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Grafting of borane-protected aliphatic and aromatic aminophosphine ligands to glassy carbon electrodes

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ABSTRACT

Phosphine–borane moieties with amino-anchoring groups were covalently grafted on glassy carbon substrates, using free radical electrografting methods. The oxidative destruction of phosphine was efficiently quenched thanks to the borane protecting group. The chelating ability of the attached phosphine ligands was exemplified with Mn.

1. Introduction

Electrode surfaces modified with organometallic complexes have been studied for their potential applications in electrocatalysis or in heterogeneous catalysis [1–5]. Phosphine compounds exhibit excellent chelating ability towards low and high oxidation-state transition metal derivatives and, therefore, would be particularly attractive to graft on a surface. However, only a few works report on the grafting of chelating phosphines on substrates [3,6,7], probably because their high sensitivity towards oxidation makes them difficult to handle. For catalytic applications, robust linkage must be built between substrates and phosphine compounds to prevent from the leaching of the transition metals. Free radical grafting methods onto carbon surface are probably the most convenient procedure to covalently introduce organic moieties on surfaces. The main related strategies consist of the electrochemical oxidation of amines or reduction of aryldiazonium salts [8,9]. However, the oxidation potential of phosphines being lower than that of amines, the phosphorus atom must be protected, especially when applying the first strategy. As phosphines protecting group, borane group was successfully reported to impede their chemical oxidation [10].

Using both strategies, we describe here the electrografting of aminophosphine–borane ligand. This work aims at demonstrating the efficiency of borane protection towards electro-oxidation and the ability of the immobilized ligands for chelating transition metals after a simple deprotection step.

2. Experimental

2.1. Syntheses of amino-phosphine borane

(3-aminopropyl)diphenylphosphine–borane (**1**) was prepared from the reaction of $PPh_2(Li).BH_3$ with 7.2 mmol 3-chloropropylamine (98%, Aldrich) at −80 °C in THF [10]. After recrystallization in diethyl ether (75% yield) and neutralization with 2 M aqueous NaOH, (**1**) was obtained as white powder.

δ (ppm) $CDCl_3$, ^1H 300 MHz: 7.70–7.30 (*m*, 10 H), 2.76 (*t*, 2 H), 2.26 (*m*, 2 H), 1.67 (*m*, 2 H), 1.20 (*bs*, 2 H), 1.00 (*m*, 3 H); ^{31}P 121 MHz: 16.15 (*m*).

(4-aminobenzyl) diphenylphosphine–borane (**2**) was obtained from $PPh_2(Li).BH_3$ and 7.2 mmol 4-nitrobenzylbromide (Aldrich, 99%). A subsequent reduction of the nitro moiety with $SnCl_2$ (Aldrich, 99%) in EtOH gave (**2**) (14% yield) [11].

δ (ppm) $CDCl_3$, ^1H 300 MHz: 7.70–7.30 (*m*, 10 H); 6.74 (*dd*, $^3J_{HH}=8.5$ Hz, $^4J_{PH}=2.1$ Hz, 2 H); 6.48 (*d*, $^3J_{HH}=8.5$, 2 H); 3.58 (*bs*, 2 H); 3.50 (*d*, $^2J_{PH}=9.2$ Hz, 2 H); ^{31}P 121 MHz: 17.15 (*m*).

2.2. Electrochemistry

Electrochemical measurements were performed using an Autolab electrochemical analyzer (PGSTAT 30, EcoChemie BV). The reference electrode was SCE, equipped with a salt bridge (and calibrated with ferrocene), and the counter electrode a Pt foil.

Glassy carbon (GC) disk or plates electrodes were used as substrates in the preparation of electrodes functionalized with the aminophosphine–borane species. The substrates were polished with DP-Nap paper 1 μm and Al_2O_3 slurry 0.3 μm (Struers). Electro-

