



Dithiafulvenylphosphine as P- and P,S-ligand towards metal carbonyl fragments

Michel Guerro, Emmanuel Di Piazza, Xin Jiang, Thierry Roisnel, Dominique Lorcy*

Sciences Chimiques de Rennes, UMR-CNRS 6226, Université de Rennes 1, Campus de Beaulieu, Bât 10A, 35042 Rennes cedex, France

ARTICLE INFO

Article history:

Received 21 March 2008

Received in revised form 9 April 2008

Accepted 9 April 2008

Available online 13 April 2008

Keywords:

Molybdenum

Manganese

Carbonyl complexes

P and P/S ligands

X-ray structure

ABSTRACT

The ability of the dithiafulvenylphosphine (P-DTF) to react as a monodentate (P) or a bidentate (P,S) ligand with metal carbonyl complexes such as $\text{Mo}(\text{CO})_6$ and $\text{MnBr}(\text{CO})_5$ is presented. A series of metal carbonyl complexes are synthesised and characterised by IR, ^1H NMR and ^{31}P NMR spectroscopy. X-ray crystallographic analyses on the $\text{Mo}(\text{CO})_5(\text{P-DTF})$ and $\text{Mo}(\text{CO})_4(\text{P,S-DTF})$ complexes are reported together with the structural investigations on the dithiafulvenes precursors. The electrochemical properties of the various complexes investigated by cyclic voltammetry are discussed.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Redox active phosphines containing a tetrathiafulvalene (TTF) core have received considerable attention in recent years particularly as building blocks for the formation of hybrid multifunctional materials or as ligands for catalytic applications [1–5]. Another interesting electroactive moiety, related to TTF, is the dithiafulvene (DTF) core. Besides being an excellent precursor of vinyllogous TTF, DTF substituted by a diphenylphosphino group has also proved to be a good (P) ligand towards transition metal complexes such as molybdenum or tungsten in $[\text{M}(\text{CO})_4(\text{P-DTF})_2]$ [6]. Moreover, this redox active vinyl phosphine (P-DTF) stands out by its ability to form upon oxidation, when two of them are coordinated to a metal carbonyl fragment $\text{M}(\text{CO})_4$ with $\text{M} = \text{Mo}$ or W , a bidentate diphosphine complex with a redox active vinyllogous tetrathiafulvalene backbone $[\text{M}(\text{CO})_4(\text{P,P-TTFV})]$ (Chart 1).

When we first studied the coordinating ability of this redox active ligand (P-DTF), we choose to prepare metal 0 complexes from $\text{cis-M}(\text{CO})_4(\text{piperidino})_2$ with $\text{M} = \text{Mo}$ and W , demonstrating that (P-DTF) can behave either as a monodentate (P) ligand or as a bidentate (P,S) ligand towards tungsten carbonyl fragment $\text{W}(\text{CO})_4$ [6b]. In continuation of our studies on this vinyl phosphine, we wish now to report the reactivity of this ligand towards $\text{Mo}(\text{CO})_6$. As compared with $\text{cis-}[\text{Mo}(\text{CO})_4(\text{piperidino})_2]$, the CO ligands are less labile than the piperidino one. We also examined the reactivity of this phosphine towards another metal carbonyl fragment such as Mn^{1+} metal ion in $\text{BrMn}(\text{CO})_5$. Using these metal

carbonyl complexes, we report that this redox active ligand behaves easily as a (P) ligand while its reactivity as a (P,S) ligand is subjected to the withdrawal facilities of one CO ligand. In addition, the structural properties of the various dithiafulvene precursors as well as the Mo complexes together with the electrochemical properties of the different complexes is presented.

2. Results and discussion

2.1. Synthesis and molecular structures of the ligand

The vinyl phosphine **2** was prepared (Scheme 1) from the phosphine borane **1** by simply treating **1** with DABCO in order to realize the decomplexation of the phosphine borane [6]. The dithiafulvene **2** is an air stable compound which can be stored for months without being oxidized. We also prepared the thioxo derivative of **2** by simply treating **2** with S_8 in dichloromethane at room temperature.

Crystals of **1**, **2** and **3** were isolated from recrystallization in MeOH. The X-ray molecular structures of **1–3** are shown in Fig. 1 and selected bond lengths are listed in Table 1. X-ray crystal structure analysis demonstrates that in all the cases the dithiafulvene cores are planar, while the diphenyl substituents on the phosphorus atom are located differently due to the orientation of either BH_3 or the thioxo groups. Concerning compound **1** and the borane group bound to the phosphorus atom, the P–B (1.922(2) Å) bond length as well as the C–P–C and C–P–B angles are in agreement with those of related phosphine borane derivatives with a slightly distorted tetrahedral environment [7,8]. As can be seen in Table 1, there is no significant influence of the electron withdrawing or releasing character of the phosphino group on the bond lengths of the

* Corresponding author. Tel.: +33 2 23 23 62 73; fax: +33 2 23 23 67 38.

E-mail address: dominique.lorcy@univ-rennes1.fr (D. Lorcy).

