

Available online at www.sciencedirect.com



Tetrahedron Letters 46 (2005) 8793-8797

Tetrahedron Letters

New tetrakis(4-aminophenyl)ethenes: synthesis and electrochemical investigations

Jean-François Kuntz,^a Raphaël Schneider,^{a,*} Alain Walcarius^b and Yves Fort^{a,*}

^aSynthèse Organométallique et Réactivité, UMR 7565, Université Henri Poincaré, BP 239, 54506 Vandoeuvre les Nancy Cedex, France ^bLaboratoire de Chimie Physique et Microbiologie pour l'Environnement, UMR 7564, CNRS-Université Henri Poincaré, 54600 Villers les Nancy, France

Received 25 August 2005; revised 30 September 2005; accepted 10 October 2005

Abstract—Four novel functional conjugated tetraarylamines containing a tetraphenylenecore were synthesized via Ni-catalyzed aryl amination followed by McMurry olefination. Their electrochemical properties were studied by cyclic voltammetry, coulometry, and electrolysis monitored by UV–vis spectroscopy, and discussed with regard to those of the known tetrakis(dimethyl-aminophenyl)ethane.

© 2005 Elsevier Ltd. All rights reserved.

Aromatic amines have been extensively used as excellent hole-transport layers (HTL) in fabricating organic electroluminescent (EL) devices,¹ which have great potential use in full color flat panel displays, as a result of their low drive voltage, high efficiency, and high brightness. Efficient hole transporting ability requires the facile oxidation of aromatic amines to stable radical cations. The ability to synthesize new arylamines allows to tune the electronic structure of these materials; this is of interest because matching the energy of the highest occupied molecular orbitals of hole-transport materials with respect to those of the anode and electron transport layer strongly influences charge injection efficiencies and therefore the overall performance of organic devices.²

In the search for new potential charge transport materials, we were interested in developing conjugated materials of branched topologies and became attracted by the two-dimensional conjugated unit 1 (Fig. 1) in which three different conjugation modes are available: diagonal conjugation, lateral conjugation, and cross-conjugation. Several studies have demonstrated that conjugated architectures based on tetraphenylethene core displayed different properties from those of their one-dimensional analogs.³ Surprisingly, despite the potential applications



1: X = NR₂; R = Me (1a), R = H (1b), R = Ar (1c) 2 : Cl

Figure 1.

of compounds **1** in constructing hole-transport materials, very little is known about their synthesis and electronic properties. The oxidation/reduction of tetrakis (aminophenyl)ethenes **1a**,**b** has been investigated by Hünig and Fox.^{4,5} Cyclic voltammetry (CV) of **1a** revealed two successive two-electron transfer processes at ca. -0.30 and +0.67 V (vs Fc/Fc⁺). The electrochemical features of **1c** ($\mathbf{R} = C_6H_5$ or *m*-MeC₆H₄) was also briefly investigated by Plater.⁶

During recent years, we have directed our efforts toward Ni- and Pd-mediated aryl amination chemistry with the goal to develop new electron-donor compounds.⁷ We have recently reported the use of a Ni(0) catalyst associated with a strong electron-donating and sterically hindered *N*-heterocyclic carbene⁸ [*N*,*N'*-bis(2,6-diiso-propylphenyl)dihydroimidazol-2-ylidene, SIPr] (Fig. 2) to allow mild amination of aryl chlorides with several classes of amines.⁹

Keywords: Diamination; Ni catalysis; *N*-Heterocyclic carbene; Tetra-kis(4-aminophenyl)ethenes; McMurry olefination.

^{*} Corresponding authors. Tel.: +33 383 68 47 84; fax: +33 383 68 47 85 (R.S.); e-mail: Raphael.Schneider@sor.uhp-nancy.fr

^{0040-4039/\$ -} see front matter @ 2005 Elsevier Ltd. All rights reserved. doi:10.1016/j.tetlet.2005.10.071



Figure 2.

We initially envisaged that Ni-catalyzed polyamination of compound **2** could give an easy access to a variety of new tetrakis(4-aminophenyl)ethenes. However, due to the strong electron-donating properties of the 4-amino substituent introduced in the course of the aryl amination reaction, the cross-coupling proceeded sluggishly and afforded mixtures of mono- and di-amination products even after extended reaction times.

