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1,5-DIHYDROPYRROL-2-ONES FROM (1,4-DIAZA-1,3-DIENE)TRICARBONYLIRON, (dad)Fe(CO)$_3$, AND ALKYNE

IV *. ELECTRONIC AND STERIC EFFECTS ALONG THE REACTION COORDINATE. REGIOSELECTIVITIES WITH UNSYMMETRICAL dad (METHYLGLYOXAL-BIS-ISOPROPYLIMINE) OR ALKYNE (METHYL PROPYNOATE)

HANS-WERNER FRÜHAUF ** and FRANK SEILS

*FB 6, Fachgebiet Organische Chemie der Universität, GH, Duisburg, Lotharstrasse 1,
D-4100 Duisburg 1 (Bundesrepublik Deutschland)*

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Summary

The [2.2.2]bicyclic intermediate observed in the title reaction in the case of dad ligands containing at least one unsubstituted imine carbon atom (aldimino group) were previously shown to be stabilized by introduction of a phosphite ligand, and on the basis of the bond distances revealed by X-ray analysis of the stabilized complex the stabilizing effect has been attributed to a strengthening of the Fe–C bond *trans*- to the P-donor atom, i.e., to one of the bonds broken in the final rearrangement reaction. By utilization of this stabilization, the heretofore unobservable [2.2.2] intermediate with a biacetyl derived dad (bis-ketimine) was observed, and identified by IR spectroscopy. Its rearrangement product, the first example of this type of species containing a phosphite ligand, was isolated. Its NMR (^{1}H, ^{13}C, ^{31}P) spectra reveal that only the isomer with the phosphorus in the thermodynamically most favorable position is formed. With sterically demanding dad-substituents, products from the final rearrangement are obtained only in poor yields. A mechanistic sequence which accounts for the findings is proposed. The initial step in the reaction sequence, in which the dad and alkyne become C–C connected, has been found to be very sensitive to electronic influences. In reactions with unsymmetrical dad (methylglyoxal-bis-isopropylimine) and alkyne (methyl propynoate), respectively, the formation of exclusively one of the possible regio-

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[*] For part III see ref. 4.

[**] Present address: Laboratorium voor Anorganische Chemie, University of Amsterdam, J.H. van 't Hoff Instituut, Nieuwe Achtergracht 166, 1018 WV Amsterdam (The Netherlands).

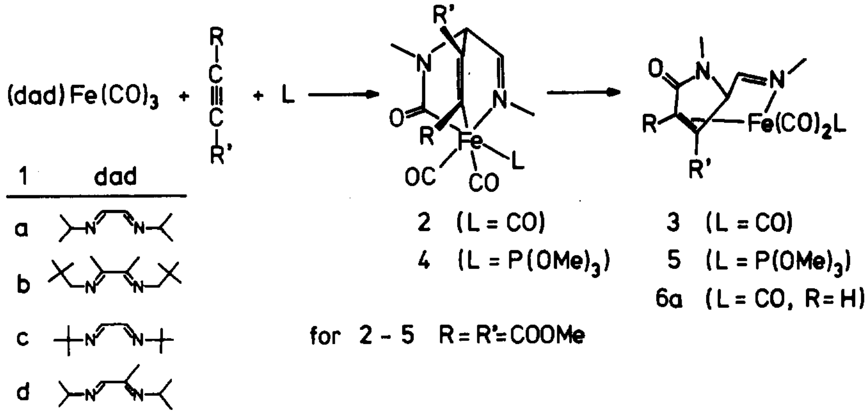
isomers is observed. The products have been characterized, and their structures determined by MS, IR, ^1H, and ^{13}C NMR spectroscopy.