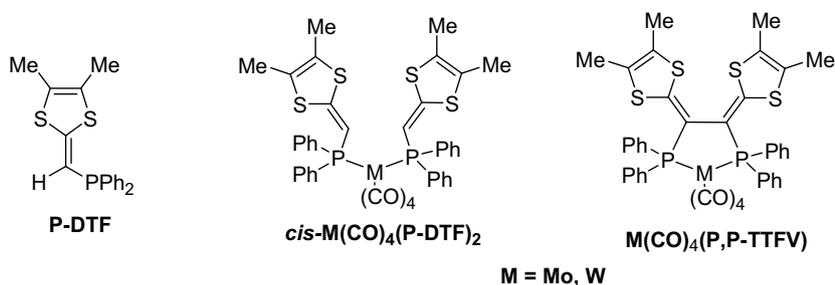
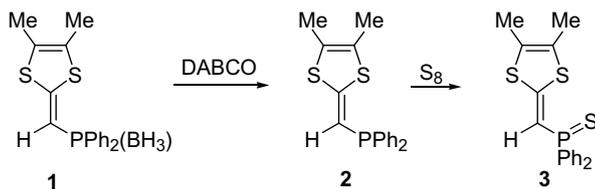


Chart 1.

dithiole ring while the oxidation potential of the dithiole core is more sensitive to this influence (*vide infra*).

2.2. Molybdenum complexes

In continuation of our work on the coordinating ability of this vinyl phosphine **2** towards transition metal complexes, we investigated its reactivity towards Mo(CO)₆. In order to coordinate only one vinyl phosphine ligand to the molybdenum atom, we heated a solution of **2** in decahydronaphthalene with one equivalent of Mo(CO)₆ (Scheme 2). After 30 min, analysis of the medium by ³¹P NMR reveals two singlets on the spectrum, at 24.1 ppm and 62.4 ppm, corresponding to the formation of two metal complexes. Chromatographic separation of the reaction mixture on silica gel affords two crystalline metal complexes **4** and **5** in 45% and 5% yield, respectively. Assignment of the structures [Mo(CO)₅(P-DTF)] (**4**) and [Mo(CO)₄(P,S-DTF)] (**5**), was realized thanks to X-ray crystal structure analysis (Fig. 2). The monosubstituted molybdenum complex [Mo(CO)₅(P-DTF)] (**4**), exhibits the signal at 24.1 ppm on the ³¹P NMR spectrum. It is worth mentioning that **4** and the bis substituted molybdenum derivative, [Mo(CO)₄(P-DTF)₂] [6], exhibit a singlet at the same chemical shift on the ³¹P NMR spectra (24.1 ppm) (Table 2). Contrariwise, the phosphorus atom in **5** resonates at lower field than in **4** and a deshielding of 38 ppm is observed consistent with the strain brought by the P,S coordination mode of P-DTF to the metal in **5**. Actually, close deshielding (36 ppm) was already noticed when going from [Mo(CO)₄(P-DTF)₂] to the five-membered metallacycle [Mo(CO)₄(P,P-TTFV)] (see Chart 1).



Scheme 1.

The molecular structures of **4** and **5** are depicted in Fig. 2, and selected bond lengths are listed in Table 1. As can be seen in Fig. 2, the dithiole core of the vinylphosphine in **4** is planar while in **5**, due to the formation of the metallacycle, the dithiole ring is folded along the S··S axis with an angle of 26°. The strain brought by the P,S coordination mode in **5** influences also the geometry of the dithiole ring itself as the C–S bond within the metallacycle (S2–C32 1.776(2) Å) is slightly longer than the other one (S3–C32 1.752(2) Å). Phosphorus–molybdenum bond lengths are in the usual range, Mo–P1: 2.5531(7) Å for **4** and Mo–P11: 2.5141(4) Å for **5** with a P11–Mo–S2 interligand angle of 76.367(15)° [9]. Compared with the bis dithiafulvene derivative [Mo(CO)₄(P-DTF)₂] we previously reported [6], it is interesting to note that the Mo–P bond length in **4** is slightly longer than in [Mo(CO)₄(P-DTF)₂] (Mo1–P1 2.5084 (10) Å).

As the reaction of Mo(CO)₆ at 150 °C in decahydronaphthalene with a stoichiometric amount of **2** leads mainly to the monosubstituted metal carbonyl complex **4**, we investigated another route for the formation of the chelated complex **5**. Assuming that the synthesis of **5** could be realized from **4** through the loss of one CO ligand followed by an intramolecular coordination of the Mo atom with one S atom of the dithiole ring, we studied three classical pathways for eliminating one CO ligand. First, we investigated the influence of the heat, under inert atmosphere, on a solution

Table 1
Selected bond distances (Å) for compounds 1–5

	1	2	3	4	5
a	1.787(2)	1.796(3)	1.7789(15)	1.796(3)	1.8120(18)
b	1.357(3)	1.347(4)	1.352(2)	1.346(4)	1.325(3)
c	1.741(2)	1.753(2)	1.7509(15)	1.748(3)	1.7517(17)
c'	1.755(2)	1.747(2)	1.7467(15)	1.751(3)	1.7762(18)
d	1.760(2)	1.759(3)	1.7527(16)	1.761(3)	1.767(2)
d'	1.760(2)	1.753(3)	1.7587(16)	1.760(3)	1.7764(18)
e	1.329(3)	1.318(4)	1.337(2)	1.320(5)	1.328(3)

