P.L. and to the University of British Columbia for the award of a graduate fellowship to G.R-A.

Registry No. $CpMo(NO)Cl_2$, 120311-08-2; $Cp^*Mo(NO)Cl_2$, 120311-09-3; $CpMo(NO)Br_2$, 120311-10-6; $Cp^*Mo(NO)Br_2$, 120311-11-7; $CpMo(NO)I_2$, 61495-99-6; $Cp^*Mo(NO)I_2$, 115364-37-9; $CpMo(NO)I_2(PMePh_2)$, 100898-79-1; $[CpMo(NO)Cl_2]^{\bullet-}$, 120311-12-8; $[Cp^*Mo(NO)Cl_2]^{\bullet-}$, 120311-20-8; $[CpMo(NO)Br_2]^{\bullet-}$, 120311-13-9; $[Cp^*Mo(NO)Br_2]^{\bullet-}$, 120311-14-0; $[CpMo(NO)I_2]^{\bullet-}$, 120311-15-1; $[Cp^*Mo(NO)I_2]^{\bullet-}$, 120311-16-2; $[Cp_2Co][Cp^*Mo(NO)Br_2]$, 120311-17-3; Me_3SiCH_2MgCl, 13170-43-9; $CpW(NO)I_2$, 120311-18-4; $Cp^*W(NO)I$, 115364-39-1; $[Cp_2Co][CpMo(NO)Cl_2]$, 120311-19-5; $[Cp_2Co][Cp^*Mo(NO)Cl_2]$, 120311-21-9; $[Cp_2Co][CpMo(NO)Br_2]$, 120311-22-0; $[Cp_2Co][CpMo(NO)I_2]$, 120311-23-1; $[Cp_2Co][Cp^*Mo(NO)I_2]$, 120311-24-2; $[CpFe(\eta^6-C_6H_6)][CpW(NO)(CH_2SiMe_3)_2]$, 120311-26-4.

Electrocatalytic Study of Iron(0)-Carbene Complexes: Electrocatalytic Dimerization of the Carbene Ligand and Synthesis of Tetrathiafulvalene Derivatives

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Received November 1, 1988

The electrochemical properties of (carbene)iron(0) complexes $Fe(:\overline{CSC(CO_2Me)=C(CO_2Me)S})(CO)_2(L)_2$ (**2**; L = PMe_3, **a**; L = PMe_2Ph, **b**; L = $PMePh_2$, **c**; L = PPh_3, **d**; L = PPh_3 and CO, **e**) are reported. Cyclic voltammetry shows that they undergo a one-electron oxidation between −0.1 and −0.3 V vs SCE and that the stability of 2^+ is markedly affected by the nature of both solvents and ligands. Controlled potential electrolysis of **2d** in acetonitrile affords TTF derivative **3** arising from the dimerization of the carbene ligand, and coulometric measurements reveals that the dimerization is electrocatalyzed (TN ≥ 100). The formation of TTF derivative **3** from **2d** can be initiated either by electrochemical oxidation or by chemical oxidation with $AgCF_3SO_3$, I_2, or $[Fe(C_5H_5)_2]PF_6$. The stoichiometric chemical oxidation of **2b** with Ag^+ or $Fe(C_5H_5)_2^+$ salts leads to a mixture of two cationic diamagnetic isomers corresponding to $(\mathbf{2b})_2^{2+}$ derivatives. A mechanism of the electrocatalyzed dimerization of carbene ligand is proposed and is shown to involve one-electron oxidation, dimerization of the resulting cation, and ligand elimination.

Introduction

Metal-carbene complexes are useful reagents for the selective formation of carbon-carbon bonds and the synthesis of organic compounds.[2] Dimerization of carbene ligands, with carbon-carbon double bond formation, is of special interest for the direct access to functional olefins displaying specific properties. Especially, the dimerization of the 1,3-dithiol-2-ylidene ligand of complexes of type I, easily produced by the cycloaddition of alkynes to $Fe(\eta^2-CS_2)$ complexes,[3] shows potential for the one-step synthesis of tetrathiafulvalene derivatives II which behave as one-electron donating compounds for the formation of charge-transfer complexes.[4] The dimerization of carbene ligands into olefins has already been achieved by the thermolysis of Fischer-type metal-carbene complexes.[5,6] As for carbene-olefin coupling reactions[7] or metal-carbene-initiated alkyne polymerization,[8,9] the initial step of the carbene ligand dimerization process involves the generation of a vacant site, by thermal or photochemical dissociation of a metal-ligand bond.[10,11] In addition, it has been established that the thermal dimerization does not proceed with the release of the uncoordinated carbene species but via a bimetallic intermediate[10] (Chart I).

Chart I

(I) (II)

We have already shown that tetrathiafulvalene derivatives II could be produced directly from (1,3-dithiol-2-ylidene)iron complexes (I) by either thermolysis or even addition of iodine.[11] The latter observation led us to investigate the role of oxidation on the dimerization of the carbene ligand, and we report herein the electrochemical study of iron-carbene complexes of type I that gives evidence for the electron-transfer catalysis and the controlled influence of ancillary PR_3 ligands in carbene ligand dimerization.

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(1) (a) Laboratoire d'Electrochimie (UA-CNRS 439). (b) Laboratoire de Chimie de Coordination Organique (UA-CNRS 415), Campus de Beaulieu, Université de Rennes.