Introduction

The title reaction of diazadiene-tricarbonyliron complexes (**1**) with electron deficient alkynes in the presence of CO as additional ligand L, which finally results in the formation of (1,5-dihydropyrrol-2-one)tricarbonyliron complexes **3** (cf. Scheme 1), has been found to very strongly depend on the substitutional pattern of the dad ligand. In our first report on the reaction [1,2] we presented evidence that in the reaction of **1a** with glyoxal-bis-isopropylimine as the diazadiene, i.e., with hydrogen attached to the imine carbon atoms, a thermally labile intermediate could be observed which eventually isomerized to the final product.

When trimethyl phosphite was used as the entering ligand L instead of CO, the intermediate, **4a**, was stabilized and its [2.2.2] bicyclic structure was determined by X-ray methods [3]. However, with diazadienes with a methyl group in place of the hydrogen atom at the imine carbon atom that becomes C–C-connected to the alkyne, there was no way of telling whether the same reaction path was being followed, the final product **3** in such cases being the first spectroscopically observable species. We now present evidence that this is due to a much lower activation energy for the isomerization of the corresponding intermediates **2** whereby the formation of **2** becomes rate determining, and an observable stationary concentration of **2** cannot be built up.

In view of the strong influence that substituents on the imine carbon atoms have on the activation energy in the last part of the reaction coordinate, it was of much interest to find out whether there was a comparable influence at the early stages of the reaction sequence. If so, a pronounced regioselectivity should result when employing an unsymmetrical diazadiene with one substituted and one unsubstituted imine carbon atom. We report here on the reaction of (methylglyoxal-bis-isopropylimine)Fe(CO)$_3$ with dimethyl acetylenedicarboxylate. The related reaction of



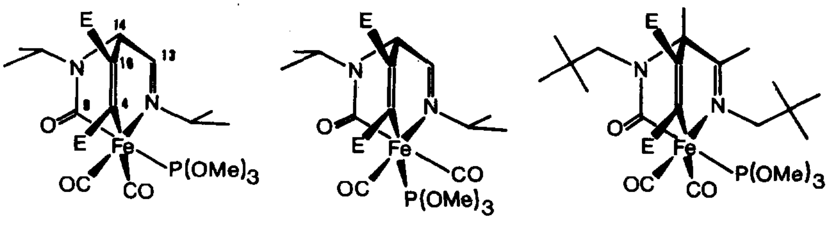
SCHEME 1

(glyoxal-bis-isopropylimine)Fe(CO)$_3$ with methyl propynoate as unsymmetrically substituted alkyne has also been examined in order to gain information on the influence of the presence of electronically different alkyne carbon atoms.

Results and discussion

The reaction of (biacetyl-bis-neopentylimine)Fe(CO)$_3$ (**1b**) with dimethyl acetylenedicarboxylate under an atmosphere of CO immediately gives the corresponding complex **3b** [2]. When the reactant solution made up at very low temperature in an IR cell is slowly allowed to warm above the temperature at which reaction takes place, the only new carbonyl stretching bands that can be detected are exclusively those of **3b**. In view of the very large increase in stability that we observed on going from **2a** to **4a**, i.e., when CO as the additional ligand was replaced by trimethyl phosphite [3], we also carried out a similar monitoring of the reaction of **1b** in the presence of trimethyl phosphite. The positions of the two new carbonyl stretching bands that progressively developed in the reaction mixture at -20 °C (ν(CO) in THF 2029, 1975 cm^{-1}) clearly indicated that the bicyclic complex **4b** indeed was being formed. This can be seen in Scheme 2, which compares the carbonyl stretching frequencies of **4b** in chloroform solution with those of the two stable, isomeric phosphite complexes **4a** and **4a'**, the [2.2.2] structures of which have previously been definitely established [3,4].