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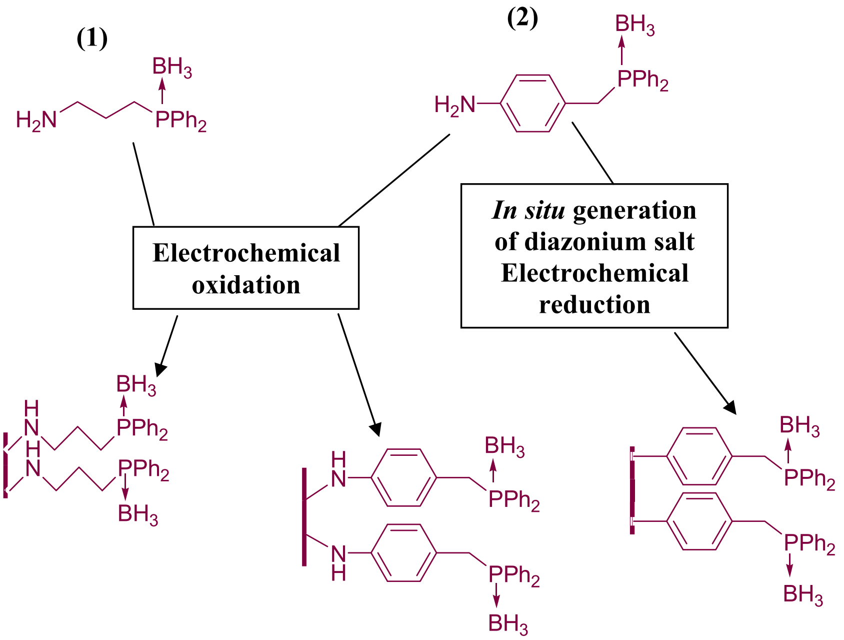

Scheme 1. Structures of the aminophosphine–borane species and their immobilization onto the electrode surfaces.

oxidative grafting of (**1**) (5 mM) was performed in MeCN containing 0.1 M Bu_4NPF_6 (Acros, electrochemical grade), by holding the potential at 2 V for 5 min while the grafting of (**2**) (5 mM) was carried out at 1 V for 5 min in MeOH + 0.1 M $LiClO_4$ (Aldrich) in the presence of 0.25 M lutidine (Acros) [12]. The aromatic aminophosphine–borane allowed to generate the corresponding diazonium salt, following the procedure by Bélanger and co-workers [13]. (4-benzyl) diphenylphosphine–borane was grafted by the electrochemical reduction of the corresponding diazonium, in situ generated in 0.5 M aqueous HCl, containing 10 mM $NaNO_2$ (Aldrich, 97%) and 5 mM of (**2**). The electrografting was achieved by applying a constant potential at −0.75 V for 5 min (Scheme 1). The electrodes were then rinsed with ultrapure water and absolute EtOH.

The disk electrodes modified by the phosphine–borane ligands were treated for 4 h in toluene containing 1,4-diazabicyclo[2.2.2] octane (DABCO) at 55 °C, for deprotecting the phosphine group [14].

