

parison to the Ti-C<sub>2</sub>H<sub>5</sub> distance involving the inherently larger Ti(O) in ( $\eta^7$ -C<sub>7</sub>H<sub>7</sub>)Ti(C<sub>2</sub>H<sub>5</sub>)(dmpe), 2.211 (5) Å,<sup>29</sup> permits the conclusion that CpVMe(dmpe) contains a somewhat long V-CH<sub>3</sub> bond.

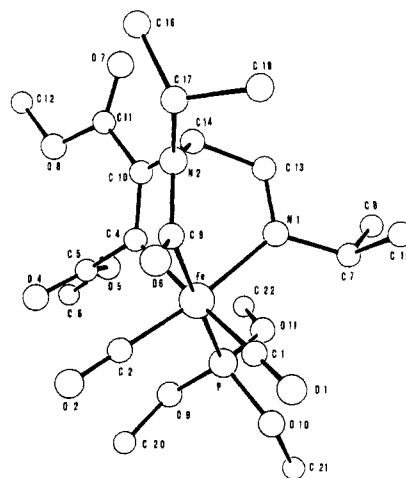
The distinctly low V-Me C-H stretching frequency in CpVMe(dmpe) thus finds no explanation in the X-ray study. We suggest that one of the half-filled orbitals is not only metal localized but also V-C and C-H antibonding. This would account for the IR anomaly, the lack of observation of the V-CH<sub>3</sub> proton resonance, and also the long V-C distance.

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**Supplementary Material Available:** Tables of atomic positional parameters and bond lengths and angles for (C<sub>5</sub>H<sub>5</sub>)-VCH<sub>3</sub>(Me<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PM<sub>2</sub>), a listing of F<sub>o</sub> and F<sub>c</sub> for CpVMe(dmpe), and tables of elemental analyses and magnetic susceptibility data (18 pages). Ordering information is given on any current masthead page.

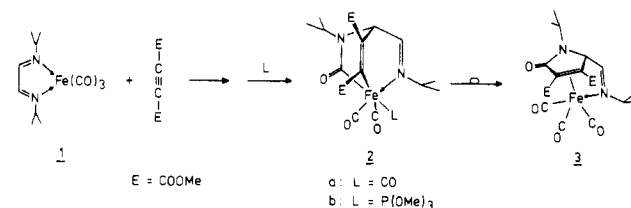
(28) Fachinetti, G.; Floriani, C.; Chiesi-Villa, A.; Guastini, A. *Inorg. Chem.* 1979, 18, 2281.

(29) Green, M. L. H.; Hazel, N. J.; Grebenik, P. D.; Mtetwa, V. S. B.; Prout, K. J. *Chem. Soc., Chem. Commun.* 1983, 356.



**Figure 1.** The molecular structure of 2b. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Fe-C(4) = 2.023 (3), Fe-C(9) = 2.023 (3), Fe-N(1) = 2.030 (2), Fe-C(1) = 1.808 (3), Fe-C(2) = 1.767 (3), Fe-P = 2.260 (1), C(4)-C(10) = 1.337 (4), C(9)-N(2) = 1.362 (4), N(1)-C(13) = 1.269 (4), C(9)-Fe-P = 178.8 (1), C(1)-Fe-C(4) = 173.7 (1), C(2)-Fe-N(1) = 170.8 (1), C(4)-Fe-C(9) = 87.6 (1).

### Scheme I



## 1,5-Dihydropyrrol-2-ones from (1,4-Diaza-1,3-diene)tricarbonyliron and Alkyne. 2.<sup>1</sup> Structure of a [2.2.2] Bicyclic Intermediate with Iron at the Bridgehead Position

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**Summary:** (1,4-Diaza-1,3-diene)tricarbonyliron complexes react with electron-deficient alkynes under an atmosphere of CO to give a thermally labile, bicyclic intermediate which rearranges to a (1,5-dihydropyrrol-2-one)tricarbonyliron complex. With trimethyl phosphite instead of CO, the intermediate is stabilized, and it has been possible to determine its structure by X-ray crystallography.

