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Investigation of the iron–carbon bonding for alkyl, alkynyl, carbene, vinylidene, and allenylidene complexes using ^{57}Fe Mössbauer spectroscopy[1]

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Abstract

The synthesis of the iron allenylidene [Cp*(dppe)Fe(=C=C=C(OCH$_3$)CH$_3$)][BPh$_4$] (**7**) was achieved in one step, from the reaction of the Cp*(dppe)FeCl (**8**) with 1 equiv. of Me$_3$–Si–C≡C–C≡CH. By working in methanol and in the presence of NaBPh$_4$, the complex **7** was isolated in 85% yield as a dark green powder. Comparison of the Mössbauer parameters of a series of 16 compounds having the same Cp*(dppe)Fe backbone and a end-bound hydrocarbon ligand shows that it is possible to identify both the oxidation state of the metal (Fe^{II} vs. Fe^{III}) and the metal–carbon bonding (single vs. double bond) of the terminal hydrocarbon ligands using Mössbauer spectroscopy. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Synthesis; Organoiron; Iron(II); Iron(III); Butadienyl; Alkyne; Carbene; Vinylidene; Allenylidene; Cumulene; Mössbauer spectroscopy

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1. Introduction

After the discovery of complexes with alkyl, vinyl and alkynyl σ-bound ligands, the emergence of the transition-metal carbene chemistry was one of the most exciting areas in molecular chemistry research during the last decades. Nowadays, the chemistry of metal–vinylidene, allenylidene and cumulene complexes have attracted considerable interest. Several synthetic methods are available to prepare this new class of compounds which constitute potential building blocks for the construction of polymeric materials or nanoscale molecular devices as molecular wires. Moreover, it has been established that metallacumulenes act as intermediates in stoichiometric reactions [1,2] and are also involved in many catalytic processes [3–11]. The low solubility of many of these complexes and the difficulty to establish their structure on the basis of ^{13}C-NMR and IR spectroscopic data prompted us to examine the possibility to get complementary insights on the metal carbon bonding by Mössbauer spectroscopy. Such an approach might be particularly interesting when growing of single crystals is unfruitful.

It is well known that ^{57}Fe Mössbauer spectroscopy is very efficient to identify the oxidation states of iron [12–19]. This technique which usually requires a solid powdered sample was used with success to characterize many mononuclear, and polynuclear derivatives and mixed-valence complexes. For instance, we have previously shown in the Cp*(dppe)Fe–R series that Mössbauer spectroscopy is a powerful tool for the

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[1] Dedicated to Professor Michael Bruce on the occasion of his 60th birthday, in recognition of his contributions to organometallic chemistry.

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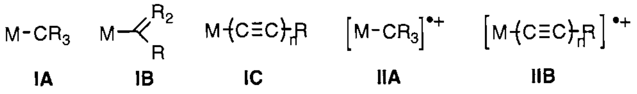
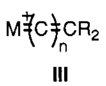


Scheme 1.



Scheme 2.

identification of the oxidation state of the metal in iron-alkyl and iron-alkynyl complexes [20–22]. In this series of compounds with a σ-bound hydrocarbon ligand, the iron(II) derivatives (Scheme 1, type **IA**, **IB**, and **IC**, Scheme 1) exhibit a quadrupole splitting close to 2 mm s^{-1}, whereas the quadrupole splitting of their 17-electron iron(III) analogues (type **IIA** and **IIB**) is lower than 1 mm s^{-1} (Table 1).

Owing to the growing interest for compounds with multiple metal–carbon bonds, the characterization of metal–carbon double bonding in iron–carbene, iron–vinylidene and iron–allenylidene (Scheme 2, type **III**, $n = 0, 1, 2$) compounds by ^{57}Fe Mössbauer spectroscopy was the goal of this work. The target molecules used in this study were all chosen in the same Cp*(dppe)Fe series and are depicted on Scheme 3. Their syntheses were previously reported for almost all of them. However, iron allenylidene complexes ($n = 3$) were unknown in this series, and for the purpose of this spectroscopic study we designed and synthesised the iron allenylidene $[Cp^*(dppe)Fe\{=C=C=C(OCH_3)CH_3\}][BPh_4]$ (**7**).