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Table I. Cyclic Voltammetric Data for the First Oxidation Process of Complex 2[a]

complex	L^1/L^2	solv	E_p^a, V	E_p^c, V	i_p^c/i_p^a
2a	PMe_3/PMe_3	CH_3CN	−0.30	−0.41	0.2
2b	PMe_2Ph/PMe_2Ph	CH_3CN	−0.29	−0.39	0.2
2b	PMe_2Ph/PMe_2Ph	CH_2Cl_2	−0.15	−0.26	0.4
2c	PPh_2Me/PPh_2Me	CH_3CN	−0.23	−0.32	0.8
2c	PPh_2Me/pPh_2Me	CH_2Cl_2	−0.12	−0.27	1.0
2d	PPh_3/PPh_3	CH_3CN	−0.19	−0.29	0.3
2d	PPh_3/PPh_3	CH_2Cl_2	−0.11	−0.20	0.9
2e	PPh_3/CO	CH_3CN	+0.27		0

[a] Performed with a 3×10^{-3} M of complex **2** in 0.1 M solution of Bu_4NBF_4, Bu_4NPF_6, or Bu_4NClO_4 at 0.1 $V\cdot s^{-1}$. Potentials are vs SCE.

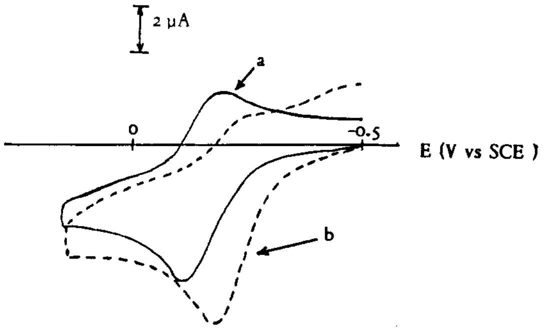
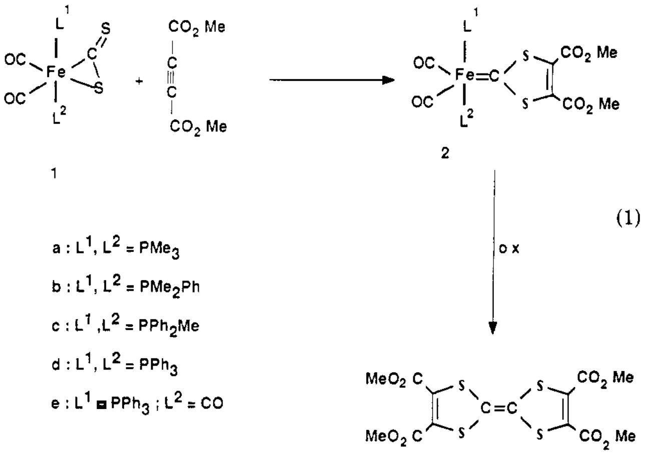


Figure 1. Cyclic voltammograms of **2d** (a) in CH_2Cl_2 (—) and (b) in CH_3CN (- - -), with Bu_4NBF_4 at 0.1 V/s.

Results

a. Cyclic Voltammetry. Complexes **2a–e** were prepared in situ by adding an excess of dimethyl acetylenedicarboxylate to the corresponding $Fe(\eta^2\text{-}CS_2)$ complexes (**1a–e**)[3,12] in the appropriate solvent (eq 1).



1 2 3 (1)

a : $L^1, L^2 = PMe_3$
b : $L^1, L^2 = PMe_2Ph$
c : $L^1, L^2 = PPh_2Me$
d : $L^1, L^2 = PPh_3$
e : $L^1 = PPh_3$; $L^2 = CO$

The cyclic voltammetry (CV) of complexes **2** was carried out at a stationary platinum electrode in acetonitrile, dichloromethane, or acetone solutions containing tetrabutylammonium perchlorate, tetrafluoroborate, or hexafluorophosphate (0.1 M) as the supporting electrolyte. The cyclic voltammetry data are summarized in Table I.

All complexes **2** show a first anodic wave between −0.1 and −0.3 V vs SCE. The chemical ability of the anodically generated species 2^+, as shown by the i_p^c/i_p^a ratio, changes according to the nature of the solvent and of the phosphine ligands: for complex **2d** ($L = PPh_3$) the peak current ratio i_p^c/i_p^a which is 0.9 in dichloromethane markedly decreases in acetonitrile ($i_p^c/i_p^a = 0.3$) (Figure 1). A similar variation of the ratio is also observed for complex **2c** (1.0 in dichloromethane and 0.8 in acetonitrile). The i_p^c/i_p^a ratio gradually increases with the scan speed—from 0.3 to 0.7 over scan rates from 0.1 to 1 $V\cdot s^{-1}$ for **2d** in acetonitrile—indicating EC behavior.

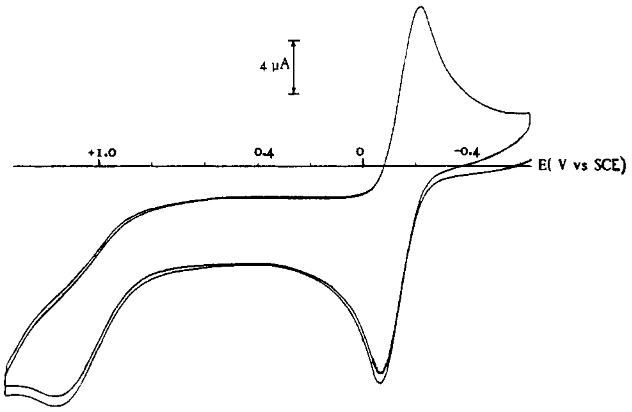


Figure 2. Cyclic voltammogram of **2c** in CH_2Cl_2, with Bu_4NBF_4 at 0.1 V/s.

