4) 3.1	
11	18.2	129		1.79 (s)
12	19.1	130		2.15 (s)
13/20	142.6/138.1			
14/18	124.1/118.3	162/156		
15/17	115.1/113.9	162/162		aryl-H
21/25	120.5/120.5	159/159		6.4-7.5 (m)
22/24	114.1/114.1	162/162		
16/23	157.7/157.5			
19/26	55.4/55.4	145/145		3.80/3.82 (s/s)
27/28	49.9/50.9	146/145	(2) 10.4/5.7	3.40/3.61 (d/d, 11.1/11.3 Hz)

[a] ±0.5 cm^{-1}; calibrated against DCl gas rotational bands.[12] [b] In CDCl$_3$ at 248 K. [c] Negative chemical shift upfield from external P(OMe)$_3$ under identical conditions. [d] TMS internal standard. [e] In CDCl$_3$ at ambient temperature. [f] Tentative assignments referring to the numbering scheme of complex 5a (cf. Figure 1).

nonbonding contacts between adjacent molecules of complex or solvent. An ORTEP diagram with the numbering scheme and a stereoscopic view of 5a are shown in Figure 1, selected bond distances and angles are given in Table III, and pertinent crystallographic details are collected in Tables IV and V.

The coordination geometry around the central iron atom is distorted octahedral whereby the coordinated hetero atoms and carbon atoms are each meridionally arranged. As had been suggested by the NMR results, i.e., the missing of one phosphite methyl group and the diastereotopicity of the remaining ones, one of the methoxy groups of the trimethyl phosphite ligand of 4a has apparently been hydrolyzed. The P-O(10) distance (1.480 Å) is remarkably short as compared to P-O(9) or P-O(11) (1.617 and 1.600 Å), indicating a pronounced double-bond character. The O(9)-P-O(11) angle of 97.6° is much smaller than O(9)-P-O(10) or O(11)-P-O(10) with 109.0 and 112.7° respectively. Concurrently the requisite hydrogen atom definitely does not reside on O(10) but instead on N(1). The short N(1)-H distance of 0.92 Å is clearly bonding, whereas the distance H(n1)-O(10) of 2.28 Å is indicative of a hydrogen-bridging interaction.[5] This intramolecular hydrogen bridge is therefore responsible for the coplanarity of N(1)-Fe-P-O(10) in the crystal (dihedral angle 1°). This bonding situation makes it appropriate to view at N(1) as a 2e-donating amine, in place of the covalently bound amide in 4a, whereas the phosphorus ligand has consequently changed from a trivalent, 2e-donating phosphite in 4a to a covalently bound, pentavalent phosphonate. Almost identical bonding distances for the Fe–phosphonate moiety have recently been reported in the structure of (cp)Fe(CO)$_2$\{P(O)(OEt)$_2$\},[6] namely, Fe-P =

(5) Olovsson, I.; Jönsson, P.-G. In *The Hydrogen Bond*; Schuster, P., Zundel, G., Sandorfy, C., Eds.; North-Holland Publishing Co.: Amsterdam, 1976; Vol. II, Chapter 8.5.3.
(6) Nakazawa, H.; Morimasa, K.; Kushi, Y.; Yoneda, H. *Organometallics* 1988, 7, 458.

Table III. Selected Distances (Å) and Angles (deg) for 5a[a]

Distances

Fe-C(1)	1.812 (4)	C(5)-C(11)	1.524 (4)
Fe-C(2)	1.763 (3)	C(5)-N(1)	1.514 (5)
Fe-C(3)	2.001 (4)	C(6)-C(12)	1.497 (5)
Fe-N(1)	2.049 (2)	C(6)-N(2)	1.272 (4)
Fe-N(2)	2.030 (3)	C(13)-N(1)	1.464 (4)
Fe-P	2.230 (3)	C(20)-N(2)	1.444 (4)
C(1)-O(1)	1.138 (5)	O(9)-P	1.617 (4)
C(2)-O(2)	1.146 (4)	O(10)-P	1.408 (3)
C(3)-C(4)	1.346 (4)	O(11)-P	1.600 (2)
C(4)-C(5)	1.531 (4)	N(1)-H(n1)	0.92 (3)
C(5)-C(6)	1.539 (4)	O(10)-H(n1)	2.28 (3)