2. Results and discussion

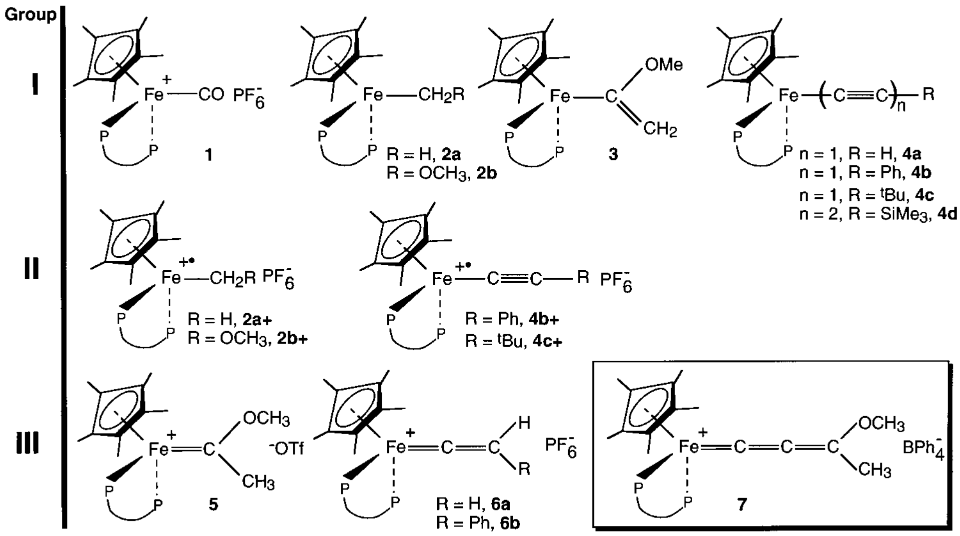
2.1. *Synthesis of the methyl methoxymethyl allenylidene complex* $[Cp^*(dppe)Fe\{=C=C=C(OCH_3)CH_3\}][BPh_4]$ *(**7**)*

Metal–allenylidene complexes were reported for the first time in 1976 [23], but these complexes became readily accessible in 1982 with the paper by Selegue which illustrated for the first time that propargylic alcohols can be converted into allenylidene ligands in the coordination sphere of an electron rich ruthenium complex [24]. More recently, a large number of mononuclear allenylidene compounds were reported for a large variety of transition metals [25–29]. The iron allenylidene complex **7** was prepared according to a one-step original procedure.

Treatment of the chloro complex Cp*(dppe)FeCl (**8**) and $NaBPh_4$ in methanol with 1 equiv. of $Me_3{-}Si{-}C\equiv C{-}C\equiv CH$ produced after 16 h a deep-green solution from which the allenylidene complex $[Cp^*(dppe)Fe(=C=C=C(OCH_3)CH_3)][BPh_4]$ (**7**) was isolated as a green forest powder in 85% yield (Scheme 4). Subsequent crystallization gave analytically pure **7** (78%) which was characterized by IR, ^{1}H-, ^{13}C-, ^{31}P-NMR and UV–vis spectroscopies. The infrared spectrum revealed two strong allenylidene C=C=C stretches at 1938 and 1947 cm^{-1} in the solid state (Nujol) and a single band stretching in solution at 1943 cm^{-1} (CH_2Cl_2). The observation of two band stretches in the solid state could be due either to the presence of isomorphous microcrystals or to a restricted rotation in the allenylidene fragment giving different rotamers quenched in the crystal lattice (vide infra). The ^{1}H-NMR spectrum ($CDCl_3$) displays a singlet at δ 1.41 for the methyl of the Cp* ring and two singlets at δ 1.71 and 3.41 for the protons of the methyl and methoxy groups of the allenylidene ligand, respectively. A

Table 1
Mössbauer parameters in mm s^{-1} for the Fe(II) and Fe(III) complexes of the $[Cp^*(dppe)FeL]^{n+}n[X^-]$ series at 80 K

