Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 40:386–390, 2010

ISSN: 1553-3174 print / 1553-3182 online
DOI: 10.1080/15533174.2010.492549

Crystal Structure and Electrochemical Properties of Ferrocenyl Aminophosphonic Esters

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A series of novel compounds of aminophosphonates bearing the ferrocenyl moiety are obtained. X-ray Crystallography of 2c reveals that it belongs to monoclinic system with space group P2(1)/c, R1 = 0.0620, wR2 = 0.1516. The cyclic voltammetric behavior of these compounds show one pair of quasi-reversible and redox waves in the potential range of 0.0–1.0 V and it is controlled by diffusion. The diffusion coefficient decrease with increasing in the molecular weight of the compounds and the size of the molecules. CCDC: 679937

Keywords aminophosphonates, crystal structure, electrochemical properties, ferrocene

INTRODUCTION

Compounds derived from the sandwich structural ferrocene have been widely employed in electroactive polymers,[1] thermotropic liquid crystal,[2] and non-liner optical materials[3] because they are characterized by their ability to make metal-centered redox systems to generate oxidized or reduced form of different properties.[4] Experiments show that the redox potential depends on the electronic effect of the ring substituent on ferrocene. Electron-withdrawing substituents increase the oxidation potential (decrease the reactivity towards oxidation), while electron-donating substituent decreases the oxidation potential, and thus enhances the reactivity of ferrocene.[5–6] Phosphines substituents on the ferrocene unit allow incorporation of a redox-active moiety into transition metal complexes, often leading to an increase in the reactivity of the complex.[7] Coordinated ferrocenylphosphine ligands usually exhibit simple, reversible electrochemistry behavior arising from one-electron oxidation of the ferrocene center, while free ferrocenylphosphine displays complex redox properties.[8–9]

More than five decades after its discovery,[10–11] ferrocene still evokes a great deal of research interest from scientists across the board. Chiral and achiral ferrocenyl phosphines have been extensively used as ligands in organic synthesis and asymmetric catalysis for carbon–carbon, carbon–heteroatom coupling, carbonylation, hydroformylation, hydrogenation, olefin polymerization and cycloaddition.[12–14] Ferrocenyl amino acids found their application in food chemistry as a possible substitute for phenylalanine in the commercial sweetener aspartame.[15]

Regarding all of the above, we want to take advantage of the properties of mixed valent phosphine bridged ferrocene moieties and obtain a series of novel compounds bearing aminophosphonates and ferrocene moiety. We systematically investigated their electrochemical behaviors by cyclic voltammetry (CV), chronoamperometry (CA), and chronocoulometry (CC). By contrast, there are few reports about the electrochemistry of ferrocenylphosphine oxide[16–17] and ferrocenylphosphonates.[18–19]

EXPERIMENTAL

X-ray Structure Determination of 2c

An orange crystal of the title compound **2c** with dimensions of 0.40 × 0.36 × 0.16 mm^3 is mounted on a glass fiber. All measurements are made on a Rigaku RAXIS-IV imaging plate area detector with graphite monochromated Mo-Kα radiation (λ =0.71073 Å). A total of 25247 reflections are collected $I > 2\sigma$ (I) reflections are 4526. The data are corrected for Lorentz and polarization effects. The structure is solved by direct methods, and expanded using Fourier techniques. The non-hydrogen atoms are refined anisotropically. Hydrogen atoms are included, but not refined. The final R factor is 0.0620, Rw = 0.1516. All calculations are performed with the SHELXL-97 crystallographic software package.[23]

Determination of Electrochemical Properties

Cyclic voltammetry, chronoamperometry and chronocoulometry studies are recorded with a CHI660B electrochemical analyzer utilizing the three-electrode configuration of a Pt

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Received 2 August 2009; accepted 22 April 2010.

The authors thank Luoyang Normal College for the diffraction measurements and Henan Province Natural Science Foundation (No. 06110214000). This work is supported by the National Natural Science Foundation of China (No. 20771093).