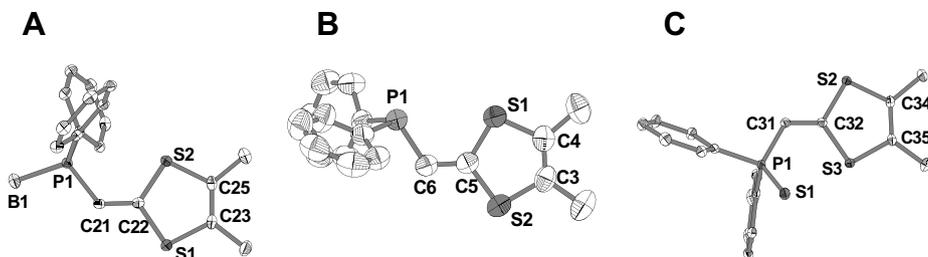
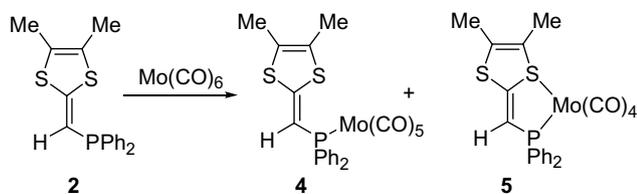


Fig. 1. Molecular structures of **1** (left A), **2** (middle B) and **3** (right C) (Hydrogen atoms omitted for clarity). Ellipsoids are drawn at 50% probability.



Scheme 2.

of **5** in various solvents and the reaction was monitored by ^{31}P NMR (Scheme 3). After 3 h of reflux in dichloromethane, it was possible to detect the formation of a small amount of complex **5** in the medium through the appearance of the signal at 62.4 ppm. Actually, by increasing the reaction time for 5 days, we were able to transform 25% of the starting complex **4** into the (P,S) chelate complex **5** (Scheme 3). Then, we realized similar experiment with a solution of **4** in toluene, expecting that the elevation of the reflux temperature will favour the departure of the CO ligand. Actually, by increasing the temperature, we induced the decoordination of the phosphine one instead of the CO, as the signature of dithiafulvene **2** was observed on the ^{31}P NMR spectrum. Therefore, we choose another approach involving the reaction of **4** at room temperature during 3 h in the presence of one equivalent of $\text{Me}_3\text{NO} \cdot 2\text{H}_2\text{O}$ [10] in dichloromethane. Actually, in these conditions, the use of this reactant with **4** did not allow the release of one coordination site as complex **4** is entirely recovered. This is surprising as it is known that similar reaction realized with $\text{Mo(CO)}_5(\text{PPh}_3)$ in the presence of Me_3NO and PPh_3 yielded the *trans* bisubstituted complex, *trans*- $\text{Mo(CO)}_4(\text{PPh}_3)_2$ [10]. One explanation for the inertia of **4** with $\text{Me}_3\text{NO} \cdot 2\text{H}_2\text{O}$ could be that the vinyl phosphine ligand behaves as a good electron donor inducing a diminution of the electrophilic character of the carbon in the $\text{C}^+\equiv\text{O}$ ligand towards the reagent. In agreement with this observation, the length of the bond between the metal and the *trans*-carbonyl carbon atom is shorter than the metal-*cis*-carbonyl bonds indicating a back donation to the *trans* carbonyl ligand due to the donating ability of the phosphine **2**.

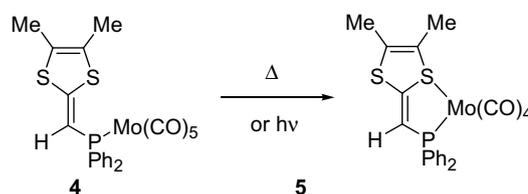
In order to check this point we also tried the formation of complex **5** directly from Mo(CO)_6 by using one equivalent of vinyl phosphine **2** in the presence of two equivalents of $\text{Me}_3\text{NO} \cdot 2\text{H}_2\text{O}$ in dichloromethane. Under these reaction conditions, after 3 h, we were able to form **5** in 40% yield besides the formation of **4** in 20% yield and the formation of the bisubstituted complex *cis*- $[\text{Mo(CO)}_4(\text{P-DTF})_2]$ in 30% yield (Scheme 4).

Photoreaction of metal carbonyl complexes is also a useful route for inducing the loss of CO ligands. Therefore, UV irradiation of **4** in a CDCl_3 solution was realized and monitored by ^{31}P NMR

Table 2

^{31}P parameters and oxidation peak potentials for the Molybdenum metal carbonyl complexes

Compound	δP (ppm)	E_{pa} (V) vs. SCE
1	14.3	1.07
P-DTF, 2	-13.2	0.73
3	32.1	1.01
$[\text{Mo(CO)}_5(\text{P-DTF})]$ (4)	24.1	0.88
$[\text{Mo(CO)}_4(\text{P,S-DTF})]$ (5)	62.4	0.92
$[\text{Mo(CO)}_4(\text{P-DTF})_2]$	24.1	0.60, 1.35



Scheme 3.

and ^1H NMR. Photolysis of **4** for 1 h at 300 nm showed the formation of the chelate ring in $[\text{Mo(CO)}_4(\text{P,S-DTF})]$ complex and after 5 h of photolysis only 30% of **4** was converted into **5**.