L	Compounds	n	Group	δ	ΔE_Q	Ref.
CH_3	**2a**	0	I	0.15	1.95	[20]
CH_2OCH_3	**2b**	0	I	0.13	1.97	[20]
$-C\equiv C-H$	**4a**	0	I	0.276	1.987	This work
$-C\equiv C-(C_6H_5)$	**4b**	0	I	0.27	2.02	This work
$-C\equiv C-{}^{t}Bu$	**4c**	0	I	0.28	2.00	This work
$-C\equiv C-C\equiv C-SiMe_3$	**4d**	0	I	0.25	1.93	[37]
$-C(=CH_2)OCH_3$	**3**	0	I	0.323	1.904	This work
CO	**1**	1	I	0.196	1.842	This work
$=C(CH_3)OCH_3$	**5**	1	III	0.216	1.223	This work
$=C=CH_2$	**6a**	1	III	0.086	1.032	This work
$=C=C(C_6H_5)H$	**6b**	1	III	0.116	1.118	This work
$=C=C=C(CH_3)OCH_3$	**7**	1	III	0.160	1.451	This work
CH_3	**2a+**	1	II	0.35	0.76	[20]
CH_2OCH_3	**2b+**	1	II	0.25	0.95	[20]
$-C\equiv C-(C_6H_5)$	**4b+**	1	II	0.25	0.90	This work
$-C\equiv C-{}^{t}Bu$	**4c+**	1	II	0.26	0. 85	This work



Scheme 3.

deshielded C_α triplet (δ_C 268.2, $^2J_{PC} = 34$ Hz), a C_β (δ_C 156.6) singlet and a C_γ (δ_C 152.4) unresolved multiplet, typical of a metalla-allenylidene, were observed in the ^{13}C-NMR.

By analogy with the reaction of the trimethylsilylacetylene with the chloro iron complex Cp*(dppe)FeCl (**8**) which provided the vinylidene derivative [Cp*(dppe)Fe(=C=CH_2)][BPF_6] under the same conditions (**6a**, Eq. (1)),[22] one can assume the formation of the butatrienylidene complex [Cp*(dppe) Fe(=C=C=C=CH_2)][BPF_6] results from the primary product of the reaction of **8** with the trimethylsilyl 1,3-butadiyne (Eq. (2)). A subsequent addition of a methanol molecule to the complex **7** yields the isolated allenylidene **7** (Eq. (3)).

$$\textbf{(8)}[(Cp^*)(dppe)FeCl] + Me_3SiC{\equiv}CH \underset{MeOH}{\overset{NH_4PF_6}{\rightarrow}} [(Cp^*)(dppe)Fe({=}C{=}CH_2)][PF_6]\ \textbf{(6a)} \qquad (1)$$

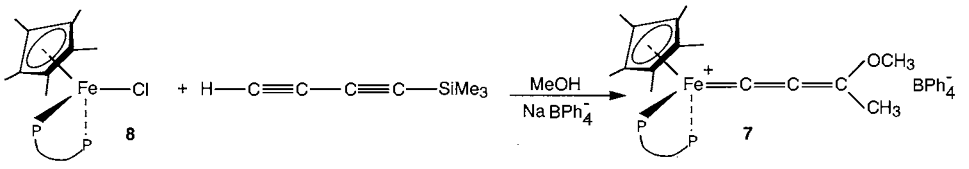
$$\textbf{(8)}[(Cp^*)(dppe)FeCl] + Me_3SiC{\equiv}C{-}C{\equiv}CH \underset{MeOH}{\overset{Na_4BPh_4}{\rightarrow}} \{[(Cp^*)(dppe)Fe({=}C{=}C{=}C{=}CH_2)][BPh_4]\} \qquad (2)$$

$$\{[(Cp^*)(dppe)Fe({=}C{=}C{=}C{=}CH_2)][BPh_4]\} + MeOH \rightarrow \textbf{7} \qquad (3)$$

Whereas the formation of a vinylidene derivative requires a 1,2 H-shift according to Eq. (1), the formation of a butatrienylidene compound from 1,3-butadiyne involves a 1,4 H-shift. Meanwhile butatrienylidene complexes were never isolated nor spectroscopically characterized to date, their existence is not inconsistent with the result of ab initio calculations. Indeed, it was possible to predict that the free energy of [M]=C=C=C=CH_2 should be close that of [M]=C=CH(C≡CH) [30]. Moreover, elegant quenching reactions of ruthenium butatrienylidene intermediates [$(PPh_3)_2$CpRu=C=C=C=CH_2] generated by reaction of the buta-1,3-diyne with [$(PPh_3)_2$CpRu(THF)] were reported from M.I. Bruce's group [1,2]. On the other hand, the synthesis of ruthenium allenylidene complexes from the reaction of a dichloro ruthenium derivative with terminal diynes in methanol also supports the proposed mechanism for the formation of the iron compound **7** [29].