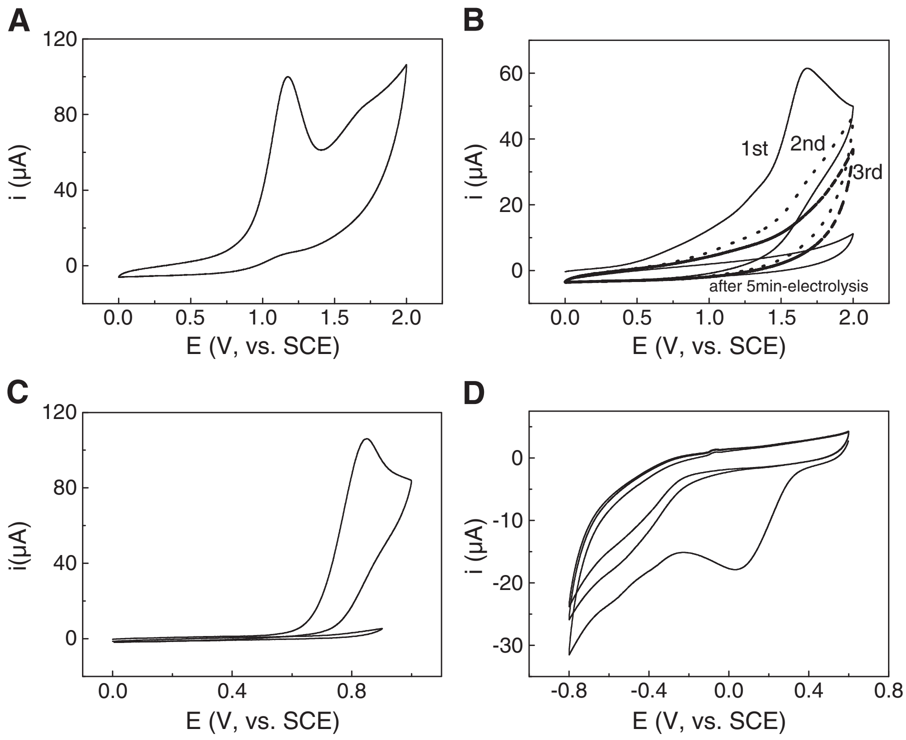

Fig. 1. (A) CV of 9 mM borane-free analog of 1 in MeCN containing 0.1 M Bu_4NPF_6 v = 200 mV/s. (B–D) CVs demonstrating the grafting of 5 mM phosphine–borane species. (B) Electrooxidation of 1 in MeCN + 0.1 M Bu_4NPF_6, v = 200 mV s^{-1} (3 scans and after 5 min electrolysis at E = 2 V). (C) Electrooxidation of 2 in MeOH + 0.1 M $LiClO_4$ + 50 eq lutidine, v = 100 mV s^{-1} (1st scan and after 5 min electrolysis at E = 1 V). (D) electroreduction of diazonium salt from 2 in 0.5 M HCl + 10 mM $NaNO_2$, v = 100 mV s^{-1}.

Table 1
P/C atomic ratio calculated from XPS analyses and surface concentrations for the modified GC surfaces.

	P/C	Γ_{XPS} mol cm^{-2}	Introduction of Mn(I) complexes E°(V)	$\Gamma_{ECHEM\text{-}Mn}$ mol cm^{-2}	$\Gamma_{thCPML\text{-}Mn}$ mol cm^{-2}
1 hydrochloride	0.072		–	–	–
Electro-oxidation of 1	0.029	$2.1 \cdot 10^{-10}$	1.52	$1.35–2.6 \cdot 10^{-10}$	$1.02 \cdot 10^{-10}$
Electro-oxidation of 2	0.022	$1.6 \cdot 10^{-10}$	1.43	$1.3–2.6 \cdot 10^{-10}$	$0.8 \cdot 10^{-10}$
Diazonium generation of 2 and electro-reduction	0.013	$0.94 \cdot 10^{-10}$	1.38	$0.6–1.2 \cdot 10^{-10}$	$0.8 \cdot 10^{-10}$

Then the electrodes were refluxing in CH_2Cl_2 containing $Mn(CO)_5Br$ for 4 h, yielding the corresponding organometallic complexes immobilized onto the GC surfaces.

2.3. XPS

XPS photoelectron spectra were collected from modified GC plates on a Thermo VG Scientific Escalab 250 system fitted with a monochromatic Al Kα X-ray source ($h\nu = 1486.6$ eV, spot size = 650 μm, power 15 kV × 200 W). The pass energy was set at 150 and 40 eV for the survey and the narrow regions, respectively. Spectral calibration was determined by setting the main C1s component at 285 eV. The surface composition was estimated using the integrated peak areas and the corresponding Scofield sensitivity factors corrected for the analyzer transmission function.

3. Results and discussion

The electrochemical oxidation of **1** and **2** was investigated in MeCN + 0.1 M Bu_4NPF_6 and compared to that of their borane-free analogs. In the absence of borane moiety, an irreversible oxidation peak corresponding to the oxidation of the phosphine group is observed at potential less positive than that corresponding to the amine group. This precludes any electrografting of the phosphine-ligand using the electro-oxidation of the amino group [8,15]. Addition of borane substituent onto the phosphine group allows the selective oxidation of amine group for **1** and **2**, keeping intact the phosphine group and its chelating ability. For instance, the cyclic voltammetry of the borane-free analog of **1** displays an irreversible oxidation peak at 1.05 V (Fig. 1A) contrariwise to **1** that does not exhibit this peak, only allowing the oxidation of amine at 1.7 V (Fig. 1B). The borane moiety is an efficient protecting group towards the electrochemical oxidation, even for highly positive potentials.

The grafting route based on the reduction of diazonium salt does not require protecting phosphine from its oxidation. However, phosphine groups are very sensitive to air oxidation. Then an additional interest to borane protection is the possibility to store and manipulate easily the phosphine-modified surfaces under ambient atmosphere.