Attempts to isolate **4b** in analytically pure state, however, were unsuccessful (see Experimental), and resulted in partial decomposition and in the formation of increasing amounts of the rearranged product **5b**. Despite the stabilizing effect of the phosphite ligand, the isomerization of **4b** into **5b** still requires little activation energy and is already evident at -20 °C, but it is accompanied by an unusually high degree of decomposition, so that the isolated yield was only 13%. We ascribed this to steric hindrance arising from the combined bulk of the dad and the phosphite ligand. For comparison we therefore prepared **2c**, derived from glyoxal-bis-t-butylimine; **2c** also proved to be thermally so labile because of its bulky t-butyl groups that we had to restrict characterization to spectroscopic methods (see Experimental). Examination by IR spectroscopy and thin layer chromatography of



4a 4a' 4b

IR: ν(CO) in n-hexane [cm^{-1}]

2040.5, 1989.0 2037.0, 1986.5 2035.5, 1981.5

SCHEME 2

the products from isomerization of **2c** revealed the presence of so many components that no attempt was made to isolate and purify **3c**.

From the results the following conclusions were drawn:

(i) Methyl substituents on the imine carbon atoms of the dad ligands do not change the reaction path, but rather lower the activation energy for the isomerization step to such an extent that a detectable stationary concentration of [2.2.2] bicyclic intermediate **2** cannot build up.

(ii) The gain in stability of the intermediate from the introduction of a phosphite ligand is sufficient to permit its spectroscopic detection and identification.

(iii) Bulky substituents on the dad nitrogen atoms are detrimental to a smooth rearrangement reaction.

We have no ready explanation of how the activation energy for rearrangement is lowered by the methyl substituents at the dad imine carbon atoms. A rationale for the stabilizing effect of the phosphite ligand, however, can be based on the molecular structure of **4a**. In Scheme 2 the relevant atoms are identified by adopting the numbering scheme of the X-ray structure determination [3]. The bonds Fe–C(4) and Fe–C(9) had identical distances of 202.3 pm. These two bonds are the most important ones in the rearrangement as they are broken in the course of the isomerization **2** → **3**, which proceeds by a reductive elimination, or 1,2-migration, thus forming a bond between C(4) and C(9) and closing the 5-membered heterocycle, which in turn coordinates to the iron via its π-bond between C(4) and C(10). The fairly long bond distance of 202.3 pm is particularly surprising for the Fe–C(9) bond, which should be shortened by increased backbonding due to the phosphorus donor ligand in a *trans*-position. Conversely, it has to be concluded that this bond must be still longer in **2**, and hence more readily broken, owing to a reduction in the π-bond order when there is a carbonyl ligand in *trans*-position.

Since neither complex **4a**, nor the isomeric **4a′** [4], with the stabilizing phosphite ligands in *trans*-positions to C(9) and C(4), respectively, could be isomerized to the corresponding complexes **5**, it was of particular interest to obtain structural information on **5b**, the first example of a rearranged phosphite complex. We had found that on formation of **2** and **4** the new ligands L are incorporated exclusively *trans* to the inserted carbonyl C(9) [4]. The question now was whether the phosphite in **5b** would be bound specifically to one of the three possible positions or be distributed more or less statistically. All the spectroscopic results indicate the presence of a single species **5b**, i.e., the phosphorus is bound to one specific position only. The proton-decoupled ^{31}P NMR spectrum shows one single resonance at 24.4 ppm downfield from the external trimethyl phosphite standard. The ^{1}H and ^{13}C NMR data are listed in Table 1, and the structure of **5b** derived therefrom also gives the numbering scheme used for assignment of the resonances.