2.2. Investigation of the iron–carbon bonding by Mössbauer spectroscopy

The Mössbauer spectra of microcrystalline samples of the iron complexes depicted on Scheme 3 are characteristic of pure organoiron complexes (Table 1, Fig. 1). Indeed, all these spectra displayed a single quadrupole doublet. As previously observed for complexes **2a** and **2b** [20] and also for many ferrocene derivatives [31], the Mössbauer parameters are almost temperature independent between 77 and 300 K. For this reason, the spectra here reported were all recorded at 80 K. Considering the Mössbauer quadrupole splittings of these compounds (Table 1), it is possible to classify them in three different groups. All the complexes having a 18-electron iron(II) center connected to a η^1-bound carbon ligand belong to the first group. Their ΔE_Q is close to 2 mm s^{-1}. In this group of compounds, the quadrupole splitting is independent of the hybridization of the carbon bound to the iron atom and weakly depends on the electronic effect of the hydrocarbon ligand. Thus, in the case of the cationic complex [Cp*(dppe)Fe(CO)][PF_6] (**1**), the less electron rich complex of this group, one can note that the quadrupole splitting ($\Delta E_Q = 1.842$ mm



Scheme 4.

s^{-1}) is not far from the values observed for the neutral complexes **2**–**4**. Generally, in an homogenous series of iron compounds the isomeric shift is related to the electron density at the metal center. This is apparently not verified for the complexes of group I which do not constitute an homogeneous enough family to allow such a statement to be made.

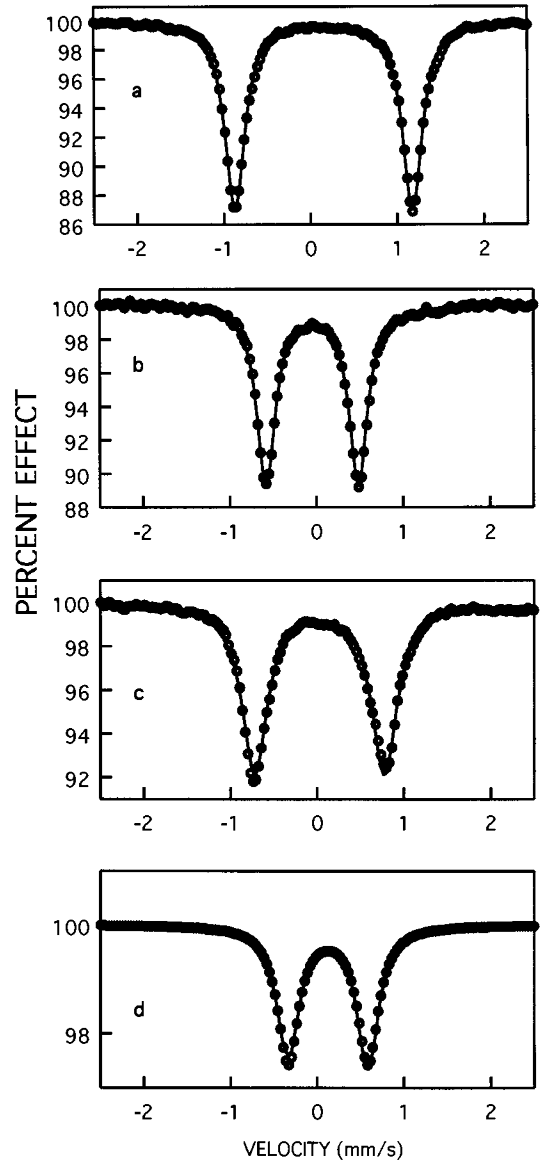
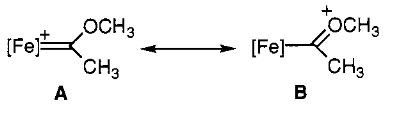


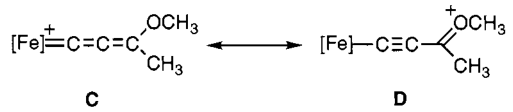
Fig. 1. Selected Mössbauer spectra at 80 K of (a) Cp*(dppe)Fe–C≡C–H (**4a**); (b) [Cp*(dppe)Fe=C=C(Ph)H][PF$_6$] (**6a**); (c) [Cp*(dppe)Fe=C=C=C(Me)OMe][BPh$_4$] (**7**); (d) [Cp*(dppe)Fe–C≡C–Ph][PF$_6$] (**4b**+).