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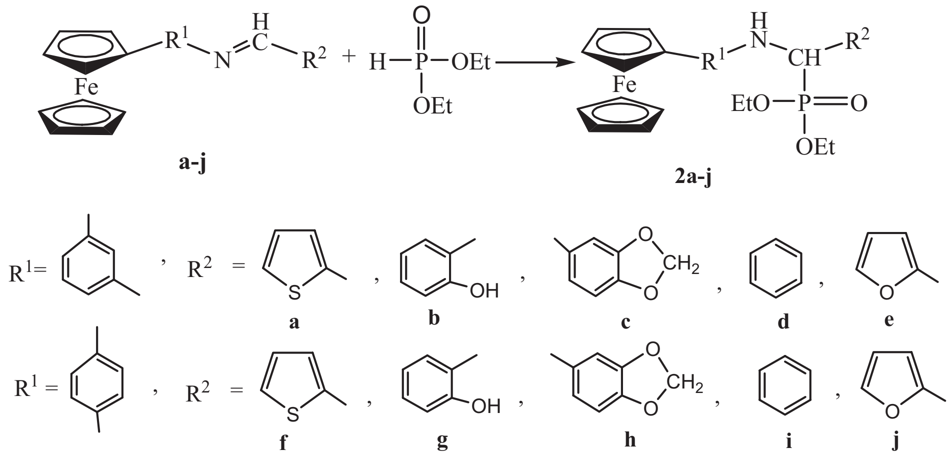


SCH. 1.

working electrode, a Pt auxiliary electrode, and a commercially available saturated calomel electrode as the reference electrode. The measurements are performed in acetonitrile solution containing tetra-n-butyl-ammonium perchlorate (TBAP) (0.1 mol·dm^{-3}) as supporting electrolyte. Pure N_2 gas is bubbled through the electrolytic solution to remove oxygen.

Electrochemical Properties

The cyclic voltammogram behaviors of compounds **2** in 0.1mol·dm^{-3} TBAP acetonitrile solution were investigated at room temperature. The CV diagrams show that compounds **2** exhibited one-pair well-defined reduction and oxidation waves in the potential range of 0.1–0.6 V at the Pt working electrode (Table 3).

It can be seen from Table 3 that the oxidation potentials and reduction potentials of derivates of m-ferrocenylaniline (**2f**, **2g**, **2h**, **2i**, **2j**) apparently shift to lower potentials compared with those of the corresponding potentials of ferrocene, ferrocenylaniline and the derivates of p-ferrocenylaniline. This might be because derivates of p-ferrocenylaniline could form an extent Π bond, as shown in Scheme 2.

The cyclic voltammetric diagrams of complounds **2a-j** at different scan rates (from 50 to 400 mV·s^{-1}) are shown in Figure 2.

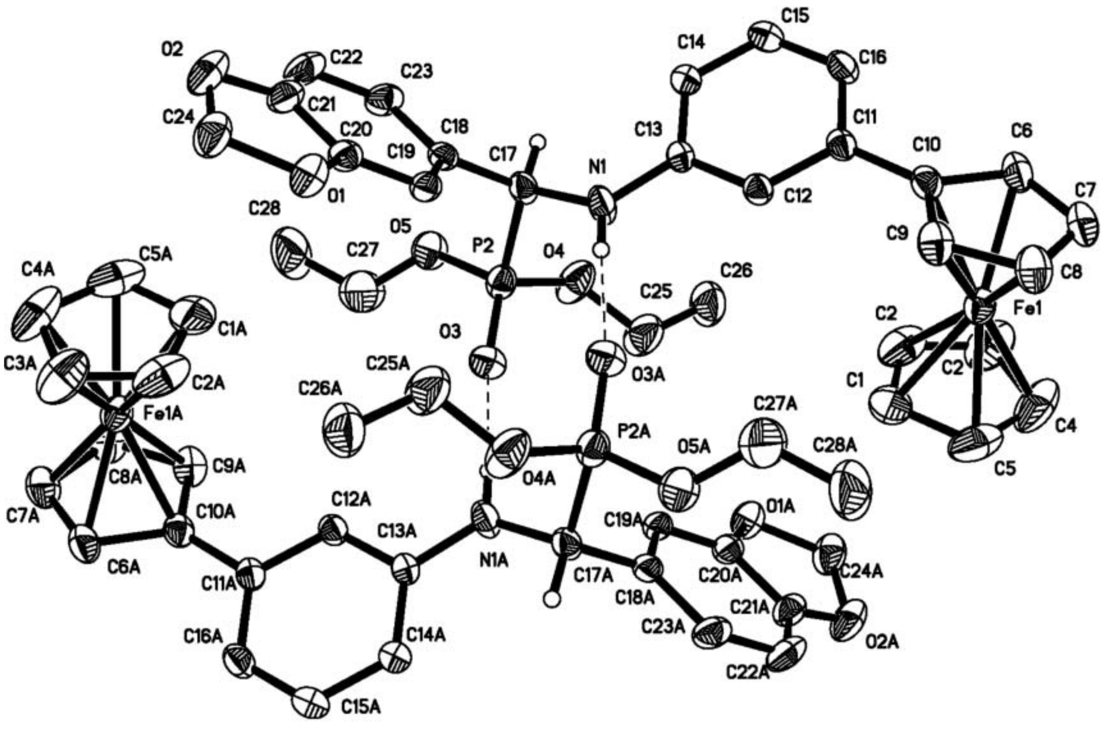


FIG. 1. The molecular structure of compound **2c**.