5b

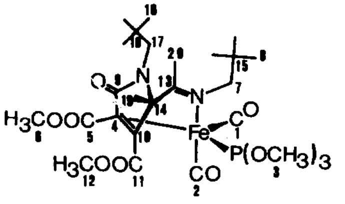


TABLE 1

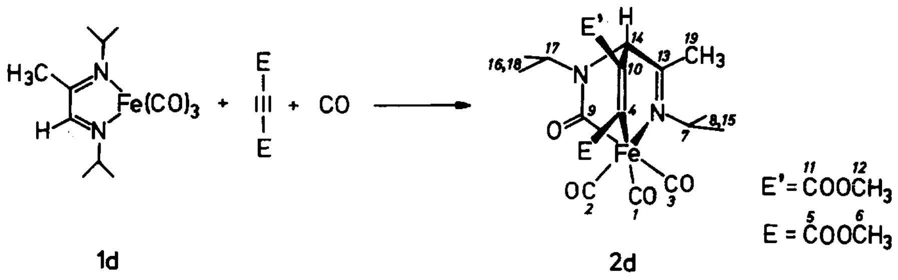
NMR DATA FOR **5b** IN $CDCl_3$ SOLUTION: ^1H (301 K, 80 and 300 MHz), AND ^{13}C (248 K, 20 MHz) (Positions are denoted by the numbering given in the structural formula of **5b**)

Position	δ(H) (ppm)	δ(C) (ppm)	^1J(C,H) (Hz)	^nJ(C,P) (Hz)
1		211.3	–	39.2
2		214.1	–	7.9
3	3.77 (d, ^3J(H,P) 10.7 Hz)	52.4	147	6.3
4		66.1	–	25.8
5		172.6 [a,b]	–	[c]
6	3.76(s) [a]	50.4 [a]	146	–
7	3.33(br)	68.9	[c]	7.4
8	0.96(s) [a]	28.7 [a]	125	–
9		172.6 [b]	–	[c]
10		64.8	–	5.5
11		173.3 [a]	–	7.3
12	3.53(s) [a]	53.0 [a]	146	–
13		196.7	–	7.6
14		77 [d]	–	
15		34.5 [a]	–	–
16	0.81(s) [a]	28.5 [a]	125	–
17	2.06(d, ^2J(H,H) 13.5 Hz) 3.36(d, ^2J(H,H) 13.5 Hz)	52.7	139	–
18		34.0 [a]	–	–
19	1.78(br)	21.2 [b]	129	–
20	1.91(d, ^5J(H,P) 3.8 Hz)	21.2 [b]	129	–

[a] Individualized assignments for respective pairs of signals are tentative. [b] Pairs of signals superimposing one another. [c] Not determined due to insufficient S/N ratio or overlaps. [d] Hidden under solvent signals.

The ^1H and ^{13}C chemical shifts very closely resemble those of the corresponding tricarbonylcomplex **3b** [2] except for C(1) and C(2), which experience a significant downfield shift due to the P-donor. The large difference in their C,P coupling constants, 39.2 and 7.9 Hz, respectively, indicates a great difference between the two OC–Fe–P angles. Very different C,P coupling constants are also observed for C(4) and C(10) namely 25.8 and 5.5 Hz, respectively. This can only be accounted for by a ligand arrangement, as shown in structure **5b**. A trigonal bipyramidal geometry has also been found for **3a** by X-ray diffraction [2], and an equatorial position of the phosphite is also plausible for electronic reasons, since it would avoid a *trans* arrangement of the σ-donating imine nitrogen and phoshorus atoms. Thus, the phosphite appears to occupy the thermodynamically most favorable position, more closely *trans* to C(4). The most surprising feature in the ^1H NMR spectra is a 3.8 Hz long range coupling of the phosphorus across five bonds to the methyl protons at C(20). By selective ^1H decoupling of the phosphite methyl protons this unusually large and far reaching coupling has been confirmed at the ^{31}P nucleus.

The conclusion that the phosphite ligand in **5b** ends up in the thermodynamically most favorable position agrees well with the picture of a coordinatively unsaturated intermediate during the rearrangement reaction **4** → **5**, when the bond between C(4) and C(9) has already been formed, but the resulting 5-ring has not yet become coordinated to the iron via its C(4)–C(10) π-bond. At this stage the conformational rigidity of **4** has been broken, and the ligands can adjust to the most favorable arrangement before the empty coordination site is filled, and rigidity is restored.