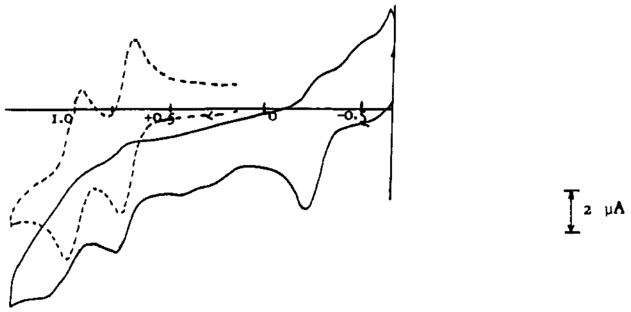


Figure 3. Cyclic voltammograms of **2d** in CH_3CN (—) and of the TTF derivative **3** (- - -), with Bu_4NBF_4 at 0.1 V/s.

This first anodic process involves a one-electron transfer as demonstrated by the oxidation of complex **2c** with 1 equiv of ferrocenium cation which is in turn totally reduced into ferrocene. An additional irreversible oxidation is observed for **2c** at a more anodic potential ($E_p^a \approx +1.1$ V) (Figure 2). Cation $\mathbf{2d}^+$ is less stable than $\mathbf{2c}^+$ in acetonitrile. The complete cyclic voltammogram of **2d** in acetonitrile (Figure 3) shows, in addition to the first anodic wave, the appearance of two new reversible waves at 0.8 V and approximately +1.1 V which have been identified as the oxidation waves of the tetrathiafulvalene (TTF) derivative **3**, resulting from the dimerization of the carbene ligand. Another wave at ca. +1.2 V is also observed and can be attributed to the oxidation of the free triphenylphosphine. Furthermore, two unidentified waves appear at more cathodic potential ($E_p^c = -0.55$ and -0.77 V). Addition of a large excess of carbon disulfide and of dimethyl acetylenedicarboxylate to **2d** in acetonitrile does not lead to any modification of CV; this is consistent only with the stoichiometric formation of the TTF derivative **3** at the electrode.

The cyclic voltammetry of **2d** in acetonitrile and in the presence of carbon monoxide leads rapidly to an irreversible substitution of one PPh_3 group by carbon monoxide and to the formation of the known complex **2e** ($L^1 = PPh_3$, $L^2 = CO$)[11] (Figure 4). Although this ligand exchange reaction has not been studied in detail, it seems likely that it occurs by a radical chain mechanism.[13] This

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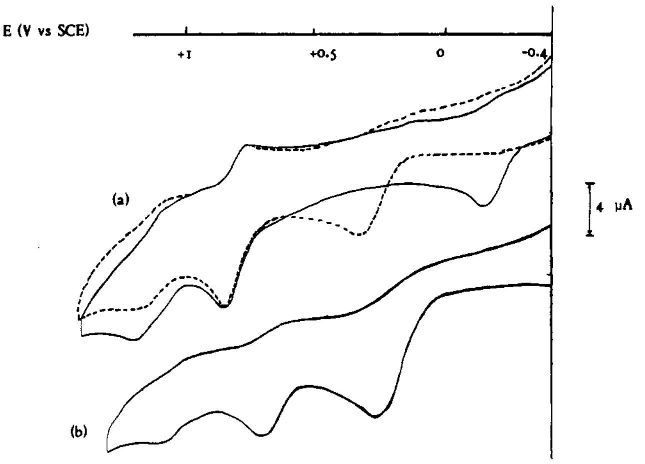

Figure 4. Cyclic voltammograms (a) of **2d** in CH_3CN before (—) and after (---) CO bubbling and (b) of **2e** in CH_3CN, with Bu_4NBF_4 at 0.1 V/s.

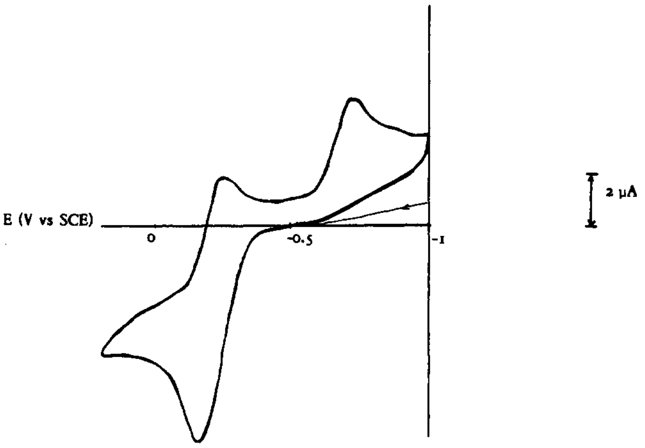

Figure 5. Cyclic voltammogram of **2b** in CH_2Cl_2, with Bu_4NBF_4 at 0.1 V/s.

facile and rapid reaction contrasts with the thermal formation of **2e** from **2d** which requires heating of **2d** under CO pressure.[11] The first anodic step given by **2e** appears at more positive potential (E_p^a = +0.27 V) than that of **2d**, and the corresponding oxidized form $\mathbf{2e}^+$ is also unstable in acetonitrile and leads to the formation of the TTF derivative **3**.