2.3. Manganese complexes

We studied also the group 7 carbonyl complexes using bromopentacarbonylmanganese, $[\text{MnBr(CO)}_5]$ as precursor as substitution of two CO ligands can easily been performed [11]. First, we investigated the reaction of **2** with half equivalent of $\text{Mn(CO)}_5\text{Br}$ in refluxing dichloromethane for 7 h with the aim of preparing the bisubstituted manganese complex $[\text{MnBr(CO)}_3(\text{P-DTF})_2]$. After purification by chromatography on silica gel column, the desired complex $[\text{MnBr(CO)}_3(\text{P-DTF})_2]$ (**6**), was obtained in 40% yield as a yellow precipitate. ^{31}P NMR investigation of this precipitate shows two signals at 41.6 and 21.3 ppm of different intensities indicating likely the presence of two isomers. It is worthnoting that three isomeric forms can be envisioned for $[\text{MnBr(CO)}_3(\text{P-DTF})_2]$: *fac*, *mer-cis* and *mer-trans* [12]. ^{31}P NMR investigation is a very convenient tool for structural determination by comparison of the chemical shift values with close derivatives [13]. Accordingly, we attributed to the signal observed at 41.6 ppm the *mer-trans*-P-Mn-P isomer and to the 21.3 ppm the *fac-cis*-P-Mn-P isomer (Scheme 5) [14]. The *cis* and *trans* configurations are also evident from the ^1H NMR spectrum for the vinylogous proton which appears as a doublet and resonates at 5.58 ppm ($^2J_{\text{PH}} = 21$ Hz) for the *fac*, *cis* and 6.56 ppm ($^2J_{\text{PH}} = 21$ Hz) for the *mer*, *trans*. From the ^1H NMR,

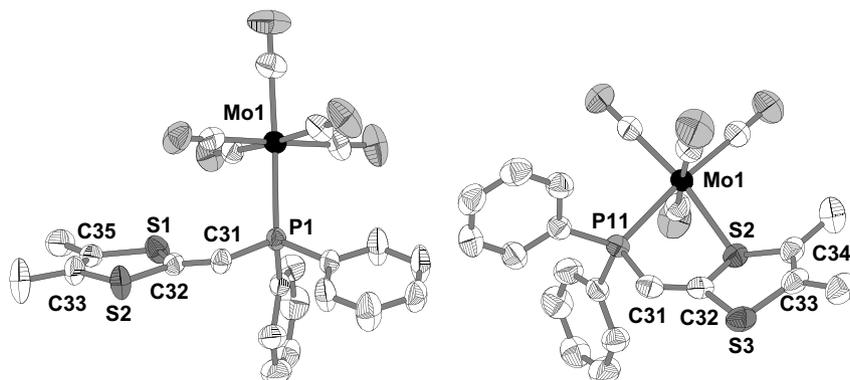
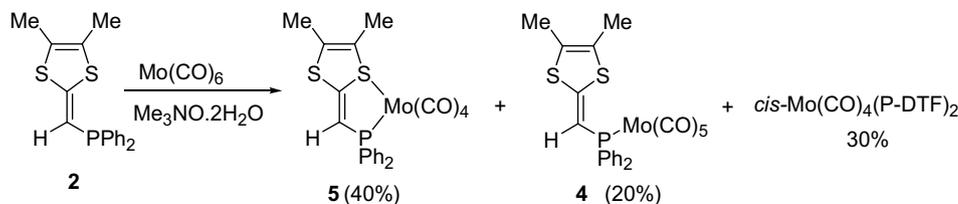
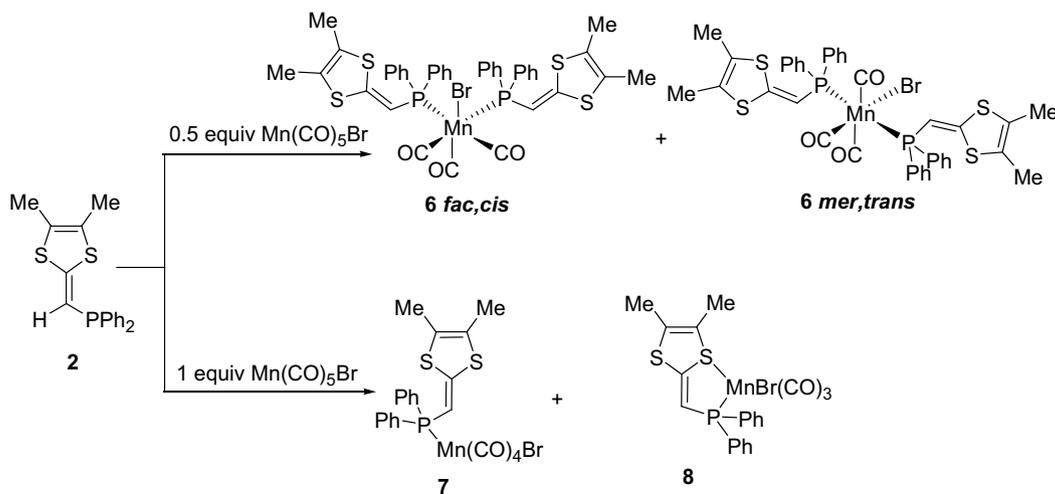


Fig. 2. Molecular structures of **4** and **5**. H atoms omitted for clarity. Ellipsoids are drawn at 50% probability.