SCHEME 3

This picture also nicely accounts for the unsatisfactory preparative yields with bulky substituents. It then just takes too long for the 5-ring to find the suitable position for recoordination and part of the coordinatively unsaturated species escapes into other reaction paths.

We believe that the new C–C bond between dad and alkyne is formed at the very beginning of the reaction coordinate. In (methylglyoxal-bis-isopropylimine)Fe(CO)$_3$ (**1d**) the two imine carbon atoms are chemically diverse. From the results for reactions with glyoxal and biacetyl derived diazadienes however, it was clear that either sort of imine carbon in **1**, aldimine or ketimine, may in principle be attacked to form the new C–C bond. The use of unsymmetrically-substituted dad or alkyne could possibly lead to regioselective product formation. This is indeed the case (vide infra), and this selectivity was used to draw conclusions pertaining to the following questions: (a) which carbon atom would form the new bond to the alkyne carbon atom, and (b) how easily would the resulting bicyclic complex **2** rearrange to **3**? The answer to the first question is indicated in Scheme 3: C–C connection to acetylenedicarboxylate is formed exclusively at the unsubstituted imine carbon to give **2d**, with unsubstituted bridgehead carbon. **2d** isomerizes in a very unsatisfactory fashion to **3d**, i.e., as in the case of **2c**, many side products are formed. Though **3d** was positively identified from its typical IR carbonyl stretching bands in the raw product (ν(CO) in n-hexane: 2061.0, 2001.0, 1975.0 cm^{-1}), it could not be isolated analytically pure.

The structure of **2d** can be unambiguously derived from its ^{1}H and ^{13}C NMR data (see Table 2). The chemical shift for the dad hydrogen atom of 5.56 ppm is typical for the bridgehead position at C(14). Complexes **2** of glyoxal-derived dad show this resonance between 5.74 and 6.23 ppm, whereas values from 8.48 to 8.76 ppm were observed for the hydrogen at the sp^2-hybridized imine carbon. The signal from the bridgehead carbon C(14) in **2d** at 51.9 ppm shows a ^1J(C,H) of 147 Hz. The corresponding geminal coupling the bridgehead hydrogen to the C–C connected alkyne carbon C(10) has a value of 5.4 Hz. The signal at 180.4 ppm from the sp^2-hybridized C(13), the imine carbon which bears the methyl substituent, is shifted downfield by ca. 10 ppm relative to the hydrogen-bearing analogs, which is in the expected range [5].

From these findings it can be concluded that the final isomerization step is fast if the C–C connected bridgehead carbon atom in **2** bears a methyl substituent, but prior to this, and if there is a choice, C–C bond formation occurs only at the unsubstituted imine carbon atom.

TABLE 2

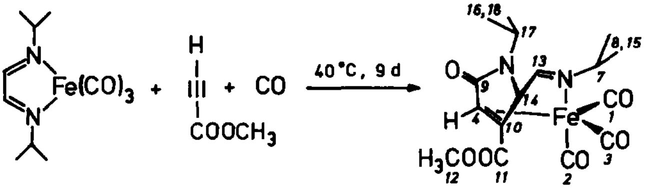
NMR DATA FOR **2d** IN $CDCl_3$: ^1H (233 K, 80 MHz) AND ^{13}C (248 K, 20 MHz) (Positions refer to the numbering given in Scheme 3)

Position	δ(H) (ppm)	δ(C) (ppm)	^1J(C,H) (Hz)	^nJ(C,H) (Hz)
1		203.9	-	-
2		205.6	-	-
3		200.7(br)	-	-
4		193.2	-	6.7
5		177.3	-	3.6
6 [a]	3.87(s)	52.3	148	-
7	4.48(m)	61.9	141	[b]
8 [a]	1.20(d)	21.7(br)	126	[b]
9		204.5(br)	-	-
10		126.9	-	5.4
11		160.1	-	3/3
12 [a]	3.81(s)	51.4	147	-
13		180.4	-	[b]
14	5.56(br)	51.9	147	[b]
15 [a]	1.20(d)	21.7(br)	126	[b]
16 [a]	1.37(d)	20.2(br)	126	[b]
17	4.15(m)	43.8	143	[b]
18 [a]	1.37(d)	20.2(br)	126	[b]
19	2.52(br)	25.5(br)	[b]	[b]

[a] Individualized assignments for signals are tentative. [b] Not determined due to insufficient S/N ratio.