Cation $\mathbf{2c}^+$ (L = $PMePh_2$) is more stable than $\mathbf{2d}^+$ in acetonitrile: the anodic waves corresponding to the oxidation of the TTF derivative **3** and of the phosphine are also observed but with a low intensity. By contrast, the oxidized species $\mathbf{2}^+$ of complexes **2a** and **2b** (**a**, L = PMe_3; **b**, L = PMe_2Ph) are chemically unstable in dichloromethane (Figure 5). Moreover, in acetonitrile, neither the anodic waves corresponding to the oxidation of the TTF derivative **3** nor the oxidative waves of the free phosphine are observed; but two cathodic waves appear at negative potential (Figure 6). This suggests that the cation $\mathbf{2a}^+$ or $\mathbf{2b}^+$ has been chemically transformed into species reducible at those potentials.

b. Controlled Potential Electrolysis and Coulometric Measurements. The observation of TTF waves during the cyclic voltammetry of complex **2d** in acetonitrile led us to examine the controlled potential electrolysis of this compound.

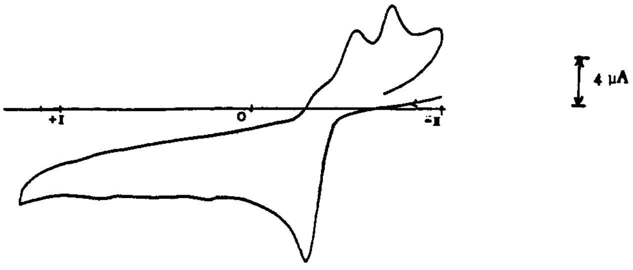

Figure 6. Cyclic voltammogram of **2b** in CH_3CN, with Bu_4NBF_4 at 0.1 V/s.

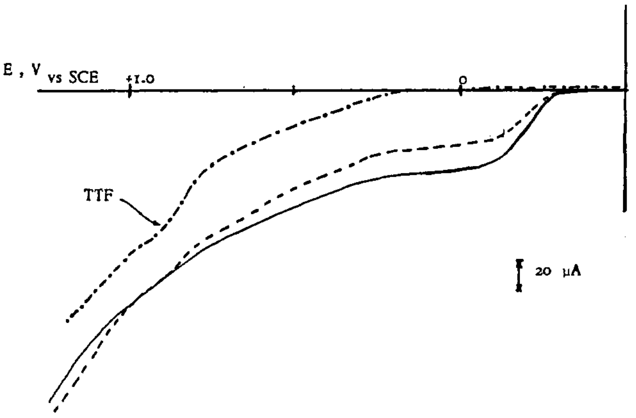

Figure 7. Voltammograms of **2d** ($c = 10^{-2}$ M) at vitreous carbon rotating disk (2000 rpm) in $LiClO_4/CH_3CN$ medium before electrolysis (—) and after the passage of 1 C: immediately after the end of electrolysis (---) and 15 min after the end of electrolysis (-·-).

The electrolysis of 1 mmol of **2d** in acetonitrile at a large vitreous carbon electrode, at 0 V vs SCE, corresponding to the first anodic wave, involves only nearly 0.1 F/mol but leads to the TTF derivative **3** in approximately 60% yield, after separation and purification by column chromatography (eq 1). The small measured amount of charge (faradays) suggests that the TTF formation, therefore the carbene ligand dimerization, is electrocatalyzed.

To confirm the electrocatalysis, the electrolysis was stopped after 0.01 F/mol of **2d** was passed through the solution and the reaction was then monitored by following the changes at a rotating disk electrode: the first oxidation wave rapidly and totally disappeared, within 15 min, with the concomitant increasing of a new wave at more positive potential, corresponding to the TTF formation (Figure 7). The electrocatalysis was also operational in dichloromethane, but the reaction was slower ($t_{1/2} \approx 0.5$ h). No increase of the yield in the TTF derivative **3** was observed by electrolysis of **2d** in acetonitrile at 0 V vs SCE, in the presence of a large excess of dimethyl acetylenedicarboxylate and of carbon disulfide (1/20/80 ratio).

The electrocatalysis has also been used to prepare the unsymmetrical TTF derivative **4** (eq 2). An equimolar mixture of complexes **2d** and **2d′** was first prepared by addition of dimethyl acetylenedicarboxylate and of diethyl acetylenedicarboxylate to complex **1d** in acetonitrile. The electrolysis of this solution gave a mixture of the two symmetrical TTF derivatives **3** and **3′** in low yield and of the unsymmetrical TTF derivative **4**, isolated in 15% yield. The low yields are related to the difficulty of the separation of the TTF derivatives which was performed by using successive column and thick-layer chromatographies.

c. Chemical Oxidations of Complexes 2c and 2d. The cyclic voltammetry showed that complexes **2d** (L = PPh_3) and **2c** (L = $PMePh_2$) on one side and complexes **2a** (L = PMe_3) and **2b** (L = PMe_2Ph) on the other side behaved quite differently. The chemical oxidation of complexes **2b** and **2d** has been performed in an attempted

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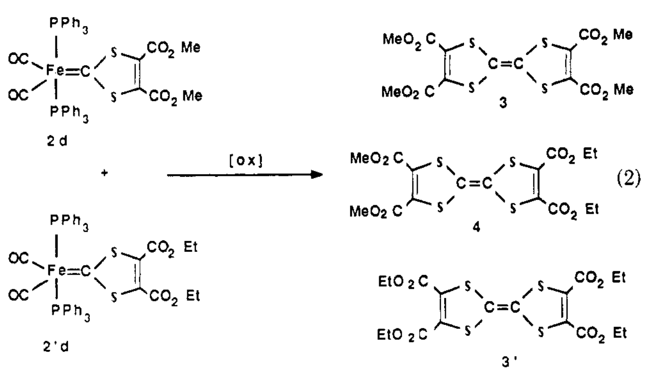
(14) Hartzler, H. D. *J. Am. Chem. Soc.* **1973**, *95*, 4379.