In the case of the 17-electon iron(III) radical cations having an η^1-bound hydrocarbon ligand, it was observed that the quadrupole splitting is systematically below 1 mm s^{-1} (see Table 1). Once again, similar ΔE_Q values are observed with hydrocarbon ligands having either a sp^3 or a sp hybridized carbon atom. These complexes constitute the group II of the compounds here considered, and they can be identified by their doublet separation in the Mössbauer spectrum. Moreover, one can note that the isomeric shift of **2a**+ and **2b**+ are significantly weaker than those of **2a** and **2b**, whereas almost the same δ values are observed for the couple of compounds **4b**, **4c** and **4b**+, **4c**+. This indicates that the ethynyl ligand should participate to the delocalization of the odd electron. As a result, the diminution of the electron density at the metal center resulting of the one-electron oxidation should be partly balanced in **4b**+, **4c**+ by the ethynyl fragment.

More interesting are the Mössbauer parameters of the carbene, vinylidene and allenylidene iron derivatives **5**–**7**. These compounds with a Fe=C double bond constitute the third group of complexes in this study, and have never been the subject of a Mössbauer spectroscopic investigation. The quadrupole splittings of these iron(II) centers are well differentiated from those of the iron(II) and iron(III) parent compounds of the groups I and II. As a consequence, the quadrupole splitting (ΔE_Q) is diagnostic of the bond order of the iron–carbon bond between the metal and the end-bound carbon ligands, at least in this Cp*(dppe)Fe series. Moreover, the quadrupole separation is significantly higher for the compounds having a methoxy group on the C_α (**5**) or C_γ (**7**) carbon atom that for the vinylidene **6a** and **6b**. This might be related to the strength of the π bond between the iron center and the C_α atom. Indeed, the contribution of the mesomeric form **B** (Scheme 5) has been recognized for a long time in the description of the electronic structure of Fischer-type carbene complexes. Such a structure also supports the observed restricted rotation about the carbene carbon–oxygen bond in many of these derivatives [32–35].



Scheme 5.



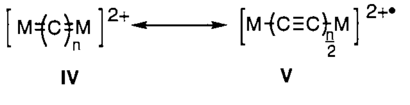
Scheme 6.

Additionally, comparison between the quadrupole splittings of the carbene (**5**) and the allenylidene (**7**) complexes revealed an important increase of ΔE_Q from 1.223 to 1.451 mm s^{-1}. As a consequence of this experimental result, one can suppose that the double bond character of the Fe=C bond in a hetero-carbene might be stronger than in the homologous hetero-allenylidene. In other words, the weight of the contribution of the mesomeric form **D** (Scheme 6) in the description of the electronic structure of the allenylidene **7** might be stronger than those of the form **B** in the description of the electronic structure of the methoxycarbene **5**. To our knowledge, comparison between the rotation barriers of heterocarbene and heteroallenylidene complexes has never been the subject of discussion in the literature.

At this point, it is important to emphasize the interest in the characterization of the metal–carbon bonding for an unsaturated end-bound hydrocarbon ligand using Mössbauer spectroscopy because this technique is complementary to infrared spectroscopy. Indeed, the alkynyl and vinylidene ligands are easily characterized by IR (i.e. $\nu_{C\equiv C}$ of **4a**, 1910 cm^{-1}; $\nu_{C=C}$ of **6a** 1612 cm^{-1}) but it is almost impossible to make the distinction between the ethynyl and allenylidene ligands using this spectroscopy (i.e. $\nu_{C=C=C} = 1943\ cm^{-1}$ for **7**). As a result of our investigation on sixteen mononuclear iron complexes of the Cp*(dppe)Fe series using Mössbauer spectroscopy, it can be concluded that the Mössbauer spectra recorded at zero field constitute a very useful mean to determine both the oxidation state of the iron center (Fe^{II} vs. Fe^{III}) and the metal–carbon bond order of end-bound hydrocarbon ligands in microcrystallised samples. Additionally, Mössbauer is a very sensitive spectroscopy and the presence of a single iron species in the sample can easily be checked by the observation of a single Mössbauer doublet.