Herein, we report a new synthesis to tetrakis(4-aminophenyl)ethenes **3** based on a two-step process involving (i) Ni(0)/SIPr catalyzed bis-amination of 4,4'-dichlorobenzophenone and (ii) McMurry olefination of 4,4'-diaminobenzophenones **4** produced (Scheme 1). This synthetic route takes advantage of the ease with which 4,4'-dichlorobenzophenone may be di-aminated in the 4 and 4' positions due to the activating effect of the carbonyl group.

First, we evaluated the feasibility of direct cross-coupling of 4,4'-dichlorobenzophenone and amines using Ni/SIPr catalyst and t-BuONa as the base. Ni(0)/SIPr/ t-BuONa was in situ generated from Ni(acac)₂ and SIPr·HCl¹⁰ by reduction of Ni(acac)₂ and deprotonation of the azolium salt using t-BuONa activated sodium hydride as previously described.9b A preliminary screening of Ni/SIPr catalyst for coupling of 4,4'-dichlorobenzophenone with morpholine revealed that the reaction required 5 mol % of Ni/SIPr complex in refluxing THF or dioxane. The optimum yield of 4a is obtained when a ratio of aryl dichloride to amine of 1:3 was used. As a control experiment, when the same reaction was carried out in the absence of Ni/SIPr catalyst, very little mono-aminated cross-coupled product (<7%) was obtained even after heating for 15 h in refluxing THF.



Scheme 1. Reagents and conditions: (i) $HNR^{1}R^{2}$ (3 equiv), *t*-BuONa, Ni/SIPr (5 mol %), THF, 65 °C; (b) TiCl₄, Zn.

CI	HNR ¹ R ² Ni(0)/SIP NaOt-Bi THF, 65°C		0 N ^{R¹} 4 R ²
Entry	Amine	Time (h)	Yield (%) ^b
a	HNO	4	99 ^c
b	H ₂ N-OMe	12	$0^{d,e}$
с	Me N	6	90 ^d
d	N H	3	93 ^d

Table 1. Cross-coupling of 4,4'-dichlorobenzophenone with amines^a

^a Reactions conditions: 5 mol % Ni, *t*-BuONa, THF, 65 °C.

^b Yields of pure products after column chromatography.

^c A Ni/SIPr ratio of 1/1 was used.

^d A Ni/SIPr ratio of 1/2 was used.

^e Imine was the only product observed after 12 h reaction.

Under these experimental conditions, we then investigated direct cross-coupling reactions using primary and secondary aromatic amines (Table 1). All sec-aromatic amine substrates underwent direct cross-coupling reactions with 4,4'-dichlorobenzophenone to afford products 4 in excellent yields. The reaction times were short (<6 h) and no side-products were detected. In contrast, p-anisidine (entry b) failed to give the di-amination product and the imine, arising from attack of the primary amine on the carbonyl group, was the only product isolated. Attempts to aminate the initially formed imine by extending the reaction time and/or forcing the reaction conditions by using an excess of *p*-anisidine (up to 6 equiv) or increasing catalyst loading (10 mol %) only gave a mixture of several unidentified products. The synthesis of di[(4-methoxyanilino)phenyl]methanone 4b could however be achieved using a dioxolane protection for the carbonyl group of 4,4'-dichlorobenzophenone (Scheme 2).

To achieve the targeted tetrakis(4-aminophenyl) ethenes **3**, compounds **4** were subjected to McMurry olefination using low valent titanium reagents (Table 2).¹¹ Among the various methodologies developed over the years to effect reductive couplings of carbonyls, the combination of TiCl₄ with Zn was the best for the preparation of compounds **3** and the reaction usually could be done in 2–5 h in refluxing dioxane. The use of TiCl₃–Li–THF or TiCl₃–LiAlH₄ afforded the substrate **3a** in lower yields (respectively, 73% and 64%).

The electrochemical behavior of novel donors 3a-c is close to that observed for the related 1a (Table 3). Figure 3 depicts the CV curves recorded for 3a as a representative example. Compounds 3a-c give rise to a first electrochemically reversible oxidation signal (I), involving the exchange of two electrons, during which the respective dications are formed. The two-electron



Scheme 2. Reagents and conditions: (a) $(CH_2OH)_2$, APTS, xylene, 120 °C, 97%; (b) *p*-anisidine (3 equiv), Ni/SIPr, *t*-BuONa, THF, 65 °C, 7 h, 86%; (c) H₂SO₄, SiO₂, acetone, rt, 2 h, 87%.