(2)

to elucidate the striking different role of PPh_3 and PMe_2Ph ligands in complexes **2**.

We have investigated the oxidation of complex **2d** in dichloromethane and in acetonitrile with a catalytic amount of iodine (iodine/complex **2d** = 1/150). The reaction was followed by voltammetry at a rotating disk electrode (Figure 8): at room temperature in acetonitrile, **2d** disappeared in a first-order reaction ($t_{1/2} \approx 20$ min) and simultaneously the TTF derivative **3** was formed as shown by the anodic wave ($E_{1/2} = 0.97$ V). The same experiment carried out in the presence of free triphenylphosphine (3 equiv) resulted in a slowing down of the reaction ($t_{1/2} \approx 35$ min). Oxidation of complex **2c** in acetonitrile with a catalytic amount of iodine gave also the TTF derivative **3**, but the rate was slower than that from complex **2d** ($t_{1/2} \approx 1.5$ h), in agreement with the higher stability of **2c**$^+$ observed by cyclic voltammetry (Figure 2).

Cyclic voltammetry of **2b** did not reveal the formation of TTF on oxidation but only two cathodic waves which could result from the chemical evolution of the oxidized species **2b**$^+$. In a attempt to isolate the species resulting from **2b**$^+$, we have examined the stoichiometric oxidation of **2b**. Reaction of **2b** with 1 equiv of silver triflate, or ferrocenium hexafluorophosphate, in dichloromethane resulted in the formation of new *diamagnetic* salts. These salts could correspond to a mixture of two isomers of the dimer (**2b**$^+$)$_2$ (58% yield after recrystallization based on (**2b**)$_2$(CF_3SO_3)$_2$($2CH_2Cl_2$) as suggested by elemental analysis and ^1H, ^{13}C, and ^{31}P NMR studies. The ^{31}P NMR spectrum shows only two lines in the 1:2 ratio suggesting the presence of two isomers, A and B. The ^{13}C NMR spectrum shows two sets of resonances for the carbene and carbonyl ^{13}C nuclei also consistent with the presence of the two isomers A and B in a 1:2 ratio [B, δ 273.93 (Fe=C<), 214.29 (FeCO); A, δ 263.28 (Fe=C<), 209.81 and 208.06 (FeCO)]. Each of these resonances appears as a triplet corresponding to the coupling of the ^{13}C nuclei with two identical ^{31}P nuclei. This suggests a structure trans for isomer B and cis for isomer A. The cyclic voltammogram of these salts in dichloromethane shows no anodic wave but two cathodic waves at $E_p = -0.58$ and -0.95 V (Figure 9) already observed by complete cyclic voltammetry of **2b** (Figure 6) (Chart II).

Discussion

The cyclic voltammetry studies (Table I) show that the nature of the phosphorus ligands L markedly affects the easiness of oxidation of complexes **2**: $E_p{}^a$ is lowered as the electron donor capability of L increases and follows the sequence $PPh_3 < PMePh_2 < PMe_2Ph < PMe_3$. The chemical stability of complex **2c**$^+$ (L = $PMePh_2$) appears to be much higher than that of **2b**$^+$ (L = PMe_2Ph) and **2a**$^+$ (L = PMe_3) which contains more basic phosphines or of **2d**$^+$ (L = PPh_3) which contains the more hindered and labile PPh_3 ligands.

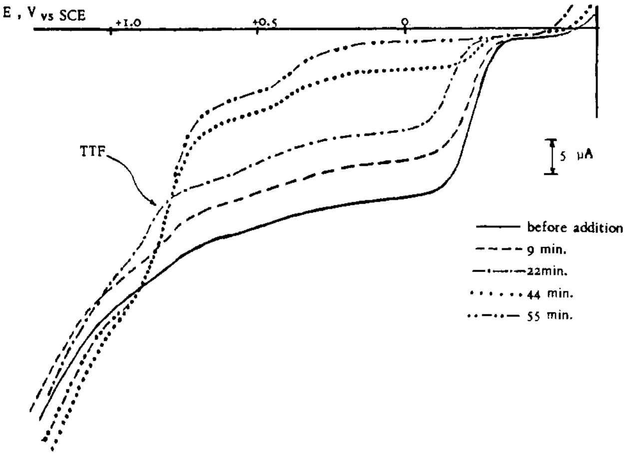


Figure 8. Voltammograms of **2d** before and after addition of 0.01 equiv of I_2, in Bu_4NBF_4/CH_3CN medium.

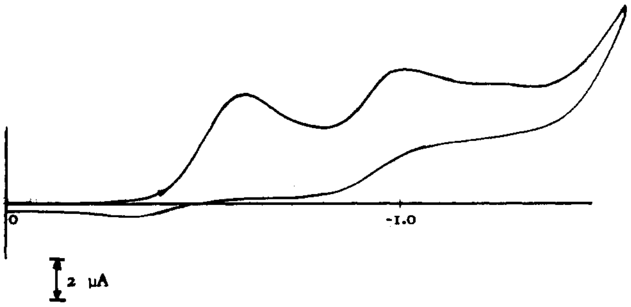
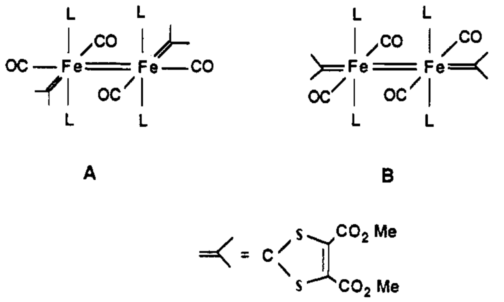


Figure 9. Cyclic voltammogram of [**2b**]$_2{}^+$ in CH_3CN, with Bu_4NPF_6 at 0.2 V/s.