In all reactions previously described, acetylenedicarboxylate was used as the alkyne component because it is readily available and its reactivity leaves nothing to be desired. Depending on the nature of the dad in complexes **1**, the reaction temperatures necessary for practically immediate C–C connecting reactions range from −20 down to −78°C. When one of the electron-withdrawing ester groups is replaced by hydrogen, as in methyl propynoate, much more forcing conditions have to be applied. Heating to +40°C for 9 days and a slight excess of propynoate were necessary for the reaction sequence in Scheme 4 to proceed to completion.

The spectroscopic properties of product **6a**, obtained in 80–90% yield, immediately indicated that it was the pyrrolinone complex. In view of the reaction conditions, it was not surprising that an observable concentration of the [2.2.2] bicyclic compound could not build up. The structure of **6a**, as shown in Scheme 4, can unequivocally be deduced from the NMR spectroscopic data shown in Table 3.



1a

6a

SCHEME 4

TABLE 3

NMR DATA FOR **6a** in $CDCl_3$: ^1H (268 K, 80 MHz) and ^{13}C (248 K, 20 MHz) (Positions refer to the numbering given in Scheme 4)

Position	δ(H) (ppm)	^3J(H,H) (Hz)	δ(C) (ppm)	^1J(C,H) (Hz)	^nJ(C,H) (Hz)
1			209.6	–	–
2			209.9	–	–
3			208.3	–	–
4	4.08(s)	–	51.5 [a]	171	–
7	4.21(m)	6.8	63.4 [a]	141	[b]
8 [c]	1.24(d)	6.8	24.2	126	[b]
9			172.5	–	5/2/2
10			70.1	–	4/4
11			175.1	–	3.5
12	3.69(s)	–	51.5 [a]	147	[b]
13	7.94(d)	2.0	175.2	172	6.5
14	4.92(d)	2.0	63.4 [a]	158	[b]
15 [c]	0.97(d)	6.8	22.1	128	[b]
16 [c]	1.30(d)	6.6	21.9	128	[b]
17	3.87(m)	6.6	43.3	140	[b]
18 [c]	1.08(d)	6.6	19.9	126	[b]

[a] Pairs of signals superimposing one another. [b] Not determined due to insufficient S/N ratio. [c] Individualized assignments for respective pairs of signals are tentative.

Only one of the two possible regioisomeric products is observed. The resonance of the former terminal alkyne proton, H(4) according to the numbering scheme in **6a**, gives a sharp singlet at 4.08 ppm. This alone is strong evidence, since in case of the opposite orientation of the alkyne a vicinal coupling to H(14) should be observed. The C,H couplings in the ^{13}C NMR spectra corroborate the structural assignment. C(4) shows only a coupling to H(4), of 171 Hz. The splitting pattern for C(9) indicates three couplings to H(4), H(14), H(17), respectively, while the C(10) signal exhibits a pseudo triplet structure which must result from two equally large couplings to H(4) and H(14).

Experimental

Spectra were recorded 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 [6], and are accurate to within ±0.5 cm^{-1}; NMR (^1H, ^{13}C, ^{31}P) were recorded with Bruker WP 80 SY WG, and WM 300 spectrometers, chemical shifts (ppm, δ-scale) for ^1H and ^{13}C are relative to internal TMS, for ^{31}P, ppm values are positive downfield from external $P(OMe)_3$. For mass spectra a Varian 311A (FD mode) spectrometer was used. Elemental analyses were performed by the Microanalytical Laboratory Dornis and Kolbe, Mülheim a.d. Ruhr, Germany. All reactions were carried out in de-aerated, dried solvents. Preparation of the starting complexes $(dad)Fe(CO)_3$ (**1**) has been described previously [7].