Until recently it was thought that C-C bond-forming reactions of 1,4-diaza-1,3-dienes (dad) in the coordination sphere of transition metals were only feasible in binuclear complexes with the dad coordinated to both metal centers in an unsymmetrical six-electron mode, involving the  $\pi$ -electrons of one C=N moiety.<sup>3,4</sup> The reaction of (dad)-

tricarbonyliron complexes 1, in which the dad is coordinated in the chelating 4-electron mode through the nitrogen lone pairs only, with dimethyl acetylenedicarboxylate under an atmosphere of CO, finally yielding tricarbonyliron complexes of 1,5-dihydropyrrol-2-ones (e.g., 3, see Scheme I) suggests that this is not the case.<sup>1</sup> This is supported by the observation of a thermally labile mononuclear intermediate 2a. In view of the importance of this reaction,<sup>5</sup> we decided to investigate the structure of 2a. The <sup>13</sup>C NMR resonances of this intermediate could be fully assigned from the proton-coupled spectra and revealed shift differences of up to 125.5 ppm with respect to the isomerized product 3 (cf. Figure 2), consistent with a [2.2.2] bicyclic structure. Unfortunately, the structure of this intermediate could not be determined by X-ray methods. However, when the reaction was performed in the presence of trimethyl phosphite,<sup>6</sup> a compound with very similar spectroscopic properties to 2a was isolated.<sup>7</sup>

(3) Frühauf, H.-W.; Landers, A.; Goddard, R.; Krüger, C. *Angew. Chem.* 1978, 90, 56; *Angew. Chem., Int. Ed. Engl.* 1978, 17, 64.

(4) van Koten, G.; Vrieze, K. *Adv. Organomet. Chem.* 1982, 21, 151.

(5) Not only are the 1,4-diaza-1,3-dienes easily accessible starting materials, but the pyrrolinones formed are of considerable synthetic interest. See: (a) Kochar, K. S.; Carson, H. J.; Clouser, K. A.; Elling, J. W.; Grames, L. A.; Parry, J. L.; Sherman, H. L.; Braat, K.; Pinnick, H. W. *Tetrahedron Lett.* 1984, 25, 1871. (b) Rio, G.; Masure, D. *Bull. Soc. Chim. Fr.* 1972, 4598 and references cited therein.

(6) Preparation of 2b: A solution of 0.87 g (2.4 mmol) of (glyoxalbis(isopropylimine)tricarbonyliron 1<sup>12</sup> in ca. 20 mL of tetrahydrofuran (THF) was cooled to -15 °C. Then 0.283 mL (298 mg, 2.4 mmol) of trimethyl phosphite (z. Synth.; E. Merck, Darmstadt) was added, followed slowly from a dropping funnel by a solution of 341 mg (2.4 mmol) of dimethyl acetylenedicarboxylate in 30 mL of THF, keeping the reaction temperature below -5 °C. After removal of the solvent in vacuo, the vesicular residue was redissolved in 25 mL of methanol at 0 °C. After the mixture was slowly cooled to -78 °C, 0.65 g of a light yellow crystalline powder was precipitated. It was dried in vacuo. The concentrated mother liquor yielded an additional 0.11 g; total yield 0.76 g (58%).

(1) Part 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) (a) Universität Duisburg. (b) Max-Planck-Institut für Strahlenchemie. (c) Max-Planck-Institut für Kohlenforschung. (d) Present address: Department of Chemistry, Lisbon University, Lisbon, Portugal.

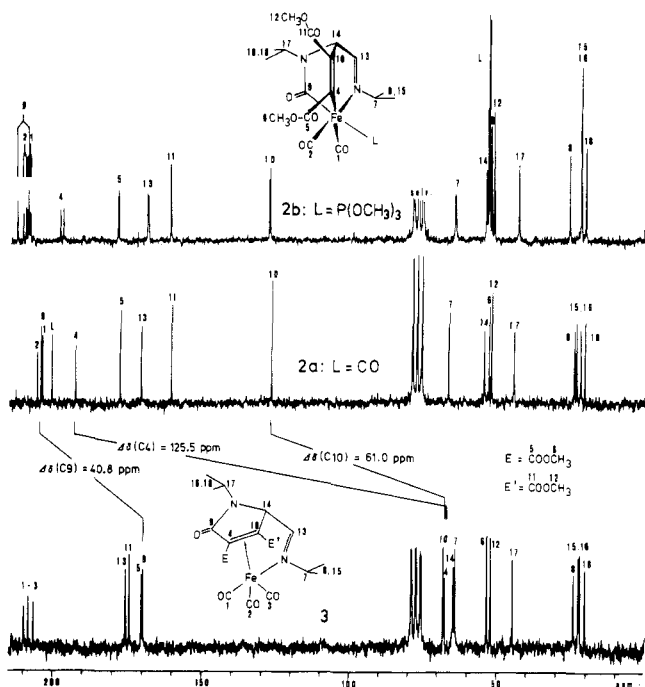


Figure 2. The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of **2b**, **2a**, and **3** (20.15 MHz, 248 K,  $\text{CDCl}_3$  solvent signals are truncated).