TABLE 1
Crystallographic data for compound **2c**

Empirical formula	C28H30FeNO5P
Formula weight	547.35
Crystal system	Monoclinic
Space group	P2(1)/c
a(Å)	16.356(3)
b(Å)	11.585(2)
c(Å)	15.404(3)
β(°)	117.92(3)
V(Å^3)	2579.1(9)
F(000)	1144
Dcalc (mg/m^3)	1.410
Temperature (K)	293(2)
Theta range for data collection(°)	2.25 – 25.00
Reflections collected	25247
Independent reflections [R(int)]	0.0330
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.098
Final R indices [I > 2r(I)]	R1 = 0.0620, wR2 = 0.1516
R indices (all data)	R1 = 0.0671, wR2 = 0.1558
Largest difference in peak and hole	0.415 and –0.274

TABLE 2
Selected bond lengths(Å) and angles(°) for **2c**

Bond lengths		Bond angles	
N(1)-C(13)	1.387(4)	O(3)-P(2)-O(5)	117.89(17)
N(1)-C(17)	1.446(4)	O(3)-P(2)-O(4)	115.92(17)
P(2)-O(3)	1.448(3)	O(5)-P(2)-O(4)	99.32(18)
P(2)-O(5)	1.559(3)	O(3)-P(2)-C(17)	115.13(16)
P(2)-O(4)	1.584(3)	O(5)-P(2)-C(17)	102.73(16)
P(2)-C(17)	1.803(4)	O(4)-P(2)-C(17)	103.51(19)
O(1)-C(20)	1.381(4)	C(13)-N(1)-C(17)	124.7(3)
O(2)-C(21)	1.374(5)	C(20)-O(1)-C(24)	104.3(3)
O(5)-C(27)	1.355(6)	C(21)-O(2)-C(24)	105.0(3)
O(2)-C(24)	1.403(6)	C(25)-O(4)-P(2)	124.9(3)
O(4)-C(25)	1.392(6)	C(27)-O(5)-P(2)	128.2(4)
N(1)-C(13)	1.387(4)	O(2)-C(24)-O(1)	108.7(4)
N(1)-C(17)	1.446(4)	O(4)-C(25)-C(26)	111.9(5)

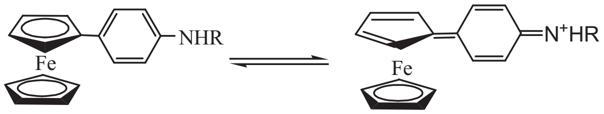
From the i_{pa}/i_{pc} ($\approx$1) values of each couple, it can be seen that the redox processes were chemically quasi-reversible processes. Additionally, as shown in Figure3, the dependence of the currents at different scan rates on the square root of the scan rates is linear. So the redox processes of compounds **2** are controlled by diffusion.

In order to determine the D values of compounds **2**, the CA and CC methods were used. The relationships between the time and the currents or the electric energies are given by Cottrell equations[24]:

$$i(t) = \frac{nFAD_o^{1/2}C_o}{(\pi t)^{1/2}} + i_c \quad Q(t) = \frac{2nFAD_o^{1/2}C_o t^{1/2}}{\pi^{1/2}} + Q_{dl}$$

where i is the current, Q is the electric energy, n is the electron numbers involved in the redox process, F is the Faraday constant, A is the area of the electrode, D is the diffusion coefficient, C is the concentration of the compound, and t is time.

As depicted in Figures 4 and 5, linear trends for **2j** are observed from the dependence of i on $t^{-1/2}$ or Q on $t^{1/2}$. According to the slope coefficients, the D value of **2j** is obtained by CA method or by CC method. In the same way, all D values of compound **2a–j** (Table 4.) can be obtained. Clearly, the D values obtained from CA and CC are close to each other. This means that the kinetic data measured are accurate and authentic. The results show that the D values decrease with the increase in the molecular weight of the compounds and the size of the molecules.[25]



SCH. 2.

