UNIVERSITE DE BOURGOGNE
U.F.R. Sciences et Techniques
Filière : **Master 2 CMPP**

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21 janvier 2015

Session : **1**

EPREUVE

Electrochimie Moléculaire

Calculatrice non autorisée
Durée : 01h00

A – 1. Par analyse électrochimique de composés de coordination, à quelle grandeur thermodynamique peut-on accéder qui fait le lien avec la structure électronique ?

2. Sur une série de composés de votre choix, expliquer comment varie cette grandeur avec les éléments constitutifs ou variables structurales de la molécule.

3. Quelle est la méthode électrochimique la plus couramment utilisée pour cette détermination ? Pour quelle raison ?

4. Quelles sont les orbitales moléculaires concernées respectivement par la première oxydation et la première réduction d'une molécule donnée ?

B – Analyse de publication : *Organometallics* **2006**, *25*, 4292.

1. Préciser les conditions expérimentales les plus essentielles utilisées pour l'analyse en voltammétrie cyclique au cours de ce travail.

2. a) Représenter schématiquement la courbe de réponse en voltammétrie cyclique du composé *dtbpf*. Faire la relation aux grandeurs (i_p^{ox} / i_p^{red}) et ΔE_p mentionnées dans la partie Results and Discussion. Quelles sont les valeurs théoriquement attendues ?

b) Connaissez-vous d'autres critères caractérisant ce type de réponse en voltammétrie cyclique ?

3. a) Que désigne le terme « formal potential » et comment est-il extrait expérimentalement du voltammogramme ?

b) Comment se situe en potentiel le *dtbpf* par rapport au ferrocène ?

c) Identifier l'élément électroactif dans ces deux molécules.

d) Commenter l'effet électronique du groupement $-P(tBu)_2$? Cet effet est-il conforme aux attentes des auteurs (justifier votre réponse sur une base quantitative) ?

Organometallics **2006,** *25,* 4292−4300

Anodic Electrochemistry of Free and Coordinated 1,1′-Bis(di-*tert*-butylphosphino)ferrocene

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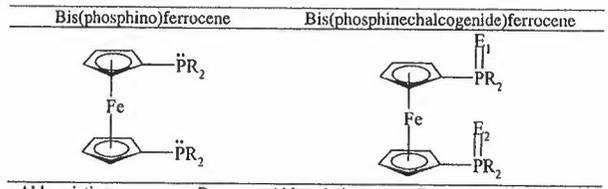
The electrochemistry of 1,1′-bis(di-*tert*-butylphosphino)ferrocene (dtbpf) was examined in methylene chloride with tetrabutylammonium hexafluorophosphate as the supporting electrolyte. Two new complexes in which dtbpf was bound to a transition metal were prepared and characterized. The two new complexes as well as two previously reported complexes were analyzed by cyclic voltammetry. In addition, the chalcogenids, dtbpfS_2 and dtbpfSe_2, were prepared and characterized by NMR and the structure of dtbpfSe_2 was determined. The oxidation of dtbpfS_2 is a simple one-electron process due to the presence of the iron center. In contrast, the oxidation of dtbpfSe_2 is electrochemically irreversible and appears to proceed by an EE mechanism. Chemical oxidation of dtbpfSe_2 resulted in the formation of [dtbpfSe_2][BF_4]$_2$, in which a Se−Se bond formed. This compound was characterized by ^{31}P NMR and X-ray crystallography. A detailed analysis of the electrochemistry suggests that the oxidation of dtbpfSe_2 occurs by two separate one-electron processes. In addition, formation of the Se−Se bond was reversible.

Chart 1. Bis(phosphino)ferrocenes and Bis(phosphinechalcogenide)ferrocenes Mentioned in This Report



Abbreviation	R	Abbreviation	R	E_1	E_2
dppf	Ph	dppfS_2	Ph	S	S
dippf	iPr	dppfSe_2	Ph	Se	Se
dtbpf	tBu	dppfOSe	Ph	O	Se
		dippfS_2	iPr	S	S
		dippfSe_2	iPr	Se	Se
		dtbpfS_2	tBu	S	S
		dtbpfSe_2	tBu	Se	Se

To further investigate the role of electronics and sterics on the oxidative electrochemistry of bis-phosphinometallocenes, we have chosen to examine 1,1′-bis(di-*tert*-butlypropylphosphino)-ferrocene (dtbpf).

Experimental Section

Electrochemical Procedures. Cyclic voltammetric, chronoamperometric, and linear scan voltammetric experiments were conducted at ambient temperature (22 ± 1 °C) with the exception of dtbpf, which was conducted at 20, 10, 0, and −10 °C using a jacketed cell connected to a constant-temperature circulating bath (±0.1 °C). Experiments were conducted using a PAR Model 263A potentiostat/galvanostat. All scans were performed under an argon atmosphere using 0.1 M tetrabutylammonium hexafluorophosphate ([NBu_4][PF_6]) as the supporting electrolyte and CH_2Cl_2 as the solvent, with the exception of the cyclic voltammograms of dtbpfSe_2 used for simulation, in which case the concentration of the supporting electrolyte was 0.5 M. Analyte concentrations were 1.0 mM, with the exception of dtbpf, which was studied at 0.50, 1.0, and 2.0 mM. Glassy carbon (1.5 mm disk) was used as the working electrode. The glassy carbon electrode was polished with two diamond pastes, first 1.0 μm and then 0.25 μm, and rinsed with CH_2Cl_2 prior to use. The experimental reference electrode was Ag/AgCl, separated by a fine frit from the solution, and the counter electrode was a platinum wire. FcH or Fc* was used as an internal standard depending on the potential of the compound being studied.[12] Cyclic voltammograms were recorded using PowerSuite software and were performed at scan rates of 50 mV/s, and from 100 to 1000 mV/s in 100 mV/s increments. Digital simulations were performed using DigiElch version 2.0.[13]