Angles

C(1)-Fe-C(2)	91.0 (2)	Fe-C(3)-C(4)	111.6 (3)
C(1)-Fe-C(3)	175.6 (2)	C(3)-C(4)-C(5)	114.5 (3)
C(1)-Fe-N(1)	96.7 (2)	C(4)-C(5)-C(11)	116.9 (3)
C(1)-Fe-N(2)	92.3 (3)	C(6)-C(5)-C(11)	115.2 (3)
C(1)-Fe-P	92.7 (2)	C(5)-C(6)-C(12)	120.1 (3)
C(2)-Fe-C(3)	92.9 (2)	C(12)-C(6)-N(2)	126.1 (3)
C(2)-Fe-N(1)	172.3 (1)	Fe-N(1)-C(5)	100.4 (2)
C(2)-Fe-N(2)	99.6 (2)	Fe-N(2)-C(6)	114.3 (3)
C(2)-Fe-P	90.7 (2)	Fe-P-O(10)	115.0 (2)
C(3)-Fe-N(1)	79.4 (2)	O(9)-P-O(10)	109.0 (3)
C(3)-Fe-N(2)	85.1 (2)	O(9)-P-O(11)	97.6 (3)
C(3)-Fe-P	89.3 (2)	O(10)-P-O(11)	112.7 (2)
N(1)-Fe-N(2)	79.9 (2)	Fe-N(1)-H(n1)	108 (3)
N(1)-Fe-P	89.2 (1)	C(5)-N(1)-H(n1)	106 (3)
N(2)-Fe-P	168.5 (1)	C(13)-N(1)-H(n1)	106 (3)

Dihedral Angles

C(5)-C(4)-C(3)-Fe	1	C(12)-C(6)-N(2)-C(20)	0
C(5)-C(6)-N(2)-Fe	2	N(1)-Fe-P-O(10)	1
C(7)-C(3)-C(4)-C(9)	1	C(11)-C(5)-N(1)-C(13)	48

[a] Standard deviations in parentheses. The H atoms refined reasonably well; C-H distances range from 0.79 to 1.06 Å.

Table IV. Crystallographic Data and Details of Data Collection and Refinement for 5a

(a) Crystal Parameters

formula: C$_{28}$H$_{33}$N$_2$O$_{11}$PFe·C$_3$H$_6$O	fw: 718.48
space group: $P\bar{1}$	cryst system: triclinic
a = 11.833 (4) Å	α = 102.94 (2)°
b = 13.740 (2) Å	β = 106.79 (2)°
c = 11.607 (3) Å	γ = 76.54 (2)°
V = 1732.0 (8) Å^3	ρ(calcd) = 1.38 g/cm^3
approx cryst size: 0.3 × 0.2 × 0.5 mm	Z = 2

(b) Data Collection

diffractometer	Nonius CAD 4
radiatn	Mo Kα
μ, cm^{-1}	5.31
monochromator	graphite
temp, K	295 ± 3
θ_{max}, deg	30
scan mode	$\theta/2\omega$
horiz and vert aperture, mm	3 + tan θ, 4
max time/reflctn, s	19
ref reflctns	2,-3,1; -3,0,3 (13% decrease)
total no. of reflctn data	10 022
total no. of unique reflctns	10 022
obsd data ($I > 2.5\sigma(I)$)	5862
X-ray exposure, h	79.4

(c) Refinement

no. of parameters	576
weighting scheme	$1/(5.8 + F_o + 0.019F_o{}^2)$
final R values	R = 0.048 (R_w = 0.075)
max shift/error	1.2
min and max residual density, e Å^{-3}	0.5

2.1999 (2) Å, P=O = 1.495 (4) Å, and P-OEt = 1.611 (4) and 1.612 (4) Å.