Chart II



Cyclic voltammetry of **2d** in dichloromethane gives a quasi-reversible wave with $E_{1/2} = -0.12$ V whereas $Fe(CO)_3(PPh_3)_2$ reversibly oxidizes at $E_{1/2} = +0.34$ V.[15] This indicates the much better donor capability of the carbene ligand than that of the CO ligand.

The chemical instability of the oxidized species **2**$^+$ contrasts with the stability of the paramagnetic carbene iron(I) salts $Fe(CO)_2L_2L^{Me}$ (L = PPh_3 or $P(OR)_3$; L^{Me} = $\overline{CN(Me)CH_2CH_2NMe}$).[16] $Fe(CO)_2(PPh_3)_2L^{Me}$ oxidizes reversibly at -0.5 V and gives a stable green paramagnetic cation, whereas oxidation of **2d** leads to the dimerization of the carbene ligand. The chemical oxidation of **2b** with 1 equiv of $Ag(CF_3SO_3)$ results in the formation of diamagnetic salts without the loss of ligands corresponding to (**2b**$^+$)$_2$($CF_3SO_3{}^-$)$_2$ and therefore to the dimerization of

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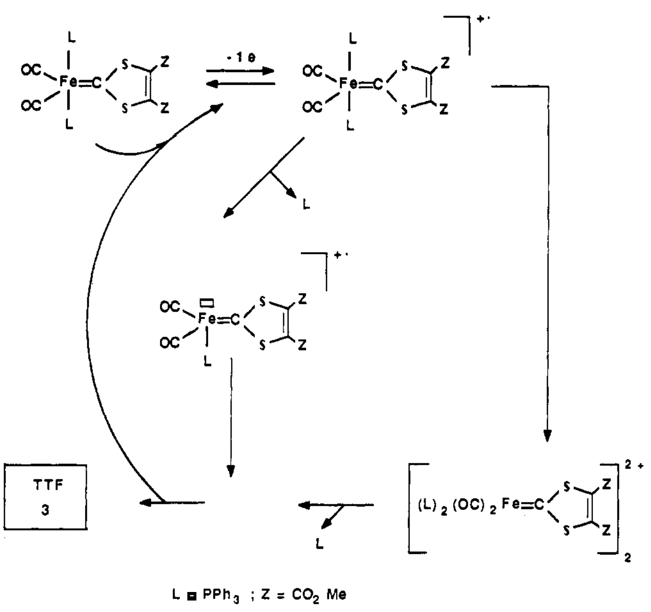
(15) Connelly, N. G.; Somers, K. R. *J. Organomet. Chem.* **1976**, *113*, C39.

(16) Lappert, M. F.; Mac Quitty, J. J.; Pye, P. L. *J. Chem. Soc., Chem. Commun.* **1977**, 411.

Scheme I



the one-electron oxidation product of **2b**.

The electrochemical studies show the crucial role of triphenylphosphine in the electrocatalytic dimerization of the carbene ligand as the fastest dimerization was observed with **2d**. The lability of the Fe–PPh$_3$ bond in **2d**$^+$ is very high, as shown by the rapid exchange with carbon monoxide leading to **2e**$^+$, and is rate-determining for the dimerization which slows down when an excess of PPh$_3$ was added. The electrocatalytic dimerization can be related to the synthesis of TTF by the thermolysis of **2d** which was shown to depend on the lability of PPh$_3$ ligands and did not result from the dimerization of a free carbene, suggesting a binuclear complex as an intermediate.[11]

From these observations it is possible to propose a mechanism which involves an electrochemical step followed by several chemical steps (Scheme I). For all complexes **2**, the first step is a one-electron oxidation leading to a paramagnetic 17-electron species. In the second step, the dimerization of the 17-electron complex gives a *diamagnetic* complex of type $(2^+)_2$ which could be observed only after the oxidation of **2b**, thus suggesting an iron–iron bond formation. With PPh$_3$ or PMePh$_2$ ligands, the formation of the dimeric species can be followed by the loss of the phosphine ligand and by an intramolecular carbene transfer to give TTF.

In support of this hypothesis, one has to point out the analogy observed in CV for the acetonitrile solution between the unidentified waves at −0.55 and −0.77 V vs SCE for **2d** and at −0.54 and −0.74 V vs SCE for **2b** and $(\mathbf{2b}^+)_2$; these waves probably correspond to the reduction of the analogous binuclear complexes (Figures 3 and 6).

An alternate route could involve the initial loss of PPh$_3$ from **2d**$^+$ since the lability of 17-electron cation radicals is well-known and has intensively been used in the ligand exchange reaction of carbonyl ligands[13,17] and even of phosphines.[18] The intermediate could then dimerize to afford TTF.

Finally, to explain the electrocatalysis one of the intermediates formed in the chemical evolution of the 17-electron complex has to be an oxidative species for the starting complex **2d**.

