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Formation of vinyl and dithioformate metallacycles by insertion of an ester-functionalized alkyne or carbon disulfide into an Fe–H bond: crystal structure of *cis*-[Fe(CH=CHCOOMe)($Ph_2PCH_2CH_2PPh_2$)$_2$][BF_4]

Sílvia S.P. Almeida, Maria T. Duarte, Luísa M.D. Ribeiro, Fiona Gormley, Adelino M. Galvão, João J.R. Fraústo Da Silva, Armando J.L. Pombeiro *

Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, Av. Rovisco Pais, 1096 Lisboa codex, Portugal

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Abstract

Treatment of a THF solution of *trans*-[FeHCl(dppe)$_2$] (dppe = $Ph_2PCH_2CH_2PPh_2$) with HC≡CCOOMe or CS_2, in the presence of Tl[BF_4], forms the vinyl complex *cis*-[Fe(CH=CHCOOMe)(dppe)$_2$][BF_4] or the η^2-dithioformate compound *cis*-[Fe(η^2-S_2CH)(dppe)$_2$][BF_4] respectively. The molecular structure of the former is authenticated by X-ray diffraction analysis.

Keywords: Iron; Alkynes; Carbon disulfide; Metallacycle; Vinyl; Dithioformate

1. Introduction

The chemistry of metallacycles is a challenging area of current research, in view of their significance [1,2] in various fields of organic synthesis and catalysis, biology, photochemistry, etc., and small unsaturated carbon molecules are useful starting materials for their formation.

Within our interest in the investigation of nitrogenase substrates, and related species, by dinitrogen-binding iron sites which can mimic the nitrogenase function (in particular the alternative form which appears to present iron as the sole transition metal in the active S-containing metal centre [3]), we have previously prepared [4] a series of isocyanide complexes, *trans*-[FeH(CNR)(dppe)$_2$][A] (R = alkyl or aryl, A = BF_4 or PF_6; dppe = $Ph_2PCH_2CH_2PPh_2$), by reaction of the appropriate isocyanide in the presence of Tl[A] with *trans*-[FeHCl(dppe)$_2$], a precursor for the dinitrogen complex *trans*-[FeH(N_2)(dppe)$_2$].

We have now extended this type of study to alkynes, i.e. other nitrogenase substrates, and to carbon disulfide, a potential sulfur-source to the metal.

2. Results and discussion

We have found that, in contrast to isocyanides [4], organonitriles, CO, N_2, etc. [5], which bind simply to the metal centre, HC≡CCO_2Me (methyl propiolate) and CS_2 insert into the Fe–H bond to give cyclometallated complexes.

Hence, treatment of a THF solution of *trans*-[FeHCl(dppe)$_2$] with HC≡CCO_2Me (four-fold molar excess), in sunlight and under argon in the presence of Tl[BF_4], leads to the formation of the vinyl complex *cis*-[Fe(CH=CHCOOMe)(dppe)$_2$][BF_4] (1) (Eq. (1)), isolated as a red solid and formulated on the basis of IR, ^{1}H, ^{31}P and ^{13}C NMR spectroscopies, elemental and

* Corresponding author.

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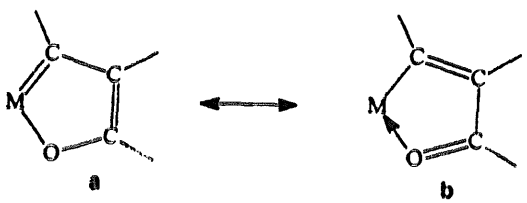
X-ray diffraction analysis [1], its molecular structure being depicted in Fig. 1.

$$trans - [FeHCl(dppe)_2] + HC{\equiv}CCO_2Me + Tl[BF_4] \rightarrow cis - [Fe(CH{=}CHCOOMe)(dppe)_2][BF_4] + TlCl \quad (1)$$

The arrangement around the iron atom is a distorted octahedron with the two *cis* dppe ligands pushing each other away, thus forcing the C(29)–Fe–O(2) angle of the chelating vinyl ligand to a value of 80.0(6)°. The data indicate that the vinyl ligand is coordinated through the α-carbon [Fe–C(29) 1.96(2) Å] and the carbonyl oxygen [Fe–O(2) 2.012(12) Å] of the ester group, forming a five-membered metallacycle which can be represented as a hybrid of the mesomeric forms **a** and **b**. This is also supported by the planarity of the whole vinyl ligand skeleton (mean deviation ±0.011 Å considering the plane including the Fe and all the C and O atoms of the vinyl ligand).