Apart from this interesting and rather unusual transformation, the most important result in the context of this paper is the conservation and confirmation of the ferrabicyclo[2.2.1] structure of 4a. The existence of such an
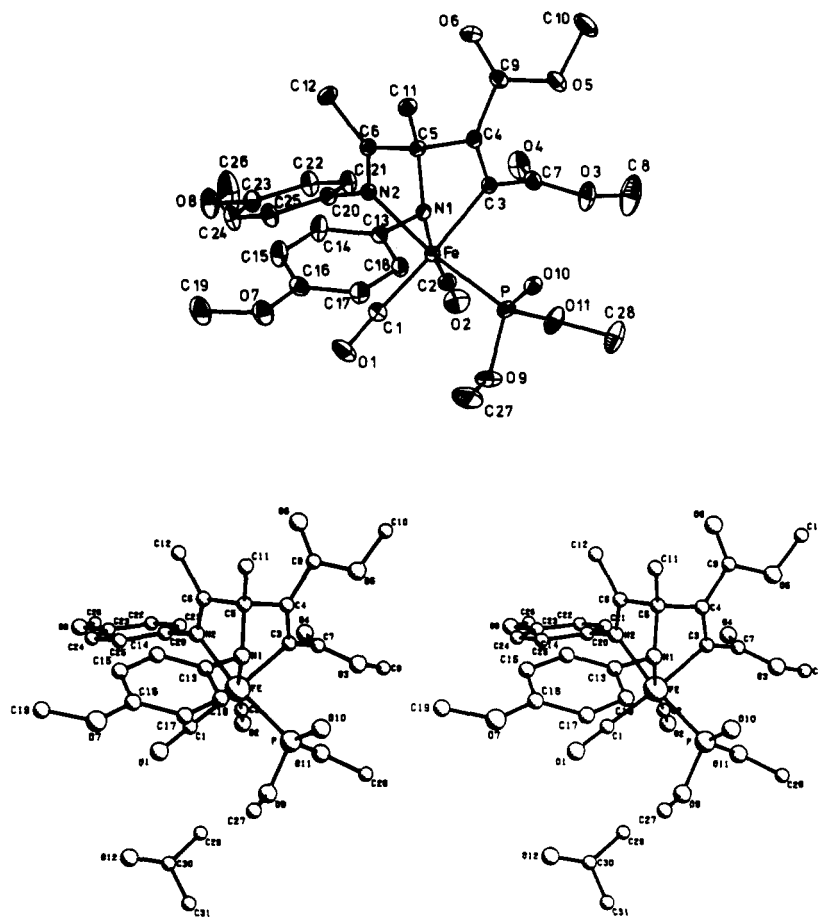
Figure 1. ORTEP diagram of **5a** showing 50% probability thermal ellipsoids and stereoscopic view also showing the acetone molecule of crystallization.

arrangement is crucial to our mechanistic understanding of the reaction of (1,4-diaza-1,3-diene)Fe(CO)$_3$ complexes **1** with dipolarophilic alkynes which will be detailed in the following.

Isolobal Analogy of the C=N—Fe Fragment and Azomethine Ylide. Huisgen[7] defined a 1,3-dipole as a species that may be described by zwitterionic octet structures **6a** ↔ **6b**[8] and may undergo cycloaddition reactions of the type 3 + 2 → 5 with suitable multiple bonds (dipolarophile U=V).
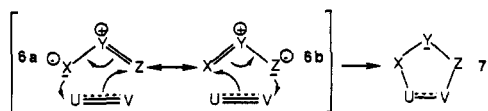