The grafting of primary amines to carbon surface by electro-oxidation is nowadays a well-documented procedure, namely concerning the aliphatic amines [8,15]. Mechanistic studies have demonstrated that the radical cation initially formed upon electron transfer deprotonates to give an aminyl radical that covalently binds to the carbon surface [15]. More recently, several works successfully applied this strategy to aromatic amines, leading to the binding of the corresponding aromatic aminyl radical to the carbon surface [12,16,17]. Cyclic voltammetry recorded for the oxidation of **1** and **2** is consistent with the grafting of a film onto the electrode surface. Irreversible peaks are observed at Epa = 1.7 V (Fig. 1B) and 0.85 V (Fig. 1C) for **1** and **2**, respectively and assigned to the amine oxidation. On successive scans, the peak current decreases and disappears after 5 scans. Similarly, after 5 min-electrolysis at 2 V and 1 V for **1** and **2**, respectively, no oxidation peak could be further detected in the voltammograms recorded in the modifier solution (Fig. 1B and C). These results indicate the formation of a blocking film on the surface.

The electrochemical reduction of in situ generated aryldiazonium salt is another efficient procedure to strongly attach organic moiety onto carbon surface via the formation of C—C bonds [13], contrariwise to the former method that produces C—N bonds. Cyclic voltammograms of **2** in aqueous HCl containing $NaNO_2$ exhibit a large irreversible reduction peak located at 0.06 V (Fig. 1D). This peak is due to the reduction of the generated diazonium cation. It produces an aryl radical species that grafts onto the carbon surface. As a result, the peaks disappear on subsequent potential scans.

In order to further confirm the grafting of the phosphine–borane ligands onto the carbon surface, XPS analyses were performed on 3 samples of modified GC plates. Low-intensity signals due to phosphorous atoms in a BH_3–PPh_2 environment were observed at 133 (P2p) and 190 (P2s) eV. It is worth outlining that the signal at 190 eV contains two distinct contributions: P2s and B1s. After subtracting the P2s contribution (estimated from the P2s/P2p intensity ratio measured on triphenylphosphine as reference sample), an atomic P/B ratio close to 1 was calculated. These analyses unambiguously demonstrate the presence of phosphine–borane ligands at the carbon surface. Assuming a carbon atom surface density equal to that of basal plane graphite, the surface concentration (Γ_{XPS}) of the phosphine–borane ligands could be roughly estimated from the atomic P/C ratio [18]. Note that this calculation provides underestimated values as only one monolayer of the carbon atoms of the substrates is considered. Because the sampling depth for XPS is ~10 nm, more than one monolayer of carbon atoms are obviously probed.

It is further interesting to evaluate the chelating ability of the immobilized phosphine group towards coordination compounds. After a deprotection step, the modified electrodes were used as an active platform for introducing metallic Mn(I) complexes using Mn$(CO)_5Br$ as a model system. Cyclic voltammograms of the Mn (I)-modified electrodes in CH_2Cl_2 + 0.2 M Bu_4NPF_6 display reversible signal centered at 1.52, 1.43 and 1.38 V, respectively (see Table 1) corresponding to the Mn(II)/Mn(I) couple (Fig. 2). The peak currents

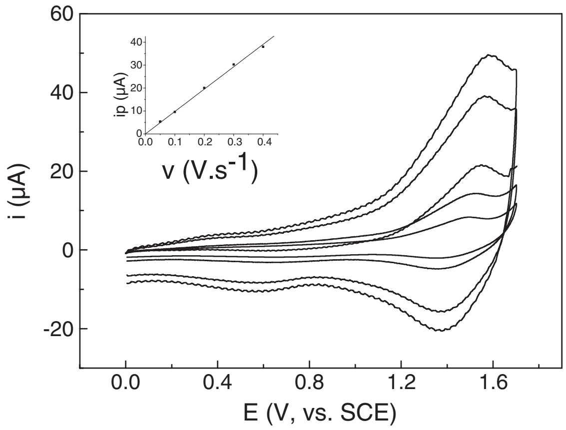

Fig. 2. CV in CH_2Cl_2 + 0.2 M Bu_4NPF_6 of surface-modified electrode after electrooxidation of 2 and formation of the corresponding Mn complex. v are 0.05, 0.1, 0.2, 0.3 and 0.4 V s^{-1}.