Scheme 4.



Scheme 5.

we can determine a ratio 4:1 for those two isomers, the main isomer being the *mer, trans* derivative. We were able to isolate **6 mer, trans** isomer by fractional crystallisation as this isomer is less soluble in MeOH. IR investigation confirms also the structural assignment, as it exhibited on the spectra three carbonyl bands, two intense bands at 2032 cm^{-1} and 1893 cm^{-1} and a weaker and sharper band at 2032 cm^{-1} supportive with the *mer, trans* derivative. For the *fac, cis* isomer three carbonyl bands of equal intensity were observed on the spectra at 2015 , 1948 and 1899 cm^{-1} .

Reaction of $[\text{MnBr(CO)}_5]$ with one equivalent of **2** in refluxing CH_2Cl_2 for 3 h leads mainly to the monosubstituted complex **7**, $[\text{MnBr(CO)}_4(\text{P-DTF})]$ in 56% yield after column chromatography. Actually, investigation of the reaction medium by ^{31}P NMR shows two signals one at 27 ppm, assigned to complex **7**, and another one at lower field, 78.7 ppm attributed to complex **8** where **2** behaves as a bidentate ligand towards Mn and form a chelate ring [15,16]. As previously observed for the molybdenum derivative described above, the signal of the phosphorus atom in this five-membered metallacycles is shifted of about 50 ppm downfield. In order to separate complex **8** from complex **7** we attempted chromatography on silica gel, but we did not isolate **8** $[\text{MnBr(CO)}_3(\text{P,S-DTF})]$ probably due to the cleavage of the weaker link of the chelate ring, the Mn–S bond.

2.4. Electrochemistry

The redox behavior of the dithiafulvenes **1–3** as well as the different complexes was investigated by cyclic voltammetry in dichloromethane. For all these derivatives, except for **6**, only one irreversible oxidation wave was observed on the voltammogram. This oxidation wave is attributed to the oxidation of the dithiafulvene core into the cation radical. Presumably, the potentials re-

quired to oxidize the metal in those complexes, Mo(0) to Mo(+1) and Mn(+1) to Mn(+2), are out of the limit of the working range of dichloromethane. This might be attributed to the electron-withdrawing effect of the oxidized phosphine coordinated to the metallic center. Comparison of the oxidation peak potentials of the various complexes with the one of the vinyl phosphine **2** shows the influence of the nature of the metal and also of the mode of coordination. For instance, for the Mo (Table 2) as well as for the Mn (Table 3) series, the oxidation of the dithiafulvene core occurs at a higher potential when it acts as a P,S-bidentate ligand than as a monodentate P ligand. Similarly when two vinyl phosphines are coordinated to the metallic center the electron-withdrawing effect of the metal center is decreased. Moreover for the $\text{M}(\text{P-DTF})_2$, $\text{M}(\text{P-DTF})$ and $\text{M}(\text{P,S-DTF})$ complexes it can be observed that the nature and the oxidation state of the metal has also a significant effect on the oxidation potential of the DTF moiety, as the Mn^{1+} complexes exhibit higher oxidation potentials than the Mo complexes. Upon recurrent scans, the cyclic voltammograms obtained for the various complexes maintained the same shape, demonstrating the absence of any C–C coupling reactions.

Table 3

^{31}P parameters and oxidation peak potentials for the manganese metal carbonyl complexes

Compound	δP (ppm)	E_{pa} (V) vs. SCE
P-DTF (2)	–13.2	0.73
$[\text{Mn Br(CO)}_3(\text{P,S-DTF})_2]$ (6)	<i>mer, trans</i> 41.6 <i>fac, cis</i> 21.3	0.80, 1.25
$[\text{Mn(CO)}_4\text{Br(P-DTF)}]$ (7)	27.0	–
$[\text{Mn(CO)}_3\text{Br(P,S-DTF)}]$ (8)	78.7	1.09
		1.21 ^a

^a Determined from a mixture of complexes **7** and **8** based on the data obtained for **7**.

Table 4
Crystal data and structure refinement parameters for **1**, **2**, **3**, **4** and **5**