This general description of a 1,3-dipole can be easily recognized in the iron–imine system with the aid of the isolobal relation 8–9 and, derived from it, 10–11.
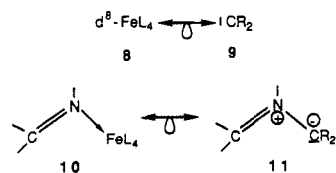
In the well-known analogy 8–9 between a d^8 ML$_4$ fragment and a carbene,[9] the four ligands L at the iron cor-

respond to, e.g., the three CO ligands and one of the two imine units in **1**. If, by way of n-donation, an imine is added to **8** and **9**, respectively, structures **10** and **11** are obtained, of which **10** is equivalent to **1** while **11** resembles one resonance structure of an azomethine ylide, a classic 1,3-dipole. Substituting our relevant atom arrangement **10** into the general formulas **6a,b** of a 1,3-dipole, we obtain **12a,b** which represent a valence-bond description of the DAD ligand properties. MO calculations on the model compound (HN=CHCH=NH)Fe(CO)$_3$[10] have shown that indeed the frontier orbitals of **1** are C=N—Fe based; i.e., both the HOMO and LUMO have strongly mixed metal d, ligand π* character.[11]
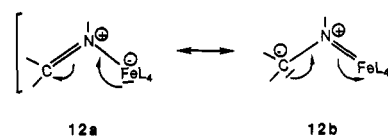
With this in mind, it seems reasonable to formulate the initial step in the reaction sequence (Scheme I) in terms of a 1,3-dipolar cycloaddition reaction of the alkyne to the C=N—Fe fragment. This results in the formation of the ferrabicyclo[2.2.1] intermediate **A**, from which the isolated products in Schemes I and II may be readily explained.

(7) Huisgen, R. *Angew. Chem.* **1963**, *75*, 604, 742.

(8) The literal 1,3-dipole results from localizing two of the four electrons at the onium centre Y, which gives rise to the sextet structures $^+$X–Y–Z$^-$ ↔ $^-$X–Y–Z$^+$. They demonstrate the ambivalence of 1,3-dipoles, which may at both termini have nucleophilic and electrophilic properties alike.

(9) Hoffmann, R. *Angew. Chem.* **1982**, *94*, 725; Stone, F. G. A. *Angew Chem.* **1984**, *96*, 85.

(10) Kokkes, M. W.; Stufkens, D. J.; Oskam, A. *J. Chem. Soc., Dalton Trans.* **1983**, 439.

(11) van Dijk, H. K.; Stufkens, D. J.; Oskam, A. *J. Am. Chem. Soc.* **1989**, *111*, 541.
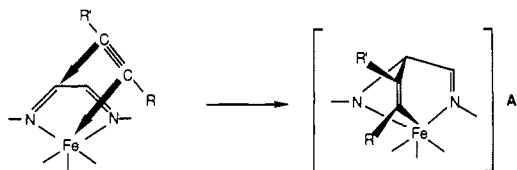
Concertedness of such a reaction cannot a priori be expected. A charge-separated intermediate in a stepwise mechanism, however, seems unlikely. With solvents of very different polarities, e.g., toluene and THF, there is no observable influence on the rate of the reaction or the isolated yields of products 2 or 3. Further pieces of evidence in favor of a cycloaddition mechanism are the observed regioselectivities with unsymmetrical alkyne or diazadiene[4] and the enormous influence of the alkyne frontier orbital energies on the reactivity which is exemplified by the different conditions that are necessary for the reaction of a given complex 1 with DMAD or methyl propynoate.[4]