transfer process was confirmed by constant potential coulometry performed at 0.8 V. It was followed by a very small peak near 1 V (denoted III in Fig. 3), which was also observed for the related 1a compound,^{4b} but its origin remains unexplained at this stage. Recording CV curves at various scan rate revealed that the electron transfer processed were diffusion controlled (peak currents directly proportional to the square root of scan rate and cathodic-to-anodic current ratios equal to unity independently on scan rate). This suggests that, under the conditions applied, the dications are stable. The corroborating evidence was obtained from the EPR spectrum of the oxidized solutions. Oxidized 3a-c exhibited a very strong EPR signal at 298 K in CHCl₃. Using 2 equiv thianthrenium perchlorate¹² (ThClO₄) as oxidant, the fluid solution showed a single broad-line EPR spectrum with a spectral width of ca. 36 G. The dications generated from compounds **3a–c** are stable at room temperature displaying a qualitative half-life of ca. 8 days. These dications can be further oxidized by extending the potential range in the anodic direction. Interestingly, compounds 3a-c exhibit extremely large potential gaps between the first and second oxidation states (ca. 0.85–0.90 V). This second signal appearing near 1.4–1.5 V (Fig. 3) is in fact constituted from two successive one-electron transfers (II_a and II_b) occurring at very close potential values (Table 3). They correspond to the successive transformation of $3^{2\cdot 2+}$ into transient $3^{3\cdot 3+}$ and then to the fully oxidized $3^{4\cdot 4+}$ product. This behavior is similar as that of $1a^4$ and was observed for all compounds 3a-c (Table 3). It is noteworthy, however, that the smaller sized compound 3a was characterized by a higher diffusion coefficient $(7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1})$ than those of larger compounds **3b** and **3c** $(4-5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1})$.

The electrochemical behavior of compound 3d was significantly different, displaying a single-electron oxidation signal at 0.61 V (I) (Fig. 4, red curve). This was confirmed by controlled potential coulometry at 0.8 V, suggesting the generation of a rather stable mono(radical cation). Once again, this signal was diffusion

Table 2. McMurry olefination of compounds 4^a



^a Reactions were carried out using 5 mmol **4**, 5.5 mmol TiCl₄, and 15 mmol Zn in refluxing dioxane.

^b Yields of pure products isolated after column chromatography.

Table 3. Electrochemical data of compounds 3a-d

	Compound				
	3a	3b	3c	3d	
$E_{\rm ox}^{\rm I}$ (V)	0.58	0.61	0.62	0.61	
$E_{\rm red}^{\rm I}$ (V)	0.55	0.58	0.58	0.55	
$E_{\rm ox}^{\rm IIa}$ (V)	1.44	1.46	1.48		
$E_{\rm red}^{\rm IIa}$ (V)	1.38	1.40	1.42	$E_{\rm ox}^{\rm II} = 1.52$	
$E_{\rm ox}^{\rm IIb}$ (V)	1.50	1.52	1.53	$E_{\rm red}^{\rm II} = 1.23$	
$E_{\rm red}^{\rm IIb}$ (V)	1.44	1.46	1.47	$E_{\rm ox}^{\rm III} = 1.08$	

controlled and the cathodic-to-anodic current ratio was independent on the potential scan rate. Compound



Figure 3. Cyclic voltammograms of 3a in CH₃CN/0.1 M Bu₄NBF₄; v = 100 mV s⁻¹; T = 293 K; $c = 10^{-3}$ M. Full potential range is in blue and restricted to the first signal is in red.



Figure 4. Cyclic voltammograms of 3d in CH₃CN/0.1 M Bu₄NBF₄; v = 100 mV s⁻¹; T = 293 K; $c = 10^{-3}$ M. Full potential range is in blue and restricted to the first signal is in red.

3d was characterized by a diffusion coefficient of $4.3 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$.

This first reversible redox process was also followed by a small irreversible signal at 1.08 V (peak III) and then by a second main peak located at 1.52 V (peak II) giving on scan reversal a small cathodic peak at 1.23 V (Fig. 4, blue curve). This second peak is characterized by an irreversible one-electron transfer leading probably to unstable di(radical cation)s that underwent follow-up reactions (e.g., dimerization¹³). It is likely that oligomerization reactions between the generated radical cations took place because 3d is unsubstituted at the para-position relative to the nitrogen atom contrary to **3b**,c for whose dimerization through *ortho*-position is difficult. This hypothesis was sustained by EPR experiments on oxidized 3d. Using ThClO₄ as oxidant, the fluid solution showed a single broad-line EPR spectrum with a spectral width of ca. 33 G. The dication $3d^{2\cdot 2+}$ was found to be less stable than those generated from 3a-c (qualitative half-life of ca. 5 h at 25 °C).