RESULTS AND DISCUSSION

Synthesis

Ferrocenylaminophosphonates are synthesized according to the following route (Scheme 1). All the Schiff bases of **a-j** are synthesized by the condensation of the m-ferrocenylaniline or

TABLE 3
Electrochemical data for ferrocene and ferrocene derivatives

Compound	E_{pa}/V	E_{pc}/V	E^0/V	ΔE	i_{pa}/i_{pc}
ferrocene	0.473	0.400	0.437	0.073	1.00
m-ferrocenylaniline	0.405	0.334	0.370	0.071	1.01
p-ferrocenylaniline	0.409	0.337	0.373	0.072	1.00
2a	0.418	0.351	0.384	0.067	1.03
2b	0.402	0.337	0.369	0.065	1.06
2c	0.415	0.347	0.381	0.068	1.00
2d	0.412	0.347	0.379	0.065	1.00
2e	0.405	0.334	0.369	0.071	1.06
2f	0.330	0.263	0.296	0.067	1.07
2g	0.337	0.270	0.303	0.067	1.03
2h	0.334	0.267	0.300	0.067	1.01
2i	0.330	0.267	0.298	0.063	1.00
2j	0.329	0.267	0.298	0.062	1.08

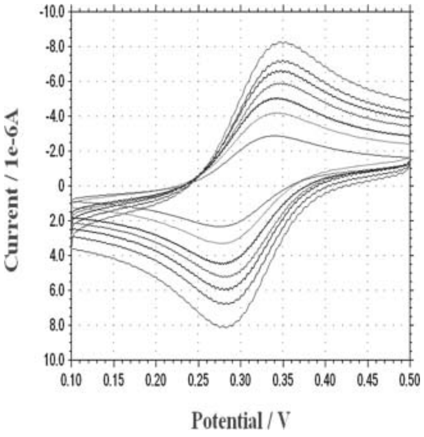


FIG. 2. CVs of compound **2j** in acetonitrile at different scan rate ($c=5\times10^{-4}mol\cdot dm^{-3}$)

p-ferrocenylaniline with aroma aldehyde following the known methodology.[20] Addition of diethyl phosphite to the azomethine bond of Schiff bases to give the corresponding ferrocenylaminophosphonates as we have previously reported.[21] The addition of phosphites to Schiff bases of ferrocenecarbaldehyde gives a racemic mixture because a chiral center is formed.

Crystal Structure of Compound 2c

The crystal structure of compound **2c** is illustrated in Figure 1. The crystal data, the selected bond lengths and angles are given in Tables 1 and 2.

Compound **2c** has two unique molecules in the symmetric unit. C17 is a chiral carbon atom. In the crystals, the two enantiomers were connected through weak hydrogen bond O(2)...H-N(1A) and O(2A)...H-N(1) (3.013 Å), forming a approximate rectangle structure. The inner diameter was 0.540 nm × 0.262 nm. Two molecular extended three-dimensional structure with Van der Waals force. The P-C bond distance is 1.803Å, which is similar to average of 1.83 Å.[22] The P2-O3 formed P=O bond for the distance of 1.448 Å is shorter than that of P2-O4, P2-O5 1.584 Å and 1.559 Å. The mean deviations from planes C(1)-C(5)(Cp1), C(6)-C(10) (Cp2) C(11)-C(16), C(18)-C(23) are 0.036Å, 0.038 Å, 0.023 Å, 0.039 Å. The Cp rings in ferrocenyl groups are planar and nearly parallel with a dihedral angle of 2.3°(Cp1, Cp2), The dihedral angle of Cp2-ring and phenyl ring C(11)-C(16) is 26.8°. The dihedral angle of the two phenyl rings C(11)-C(16), C(18)-C(23) is 55.2°.

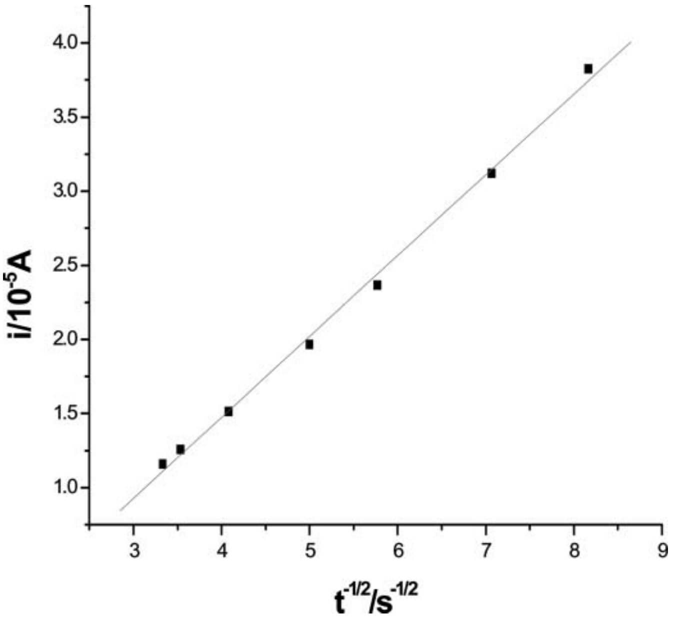


FIG. 4. The relation between i and $t^{-1/2}$.