$\overline{N(CH_2CMe_3)C(O)C(COOMe)}\underline{=C(COOMe)C(Me)C(Me)=N(CH_2CMe_3)Fe}\{(CO)_2[P(OMe)_3]\}$ *(**5b**)*

A solution of 0.70 g (1.92 mmol) of **1b** in 10 ml of tetrahydrofuran (THF) was cooled to −20°C, and one equivalent of $P(OMe)_3$ was added. Cooling was maintained as a solution of 0.24 ml (1.95 mmol) of dimethyl acetylenedicarboxylate in 40 ml of THF was slowly added. After evaporation of the solvent at −20 °C, the residue was washed with four 10 ml portions of cold n-hexane and dried in vacuo. The IR (ν(CO) in $CHCl_3$ 2035.5, 1981.5 cm^{-1}) spectrum of the crude ochre-coloured product (1.05 g, 87%) indicated that it consisted primarily of the [2.2.2] bicyclic intermediate **4b**. After three consecutive washings with diethyl ether at −70 °C the solid dissolved in cold acetone and the solution was filtered then cooled in a dry ice slurry to give 86 mg of yellow, fine crystalline **5b**. 72 mg of identical material crystallized from the concentrated mother liquor. Crystalline **4b** could not be obtained. Total yield **5b** 158 mg (13%). IR ν(CO) in $CHCl_3$ 2002.5, 1945.5 cm^{-1}, ν(CO) in KBr: 1997, 1933 cm^{-1}; MS (FD mode): *m/e* 630 (M^+); for ^1H and ^{13}C NMR data cf. Table 1; $^{31}P\{^1H\}$ NMR ($CDCl_3$, 248 K, 32.5 MHz): 24.40 ppm. Analysis found: C, 49.72; H, 6.48. $C_{26}H_{43}O_{10}N_2FeP$ (630.46) calcd.: C, 49.53; H, 6.88%.

N(t-Bu)C(O)Fe[(CO)$_3$]C(COOMe)=C(COOMe)CHCH=N(t-Bu) (**2c**)

A solution of 0.52 g (1.69 mmol) of **1c** in 15 ml of tetrahydrofuran (THF) was cooled to −15 °C under an atmosphere of CO and a solution of 0.20 ml (1.63 mmol) of dimethyl acetylenedicarboxylate in 40 ml of THF was added during 1.5 h. After evaporation of the solvent in vacuo, the residue was washed at −5 °C with five 10 ml portions of n-hexane, then, at −70 °C, with 5 ml of methanol, and dried in vacuo. Spectroscopy of the crude complex **2c**, which was obtained as light yellow powder (yield 0.54 g, 67%), revealed the presence of minor unidentified impurities. Since **2c** was evidently very labile, in solution and in the solid state, not only rearranging to **3c** (IR: ν(C≡O) in $CHCl_3$: 2063.5, 2000.0, 1973.0 cm^{-1}; in KBr ν(C≡O): 2053, 1990, 1965 cm^{-1}, ν(C=O): 1710, 1692 cm^{-1}), but also decomposing to a major extent, further purification procedures were avoided, and the following spectroscopic data were obtained from the raw product. IR: ν(C≡O) in $CHCl_3$: 2083.5, 2028.5 (vbr) cm^{-1}; in KBr ν(C≡O): 2079, 2020 (vbr) cm^{-1}, ν(C=C): 1585 cm^{-1}; MS (FD mode) *m/e* 478 (M^+); ^1H NMR ($CDCl_3$, 233 K, 80 MHz): δ 8.60 (1H, d, CH=N, ^3J(H,H) 5.8 Hz), 6.23 (1H, d, bridgehead-H, ^3J(H,H) 5.8 Hz), 3.89/3.80 (3H/3H, s/s, ester-OCH_3), 1.44 (18H, s, 2 × t-Bu); ^{13}C NMR ($CDCl_3$, 233 K, 20 MHz, BB- and gated decoupling; resonances of the C-atoms of the bicyclic frame are referred to by the numbering given for **4a** in Scheme 2): δ 205.8, 204.4, 201.6 (CO ligands), 205.3 (C(9), *J*(C,H) 10.1 Hz), 194.3 (C(4), *J*(C,H) 6.9 Hz), 177.6 (ester COO at C(4), *J*(C,H) 3.9 Hz), 170.8 (C(13), *J*(C,H) 172, and 3.6 Hz), 160.4 (ester COO at C(10), *J*(C,H) 4, and 4 Hz), 127.5 (C(10), *J*(C,H) 5.7 Hz), 65.7/59.2 (quaternary C t-Bu), 56.4 (C(14), *J*(C,H) 141, and 14.2 Hz), 52.6/51.8 (ester OCH_3, *J*(C,H) 148/147 Hz), 31.4/29.2 (CH_3 t-Bu, *J*(C,H) 127 Hz).

