Journal of Organometallic Chemistry, 302 (1986) 59–64
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

1,5-DIHYDROPYRROL-2-ONES FROM (1,4-DIAZA-1,3-DIENE)TRICARBONYLIRON AND ALKYNE

III *. STEREOSPECIFIC LIGAND INCORPORATION ON FORMATION OF THE [2.2.2]-BICYCLIC INTERMEDIATE

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(Received August 15th, 1985)

Summary

Examples of the [2.2.2.]-bicyclic intermediate formed in the reaction of (1,4-diaza-1,3-diene)tricarbonyliron complexes, (dad)Fe$(CO)_3$, with dimethyl acetylenedicarboxylate and an additional ligand L [L = ^{13}CO, $P(OMe)_3$] have been isolated and characterized by elemental analysis, field desorption mass spectrometry and NMR (^{1}H, ^{13}C, ^{31}P) and IR spectroscopy. The ligand L which completes the octahedral coordination around the bridge head iron atom, is incorporated stereospecifically *trans* to the inserted carbonyl group of the [2.2.2] system. This is found to be the case with complexes of diazadienes of differing donor/acceptor abilities and also for the two electronically different ligands L. From the results it is concluded that a stereochemically rigid intermediate is initially formed, which for steric reasons and so in a kinetically controlled reaction, allows access of L to the iron from only one direction, consequently closing the [2.2.2] structure. Conclusive evidence that the reaction is kinetically controlled is provided by the isolation of two isomeric complexes (**2b** and **7**, respectively) from the reactions of (dad)Fe$(CO)_3$ in the presence of $P(OMe)_3$, and of (dad)Fe$[P(OMe)_3](CO)_2$ from reaction in the presence of CO.

Introduction

Under an atmosphere of CO, (1,4-diaza-1,3-diene)tricarbonyliron complexes, e.g. **1**, react with an electron deficient alkyne, e.g. dimethyl acetylenedicarboxylate, to give finally (1,4-dihydropyrrol-2-one)tricarbonyliron complexes **3** [1,2]. With di-

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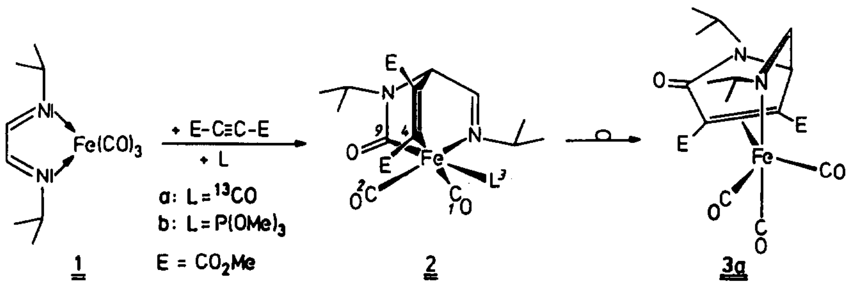
* For part II see ref. 1.



SCHEME 1

azadienes having at least one aldimino group, C(H)=N, a thermally labile [2.2.2]-bicyclic intermediate **2** (cf. Scheme 1) can be isolated at lower temperatures.

The highly functionalized α,β-unsaturated γ-lactams, such as in **3a**, which can be displaced from the metal at elevated temperatures by other ligands, e.g. diazadiene, $P(OMe)_3$, or CO, are of wide synthetic interest [3]. Obviously, the intermediate **2** plays a key role in their metal-mediated synthesis, and so we are studying the properties of **2** and details of the mechanism of its formation. When the reaction depicted in Scheme 1 is performed in the presence of trimethylphosphite instead of CO, the bicyclic species is stabilized, and in the case of **2b** the structure could be determined by X-ray methods [1]. It turned out that the entering phosphite ligand had been incorporated stereospecifically *trans* to the inserted carbonyl group, and we now present evidence that this positional preference is general, and is not controlled by electronic factors, a conclusion that had previously been suggested by the structural features of **2b** [1].