The carbene form **a** has a substantial contribution as indicated by (i) the short Fe–C bond length, 1.96(2) Å, a value significantly smaller than the average one, 2.13 Å, for the single bond Fe–CH_2R [R = C(sp^3)] [8], (ii) the unpronounced difference [0.09(3) Å] between the two C–C bond lengths in the ring (although the C_α29–C_β is smaller than the C_β–C_γ bond), (iii) the elongated C≡O bond [C(24)–O(2) 1.25(2) Å] relative to the average value, 1.19 Å, expected for an ester group [8], and (iv) the low-field ^{13}C NMR of the α-carbon which is observed as a quintet [^2J(CP) = 24.4 Hz] at δ 239.8 ppm (in CD_2Cl_2) relative to $SiMe_4$. This resonance splits into the expected doublet [J(CH) = 144.1 Hz] in the ^{13}C–^1H coupled spectrum. In the ^1H NMR spectrum,

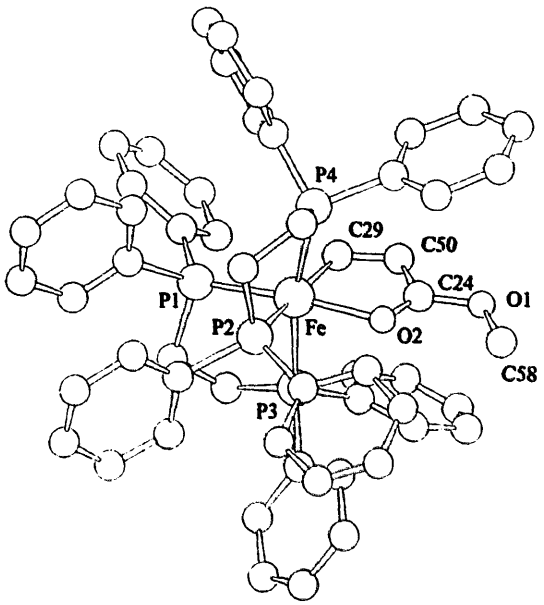


Fig. 1. Molecular structure of the complex cation of *cis*-[Fe(CH=CHCOOMe)(dppe)$_2$][BF_4] (**1**). Selected bond lengths (Å) and angles (°): Fe–C(29) 1.96(2), Fe–O(2) 2.012(12), mean Fe–P 2.305(5), C(29)–C(50) 1.33(2), C(50)–C(24) 1.42(3), C(24)–O(2) 1.25(2), C(24)–O(1) 1.33(2), O(1)–C(58) 1.45(3); C(29)–Fe–O(2) 80.0(6), P(1)–Fe–P(3) 85.8(2), P(2)–Fe–P(4) 84.6(2), P(1)–Fe–P(2) 92.2(2), P(3)–Fe–P(4) 168.8(2), Fe–C(29)–C(50) 117.1(13), C(29)–C(50)–C(24) 109(2), C(50)–C(24)–O(2) 123(2), C(24)–O(2)–Fe 110.3(13), C(24)–O(1)–C(58) 115(2).

the vinylic protons are detected as unresolved resonances at δ 11.8 and 5.9 (each integrating for one proton), whose coupling was demonstrated by selective decoupling experiments.

In the IR spectrum, a strong band at 1540 cm^{-1} is assigned to ν(CO) of the coordinated carbonyl group which, in the free alkyne, occurs at a significantly higher wavenumber (ca. 1650 cm^{-1}). A complex ABCD spin system pattern is observed in the ^{31}P-{^1H} NMR spectrum.