vary linearly as a function of the scan rates in the range 0.05–0.5 V s^{-1} as expected for surface-immobilized redox species (Fig. 2) [19]. Surface concentration of the immobilized Mn complexes ($\Gamma_{ECHEM\text{-}Mn}$) for the three experiments could be derived from the Faraday's law by taking account the large roughness of our GC electrodes

$$\Gamma_{ECHEM-Mn} = Q/nFA\rho$$

where Q is the charge obtained from integration under the oxidation peak (baseline corrected), n = 1 the number of electrons exchanged, F the Faraday constant (96,500 C mol^{-1}), A the geometric area of the electrode (0.076 cm^2) and ρ is the roughness of the electrode, lying between 4 and 8 [20]. Molecular mechanics optimization (MM2) allows to roughly estimate the molecular surfaces of Mn-**1** and Mn-**2** complexes to be 150 and 190 $Å^2$, respectively. The experimental surface coverage determined from electrochemical data was then found to correspond to 1–3 close-packed monolayers (Table 1).

4. Conclusions

In this work, phosphine-chelating ligands were strongly attached to carbon surfaces using free radical grafting methods, namely the electrooxidation of aliphatic or aromatic amines and the electroreduction of aryldiazonium salt in situ generated from its corresponding aromatic amine precursor. The high sensitivity of phosphine group towards oxidation, even for highly positive potentials, was demonstrated to be efficiently quenched by adding a borane protecting group on the phosphine substituents. The solid-phase deprotection step was easily achieved, allowing the chelation of transition metals as exemplified with Mn. Since phosphine compounds are excellent ligands towards transition metals, this work provides a simple and versatile method for immobilizing such organometallic complexes onto carbon surfaces, allowing the possible electrochemical tuning of their oxidation state. Further work is currently in progress to use these phosphine-modified electrodes in catalytic reactions.

References

[1] N. Riegel, C. Darcel, O. Stéphan, S. Jugé, J. Organomet. Chem. 567 (1998) 219.
[2] E.M. Sussuchi, A.A. de Lima, W.F. De Giovani, J. Mol. Cat A : Chem. 259 (2006) 302.
[3] E.K. Beloglazkina, A.G. Mazhuga, R.D. Rakhimov, N.V. Zyk, Russ. J. Gen. Chem. 80 (2010) 227.
[4] F. Geneste, C. Moinet, J. Electroanal. Chem. 594 (2006) 105.
[5] M. Sandroni, G. Volpi, J. Fiedler, R. Buscaino, G. Viscardi, L. Milone, R. Gobetto, C. Nervi, Catalysis Today 158 (2010) 22.
[6] C. Willocq, S. Hermans, M. Devillers, J. Phys. Chem. C. 112 (2008) 5533.
[7] M.C. Román-Martínez, J.A. Díaz-Auñón, C. Salinas-Martínez de Lecea, H. Alper, J. Mol. Cat A: Chem. 213 (2004) 177.
[8] A.J. Downard, Electroanalysis 11 (2000) 1085.
[9] J. Pinson, F. Podvorica, Chem. Soc. Rev. 34 (2005) 429.
[10] P. Pellon, Tet. Lett. 33 (1992) 4451.
[11] F.D. Bellamy, K. Ou, Tet. Lett. 25 (1984) 839.
[12] O. Buriez, E. Labbé, P. Pigeon, G. Jaouen, C. Amatore, J. Electroanal. Chem. 619–620 (2008) 169.
[13] S. Baraton, D. Bélanger, J. Phys. Chem. B 109 (2005) 24401.
[14] H. Brisset, Y. Gourdel, P. Pellon, M. Le Corre, Tet. Lett. 34 (1993) 4523.
[15] A. Adenier, M.M. Chehimi, I. Gallardo, J. Pinson, N. Vila, Langmuir 20 (2004) 8243.
[16] X. Li, Y. Wan, C. Sun, J. Electroanal. Chem. 569 (2004) 79.
[17] C. Cougnon, J. Mauzeroll, D. Bélanger, Angew. Chem. Int. Ed. 48 (2009) 7395.
[18] R.S. Deinhammer, M. Ho, J.W. Anderegg, M.D. Porter, Langmuir 10 (1994) 1306.
[19] A.J. Bard, L.R. Faulkner (Eds.), Electrochemical Methods. Fundamentals and Applications, 2nd Edition, John Wiley & Sons, New York, 2001.
[20] J.-M. Chrétien, M.A. Ghanem, P.N. Bartlett, J.D. Kilburn, Chem. Eur. J. 14 (2008) 2548.