Conclusion

The one-electron oxidation of complex **2d** leads to the formation of tetrathiafulvalene derivative **3** by the carbon–carbon coupling of two carbene ligands, with a high turnover number (>100). This process occurs either electrochemically or chemically with the use of traces of an appropriate oxidant (Ag$^+$, iodine). As the η^2-CS$_2$ precursor complex **1d** can be made, in more than 80% yield, in only one step from iron pentacarbonyl,[19] this reactions appears to be an efficient and very simple method to prepare the TTF derivative **3** and could be used for the preparation of other tetrathiafulvalene derivatives.

Finally it is important to point out that when many ligand substitution reactions are known to occur by electron transfer catalysis,[13,17,18] this reaction seems to be the first evidence of carbene ligand dimerization promoted by a one-electron oxidation.

Experimental Section

Infrared spectra were recorded on a Pye Unicam SP 1100 infrared spectrometer. NMR spectra were obtained on Varian AM 360 and on Brucker AM 300 WB instruments. Mass spectra were determined at 70 eV with use of a Varian MAT 311 double-focusing spectrometer (Centre de Mesures Physiques, Rennes, France).

Solvents were dried by reflux over appropriate drying agents. Acetonitrile was distilled over calcium hydride, dichloromethane was distilled over phosphorus pentoxide, and acetone was purchased from Merck and was used as received. Fe(η^2-CS$_2$)(CO$_2$)(PR$_3$)$_2$ complexes (**1**) were prepared according to published methods.[12,19] Complexes **2** were made directly in the cell by adding a slight excess of dimethyl acetylenedicarboxylate to a solution of Fe(η^2-CS$_2$)(CO$_2$)(PR$_3$)$_2$ complexes (**1**) at room temperature.[3]

Electrochemical Studies. Conventional electrochemical equipment was used for voltammetry (EGG PAR Model 362 scanning potentiostat with an XY recorder) and controlled potential electrolysis (Tacussel PRT 20-2 potentiostat and Tacussel IG 5 coulometer).

For voltammetry, the working electrode was a stationary (cyclic voltammetry) or a rotating (voltammetry) platinum disk electrode of 2 mm of diameter (Tacussel EDI electrode), the auxilliary electrode was a platinum electrode and the reference electrode was an aqueous saturated calomel electrode (SCE) isolated from the electrolysis by a bridge with the same electrolyte as the cell electrolyte. The ohmic drop was not corrected.

For controlled potential electrolysis, the cell was equipped with a vitreous carbon working anode of a 4-cm diameter.[20]

All measurements were made at room temperature with deoxygenated solutions. Purified Bu$_4$NBF$_4$, Bu$_4$NPF$_6$, Bu$_4$NClO$_4$, or LiClO$_4$ was used as electrolytes.

Rates (half-life) of electrochemical and chemical oxidations of complex **2d** were followed by voltammetry and measured by relating the magnitude of the current vs time.

Synthesis of the Tetrathiafulvalene Derivative 3 by Preparative Electrolysis of 2d. Complex **1d** (712 mg; 1 mmol) was added to 100 mL of CH$_3$CN containing LiClO$_4$ (0.1 M) under a nitrogen atmosphere in the electrolysis cell. An excess of dimethyl acetylenedicarboxylate (1.2 mmol) was added to prepare in situ complex **2d**.[3] The solution was stirred for 10 min at room temperature and was then oxidized at 0 V vs SCE. The electrolysis was stopped after 1 C was passed through the solution. The disappearance of complex **2d**, monitored at a rotatory disk electrode, was complete after 15 min. Water (100 mL) was then added to the solution, and after removal under vacuum of acetonitrile, diethyl ether was added., The red organic layer was

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extracted and dried on dry magnesium sulfate. Solvent evaporation followed by a silica gel column chromatography using a mixture of hexane–ether as eluant gave 130–140 mg of the tetrathiafulvalene derivative **3** (60–64%): mp 165 °C; IR (Nujol) 1743, 1715, 1575 cm^{-1}; ^{1}H NMR ($CDCl_3$, 60 MHz, 309 K) δ 3.93 (s, CO_2Me) [lit.[14] mp 169 °C; IR (KBr) 1740, 1710, 1570 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.85 (s, CO_2Me)].

Preparative Electrolysis of a Mixture of Complexes 2d and 2d′. A solution of 2 mmol of **2d** and **2d′** was first prepared by adding 2 mmol of dimethyl acetylenedicarboxylate and 2 mmol of diethyl acetylenedicarboxylate to 2850 mg (4 mmol) of **1d** in 120 mL of acetonitrile containing $LiClO_4$ (0.1 M). The electrolysis of this solution was performed at 0 V vs SCE, and the reaction products were extracted as those of the electrolysis of **2d**. A silica gel column chromatography followed by a silica gel thick-layer chromatography, using a mixture of hexane-ether as eluant, gave 110 mg of the TTF derivative **3** (12%), 140 mg of the TTF derivative **4** (15%), and 30 mg of the TTF derivative **3′** (3%).

4: IR (Nujol) 1740, 1720, 1700, 1570 cm^{-1}; ^{1}H NMR ($CDCl_3$, 60 MHz, 309 K) δ 4.23 (q, OCH_2, $^3J_{HH}$ = 7.5 Hz), 3.76 (s, OCH_3), 1.33 (t, CH_3, $^3J_{HH}$ = 7.5 Hz); MS, *m/e* calcd for $M^+(C_{16}H_{10}O_8S_4)$ 463.973, found 463.972.

3′: IR (Nujol) 1750, 1720, 1570 cm^{-1}; ^{1}H NMR ($CDCl_3$, 60 MHz, 309 K) δ 4.13 (q, OCH_2, $^3J_{HH}$ = 7.5 Hz), 1.10 (t, CH_3, $^3J_{HH}$ = 7.5 Hz).