The above-mentioned structural features of the metallacycle are comparable with those indicated [9] for the dinuclear complex [$Fe_2(CO)_4$-{C(COOMe)=CHCOOMe}(μ-$Ph_2PCH_2PPh_2$)], in which the vinyl ligand was formed upon insertion of the activated alkyne C(COOMe)≡C(COOMe) into a bridging hydride at a diiron centre.

Moreover, a complex formulated similarly to **1**, *cis*-[Fe(CH=CHCOOMe)(dmpe)$_2$][BPh_4] (dmpe = $Me_2PCH_2CH_2PMe_2$) on the basis of IR, ^1H and ^{31}P-{^1H} NMR spectroscopic and analytical data, was reported [10] as the product of the reaction of HC≡CCOOMe with [$FeCl_2$(dmpe)$_2$] in ethanol and in the presence of Na[BH_4]. Its formation was interpreted [10] in terms of insertion of the acetylene into the metal–hydride bond of [$FeH(H_2)$(dmpe)$_2$]$^+$ generated

[1] Crystal data for **1**. $FeP_4F_4BO_2C_{56}H_{54}$, crystallizes in the monoclinic system, space group $P2_1/c$, with a = 11.950(2), b = 20.756(4), c = 20.823(6) Å, β = 103.41(1)°, U = 5507(1) Å^3, Z = 4, D_c = 1.323 g cm^{-3}, F(000) = 2268. Mo radiation was used for data collection in an Enraf-Nonius TURBO CAD-4. At the present stage of refinement, where the disorder in neither the [BF_4] anion nor the solvent molecule is taken into account, the R value (based on $I > 2\sigma(I)$ is 0.123. Solution and refinement of the structure were carried out using SHELX86 and SHELX93 [6], and illustrated using SHAKAL92, Vers. 16 [7].

in the reaction mixture. Our results support this formulation and such a proposal. The related molybdenum complexes $[MoH_2(CH{=}CHCOOR)(dppe)_2][BF_4]$ (R = Me or Et), obtained from the reaction of $[MoH_4(dppe)_2]$ with HBF_4 and $HC{\equiv}CCOOR$ [11], and $[MoH\{CH{=}C(Me)COOR\}(dppe)_2]$ (R = Et, ^{i}Pr or ^{n}Bu), formed by thermal or photochemically induced reactions of $[MoH_4(dppe)_2]$ with various alkyl methacrylates (a process which involves cleavage of the olefinic C–H bond) [12], have also been reported, but their formulations were not confirmed by X-rays. Nevertheless, the carbenoid form **a** for the dihydride–molybdenum complexes conceivably has a weaker significance in the representation of the metallacycle than in our complex **1**, since the ^{13}C NMR signal of the α-carbon of the vinyl ligand resonates at a much higher field (ca. 157 ppm [12]).

The generation of the five-membered metallacycle in our system is a simpler process than those followed in the cases cited above as well as in other more complex routes involving, for example, coupling of CO, two alkyne and a hydride ligands at the $\{Mo(\eta^5\text{-}C_5H_5)(CO)\}$ centre [13], or photochemically induced insertion of the $\{Fe(CO)_4\}$ group into a three-membered ring system derived from 1,2-diphenyl-4,4-diacetyltriafulvene [14].

In fact, the formation of complex **1** simply involves a formal insertion of the alkyne into the unique Fe–H bond of *trans*-$[FeHCl(dppe)_2]$. However, it should be promoted by further coordination of the ester group (chelating effect), since this type of insertion is not observed for alkynes without such a chelating capacity (e.g. HC≡CR, R = aryl) either in our or related systems, in particular *trans*-$[FeH(H_2)(dmpe)_2]^+$ [or analogous $Et_2PCH_2CH_2PEt_2$(depe) complexes] [15,16] or *trans*-$[MoH_4(dppe)_2$ [11]. In addition, the enhanced electrophilic character of the former alkyne, due to the presence of the ester group, could also play a significant role.