Experimental Section

Spectra were recorded by using the following spectrometers: IR, Perkin-Elmer 283, carbonyl stretching band positions in solution spectra were individually calibrated against appropriate rotational bands of DCl gas[12] and are accurate to within ± 0.5 cm^{-1}; NMR (^{1}H, ^{13}C, ^{31}P) spectra were recorded with Bruker spectrometers WP 80 SY WG, WM 300, and WM 250. Chemical shifts (ppm, δ scale) for ^{1}H and ^{13}C are relative to internal TMS; for ^{31}P, parts per million values are positive downfield from external trimethyl phosphite. For mass spectra of a Varian 311A spectrometer (EI and FD mode) was used. Elemental analyses were performed by the Microchemical Laboratory Dornis & Kolbe, Mülheim a.d. Ruhr, West Germany, and by the section Elemental Analyses of the Institute of Applied Chemistry, TNO, Zeist, The Netherlands. Tetrahydrofuran solvent (E. Merck, Darmstadt; pro analysi grade) was percolated through alumina and purged with and stored under argon. All other solvents were dried and deaerated by circular distillation under argon with appropriate drying agents. Preparation of the starting complex 1a has been described previously.[13]

Preparation of N(p-anisyl)C(O)C(COOMe)=C-(COOMe)C(Me)C(Me)=N(p-anisyl)Fe(CO)$_3$ (3a). Under an atmosphere of CO (1 bar) a solution of 0.945 g (2.17 mmol) of 1a in 20 mL of tetrahydrofuran (THF) was cooled to -20 °C, and a solution of 0.27 mL (2.2 mmol) of DMAD in 40 mL of THF was slowly added. After being stirred for 24 h under CO at room temperature, the initially red reaction mixture, which showed at least 10 IR bands in the CO stretching region, has turned to yellow-brown, and only the three CO stretching bands of product 3a can be seen. The solvent was evaporated, the residue was washed with n-hexane and, at -78 °C, with little methanol, which dissolved most of the brown impurities. Crystallization from 12 mL of methanol gave 550 mg of 3a. Another crop of 280 mg of identical yellow crystals was obtained from the concentrated mother liquor (ca. 4 mL) at -30 °C after seeding. Total yield of 3a: 0.83 g (64%). IR: ν(CO) in THF 2056.5, 1996.5, 1972.5 cm^{-1}; ν(CO) in CHCl$_3$ 2064, 2003, 1982.5 cm^{-1}. MS (FD mode): m/e 606 (M$^+$) and 466 (M$^+$ - Fe(CO)$_3$). ^{1}H NMR (CDCl$_3$, 248 K, 80.13 MHz): δ 3.85 (s, 6 H, OCH$_3$), 3.77 (s, 3 H, O-CH$_3$), 3.73 (s, 3 H, OCH$_3$), 1.97 ((br), 3 H, C-CH$_3$), 1.36 (s, 3 H =CCH$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 248 K, 20.15 MHz): δ 209.3, 207.4, and 206.2 (CO ligands), 195.4 (N=C), 172.0 and 170.5 (ester CO), 171.1 (ring CO), 158.9, 157.8, 142.7, and 126.8 (quaternary aryl C), 130.5 (2 C), 121.8, 121.4, 114.4 (2 C), and 114.1 (2 C) (aryl CH), 76.7 (ring sp^3 C), 70.3, and 67.7 (ring C=C), 55.4 and 55.3 (anisyl OCH$_3$), 53.3 and 51.4 (ester OCH$_3$), 21.4 (N=CCH$_3$), 19.1 (br) (CH$_3$ at

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Table V. Fractional Coordinates of the Non-Hydrogen Atoms and Equivalent Isotropic Thermal Parameters