Structure parameter	1	2	3	4	5
Empirical formula	C ₁₈ H ₂₀ BPS ₂	C ₁₈ H ₁₇ PS ₂	C ₁₈ H ₁₇ PS ₃	C ₂₃ H ₁₇ MoPO ₅ S ₂	C ₂₂ H ₁₇ MoPO ₄ S ₂
Molecular weight	342.24	328.41	360.47	564.4	536.39
Crystal system	orthorhombic	monoclinic	monoclinic	triclinic	monoclinic
Space group	<i>Pbca</i>	<i>C2/c</i>	<i>Pn</i>	<i>P1</i>	<i>P2₁/c</i>
<i>a</i> (Å)	12.9378(2)	21.3825(6)	9.7597(4)	8.4587(2)	11.3306(2)
<i>b</i> (Å)	16.3803(2)	9.5756(2)	9.2355(4)	11.7987(3)	10.8819(2)
<i>c</i> (Å)	16.5194(2)	17.0144(4)	10.0459(4)	12.9315(3)	18.8649(3)
α (°)	90	90	90	71.8085(14)	90
β (°)	90	101.597(2)	108.422(2)	86.6956(15)	100.1857(7)
γ (°)	90	90	90	81.6192(10)	90
<i>V</i> (Å ³)	3500.87(8)	3412.59(14)	859.09(6)	1212.86(5)	2289.35(7)
<i>T</i> (K)	120(2)	293(2)	100(2)	293(2)	293(2)
<i>Z</i>	8	8	2	2	4
<i>D</i> _{calc} (g/cm ³)	1.299	1.278	1.393	1.545	1.556
μ (mm ⁻¹)	0.388	0.397	0.518	0.812	0.850
Total reflections	48360	7356	12370	18961	48124
Unique data (<i>R</i> _{int})	4004 (0.0743)	3874 (0.0289)	3308 (0.0236)	5277 (0.0455)	5186 (0.0296)
Observed reflections (<i>I</i> > 2 σ (<i>I</i>))	3120	3051	3283	3734	4591
<i>R</i> ₁ , <i>wR</i> ₂	0.0365, 0.0813	0.0525, 0.1465	0.0194, 0.0515	0.0312, 0.0619	0.0222, 0.0573
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0594, 0.0923	0.0660, 0.1573	0.0192, 0.0515	0.0621, 0.0745	0.0275, 0.0607
Goodness-of-fit	1.092	1.050	1.081	1.069	1.047

3. Conclusions

To summarize, we have investigated the coordinating ability of the electroactive dithiafulvenyl phosphine towards Mo(CO)₆ and MnBr(CO)₅ complexes. In both cases we have formed a new series of mononuclear complexes with this hemilabile ligand and have shown that, no matter the nature of the metallic center, it readily reacts as a monodentate (P) ligand and also forms P,S-chelate complexes if a coordination site is available for the ring closure. Comparison of the Mn complexes formed with the Mo complexes shows that in general they are less stable even if their oxidation potentials occur at higher potentials.

4. Experimental

4.1. General

¹H NMR, ³¹P NMR and ¹³C NMR spectra were recorded on Bruker AC 300P spectrometers. Chemical shifts are reported in ppm referenced to TMS for ¹H NMR and ¹³C NMR and to H₃PO₄ for ³¹P NMR. Melting points were measured using a Kofler hot stage apparatus. Elemental analyses results and Mass spectra were performed by the Centre Régional de Mesures Physiques de l'Ouest, Rennes. Methanol was distilled from calcium and dichloromethane from P₂O₅. Chromatography were performed using silica gel Merck 60 (70–260 mesh). The vinyl phosphine borane **1** and the vinyl phosphine **2** were prepared according to previously published procedures [6]. Cyclic voltammetry were carried out on a 10⁻³ M solution of the derivatives in dichloromethane, containing a 0.1 M *n*Bu₄NPF₆ as the supporting electrolyte. Voltammograms were recorded at 0.1 V s⁻¹ at a platinum disk electrode (*A* = 1 mm²). The potentials were measured vs. Saturated Calomel Electrode.

4.2. Synthesis and characterization

4.2.1. [(4,5-dimethyl-1,3-dithiol-2-ylidene)methyl](diphenyl)phosphine sulphide (**3**)

To a solution of **2** (0.32 g, 1 mmol) in 15 ml of dry and degassed dichloromethane sulfur S₈ (0.07 g, 2 mmol) was added under nitrogen. The reaction mixture was stirred at room temperature for 16 h and the solvent was removed in vacuo. Recrystallisation of the precipitate in ethylacetate: diethylether leads to **3** as white crystals in 88% yield. m.p. = 181 °C; ¹H NMR (300 MHz, CDCl₃) δ 1.90 (s, 3H,

CH₃), 1.94 (s, 3H, CH₃), 5.90 (d, H, CH, ²J_{PH} = 14 Hz), 7.3–7.9 (m, 10H, Ar); ¹³C RMN (75 MHz, CDCl₃) δ = 12.7, 13.5, 93.9 (d, ²J_{PC} = 97.4 Hz), 121.5, 124.9, 128.4, 128.6, 131.0, 131.1, 131.2, 131.3, 133.5, 134.7, 159.7 (d, ²J_{PC} = 16.5 Hz); ³¹P NMR (121 MHz, CDCl₃) δ = 32.1; HRMS calcd for C₁₈H₁₇PS₃: 360.0230. Found: 360.0228.

4.2.2. Mo(CO)₅(P-DTF) (**4**) and cis-Mo(CO)₄(P,S-DTF) (**5**)

To a solution of phosphine **2** (1 g, 3 mmol) in 15 mL of dry and degassed decahydronaphtalene added (790 mg, 3 mmol) of Mo(CO)₆ and the reaction mixture was heated to 150 °C for 30 min under nitrogen. The heterogeneous medium becomes rapidly an homogeneous solution. The solvent was removed under reduced pressure and the residue was chromatographed over silica gel using CH₂Cl₂/pentane (1/5) as eluent. Mo(CO)₅(P-DTF) (**4**) was obtained in 44% yield as white crystals and cis-Mo(CO)₄(P,S-DTF) (**5**) was obtained in 5% yield as white crystals.