The compound is stable and crystalline, and its structure has been determined by X-ray crystallography (Figure 1).<sup>8</sup>

The results of the X-ray analysis show that one molecule each of CO and alkyne have combined with the (dad)iron unit to give a molecule with a [2.2.2] structure, as indicated by its NMR spectrum. The coordination around the iron atom is a distorted octahedral with the phosphite ligand occupying a position trans to the carbon atom C(9) of the inserted carbonyl group. There is, however, no evidence that the positional preference of the phosphite ligand is a result of C(9) being a better acceptor than its neighbor C(4), since both atoms are equidistant from iron ( $\text{Fe}-\text{C}(4) = \text{Fe}-\text{C}(9) = 2.023$  (3) Å). Bond distances indicate that double bonds are retained at N(1)-C(13) (1.269 (4) Å) and between C(4) and C(10) (1.337 (4) Å), the original site of the alkyne bond.<sup>1,9</sup> Even though both carboxymethyl groups are planar ( $\pm 0.02$  Å), they do not appear to enter into  $\pi$ -conjugation with the double bond between them since the plane defined by the carbomethoxy group at C(4) lies almost perpendicular to the plane of the double bond,

(7) **2b**: mp 146 °C dec; mass spectrum (FD mode),  $m/e$  546 ( $M^+$ ); IR ( $\text{CHCl}_3$ ,  $\text{cm}^{-1}$ )  $\nu_{\text{CO}}$  2040.5, 1989;  $^1\text{H}$  NMR (80.13 MHz, 300 K,  $\text{CDCl}_3$ )  $\delta$  8.48 (1 H13, dd,  $J_{\text{H,H}} = 5.2$  Hz,  $J_{\text{H,P}} = 3.0$  Hz), 5.77 (1 H14, d,  $J_{\text{H,H}} = 5.2$  Hz), 4.76 (1 H7, m,  $J_{\text{H,H}} = 6.7$  Hz), 3.97 (1 H17, m,  $J_{\text{H,H}} = 6.6$  Hz), 3.76 (3 H6, s), 3.73 (3 H12, s), 3.71 (9 H, phosphite OMe, d,  $J_{\text{H,P}} = 10.4$  Hz), 1.27 (9 H16/18, d,  $J_{\text{H,H}} = 6.6$  Hz), 1.04 (3 H8 (or H15), d,  $J_{\text{H,H}} = 6.7$  Hz), 1.02 (3 H15 (or H8), d,  $J_{\text{H,H}} = 6.7$  Hz);  $^{31}\text{P}$  NMR (32.442 MHz, 248 K,  $\text{CDCl}_3$ )  $\delta$  14.75 ppm downfield from  $\text{P}(\text{OMe})_3$  ( $^3J_{\text{P,H}} = 10.4$  Hz,  $^4J_{\text{P,H}} = 29$  Hz). Anal. Calcd for  $\text{C}_{20}\text{H}_{31}\text{N}_2\text{O}_{10}\text{PFe}$ : C, 43.97; H, 5.72; N, 5.13; Fe, 10.22. Found: C, 43.34; H, 5.99; N, 5.04; Fe, 10.11.

(8) Crystal data for  $\text{N}(i\text{-Pr})\text{C}(\text{O})\text{Fe}[(\text{CO})_2\text{P}(\text{OMe})_3\text{C}(\text{CO}_2\text{Me})=\text{C}$

$(\text{CO}_2\text{Me})\text{CHCH}=\text{N}(i\text{-Pr})$  (**2b**): space group  $P2_1/c$  (No. 14),  $a = 10.065$  (2) Å,  $b = 14.710$  (4) Å,  $c = 17.442$  (2) Å,  $\beta = 98.10$  (1)°,  $Z = 4$ ,  $M_r = 546.3$ ,  $d_{\text{calcd}} = 1.42$  g  $\text{cm}^{-3}$ ,  $\mu(\text{MoK}\alpha) = 7.0$   $\text{cm}^{-1}$ . Pale yellow crystals were grown from concentrated acetone solution. Intensity data were collected on an Enraf-Nonius CAD-4 diffractometer by a  $\theta$ - $2\theta$  scan technique with scan speeds varying from 1 to 10°  $\text{min}^{-1}$  depending on the intensity to standard deviation ratio of a 10°  $\text{min}^{-1}$  prescan. The structure was solved by the heavy-atom method and refined by least-squares to  $R = 0.039$  and  $R_w = 0.046$  (4045 independent observed ( $I \geq 2 \sigma(I)$ ) reflections), where the function minimized was  $w(|F_o| - |F_c|)^2$  and  $w = 1/\sigma^2(F_o)$ . On the final refinement cycle the average shift/error was 0.1, and a subsequent difference Fourier synthesis showed no peaks greater than +0.32 e Å<sup>-3</sup>.