atom	x	y	z	U_{eq}, Å^2
Fe	0.62540 (4)	0.77349 (3)	0.15846 (4)	0.0284 (2)
C(1)	0.5199 (3)	0.6867 (3)	0.1100 (4)	0.044 (2)
C(2)	0.6573 (3)	0.7550 (3)	0.3109 (3)	0.039 (2)
C(3)	0.7439 (3)	0.8665 (2)	0.1992 (3)	0.031 (1)
C(4)	0.7853 (3)	0.8656 (2)	0.1024 (3)	0.033 (1)
C(5)	0.7352 (3)	0.7934 (2)	-0.0127 (3)	0.031 (1)
C(6)	0.7943 (3)	0.6876 (2)	0.0203 (3)	0.033 (1)
C(7)	0.8017 (3)	0.9118 (3)	0.3244 (3)	0.042 (2)
C(8)	0.8023 (8)	1.0508 (5)	0.4837 (6)	0.116 (5)
C(9)	0.8905 (3)	0.9096 (3)	0.1081 (3)	0.039 (2)
C(10)	0.9931 (6)	1.0461 (5)	0.1996 (6)	0.086 (4)
C(11)	0.7477 (3)	0.8107 (3)	-0.1334 (3)	0.041 (2)
C(12)	0.8931 (4)	0.6247 (3)	-0.0351 (4)	0.048 (2)
C(13)	0.5247 (3)	0.7576 (2)	-0.1165 (3)	0.033 (1)
C(14)	0.5518 (4)	0.6562 (3)	-0.1640 (4)	0.055 (2)
C(15)	0.4691 (4)	0.6105 (3)	-0.2608 (4)	0.056 (2)
C(16)	0.3597 (3)	0.6660 (3)	-0.3092 (3)	0.044 (2)
C(17)	0.3332 (3)	0.7677 (3)	-0.2625 (4)	0.049 (2)
C(18)	0.4152 (3)	0.8138 (3)	-0.1670 (3)	0.039 (2)
C(19)	0.2962 (5)	0.5209 (4)	-0.4479 (5)	0.080 (3)
C(20)	0.8097 (3)	0.5729 (2)	0.1505 (3)	0.034 (2)
C(21)	0.8946 (3)	0.5762 (3)	0.2605 (3)	0.044 (2)
C(22)	0.9498 (4)	0.4866 (3)	0.3075 (4)	0.050 (2)
C(23)	0.9171 (4)	0.3962 (3)	0.2459 (3)	0.043 (2)
C(24)	0.8293 (4)	0.3934 (3)	0.1367 (4)	0.050 (2)
C(25)	0.7751 (4)	0.4814 (3)	0.0898 (4)	0.045 (2)
C(26)	1.0487 (8)	0.3029 (4)	0.3976 (6)	0.112 (4)
C(27)	0.2668 (5)	0.8721 (5)	0.0781 (7)	0.089 (4)
C(28)	0.4652 (6)	1.0605 (4)	0.3732 (4)	0.074 (3)
C(29)	0.3720 (6)	0.6939 (5)	0.3679 (6)	0.085 (4)
C(30)	0.2657 (5)	0.6494 (4)	0.2920 (5)	0.074 (2)
C(31)	0.1487 (7)	0.7188 (7)	0.2772 (9)	0.126 (6)
N(1)	0.6050 (2)	0.8076 (2)	-0.0102 (2)	0.030 (1)
N(2)	0.7565 (2)	0.6656 (2)	0.1016 (2)	0.031 (1)
O(1)	0.4554 (3)	0.6312 (3)	0.0861 (4)	0.076 (2)
O(2)	0.6763 (3)	0.7429 (3)	0.4098 (3)	0.062 (2)
O(3)	0.7522 (3)	1.0063 (2)	0.3597 (3)	0.066 (2)
O(4)	0.8844 (3)	0.8639 (2)	0.3894 (3)	0.065 (2)
O(5)	0.8915 (3)	0.9984 (2)	0.1830 (3)	0.061 (2)
O(6)	0.9661 (3)	0.8712 (3)	0.0527 (3)	0.062 (2)
O(7)	0.2730 (3)	0.6282 (2)	-0.4051 (3)	0.060 (2)
O(8)	0.9674 (3)	0.3035 (2)	0.2817 (3)	0.063 (2)
O(9)	0.3589 (3)	0.8767 (3)	0.1886 (3)	0.065 (2)
O(10)	0.4585 (2)	0.9833 (2)	0.1107 (2)	0.039 (1)
O(11)	0.5176 (3)	0.9561 (2)	0.3335 (2)	0.060 (2)
O(12)	0.2750 (6)	0.5632 (4)	0.2453 (6)	0.134 (4)
P	0.48371 (8)	0.90758 (7)	0.19191 (8)	0.0353 (4)

the pyrrolinone 5-position). Anal. Calcd for C$_{28}$H$_{26}$FeN$_2$O$_{10}$: C, 55.46; H, 4.32; N, 4.62; Fe, 9.21. Found: C, 55.38; H, 4.53; N, 4.84; Fe, 9.47.