2.3. Conclusion and perspectives

Concomitantly to our activity on the mononuclear polyyne, carbene, vinylidene, allenylidene and more generally cumulene iron compounds, we have an ongoing interest in the synthesis and physical properties of bimetallic complexes where the metals are connected by an all-carbon chain. These iron compounds which have the general formula $[L_nFe-(C\equiv C)_x-FeL'_n]^{z+}z[X^-]$ have been prepared for different lengths of the carbon linkage ($4 < x < 8$) and different oxidation states ($z = 0$, 1, 2) [22,36,37]. Similar systems were also isolated in different oxidation states using rhenium, [38–40] ruthenium [41] and tungsten [42] metal centers. In the case of dicationic complexes ($n = 4$, $z = 2$) a cumulenic structure (Scheme 7, type **IV**) was attributed to the rhenium and tungsten compounds, whereas we found a polyyne structure with two 17-electron end-capping metal centers (type **V**) in the Cp*(dppe)Fe series. This versatility of the electronic structure of all-carbon chains also emphasizes the interest for implementing the set of spectroscopic tools allowing the determination of the metal–carbon bonding and makes Mössbauer spectroscopy a particular interesting technique in this respect.



Scheme 7.

3. Experimental section

3.1. General data

Reagent grade tetrahydrofuran (THF), diethylether and *n*-pentane were dried and distilled from sodium benzophenone ketyl prior to use. Pentamethylcyclopentadiene was prepared according to the published procedure [43] and other chemicals were used as received. All the manipulations were carried out under an argon atmosphere using Schlenk techniques or in a Jacomex 532 dry box under nitrogen. The FTIR spectra were recorded using Nicolet instrument (Model 205) and KBr windows. High field NMR spectra experiments were performed on a multinuclear Bruker 300 MHz instrument (AM300WB). Chemical shifts are given in parts per million relative to tetramethylsilane (TMS) for ^1H- and ^{13}C-NMR spectra, H_3PO_4 for ^{31}P-NMR spectra. Elemental analyses were performed at the Center for Microanalyses of the CNRS at Lyon-Solaise, France. The syntheses of the compounds **1** [45], **2** [20], **3** [46], **4a** [22], **4b** [47], **4c** [37], **5** [46], **6a** [22], **6b** [47], **2**+ [20], and **4b**+ [47] were reported elsewhere.

Mössbauer spectra were recorded with a 2.5×10^{-2} C (9.25×10^8 Bq) ^{57}Co source using a symmetric triangular sweep mode

3.2. ^{57}Fe Mössbauer spectroscopy

The ^{57}Fe Mössbauer spectra were obtained by using a constant acceleration spectrometer previously described with a 50 mCi ^{57}Co source in a Rh matrix [49]. The sample temperature was controlled by a Oxford MD306 cryostat and a Oxford ITC4 temperature controller. Computer fitting of the Mössbauer data to Lorenzian line shapes were carried out with a previously reported computer program [44,50]. The isomer shift values are reported relative to iron foil at 298 K and are not corrected for the temperature-dependent second-order Doppler shift. The Mössbauer sample cell consists of 2 cm diameter cylindrical plexiglass holder.

3.2.1. *Cp*(dppe)Fe(=C=C=C(OCH$_3$)CH$_3$)* (**7**)