Results and discussion

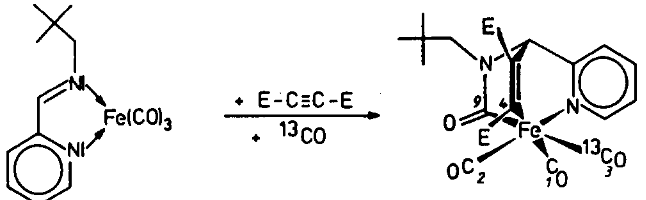
With the structure of **2** being firmly established it is possible to assign the ^{13}C NMR resonances of all individual C-atoms bonded to the iron (cf. Table 1). The C(9) resonance [4] of the inserted carbonyl group is easily identified in the proton

TABLE 1

SELECTED ^{13}C NMR DATA FOR COMPOUNDS **2a**, **2b**, **5**, AND **7**: CHEMICAL SHIFTS AND C,P COUPLING CONSTANTS FOR THE CARBON ATOMS DIRECTLY BONDED TO THE IRON (The position of the trimethylphosphite ligand (tmp) is indicated for **2b** and **7**)

Nucl. [a]	**2a**	**2b**		**5**	**7**	
	δ (ppm)	δ (ppm)	$^2J(C,P)$ (Hz)	δ (ppm)	δ (ppm)	$^2J(C,P)$ (Hz)
1	203.66	208.80	18.1	203.60	tmp	
2	205.49	210.34	19.9	205.75	211.09	27.9
3	200.49 [b]	tmp		200.38 [b]	205.08 [b]	17.7
4	192.55	197.67	21.8	189.62	202.98	41.4
9	204.22	210.91	78.5	204.82	210.06	30.5

[a] Numbering according to the X-ray structure of **2b** [1], cf. Scheme 1. [b] Position of the ^{13}C-labelled CO ligand.



4 5

SCHEME 2

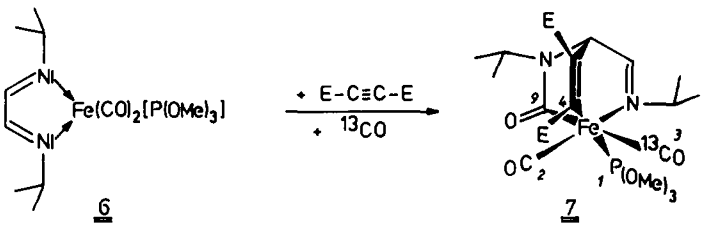
coupled spectra from its ${}^3J$(C,H) of 9–10 Hz, which is absent in the C(1), C(2), and C(3) resonances of the terminal CO ligands. For the latter the sequence of chemical shift is related to the influence of their respective *trans*-ligands. Thus, C(2), *trans* to the strongly σ-donating imine-N-atom, resonates at lowest field, while C(3), *trans* to carbonyl-C(9), experiences the least downfield shift, and that for C(2), *trans* to σ-vinyl-C(4), is intermediate. The shift information in Table 1 for the other complexes described below is consistent with these observations, and corroborates the assignments.

To find out if the stereospecificity observed for phosphite incorporation in **2b** would also be found when CO is the entering ligand, the reaction in Scheme 1 was performed under a CO-atmosphere enriched in ^{13}CO. To prevent the resulting **2a** from isomerizing into **3a** the temperature was kept below −10°C during reaction and isolation. The IR spectrum even of the crude product in the reaction mixture indicated that only one of the terminal CO ligands contained the ^{13}CO label. The ^{13}C NMR spectrum confirmed that neither CO-equilibration nor isomerization had taken place, and the C(3) resonance alone was enhanced in intensity relative to the compound with natural isotopic distribution [2].

An additional experiment proved that the stereospecificity of the ligand incorporation is not only independent of the nature of the entering ligand (CO as compared to trimethyl phosphite), but also of the type of diazadiene in the starting tricarbonyliron complex. In **4**, (2-pyridinealdehyde-neopentylimine)Fe(CO)$_3$ (cf. Scheme 2) one of the two C=N moieties of the diazadiene is an integral part of an aromatic 6π-system. Thus, only one of the two imine carbon atoms is available to form a bridge head in the [2.2.2]-bicyclic system, because if the reaction took place at the heteroaromatic ring the aromatic resonance stabilization energy would be sacrificed.

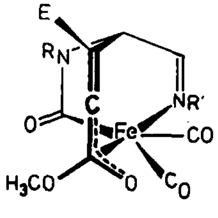
Like **1**, dimethyl acetylenedicarboxylate in THF reacted smoothly with **4** under CO enriched in ^{13}CO. The analytical data for the product, isolated in more than 60% yield, are in full agreement with structure **5** in Scheme 2. The ^{1}H NMR resonances of the pyridine protons, at δ 8.56, 7.86, 7.56, and 7.22 ppm, respectively, show that the aromatic 6π-system is intact. Comparison of the ^{12}CO stretching frequencies in the IR spectra of **2a** [ν(CO) 2088, 2029br cm^{-1} in CHCl$_3$] and **5** [ν(CO) 2089.5, 2030br cm^{-1} in CHCl$_3$], and of their relevant ^{13}C NMR data (cf. Table 1) suggests that, in spite of the different donor/acceptor properties between the two original diazadienes, the electronic and steric situation around the central iron atom in the two bicyclic complexes must be very similar.