Liberation from 3a of the Coordinated 1-(Methoxyphenyl)-3,4-dicarbomethoxy-5-methyl-5-{1-[N-(4-methoxyphenyl)imino]ethyl}-1,5-dihydropyrrol-2-one. In a 50-mL steel autoclave with glass insert, 0.23 g (0.38 mmol) of 3a, dissolved in 15 mL of acetone, was kept for 4 days at 75-90 °C under 180 bar of CO pressure. After evaporation of the solvent and Fe(CO)$_5$, the residue was chromatographed (2-mm silica gel plate developed twice with 3:1 toluene/ethyl acetate). The pale yellow main zone was scraped off and eluted with acetone, and the product was recrystallized from 2 mL of methanol by stepwise cooling to -78 °C, yielding 160 mg (90%) of the expected pyrrolinone (mp 127-130 °C). MS (EI mode, 70 eV/17 eV, 198 °C): m/e 466 (M$^+$), 435/434, 407, 348, 319, 287, 260, 148 (base peak); high-resolution MS (reference peak m/e 454.972 885) m/e 466.1739 (5); C$_{25}$H$_{26}$-N$_2$O$_7$ requires 466.17401. ^{1}H NMR (CDCl$_3$, 268 K, 80.13 MHz): δ 1.66 (br, CH$_3$), 1.81 (s, CH$_3$), 3.81 (s, OCH$_3$), 3.84 (s, OCH$_3$), 3.94 (s, OCH$_3$), 3.97 (s, OCH$_3$), 6.5-7.2 (mult, aryl-H).

Preparation of 4a and 5a. 1a (0.84 g, 1.93 mmol) was dissolved in 10 mL of THF and cooled to <-30 °C when 0.23 mL (1.95 mmol) of P(OMe)$_3$ was added. During 3 h, a solution of 0.24 mL (1.95 mmol) of DMAD in 25 mL of THF was added to the stirred mixture from a dropping funnel, keeping the temperature at or below -20 °C. After evaporation of the solvent, the residue

was washed with the precooled (-30 °C) solvents n-hexane (4 × 10 mL) and ether (4 × 5 mL). The residue was digested at -20 °C with 12 mL of methanol. Most of the red liquid phase was inversely filtered off at -50 °C. The remaining slurry was re-dissolved in 15 mL of acetone, inversely filtered, and cooled on dry ice, giving at first 60 mg and after concentrating the mother liquor to half its volume, another 360 mg of bright yellow, microcrystalline 4a. Isolated yield: 420 mg (31%) of 4a. For spectroscopic properties cf. Table I.

To NMR monitor the formation of 4a and 5a, the reaction was carried out in a 10-mm NMR tube as follows. To a THF/THF-d_6 (2.5 mL) solution of 0.48 g (1.1 mmol) of 1a at -78 °C was added neat DMAD (0.17 mL, 1.38 mmol) with stirring and then at -50 °C was added 0.13 mL (1.1 mmol) of P(OMe)$_3$. The mixture was left standing for 4 days at -30 °C. ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectra indicated a virtually complete transformation into 4a. The solution was further kept at 0 °C for 6 days, giving, after evaporation of the solvent and drying in high vacuum, 0.76 g (102%) of crude 5a. The residue was redissolved in 8 mL of THF and cooled to -30 °C, giving a pale yellow precipitate and a dark brown mother liquor. At 0 °C the precipitate was washed with 1 mL of THF and dried in vacuo. Spectroscopically, the sample was found pure enough to be combined with 5a that had been prepared analogously from spectroscopically pure microcrystalline 4a that had been prepared as described above. Anal. Calcd for C$_{28}$H$_{33}$FeN$_2$O$_{11}$P: C, 50.93; H, 5.04; N, 4.24. Found: C, 50.44; H, 5.18; N, 4.06. For spectroscopic properties of 5a cf. Table II.