To a solution (20°C) of Cp*(dppe)FeCl (0.430 g, 0.69 mmol) in methanol (40 ml) was added 1.25 equiv. of trimethylsilyl-1,3-butadiyne [48] and 1.1 equiv. of $NaBPh_4$. The mixture was stirred for 16 h and the resulting green solution was evaporated to dryness. The crude residue was extracted with dichloromethane, then concentrated to 5 ml, and diethyl ether (50 ml) was slowly added to precipitate 0.570 g (85%) of **7** as a dark green powder. Anal. Calcd. for $C_{65}H_{65}BFeOP_2$. 0.25 CH_2Cl_2: C, 77.44; H, 6.52. Found: C, 77.64; H, 6.21. FT-IR (Nujol/CH_2Cl_2 cm^{-1}) ν 1938, 1947/1943 (s, C=C=C). ^{1}H-NMR (300 MHz, $CDCl_3$) δ_H 7.4–6.8 (m, 20H, 4 C_6H_5); 3.41 (s, 3H, OCH_3); 2.66, 2.32 (m, 4H, CH_2); 1.71 (s, 3H, =C(OMe)C$\underline{H}_3$); 1.41 (s, 15H, C_5Me_5). ^{13}C-NMR (75 MHz, $CDCl_3$) δ_C 268.2 (t, $^2J_{CP} = 34$ Hz, C_α); 156.6 (s, C_β); 152.4 (m, C_γ); 97.0 (s, $\underline{C}_5Me_5$); 59.5 (q, $^1J_{CH} = 147$ Hz, OCH_3); 32.7, 28.5 (2m, CH_2); 27.4 (q, $^1J_{CH} = 130$ Hz, =C(OMe)CH_3); 10.0 (q, $^1J_{CH} = 128$ Hz, $C_5\underline{Me}_5$). ^{31}P-NMR (121 MHz, $CDCl_3$) δ_C 93.2 (s). UV–vis (nm, (ε, M^{-1} cm^{-1}), CH_2Cl_2) 455 (3260).

Acknowledgements

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References

[1] M.I. Bruce, P. Hinterding, P.J. Low, B.W. Skelton, A.H. White, Chem. Commun. (1996) 1009.

[2] M.I. Bruce, P. Hinterding, M. Ke, P.J. Low, B. W. Skelton, A.H. White, Chem. Commun. (1997) 715.

[3] B.M. Trost, J. Flygare, J. Am. Chem. Soc. 114 (1992) 5476.

[4] B.M. Trost, Chem. Ber. 129 (1996) 1313.

[5] J. Höfer, H. Doucet, C. Bruneau, P.H. Dixneuf, Tetrahedron Lett. 32 (1991) 7409.

[6] H. Doucet, J. Höfer, C. Bruneau, P.H. Dixneuf, J. Chem. Soc. Chem. Commun. (1993) 850.

[7] T. Rappert, A. Yamamoto, Organometallics 13 (1994) 4984.

[8] C. Bianchini, P. Frediani, D. Masi, M. Reruzzini, F. Zanobini, Organometallics 13 (1994) 4616.

[9] H. Doucet, B.M. Martin-Vaca, C. Bruneau, P.H. Dixneuf, J. Org. Chem. 60 (1996) 7247.

[10] C.S. Yi, N. Liu, Organometallics 15 (1996) 3968.

[11] C. Slugovc, K. Mereiter, E. Zobetz, R. Schmid, K. Kirchner, Organometallics 15 (1996) 5275.

[12] N.N. Greenwood, Mössbauer Spectroscopy, Chapman and Hall, London, 1971.

[13] T.-Y. Dong, D. Hendrickson, C.G. Pierpont, M.F. Moore, J. Am. Chem. Soc. 108 (1986) 963.

[14] M.F. Moore, S.R. Wilson, M.J. Cohn, T.Y. Dong, T. Kampara, D.N. Hendrickson, Inorg. Chem. 24 (1985) 4559.

[15] T.-Y. Dong, T. Kampara, D.N. Hendrickson, J. Am. Chem. Soc. 108 (1986) 5857.

[16] T. Kampara, D.N. Hendrickson, T.-Y. Dong, M.J. Cohn, J. Chem. Phys. 86 (1987) 2362.

[17] W.H. Morrison, D.N. Hendrickson, J. Chem. Phys. 59 (1973) 380.

[18] C. Le Vanda, D.O. Cowan, C. Leitch, K. Bechgaard, J. Am. Chem. Soc. 96 (1974) 6788.

[19] C. Le Vanda, K. Bechgaard, D.O. Cowan, J. Org. Chem. 41 (1976) 2700.

[20] C. Roger, P. Hamon, L. Toupet, H. Rabaâ, J.-Y. Saillard, J.-R. Hamon, C. Lapinte, Organometallics 10 (1991) 1045.

[21] N. Le Narvor, C. Lapinte, Organometallics 14 (1995) 634–639.