N(i-Pr)C(O)Fe[(CO)$_3$]C(COOMe)=C(COOMe)CHC(Me)=N(i-Pr) (**2d**)

The procedure described above for **2c** was used starting with 0.52 g (1.77 mmol) of **1d** and 0.22 ml (1.79 mmol) of acetylenedicarboxylate at −25 to −15 °C. The cooling was maintained as the solvent was evaporated in vacuo and the residue was washed with n-hexane then with ether (2 ×), and dried in vacuo to give 630 mg (77%) of a light yellow raw product. All attempts at recrystallization from solvents or solvent mixtures that had been used successfully in other cases failed, resulting only in rearrangement and unspecific decomposition. As with **2c**, the spectral data were therefore obtained from the slightly impure raw product. IR: ν(C≡O) in $CHCl_3$: 2085.0, 2026.0 (vbr) cm^{-1}; ν(C≡O) in KBr: 2080, 2015 (vbr) cm^{-1}, ν(C=C): 1575 cm^{-1}. MS (FD mode) 464 (M^+). For ^1H and ^{13}C NMR data cf. Table 2.

$N(i\text{-}Pr)C(O)CH{=}C(COOMe)CHCH{=}N(i\text{-}Pr)Fe(CO)_3$ (**6a**)

A solution of 1.20 g (4.28 mmol) of **1a** and 0.40 ml (4.49 mmol) of methyl propynoate (Aldrich, GC 99%) in 30 ml of toluene was heated to 40°C under an atmosphere of CO. After 3 days another 0.08 ml (0.45 mmol) of the propynoate was added. After a total of 9 days at 40°C the originally deep red solution had become orange, and the IR spectrum indicated almost complete consumption of **1a**. The solution was evaporated to dryness under vacuum, and the residue was washed under argon with five 10 ml portions of n-hexane, then with cooling with a little methanol, in order to remove residual starting materials. The raw product was dissolved in 5 ml of warm methanol, and the solution was filtered, and cooled to −30°C, to give 0.89 g (53%) of orange crystals. From the concentrated mother liquor another 0.62 g (37%) **6a** of somewhat lower purity were obtained. IR: ν(C≡O) in $CHCl_3$: 2056.0, 1994.0, 1973.0 cm^{-1}; ν(C≡O) in KBr: 2046, 1990, 1959 cm^{-1}, ν(C=O): 1698, 1658 cm^{-1}. MS (FD mode): m/e 392 (M^+). For ^1H and ^{13}C NMR data cf. Table 3. Analysis found: C, 49.95; H, 5.10; N, 7.20; Fe, 14.15. $C_{16}H_{20}FeN_2O_6$ (392.19) calcd.: 49.00; H, 5.14; N, 7.14; Fe, 14.24%.

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