Bulk electrolyses were performed under argon using a CH Instruments Model 630B electrochemical analyzer. The working and auxiliary electrodes were platinum mesh baskets that were in compartments separated by a fine glass frit. The Ag/AgCl reference electrode was in the same compartment as the working electrode, but was also separated by a fine glass frit. A 1.5 mm glassy carbon electrode was used to obtain the cyclic voltammogram after the bulk electrolysis. The solvent was CH_2Cl_2, and the supporting electrolyte was 0.1 M [NBu_4][PF_6]. The analyte concentration was 5.0 mM, and the temperature was 22 ± 1 °C.

Results and Discussion

The oxidative electrochemistry of dtbpf was examined in CH_2Cl_2 with $[NBu_4][PF_6]$ as the supporting electrolyte. At all temperatures and concentrations employed in this study, the oxidation of dtbpf was chemically and electrochemically reversible; the ratio of the peak currents (i_p^{ox}/i_p^{red}) was greater than 0.95, and the peak separation (ΔE_p) was approximately 83 mV; under identical conditions the ΔE_p for FcH was 91 mV. The potential at which oxidation of dtbpf occurs is 0.06 V vs $FcH^{+/0}$. The potential at which oxidation of 1,1′-(disubstituted)ferrocene compounds occurs has been correlated with the Hammett parameter (σ_p) for the substituents according to eq 1 ($E_L = 1/2E^0$ vs NHE).[17] The value of σ_p for the $-P(tBu)_2$ group is 0.15,[18] which, according to eq 1, would predict the potential at which oxidation of dtbpf occurs to be 0.20 V vs $FcH^{0/+}$. In general

$$E_L = 0.45\sigma_p + 0.36 \quad (1)$$

there is good agreement between the experimental potential and that predicted by eq 1, so it is surprising that there is such a large difference in this case.

The reversible oxidation of dtbpf is somewhat surprising, as the oxidative electrochemistry of two closely related compounds, dppf[2] and dippf,[3] are complicated by a chemical reaction after oxidation. The reaction has been proposed to be a dimerization of the oxidized species through one of the phosphorus atoms.[4] Since the product of the oxidation of dtbpf is stable on the cyclic voltammetric time scale, it would seem either that $dtbpf^+$ does not undergo the same reaction as the products of dppf or dippf oxidation or that the reaction is significantly slower. Given that the potential at which dtbpf oxidation occurs is nearly identical to dippf (+0.05 V vs $FcH^{+/0}$),[3] it is unlikely that the stability of $dtbpf^+$ is due to electronic factors. It would seem that the bulky *tert*-butyl groups prevent the dimerization of $dtpbf^+$ from occurring.

To further examine the electrochemistry of dtbpf, the anodic electrochemistry of four dtbpf metal complexes was investigated.

Table 2. Formal Potentials (V vs $FcH^{0/+}$),[a] Potential Difference, ΔE (defined as $E^0_{cmpd} - E^0_{dtbpf}$), and Reversibility for dtbpf and Compounds Containing dtbpf (a scan rate of 100 mV/s was used for all data)

	E^0	ΔE	i_p^{ox}/i_p^{red}
dtbpf	0.06		0.95
$[NiCl_2(dtbpf)]$	0.35[b]	0.29[d]	0
$[PdCl_2(dtbpf)]$	0.47	0.41	0.99
$[PtCl_2(dtbpf)]$	0.46	0.40	1.00
$[Au_2Cl_2(dtbpf)]$	0.56	0.50	0.98
$dtbpfS_2$	0.36	0.30	0.96
$dtbpfSe_2$	0.24, −0.07[c]	0.18[d]	

[a] Determined from the midpoint of E_p^{ox} and E_p^{red}. [b] The oxidation of this compound is chemically irreversible, and therefore this value is the E_p^{ox} and not E^0. [c] The oxidation of this compound is electrochemically irreversible; the first value given is E_p^{ox} and the second is E_p^{red}. [d] The value ΔE is defined as $E_p^{ox} - E^0_{dtbpf}$.

Upon coordination, the potential at which oxidation of the iron center of dtbpf occurs shifts to more positive potentials. Similar to the dppf and dippf analogues, the oxidation of $NiCl_2(dtbpf)$ is chemically irreversible, while the oxidation of the Pd and Pt analogues is chemically and electrochemically reversible.[2,3] As with the free phosphines, the potentials at which oxidation of the dtbpf complexes occur (Table 2) are very similar to those of the analogous dippf complexes.[3] The oxidation of $[Au_2Cl_2(dtbpf)]$ is also chemically and electrochemically reversible and occurs at a potential similar to that of the dippf analogue There is a gold atom bonded to each phosphorus in $[Au_2Cl_2(dtbpf)]$, so eq 1 can be used to estimate the Hammett parameter for the $-P(tBu)_2AuCl$ group as 0.56.