(9) Hoffmann, K.; Weiss, E. *J. Organomet. Chem.* 1977, 128, 399.

and the bond distances C(4)-C(5) and C(10)-C(11) are almost equal.

Evidence for the structural equivalence of **2a** and **2b** was obtained from their  $^{13}\text{C}$  NMR spectra, which are given in Figure 2 together with the spectrum of **3**, the final product when  $L = \text{CO}$ . Inspection of the two uppermost spectra, those of **2a** and **2b**, clearly shows that except for the differences due to the inequivalence of the respective ligands  $L$ , each single resonance in **2a** has its counterpart in the spectrum of **2b**.

The assignments given for **2a** and the assumption of the bicyclic structure were initially based on the chemical shifts and the  $^nJ_{\text{C,H}}$  values observed in the proton-coupled spectra. The additional C,P couplings in **2b** corroborated the partly tentative assignments and even allowed a distinction to be made between the resonances of the two different  $N$ -isopropyl groups since, whereas there is no  $^4J$  coupling to C(17) of the more distant isopropyl group,  $^3J_{\text{C}(7),\text{P}}$  is 5.3 Hz.

The observed C,P couplings in **2b** deserve some comment. It is well-known that in coordination compounds the coupling of nuclei in ligands that are trans to one another are larger than those that are cis related<sup>10</sup> and that coupling is greater where nuclei are connected by  $\pi$ -systems<sup>11</sup>. Both these effects can be clearly observed in **2b**. The bridgehead carbon atom C(14) is the only carbon atom of the bicyclic frame that does not show a phosphorus coupling. C(11), on the other hand, which is also four bonds away from the phosphorus atom, exhibits a  $^4J_{\text{C,P}}$  coupling of 2.3 Hz, presumably as a result of coupling through the  $\pi$ -system. Whereas the three cis  $^2J_{\text{C,P}}$  couplings across the central metal atom are of the order of 20 Hz, the resonance of carbon atom C(9) of the inserted carbonyl group is split by almost 80 Hz. Although there is, to our knowledge, no octahedral, sterically rigid iron complex directly comparable to **2b**, this coupling of 78.5 Hz exceeds the normal range of  $^2J_{\text{C-M-P}}$  couplings by more than 30 Hz; the largest values we have been able to find in the literature were around 40 Hz.<sup>10</sup>

The isomerization of **2a** to **3** results in considerable shifts of the resonances, particularly of C(4), C(9), and C(10), the atoms originally most strongly deshielded due to the Fe-C  $\sigma$ -bonding in **2a**. Comparison of the two structures leads to the formulation that the isomerization proceeds by migration of C(4) from the iron atom to C(9), thus forming the five-membered heterocycle, which in turn coordinates to the iron atom via its C(4)-C(10)  $\pi$ -bond, so retaining the 18-electron count on the metal. In spite of the similarity of **2b** to **2a** it has not been possible to cause a similar isomerization of **2b** to take place, even under extreme reaction conditions.

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**Registry No.** 1, 54446-62-7; **2a**, 95763-40-9; **2b**, 95763-41-0; **3**, 87922-39-2; dimethyl acetylenedicarboxylate, 762-42-5.

**Supplementary Material Available:** Crystal data and details of X-ray data collection, tables of atomic fractional coordinates, thermal parameters, selected interatomic distances and angles, a list of observed and calculated structure factors, and a table of  $^{13}\text{C}$  NMR data for **2a** and **2b** (23 pages). Ordering information is given on any current masthead page.

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(11) Kalinowski, H.-O.; Berger, S.; Braus, S.  $^{13}\text{C}$ -NMR-Spektroskopie"; Georg Thieme Verlag: Stuttgart, FRG, 1984.

(12) Frühauf, H.-W.; Wolmershäuser, G. *Chem. Ber.* 1982, 115, 1070.