4.2.3. Mo(CO)₅(P-DTF) (**4**)

m.p. 164 °C; ¹H NMR (300 MHz; CDCl₃) δ = 1.86 (s, 3H, CH₃), 1.96 (s, 3H, CH₃), 6.17 (d, 1H, CH, ²J_{PH} = 14 Hz), 7.30–7.60 (m, 10H, Ar); ¹³C NMR (75 MHz, CDCl₃) δ = 12.9, 13.5, 99.9 (*J*_{PC} = 160 Hz), 122.9, 123.8, 128.6, 128.7, 129.9, 132.0, 132.1, 134.6, 135.1, 152.0, 205.8, 210.5; ³¹P NMR (121 MHz; CDCl₃) δ = 24.1; IR (cm⁻¹) ν (CO): 1904, 1924, 1987, 2027, 2067; Anal. Calc. for C₂₃H₁₇MoO₅PS₂: C, 48.94; H, 3.04; S, 11.36. Found: C, 48.85; H, 3.01; S, 11.50%.

4.2.4. cis-Mo(CO)₄(P,S-DTF) (**5**)

m.p. 166 °C; ¹H NMR (300 MHz; CDCl₃) δ = 2.07 (s, 3H, CH₃), 2.09 (s, 3H, CH₃), 6.54 (d, 1H, CH, ²J_{PH} = 0.9 Hz), 7.40–7.60 (m, 10H, Ar); ³¹P NMR (121 MHz; CDCl₃) δ = 62.4; IR (cm⁻¹) ν (CO): 1876, 1897(br), 2022; HRMS (FAB): Calc. for C₂₂H₁₇MoO₄PS₂ 537.9360. Found: 537.9373.

4.2.5. [MnBr(CO)₃(P-DTF)₂] (**6**)

To a solution of vinyl phosphine **2** (0.16 g, 0.5 mmol) in 3 mL of dry and degassed CH₂Cl₂ was added (70 mg, 0.25 mmol) of BrMn(CO)₅. The reaction mixture was heated to reflux for 7 h. After evaporation of the solvent the residue was chromatographed on silica gel column using CH₂Cl₂:pentane (1:1) as eluent. The complex **6**, MnBr(CO)₃(P-DTF)₂ was obtained as a mixture of two isomers in 40% yield. The *mer*, *trans* isomer was isolated by fractional crystallisation as this isomer is less soluble in MeOH.

m.p. = 165 °C; ^1H NMR (300 MHz, CDCl_3) δ = 1.69 (s, CH_3 , 6H), 1.87 (s, CH_3 , 6H), 6.56 (d, 2H, $^2J_{\text{PH}} = 21$ Hz), 7.30–7.90 (m, Ar, 20H); ^{31}P NMR (121 MHz, CDCl_3) δ = 41.6; IR (KBr) $\nu_{\text{CO}} = 2032$ (w), 1943(s), 1893(s) cm^{-1} ; The *fac, cis* isomer ^1H NMR (300 MHz, CDCl_3) δ = 1.68 (s, CH_3 , 6H), 1.89 (s, CH_3 , 6H), 5.58 (d, 2H, CH, $^2J_{\text{PH}} = 21$ Hz), 7.30–7.90 (m, Ar, 20H); ^{31}P NMR (121 MHz, CDCl_3) δ = 23.4 ppm; IR (KBr) $\nu_{\text{CO}} = 2015$ (s), 1948(s), 1899(s) cm^{-1} ; HRMS calcd for $\text{C}_{39}\text{H}_{34}\text{BrMnO}_3\text{P}_2\text{S}_4$: $[\text{M}-\text{Br}]^+$: 795.0246. Found: 795.0213.

4.2.6. $[\text{MnBr}(\text{CO})_4(\text{P-DTF})]$ (7)

To a solution of vinyl phosphine **2** (0.20 g, 0.6 mmol) in 5 mL of dry and degassed CH_2Cl_2 was added (165 mg, 0.6 mmol) of $\text{BrMn}(\text{CO})_5$. The reaction mixture was heated to reflux for 2 h. Investigation of the medium by ^1H NMR and ^{31}P NMR allowed us to determine the spectroscopic characteristics of **8** $[\text{MnBr}(\text{CO})_3(\text{P,S-DTF})]$ ^1H NMR (300 MHz, CDCl_3) δ = 1.72 (s, CH_3 , 3H), 1.90 (s, CH_3 , 3H), 6.65 (d, $J_{\text{PH}} = 0.3$ Hz), 7.20–7.60 (m, 10H, Ar); ^{31}P NMR (121 MHz, CDCl_3) δ = 78 ppm; After evaporation of the solvent the residue was chromatographed on silica gel column using CH_2Cl_2 :pentane (1:2) as eluent. The complex **7**, $[\text{MnBr}(\text{CO})_4(\text{P-DTF})]$ was obtained as an orange powder in 56% yield. m.p. = 144 °C; ^1H NMR (300 MHz, CDCl_3) δ = 1.79 (s, CH_3 , 3H); 1.96 (s, CH_3 , 3H); 6.42 (d, 1H, $^1J_{\text{PH}} = 21$ Hz), 7.40–7.90 (m, 10H, Ar); ^{31}P NMR (121 MHz, CDCl_3) δ = 27; IR (KBr) $\nu_{\text{CO}} = 1956$, 1999 cm^{-1} ; HRMS calcd for $\text{C}_{22}\text{H}_{17}\text{O}_4\text{BrPS}_2\text{Mn}$: 573.8869. Found: 573.8862.