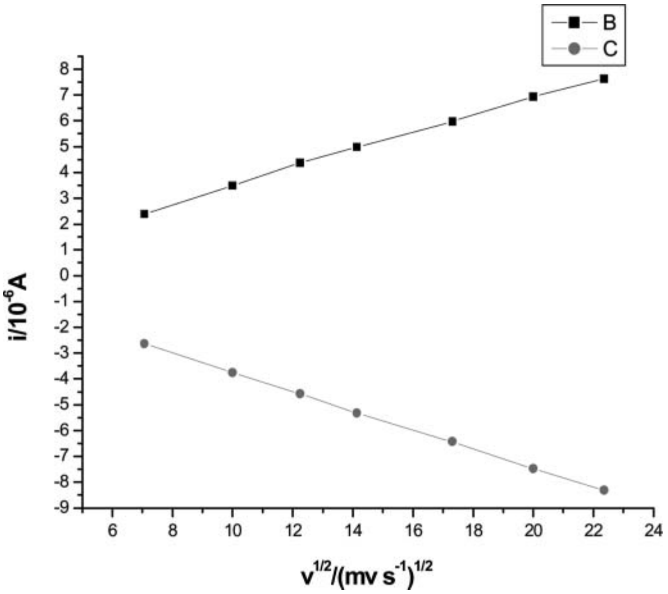


FIG. 3. The reaction between $i_p$and $\upsilon^{1/2}$ of **2j**.

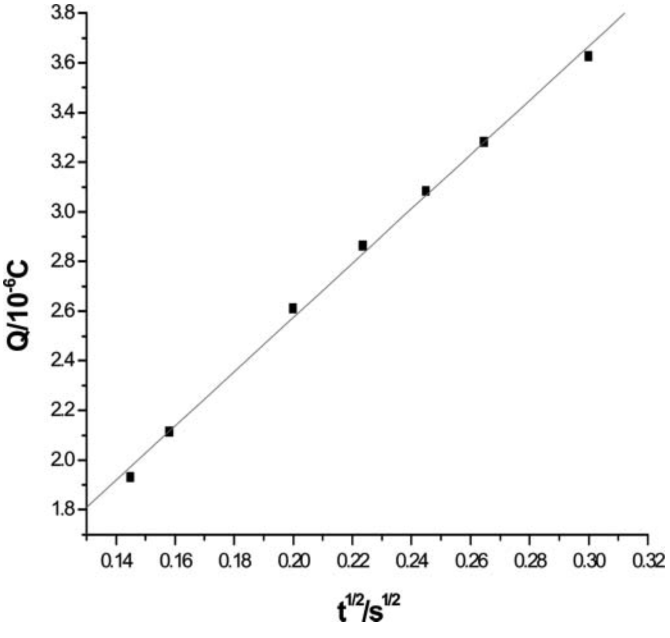


FIG. 5. The relation between Q and $t^{1/2}$.

TABLE 4
Electrochemical kinetics data

Compound	$D_o \times 10^5/(cm^2/s)$	
	CA	CC
2a	0.80	0.80
2b	0.84	0.82
2c	0.82	0.81
2d	0.83	0.82
2e	0.82	0.80
2f	0.81	0.80
2g	0.85	0.84
2h	0.82	0.85
2i	0.85	0.84
2j	0.82	0.81

CONCLUSIONS

A series of novel aminophosphonates bearing the ferrocenyl moiety are synthesized. The results of electrochemistry show that these derivatives have high electroactivity. They may have potential applications as materials for biomolecular sensors and switches. In addition, study of the applications of these compounds in asymmetric catalytic reactions is necessary. At present, these applications are under way in our lab.

SUPPLEMENTARY MATERIAL

Supplementary data Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Center, CCDC-708122. 12 Union Road, Cambridge CB2 1EZ, UK. E-mail: deposit@ccdc.cam.ac.uk. (Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk).

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