To provide further evidence for dimerization, we carried out oxidation of compound **3d** in CH₂Cl₂ with AgNO₃ (2 equiv), in the dark, under nitrogen atmosphere, according to the report of Effenberger et al. describing the synthesis of dimeric σ -complexes.¹⁴ After 10 min of stirring, the reaction mixture was evaporated to dryness and a solution of MeONa (2 equiv) in MeOH was added. The presence of a benzidine moiety could clearly be observed on the ¹H NMR spectra of the crude reaction mixture. This result argued strongly for the σ -dimeric nature of the materials obtained after oxidation of compound **3d**.

Interestingly, all compounds **3** exhibit an inferior electron-donor ability in comparison with tetrakis(dimethyl-aminophenyl)ethene **1a**. The shift in oxidation potential can be rationalized in terms of amine substitution. Indeed, dialkylamino groups exhibit the most pronounced resonance effect and the strongest donor character.¹⁵

The oxidation process of compounds **3** was also monitored by UV-vis spectroscopy. Figure 5 shows the UV-vis spectra recorded for **3a** in CH_2Cl_2 solution; the spectra of **3b,c** show similar optical absorption features. The neutral **3** were yellow in a CH_2Cl_2 solution



Figure 5. UV-vis spectra of the stepwise electrochemical oxidation of **3a** over Pt electrode.

that exhibit two bands at ca. 290 and 360 nm. When the solution of **3a** was treated with ThClO_4 or oxidized over Pt electrode, the solution turned rapidly blue and three broad bands appeared gradually in the lower energy region at ca. 490, 550, and 715 nm, in agreement to what was reported for compound **1a**.^{4b} These peaks did not decay with time confirming the formation of stable radical cations.

In summary, we have shown that Ni-catalyzed aryl amination between 4,4'-dichlorobenzophenone or its dioxolane and amines followed by McMurry reductive homocoupling of 4,4'-diaminobenzophenones 4 produced allows a rapid and efficient synthesis of new tetrakis(4-aminophenyl)ethylene 3. Cyclic voltammetry measurements reveal that compounds 3a-c exhibit good donor properties and give thermally stable radical cations. The electrochemical behavior of 3d is more complicated and it is likely that the oxidized species of *para*unsubstituted 3d caused follow-up reactions. Efforts are underway to study the hole transporting ability of new compounds 3 in electroluminescent devices.

Supplementary data

Synthetic and characterization details for compounds **3a–d** and **4a–d** are available. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2005.10.071.

References and notes

 (a) Van Slyke, S. A.; Tang, C. W.; O'Brien, M. E.; Chen, C. H. U.S. Patent 5,061,569, 1991; *Chem. Abstr.* 1992, 117, 16860a; (b) Young, R. H.; Fitzgerald, J. J. J. Phys. Chem. 1995, 99, 4230; (c) Tanaka, H.; Tokito, S.; Taga, Y.; Okada, A. Chem. Commun. 1996, 2175; (d) Bushby, R. J.; Ng, K. M. Chem. Commun. 1996, 659; (e) Sato, K.; Yano, M.; Furuichi, M.; Shiomi, D.; Takui, T.; Abe, K.; Itoh, K.; Higuchi, A.; Katsuma, K.; Shirota, Y. J. Am. Chem. *Soc.* **1997**, *119*, 6607; (f) Wienk, M. M.; Janssen, R. A. J. *J. Am. Chem. Soc.* **1997**, *119*, 4492; (g) *Handbook of Conducting Polymers*, 2nd ed.; Skotheim, T. A., Elsenbaumer, R. L., Reynolds, J. R., Eds.; Marcel Dekker: New York, 1998.