[22] N. Le Narvor, L. Toupet, C. Lapinte, J. Am. Chem. Soc. 117 (1995) 7129.

[23] E.O. Fischer, H.J. Kalder, A. Frank, F.H. Köhler, G. Huttner, L. Zsolnai, Angew. Chem. Int. Ed. Engl. 15 (1976) 623.

[24] J.P. Selegue, Organometallics 1 (1982) 217.

[25] M.I. Bruce, A.G. Swincer, Adv. Organomet. Chem. 22 (1983) 59.

[26] M.I. Bruce, Chem. Rev. 91 (1991) 197.

[27] H. Werner, Chem. Commun. (1997) 903.

[28] V. Cadierno, P. Gamasa, J. Gimeno, J. Borge, S. Garcia-Granda, Organometallics 16 (1997) 3178.

[29] D. Touchard, N. Pirio, L. Toupet, M. Fettouhi, L. Ouahab, P. Dixneuf, Organometallics 14 (1995) 5263.

[30] C.E. Dykstra, C.A. Parsons, C.L. Oates, J. Am. Chem. Soc. 101 (1979) 1962.

[31] R.L. Collins, J. Phys. Chem. 42 (1965) 1072.

[32] K.H. Dötz, H. Fisher, P. Hofmann, F.R. Kreissl, U. Schubert, K. Weiss, Transition Metal Carbene Complexes, Verlag Chemie, Weinheim, 1983.

[33] W.E. Burho, A. Wong, J.H. Merrifield, G.-Y. Lin, A.C. Constable, J.A. Gladysz, Organometallics 2 (1983) 1852.

[34] C.G. Kreiter, E.O. Fischer, Angew. Chem. Int. Ed. Engl. 8 (1969) 761.

[35] V. Guerchais, C. Lapinte, J.-Y. Thépot, Organometallics 7 (1988) 604.

[36] F. Coat, C. Lapinte, Organometallics 15 (1996) 477.

[37] F. Coat, M.-A. Guillevic, L. Toupet, F. Paul, C. Lapinte, Organometallics (in press).

[38] Y. Zhou, J.W. Seyler, W. Weng, A.M. Arif, J.A. Gladysz, J. Am. Chem. Soc. 115 (1993) 8509.

[39] J. Seyler, W. Weng, Y. Zhou, J.A. Gladysz, Organometallics 12 (1993) 3802.

[40] M. Brady, W. Weng, Y. Zhou, J.W. Seyler, A.J. Amoroso, A.M. Arif, M. Böhme, G. Frenking, J.A. Gladysz, J. Am. Chem. Soc. 119 (1997) 775.

[41] M.I. Bruce, L.I. Denisovich, P.J. Low, S.M. Peregudova, N.A. Ustynyuk, Mendeleev Commun. (1996) 200.

[42] B.E. Woodworth, P.S. White, J.L. Templeton, J. Am. Chem. Soc. 119 (1997) 828.

[43] F.X. Kohl, P. Jutzi, J. Organomet. Chem. 243 (1983) 119.

[44] F. Varret, J.-P. Mariot, J.-R. Hamon, D. Astruc, Hyperfine Interact. 39 (1988) 67.

[45] D. Catheline, D. Astruc, J. Organomet. Chem. 226 (1982) C52.

[46] V. Mahias, S. Cron, L. Toupet, C. Lapinte, Organometallics 15 (1996) 5399.

[47] N.G. Connelly, M.P. Gamasa, J. Gimeno, C. Lapinte, E. Lastra, J.P. Maher, N. L. Narvor, A.L. Rieger, P.H. Rieger, J. Chem. Soc. Dalton Trans. (1993) 2575.

[48] A.B. Holmes, C.L.D. Jennings-White, A.H. Schulthess, B. Akinde, D.R.M. Walton, J. Chem. Soc. Chem. Commun. (1979) 840–842.

[49] D. Boinnard, A. Boussekssou, A. Dworkin, J.-M. Savariault, F. Varret, J.-P. Tuchagues, Inorg. Chem. 33 (1994) 271.

[50] F. Varret, Proceedings of the International Conference on Mössbauer Effect Applications, Jaipur, India, 1981; Indian Science Academy, New Delhi, 1982.