4.3. Crystallography

Single-crystal diffraction data were collected on Nonius KappaCCD diffractometer for compounds **1**, **2** and **4** and on APEX II Bruker AXS diffractometer for compounds **3** and **5** (Centre de Diffraction X, Université de Rennes, France). Details of the crystallographic are given in Table 4.

Appendix A. Supplementary material

CCDC 682242, 682243, 682244, 682245 and 682246 contain the supplementary crystallographic data for **1**, **2**, **3**, **4** $[\text{Mo}(\text{CO})_5(\text{P-DTF})]$ and **5** $[\text{Mo}(\text{CO})_4(\text{P,S-DTF})]$. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associ-

ated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.04.011.

References

- [1] (a) M. Fourmigué, P. Batail, Bull. Soc. Chim. Fr. 129 (1992) 29; (b) M. Fourmigué, C.E. Uzelmeier, K. Boubekeur, S.L. Bartley, K.R. Dunbar, J. Organomet. Chem. 520 (1997) 343; (c) C.E. Uzelmeier, S.L. Bartley, M. Fourmigué, R. Rogers, G. Grandinetti, K.R. Dunbar, Inorg. Chem. 37 (1998) 6706; (d) N. Avarvari, D. Martin, M. Fourmigué, J. Organomet. Chem. 643–644 (2002) 292; (e) T. Devic, P. Batail, M. Fourmigué, N. Avarvari, Inorg. Chem. 43 (2004) 3136; (f) N. Avarvari, M. Fourmigué, Chem. Commun. (2004) 1300; (g) C. Réthoré, M. Fourmigué, N. Avarvari, Chem. Commun. (2004) 1384; (h) S. Perruchas, N. Avarvari, D. Rondeau, E. Levillain, P. Batail, Inorg. Chem. 44 (2005) 3459; (i) C. Rethore, I. Suisse, F. Agbossou-Niedercorn, E. Guillaumon, R. Llusar, M. Fourmigué, N. Avarvari, Tetrahedron 62 (2006) 11942.
- [2] (a) J.M. Asara, C.E. Uzelmeier, K.R. Dunbar, J. Allison, Inorg. Chem. 37 (1998) 1833; (b) B.W. Smucker, K.R. Dunbar, J. Chem. Soc., Dalton Trans. (2000) 1309; (c) C.E. Uzelmeier, B.W. Smucker, E.W. Reinheimer, M. Shatruck, A.W. O'Neal, M. Fourmigué, K.R. Dunbar, Dalton Trans. 44 (2006) 5259.
- [3] E. Cerrada, C. Diaz, M.C. Diaz, M.B. Hursthouse, M. Laguna, M.E. Light, J. Chem. Soc., Dalton Trans. 6 (2002) 1104.
- [4] (a) P. Pellon, G. Gachot, J. Le Bris, S. Marchin, R. Carlier, D. Lorcy, Inorg. Chem. 42 (2003) 2056; (b) G. Gachot, P. Pellon, T. Roisnel, D. Lorcy, Eur. J. Inorg. Chem. (2006) 2604.
- [5] M. Yuan, B. Ulgut, M. McGuire, K. Takada, F.J. DiSalvo, S. Lee, H. Abruna, Chem. Mater. 18 (2006) 4296.
- [6] (a) D. Lorcy, M. Guerro, R. Carlier, P. Pellon, Chem. Commun. (2004) 212; (b) M. Guerro, T. Roisnel, P. Pellon, D. Lorcy, Inorg. Chem. 44 (2005) 3347.
- [7] S. Dilsky, W.A. Schenk, Eur. J. Inorg. Chem. (2004) 4859.
- [8] S. Jugé, M. Stephan, R. Merdès, J.P. Genet, S. Halut-Desportes, J. Chem. Soc., Chem. Commun. (1993) 531.
- [9] L. Hirsivaara, M. Haukka, S. Jääskeläinen, R.H. Laitinen, E. Niskanen, T.A. Pakkanen, J. Pursiainen, J. Organomet. Chem. 579 (1999) 45.
- [10] Y.-L. Shi, Y.-C. Gao, Q.-Z. Shi, D.L. Kershner, F. Basolo, Organometallics 6 (1987) 1528.
- [11] S.J.A. Pope, G. Reid, J. Chem. Soc., Dalton Trans. (1999) 1615.
- [12] A.M. Bond, R. Colton, M.E. McDonald, Inorg. Chem. 17 (1978) 2842.
- [13] P.E. Garrou, Chem. Rev. 81 (1981) 229.
- [14] M.A. Beckett, D.S. Brassington, S.J. Coles, T. Gelbrich, M.E. Light, M.B. Hursthouse, J. Organomet. Chem. 688 (2003) 174.
- [15] E. Lindner, R. Fawzi, H.A. Mayer, K. Eichele, K.K. Pohmer, Inorg. Chem. 30 (1991) 1102.
- [16] B. Heuer, M.L. Matthews, G. Reid, M. Ripley, J. Organomet. Chem. 655 (2002) 55.