- (a) Koene, B. E.; Coy, D. E.; Thompson, M. E. Chem. Mater. 1998, 10, 2235; (b) Hill, I. G.; Kahn, A. J. Appl. Phys. 1999, 86, 2116; (c) Biebeler, C.; Antoniudis, H.; Bradley, D. D. C.; Shirota, Y. J. Appl. Phys. 1999, 85, 608; (d) Yanashita, K.; Mori, T.; Mizutani, T.; Miyazaki, H.; Takeda, T. Thin Solid Films 2000, 363, 33.
- (a) Van Loon, J.-D.; Seiler, P.; Diederich, F. Angew. Chem., Int. Ed. Engl. 1993, 32, 1653; (b) Bunz, U. H. F.; Enkelmann, V. Angew. Chem., Int. Ed. Engl. 1993, 32, 1653; (c) Kondo, K.; Yasuda, S.; Sakaguchi, T.; Miya, M. J. Chem. Soc., Chem. Commun. 1995, 55; (d) Diederich, F. Chem. Commun. 2001, 219; (e) Sengupta, S. Synlett 2004, 1191; (f) Ito, A.; Nakano, Y.; Kato, T.; Tanaka, K. Chem. Commun. 2005, 403.
- (a) Hünig, S.; Kemmer, M.; Wenner, H.; Perepichka, I. F.; Bäuerle, P.; Emge, A.; Gescheid, G. *Chem. Eur. J.* **1999**, *5*, 1969; (b) Hünig, S.; Kemmer, M.; Wenner, H.; Barbosa, F.; Gescheidt, G.; Perepichka, I. F.; Bäuerle, P.; Emge, A.; Peters, K. *Chem. Eur. J.* **2000**, *6*, 2618.
- 5. Muzyka, J. L.; Fox, M. A. J. Org. Chem. 1991, 56, 4549.
- 6. Plater, M. J.; Jackson, T. Tetrahedron 2003, 59, 4673.
- (a) Brenner, E.; Fort, Y. Tetrahedron Lett. 1998, 39, 5359;
 (b) Brenner, E.; Schneider, R.; Fort, Y. Tetrahedron 1999, 55, 12829;
 (c) Desmarets, C.; Schneider, R.; Fort, Y. Tetrahedron Lett. 2000, 41, 2875;
 (d) Brenner, E.; Schneider, R.; Fort, Y. Tetrahedron Lett. 2000, 41, 2881;
 (e) Desmarets, C.; Schneider, R.; Fort, Y. Tetrahedron Lett. 2001, 42, 247;
 (f) Desmarets, C.; Schneider, R.; Fort, Y. Tetrahedron 2001, 57, 7657;
 (g) Brenner, E.; Schneider, R.; Fort, Y. Tetrahedron 2002, 58, 6913;
 (h) Desmarets, C.; Schneider, R.; Fort, Y. Tetrahedron 2002, 1844;
 (i) Omar-Amrani, R.; Fort, Y. Org. Lett. 2003, 5, 2311;
 (j) Omar-Amrani, R.; Schneider, R.; Fort, Y. Synthesis 2004, 2527.
- (a) Herrmann, W. A.; Reisinger, C. P.; Spiegler, M. J. Organomet. Chem. **1998**, 557, 93; (b) Böhm, V. P. W.; Gstöttmayr, C. W. K.; Weskamp, T.; Herrmann, W. A. J. Organomet. Chem. **2000**, 595, 186; (c) Bourissou, D.; Guerret, O.; Gabbaï, F. P.; Bertrand, G. Chem. Rev. **2000**, 100, 39; (d) Herrmann, W. A. Angew. Chem., Int. Ed. **2002**, 41, 1290.
- (a) Gradel, B.; Brenner, E.; Schneider, R.; Fort, Y. *Tetrahedron Lett.* 2001, 42, 5689; (b) Desmarets, C.; Schneider, R.; Fort, Y. J. Org. Chem. 2002, 67, 3029.
- 10. SIPr·HCl is commercially available from Strem Chemicals Inc.
- (a) McMurry, J. E. Chem. Rev. 1989, 89, 1513; (b) Lenoir, D. Synthesis 1989, 883; (c) Fürstner, A.; Bogdanovic, B. Angew. Chem., Int. Ed. 1996, 35, 2442.
- 12. Murata, Y.; Shine, H. J. J. Org. Chem. **1969**, 34, 3368. Caution! Thianthrenium perchlorate is a shock-sensitive solid that should be handled only a small scale and with due care.
- (a) Seto, E. T.; Nelson, R. F.; Fritsch, J. M.; Marcoux, L. S.; Leedy, D. W.; Adams, R. N. J. Am. Chem. Soc. 1966, 88, 3498; (b) Ito, A.; Ino, H.; Tanaka, K.; Kanemoto, K.; Kato, T. J. Org. Chem. 2002, 67, 491.
- Effenberger, F.; Stahrer, W.-D.; Mack, K.-E.; Reisinger, F.; Seufert, W.; Kramer, H. E. A.; Föll, R.; Vogelmann, E. J. Am. Chem. Soc. 1990, 112, 4849.
- Brown, H. C.; Okamoto, Y. J. Am. Chem. Soc. 1958, 80, 4979.