To account for the observed stereospecificity of ligand incorporation we assume that the alkyne addition and concomitant, but not necessarily simultaneous CO



SCHEME 3

insertion precede to give an initial, stereochemically rigid, intermediate. Inspection of a molecular model shows that stereoelectronically structure **A** is a possible candidate. The acetylenic C-atom in **A** (shown bold) is *sp*-hybridized, with its two *p*-orbitals belonging to the mutually orthogonal C=C π-bond and the η^3-hetero-π-allyl group.



A

But regardless of the exact nature of the primary intermediate, before steric effects alone can be held responsible for the directional specificity of the entering ligand, as we concluded from the outcome of the experiments described above, it is necessary to provide rigorous proof that the product formation is kinetically controlled.

Under kinetic control it should be possible to vary the reactants of Scheme 1 as shown in Scheme 3 so as to obtain a product isomeric with **2b**, in which two of the monodentate ligands have mutually exchanged their positions.

Fortunately, the trimethylphosphite substituted complex **6** was at hand from investigations on P-donor substituted (dad)carbonyliron complexes [5]. When **6** was treated with dimethyl acetylenedicarboxylate in THF under a ^{13}CO-enriched atmosphere, the yellow crystalline product **7** was isolated in more than 85% yield. The elemental analysis and mass spectrum of **7** confirmed that it was identical in composition to **2b**. The spectroscopic properties of **7** indicate structural analogy with **2b**, but show significant differences. From inspection of the ^{13}C NMR spectrum it was obvious that only one of the terminal CO ligands carried a ^{13}C label. Comparison of the chemical shifts and the coupling constants in **7** with those of **2a**, **5**, and **2b**, especially ^2J(C,P) (cf. Table 1), provides sufficient information to establish the structural configuration as shown in Scheme 3, i.e., with the phosphite *trans* to the σ-vinyl C(4) atom. This follows from the significant downfield shift of the C(4) resonance of 5.31 ppm relative to **2b**, and from the ^2J(C,P) coupling constant of 41.4 Hz, which has the high value typical of *trans*-coupling. Of interest in this connection are the very unusual high values of the ^2J(C,P) *cis*-couplings to C(2) and C(9), 27.9 and 30.5 Hz, respectively. Only C(3), which bears the ^{13}C label, exhibits a *cis*-coupling constant of ^2J(C,P) 17.7 Hz which is in the normal range [6].

Experimental

Spectra were recorded using the following spectrometers: MS, Varian MAT 311 A; NMR, Bruker WP 80 SY WG: chemical shifts (ppm, δ-scale) for ^{1}H and ^{13}C are based on internal TMS standard, for ^{31}P, ppm values are given positive downfield from P(OMe)$_3$ measured under identical conditions (solv., temp.); IR, Perkin–Elmer 583. Elemental analyses were performed by Mikroanalytisches Labor Dornis und Kolbe, Mülheim a. d. Ruhr.

Syntheses

De-aerated, dried solvents were used throughout. **2b** has been described previously [1]. The ^{13}CO labelled compounds **2a**, **5**, and **7** were prepared by adapting the procedure given for the unlabelled **2a** [2] in the following way. A three-necked reaction flask was charged with the solid complex **1**, **4** or **6** under argon and in a cold bath below −15°C. One neck was connected to a pressure-equalizing dropping funnel with an additional stopcock in the pressure equalizing tube, containing an equivalent amount of dimethyl acetylenedicarboxylate in the total volume (ca. 60–70 ml) of tetrahydrofuran (THF) solvent under argon. The other neck was connected through a manifold valve to the vacuum line, to a given volume of ^{13}CO, and to the ^{12}CO cylinder, to allow for consecutive evacuation, expansion of ^{13}CO, and filling with ^{12}CO to normal pressure. After all the THF solution had been slowly added the solvent was removed in vacuo. The crude products were washed with precooled solvents as specified below, and subsequently dissolved in methanol at −10°C. The solution was filtered and kept at −78°C to give crystals of the required product.