The promotion by chelation of an insertion into the Fe–H bond was also tested in our system for carbon disulfide and, in fact, treatment of a THF solution of *trans*-$[FeHCl(dppe)_2]$ with CS_2 (stoichiometric amount) in the presence of $Ti[BF_4]$ leads to the formation (Eq. (2)) of the η^2-dithioformato complex *cis*-$[Fe(\eta^2\text{-}S_2CH)(dppe)_2][BF_4]$ (**2**), which was isolated as a violet solid and characterized by IR, ^1H, $^{31}P\text{-}\{^1H\}$ and ^{13}C NMR spectroscopies and elemental analysis. Hence, for example, the bidentate dithioformate ligand presents IR bands at 1195(w) and 910(s) cm^{-1}, in the ^1H NMR spectrum the proton resonance occurs as a complex multiplet centred at δ 9.52 and analysed as the X part of an A_2B_2X spin system [A, B = ^{31}P; X = ^1H; $^4J(HP_A)$ = 8.1 Hz, $^4J(HP_B)$ = 5.6 Hz], and in the $^{13}C\text{-}\{^1H\}$ NMR spectrum the S_2CH resonates as a singlet at δ 232.7 which splits into the expected doublet [$J(CH)$ = 185.5 Hz] in the proton-coupled spectrum. Such features are in good agreement [17–19] with the proposed η^2-coordination for the dithioformate ligand.

$$trans\text{-}[FeHCl(dppe)_2] + CS_2 + Tl[BF_4] \rightarrow cis\text{-}[Fe(\eta^2\text{-}S_2CH)(dppe)_2][BF_4] + TlCl \quad (2)$$

The $^{31}P\text{-}\{^1H\}$ NMR spectrum of **2** exhibits a pair of triplets typical of an A_2B_2 spin system, in accord with the *cis* stereochemical arrangement of the diphosphines.

The $\eta^2\text{-}S_2CH$ ligand in **2**, in THF, is deprotonated by $Li[B\{CH(Me)Et\}_3H]$ to afford the carbon disulfide species $[Fe(\eta^2\text{-}CS_2)(dppe)_2]$ isolated as a white solid [strong IR bands at 1180 and 1120 cm^{-1} assigned to ν(CS); δ (CS_2) at 206.6 in the ^{13}C NMR spectrum; singlet at δ −111.9 ppm relative to $P(OMe)_3$ in the $^{31}P\text{-}\{^1H\}$ NMR spectrum].

A complex related to **2**, *cis*-$[Fe(\eta^2\text{-}S_2CH)(dmpe)_2][BPh_4]$, has been reported briefly (no NMR spectroscopic details of the η^2-dithioformate ligand were given) [16,20] as being obtained from the reaction of CS_2 with *trans*-$[FeH(H_2)(dmpe)_2][BPh_4]$ in THF or with $[FeCl_2(dmpe)_2]$ and $Na[BH_4]$ in ethanol. In addition, the analogous depe species was prepared by quite a different route, involving a hydride attack at the Et_3PCS_2 adduct in *cis*-$[Fe(\eta^2\text{-}S_2CPEt_3)(depe)_2][BPh_4]_2$ with subsequent loss of PEt_3 [17]; this procedure was unsuccessful in the case of the dppe complex, possibly for steric reasons [13]. However, this product (see complex **2**) was easily obtained in our study by the ready insertion of CS_2 into the Fe–H bond of *trans*-$[FeHCl(dppe)_2]$. Our work indicates that the latter complex constitutes a convenient starting material for the activation of adequate unsaturated species towards insertion into the metal–hydride bond to form cyclometallated complexes, provided the substrates have a second coordinating centre to chelate the metal, and the process is assisted by a chloride ligand abstractor, such as $Tl[BF_4]$. We are trying to extend this approach to the synthesis of other types of metallacycle.

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