NJC

RSCPublishing

PAPER

View Article Online
View Journal | View Issue

New azaheterocyclic aromatic diphosphonates for hybrid materials for fuel cell applications†

Cite this: New J. Chem., 2013, 37, 3084

Fátima C. Teixeira,*[a] C. M. Rangel[a] and António P. S. Teixeira[bc]

Received (in Porto Alegre, Brazil) 1st June 2013, Accepted 12th July 2013

DOI: 10.1039/c3nj00585b

www.rsc.org/njc

New azaheterocyclic aromatic diphosphonate derivatives of benzimidazole and benzotriazole were synthesized by nickel-catalyzed Arbuzov reaction of 4,7-dibromo-2,1,3-benzothiadiazole with triethyl phosphite, followed by reductive sulfur extrusion reaction and cyclization. This new strategy allowed us to obtain these compounds with high efficiency, with the generation of these azaheterocyclic aromatic diphosphonate derivatives in good to excellent yields, since these compounds could not be synthesized by direct cross-coupling reactions catalyzed by palladium or nickel. All compounds were characterized by NMR, IR spectroscopy and mass spectrometry (low and high resolution). NMR studies of compound **9** showed the presence of only one tautomeric form, on the NMR time scale, in different solvents and at different concentrations.

Introduction

The development of cleaner and sustainable sources of energy is one of the major challenges of the 21st century. Alternative energy systems are crucial in order to deal with the environmental threat of global warming and the use of fossil energy sources. Fuel cells are electrochemical devices that convert the chemical energy stored directly into electrical energy. Fuel cells can provide electrical energy with high efficiency and low environmental impact. But, their performance depends crucially on the properties of component materials.[1–7]

Among the various kinds of fuel cells, the proton-exchange membrane fuel cells (PEMFCs) are considered promising power sources, due to their high power density and high power-to-weight ratio. A key material for the operation of PEMFCs is the proton-exchange membrane (PEM). Usually, these membranes are made of organic polymers containing acidic functionalities (*e.g.* Nafion®), but the proton transport properties of these membranes strongly depend on their water content and, consequently, limit their operation temperatures up to 90 °C. These limitations have fostered the interest in research and development of new alternative membranes for the operation of fuel cells at temperatures above 100 °C. Above this temperature, the performance of fuel cells increases, due to faster electrode reaction without CO poisoning of the Pt electro-catalyst.[1–7] New alternative membranes include polybenzimidazole (PBI)-doped membranes, composites of Nafion® and metal oxides, sulfonated polymers based on aromatic hydrocarbons and organosiloxane-based inorganic–organic hybrids with various acidic species.[1–7]

Phosphonic acids are considered to be promising proton carriers because of their good proton donating and accepting properties.[8–10] In addition, phosphonic acids are an alternative to sulfonic acid groups due to their high proton conductivities, oxidation resistance and better thermal stabilities.[9–11]

Arylphosphonates have numerous practical applications, including in the design of fuel cell membranes.[10,12,13] Continuous efforts have been made to construct C–P bonds directly through metal-catalyzed C–P coupling of arylhalides to obtain arylphosphonates.[14] The Hirao reaction[15] and the nickel-catalyzed Arbuzov reaction[16] are widely used methods employed for the synthesis of arylphosphonates.

Phosphonylated azaheterocycles have gained a lot of interest over the years. Direct phosphonylation of aromatic azaheterocycles increased significantly and was reviewed by Van der Jeught and Stevens in 2009.[17] Direct phosphonylation of 6-bromobenzimidazole derivatives by Hirao reaction, using diethyl phosphite in the presence of catalytic amounts of tetrakis(triphenylphosphine)palladium, was reported to obtain the (1-ethyl-2-methyl-6-benzimidazolyl)phosphonate and diethyl (1-phenyl-2-methyl-6-benzimidazolyl)phosphonate.[17] Recently Li *et al.* reported the first palladium-catalyzed direct phosphonation

[a] *Laboratório Nacional de Energia e Geologia, I.P., Estrada do Paço do Lumiar, 22, 1649-038 Lisboa, Portugal. E-mail: fatima.teixeira@lneg.pt, carmen.rangel@lneg.pt; Fax: +351 217 162 641*

[b] *Centro de Química de Évora & Departamento de Química, Escola de Ciências e Tecnologia, Universidade de Évora, R. Romão Ramalho, 59, 7000-671 Évora, Portugal*

[c] *Centro de Química Estrutural, IST, Universidade Técnica de Lisboa, Av. Rovisco Pais 1, 1049-001 Lisboa, Portugal*

† Electronic supplementary information (ESI) available: NMR data (^{1}H, ^{13}C and ^{31}P NMR spectra) for new compounds. See DOI: 10.1039/c3nj00585b