*rac-N(i-Pr)-d-C(O)-Fe[b-(^{13}CO)-cf-(CO)$_2$]-e-C(CO$_2$Me)=C(CO$_2$Me)-CH-CH=a-N(i-Pr) (**2a**) [7]*

Starting with 0.4 g (1.41 mmol) **1**; consecutive washings with n-hexane and methanol; yield after recrystallization 0.35 g (55%) **2a**. Except for the spectroscopic changes due to the ^{13}CO content, the properties of **2a** are identical with the unlabelled compound [2].

*rac-N(CH$_2$CMe$_3$)-d-C(O)-Fe[b-(^{13}CO)-cf-(CO)$_2$]-e-C(CO$_2$Me)=C(CO$_2$Me)-CH-C-a-NCHCHCHCH (**5**) [7]*

Starting with 1.12 g (3.54 mmol) **4**; consecutive washings with n-hexane, ether, and methanol; yield after recrystallization 1.06 g (62%) **5**. MS (FD-mode): *m/e* 486(^{12}CO), 487(^{13}CO) (M^+); IR (CHCl$_3$, cm^{-1}) ν(^{12}CO) 2089.5, 2030br; ^{1}H NMR (80.13 MHz, 283 K, CDCl$_3$, ppm): δ 8.56 (1H, m), 7.86 (1H, m), 7.56 (1H, m), 7.22 (1H, m), 5.89 (1H, s), 3.85 (3H, s), 3.75 (3H, s), 3.25 (2H, d, *J*(H,H) 1.9 Hz), 0.87 (9H, s); Analysis Found: C, 51.80; H, 4.67; N, 5.88. $C_{21}H_{22}FeN_2O_8$ (486.26) calcd.: C, 51.87; H, 4.56; N, 5.76%.

*rac-N(i-Pr)-d-C(O)-Fe{b-[^{13}CO]-c-[P(OMe)$_3$]-f-[CO]}-e-C(CO$_2$Me)-=C(CO$_2$Me)-CH-CH=a-N(i-Pr) (**7**) [7]*

Starting with 0.61 g (1.62 mmol) **6**; washing with n-hexane; yield after recrystallization 0.76 g (86%) **7** of m.p. 117°C (dec.); MS (FD-mode) *m/e* 546(^{12}CO), 547(^{13}CO) (M^+); IR (CHCl$_3$, cm^{-1}) ν(^{12}CO) 2037, 1986.5; ^{1}H NMR (80.13 MHz, 300 K, CDCl$_3$, ppm): δ 8.41 (1H, dd, *J*(H,H) 5.4, *J*(H,P) 4.3 Hz), 5.83 (1H, d, *J*(H,H) 5.4 Hz), 4.81 (1H, m, *J*(H,H) 6.7 Hz), 4.10 (1H, m, *J*(H,H) 6.5 Hz), 3.79 (3H, s), 3.78 (9H, d, *J*(H,P) 10.4 Hz), 3.71 (3H, s), 1.28 (3H, d, *J*(H,H) 6.6 Hz), 1.08 (6H, 2d), 1.04 (3H, d, *J*(H,H) 6.8 Hz); ^{31}P NMR (32.442 MHz, 248 K, $CDCl_3$) 17.55 ppm downfield from $P(OMe)_3$, $^3J(P,H)$ 10.4, $^4J(P,H)$ 4.3, $^2J(P,C(3))$ 17.7 Hz; Analysis Found: C, 43.83; H, 5.74; N, 5.24. $C_{20}H_{31}FeN_2O_{10}P$ (546.29) calcd.: C, 43.97; H, 5.72; N, 5.13%.

Acknowledgment

Financial support from the Deutsche Forschungsgemeinschaft (Project No. Fr 409/3-1) and the Fonds der Chemischen Industrie is gratefully acknowledged.

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4 The numbers ascribed to the Fe-bonded carbon atoms of **2** in Scheme 1 are adopted from the numbering scheme in the X-ray molecular structure of **2b** in ref. 1, and are used throughout the rest of the text to identify the respective positions.
5 Unpublished results; we thank Mrs. I. Pein for supplying a generous sample of **6**.
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7 The italicized lower case letters indicate the relative positions in the octahedral coordination sphere around the central iron atom, where *a* and *f*, *b* and *d*, and *c* and *e*, respectively, are mutually *trans*, cf. IUPAC rule 7.512.