Stoichiometric Oxidation of Complex 2b. To a solution of **2b** (1 mmol) in 30 mL of CH_2Cl_2, prepared in situ from 464 mg of **1b** (1 mmol) and a slight excess of dimethyl acetylenedicarboxylate (0.2 mL, 1.6 mmol), was added 257 mg of silver triflate (1 mmol). The dark brown solution turned red brown with formation of a black precipitate. The solution was stirred for 1 h and then filtered on a frit. The filtrate was concentrated to 5 mL, and ether was added. On cooling to −18 °C, 490 mg of a yellow powder was obtained. Addition of 1 mmol of ferrocenium hexafluorophosphate (331 mg) instead of triflate gave the same type of salt with the PF_6^- counteranion.

Anal. Calcd for $[Fe(CS_2C_2(CO_2Me)_2)(CO)_2(PMe_2Ph)_2](CF_3SO_3)(CH_2Cl_2)$ (M = 840; $C_{26}H_{28}O_9S_3P_2F_3Fe{\cdot}CH_2Cl_2$): C, 38.57; H, 3.57; S, 11.43; P, 7.38; Found: C, 38.01; H, 3.53; S, 11.87; P, 7.32. IR (Nujol): 2080, 2010, 1750 cm^{-1}. The NMR spectra were recorded with the sample prepared from **2b** and $Fe(C_5H_5)_2{}^+PF_6^-$ and thus containing an PF_6^- anion. ^{1}H NMR (CD_3CN, 300 MHz, 297 K): δ 7.31 (m, C_6H_5), 3.96, 3.92, 3.88 (s, CO_2Me), 2.01 (m, PMe_2). ^{31}P NMR (CD_3CN, 32.38 MHz, 309 K): δ 21.34 (s, A), 14.54 (s, B). $^{13}C\{^1H\}$ NMR (CD_3CN, 75.47 MHz, 297 K): δ 273.93 (t, Fe=C<, $^2J_{PC}$ = 22.4 Hz, B), 263.88 (t, Fe=C<, $^2J_{PC}$ = 20.6 Hz, A), 214.29 (t, CO, $^2J_{PC}$ = 24.2 Hz, B), 209.81 (t, CO, $^2J_{PC}$ = 20.6 Hz, A), 208.06 (t, CO, $^2J_{PC}$ = 20.6 Hz, A). Identification of the signals due to isomer A or B is based on the relative intensity (A/B = 1/2).

Synthesis and Characterization of (Trifluoromethyl)gold Complexes

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Received November 4, 1988

The synthesis of $(CF_3)AuL$ (L = PMe_3, PEt_3, PPh_3) from LAuCl and $Cd(CF_3)_2{\cdot}DME$ is described. These linear gold(I) compounds readily add excess halogen to form the predominantly trans square-planar gold(III) dihalides $(CF_3)AuX_2(L)$ (X = Br, I). The use of stoichiometric (or less) halogen leads to a significant quantity of $(CF_3)_2AuX(L)$ (L = PMe_3, PEt_3) which is shown to arise from trifluoromethyl/halogen ligand exchange between $(CF_3)AuL$ and $(CF_3)AuX_2(L)$. No evidence for ligand exchange is found when L = PPh_3. $(CF_3)_2AuI(L)$ (L = PMe_3, PEt_3) may also be prepared in 80% yield from the oxidative addition of trifluoromethyl iodide to $(CF_3)AuL$; experiments with the radical scavenger galvinoxyl suggest a radical chain mechanism for this CF_3I addition. Close examination of the ^{1}H and ^{19}F NMR spectra for the new square-planar complexes reveals that downfield shifts occur for both nuclei when a cis halide is changed from Br to I; a trans halide causes an upfield shift upon this substitution. The cadmium reagent is, in general, ineffective for the preparation of Au(III) complexes since reduction to $(CF_3)AuL$ usually occurs. However, treatment of $(CF_3)_2AuI(PMe_3)$ with $Cd(CF_3)_2{\cdot}DME$ in the presence of excess CF_3I leads to the high-yield synthesis of the tris(trifluoromethyl) species $(CF_3)_3AuPMe_3$.

Introduction

Although the first trifluoromethyl derivative of a transition metal was reported nearly 30 years ago,[1] the synthesis and study of such complexes have received limited investigation.[2] This may be due, in part, to the paucity of trifluoromethylating reagents available. While the synthetic chemist may choose among Grignard reagents, methyllithium, dimethylzinc, or other common alkylating agents, trifluoromethyl analogues of these standard reagents are either unknown or ineffective in the preparation of transition-metal compounds. Until recently, all trifluoromethyl complexes were synthesized by either decarbonylation of a trifluoroacetyl ligand or oxidative addition of trifluoromethyl iodide to a metal complex; both of these methods have severe limitations. A third approach has been reported by Morrison in which $Cd(CF_3)_2$ is used as the trifluoromethylating reagent.[3,4] The dimethoxyethane (DME) adduct of this species is stable enough to permit its isolation and storage, yet it is reactive enough to displace halides in nickel, palladium, platinum,[4] and cobalt[6] compounds, forming both mono- and bis(trifluoromethyl) complexes.

As part of our studies on gold alkyl compounds, we set out to synthesize the mono-, bis-, and tris(trifluoromethyl)gold phosphine complexes, $(CF_3)AuL$, $(CF_3)Au$-

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