Crystal Structure of 5a. Single crystals suitable for X-ray diffraction were obtained by slowly cooling an acetone solution of 5a. A pale yellow crystal of ca. 0.3 × 0.2 × 0.5 mm^3 was chosen, and 10022 intensities ($\theta \leq 30°$, h -16 to 16, k -19 to 19, l 0 to 16) were measured on a Nonius CAD4 diffractometer employing graphite-monochromated Mo Kα radiation. A total 4160 intensities were below the 2.5σ(I) level and were treated as unobserved. Pertinent experimental and crystallographic details are collected

in Tables IV and V. Fe, P, and one ring were found by means of direct methods (SIMPEL[14]); subsequent Fourier syntheses yielded the rest of the structure including one molecule of acetone. Refinement proceeded by means of block-diagonal least-squares calculations. An empirical absorption correction (DIFABS[15]) was applied. The positions of the H atoms were indicated in a ΔF synthesis and included in the refinement with isotropic temperature parameters. Continued refinement converged to an R value of 0.048 (R_w = 0.075) for the 5862 observed reflections. A weighting scheme $w = 1/(5.8 + F_o + 0.019F_o{}^2)$ was applied, and the anomalous scattering of Fe was taken into account. The further programs used were from XRAY 76.[16]

Registry No. 1a, 65016-01-5; 3a, 122190-26-5; 4a, 122190-27-6; 5a, 122190-29-8; N(p-anisyl)C(O)C(COOMe)=C(COOMe)C-(Me)C(Me)=N(p-anisyl), 122190-25-4.

Supplementary Material Available: Tables of fractional coordinates of the hydrogen atoms and isotropic thermal parameters and anisotropic thermal parameters of the non-hydrogen atoms and complete lists of bond distances and angles of the non-hydrogen atoms (4 pages); a listing of structure factor amplitudes (27 pages). Ordering information is given on any current masthead page.

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Coordination Chemistry of Group 14 Metalloles. 5.[1] Use of Dicarbonyl(η^5-cyclopentadienyl)(1-methyl-2,5-diphenyl-silacyclopentadien-1-yl)iron as a Four-Electron Ligand: Chemical Properties and Dynamic Stereochemistry of the Complexes

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Chlorine is displaced in 1-chloro-1-methyl-2,5-diphenylsilole by dicarbonyl(η^5-cyclopentadienyl)ferrate(I) to give a silole with a Si–Fe σ bond. Attempts to displace the carbonyl ligands to give the corresponding silaferrocene were unsuccessful. This new silole behaves as an efficient η^4-ligand with transition metals, giving a new series of complexes which present an interesting reactivity. Thus the Si–Fe bond can be cleaved without decoordination of the η^4-ligand, and the Co–Co bond in (CO)$_6$(η^4-silole)Co$_2$ can be cleaved without cleavage of the Fe–Si bond. These η^4-complexes are fluxional as observed for other series. The interconversion, in solution, of the two enantiomers cis-Λ_{uu} and cis-Λ_{uu} has an activation energy of ~35 kJ mol^{-1} and a coalescence temperature of ~200 K. However, contrary to other cases, the presence of diastereoisomers cannot be detected.

Introduction

In the rapidly developing field of group 14 metalloles,[2,3] numerous papers have dealt with the search for the η^5-

metallacyclopentadienyl species. The similarities between cyclopentadienes and siloles make attractive the stabilization of the latter by coordination to a transition metal. Its observation in mass spectrometry has been reported[4,5] without further evidence.

Functionalization at silicon could be approach to η^5-

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