Diatomic phenols as nucleophilic components in the carbonylation of the chelated C,N-palladacycle of the ferrocene series

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The carbonylation of the chelated palladium derivative of dimethylaminoferrocene in the presence of diatomic phenols affords mixtures of the corresponding mono- and diacylated dihydroxybenzenes containing a 2-dimethylaminomethylferrocenyl fragment in the acyl moiety.

Key words: diatomic phenols, ferrocene derivatives, carbonylation, C,N-palladacycles.

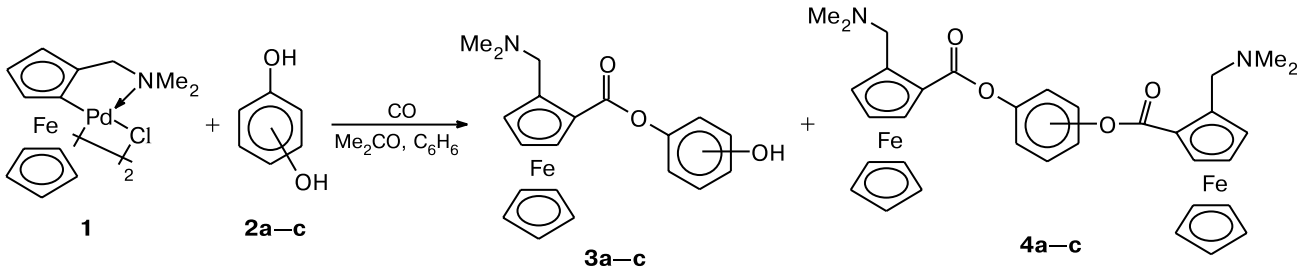
The development of a strategy for the syntheses of optically active ferrocene-based dendrimers required to study the behavior of polyatomic phenols as alcohol nucleophilic components in the carbonylation of chelated palladacycles, affording metallic palladium and respective esters. This reaction involving alkanols was repeatedly used for the synthesis of planar chiral, including optically active, 1,2-derivatives of ferrocene.[1—3] However, no information on the behavior of more acidic phenols in this reaction was available. Therefore, in this work, we studied the carbonylation of cyclopalladated dimethylaminomethylferrocene (**1**) with isomeric dihydroxybenzenes, *viz.*, pyrocatechol (**2a**), resorcinol (**2b**), and hydroquinone (**2c**), in a non-hydroxylic solvent (Scheme 1). The choice of these models was additionally favored by the fact that the expected products can serve as polydentate ligands to coordinate metal ions, because they contain two N- and O-donors each and the π-donating aryl group.

The products of carbonylation of compound **1** with pyrocatechol (**2a**) are 1-(2-hydroxyphenoxycarbonyl)-2-dimethylaminomethylferrocene (**3a**) and 1,2-bis(2-dimethylaminomethyl-1-ferrocenecarbonyloxy)benzene (**4a**). In the case of resorcinol (**2b**), the carbonylation products are 1-(3-hydroxyphenoxycarbonyl)-2-dimethylaminomethylferrocene (**3b**) and 1,3-bis(2-dimethylaminomethyl-1-ferrocenecarbonyloxy)benzene (**4b**). The carbonylation in the presence of hydroquinone (**2c**) affords 1-(4-hydroxyphenoxycarbonyl)-2-dimethylaminomethylferrocene (**3c**) and 1,4-bis(2-dimethylaminomethyl-1-ferrocenecarbonyloxy)benzene (**4c**). Their structures were established by ^{1}H NMR spectroscopy and mass spectrometry (Table 1).

The upfield shift of one of the protons of the CH_2 group in the ^{1}H NMR spectrum of compound **3a** and an inverted chromatographic behavior (monosubstituted derivative **3a** is eluted on SiO_2 more rapidly than bis-derivative **4a**) are in the agreement with a strong hydrogen bond of the free *ortho*-positioned OH group.

Since the bis-derivatives contain two planar chiral ferrocenyl fragments, diastereomers can form, which ex-

Scheme 1



Substitution pattern in the benzene ring	Yield (%)		Ratio **3** : **4**
	3	**4**	
ortho (**a**)	77	16	4.8 : 1
meta (**b**)	14	37	1 : 2.6
para (**c**)	12	48	1 : 4

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 12, pp. 2756—2758, December, 2004.

1066-5285/04/5312-2874

Table 1. ^{1}H NMR spectra, elemental analysis data, and mass spectrometry for the reaction products

Compound	Found / Calculated (%)			Molecular formula	^{1}H NMR, δ (*J*/Hz)					MS, *m/z* $[M]^+$
	C	H	N		$N(C\underline{H}_3)_2$	$C\underline{H}_2N$	C_5H_5	C_5H_3	C_6H_4	
3a	63.36 63.34	5.68 5.58	3.74 3.69	$C_{20}H_{21}FeNO_3$	2.15 (s, 6 H)	2.86, 4.43 (AB system, 2 H, *J* = 12.0)	4.25 (s, 5 H)	4.37, 4.40, 4.92 (all s, 3 H each)	6.82 (t, 1 H); 6.94 (d, 1 H); 7.07 (t, 1 H); 7.26 (d, 1 H)	379
3b	63.48 63.34	5.71 5.58	3.74 3.69	$C_{20}H_{21}FeNO_3$	2.25 (s, 6 H)	3.29, 4.23 (AB system, 2 H, *J* = 12.47)	4.20 (s, 5 H)	4.43, 4.52, 4.93 (all s, 3 H each)	6.41 (s, 1 H); 6.59 (d, 2 H); 7.07 (t, 1 H)	379
3c	68.01 68.28	6.19 5.95	3.48 3.06	$C_{20}H_{21}FeNO_3 \cdot \cdot C_6H_6$	2.30 (s, 6 H)	3.35, 4.44 (AB system, 2 H, *J* = 12.76)	4.25 (s, 5 H)	4.48, 4.54, 4.99 (all s, 3 H each)	6.89, 7.75 (both d, 2 H each)	379
4a	62.97 62.99	5.69 5.60	4.41 4.32	$C_{34}H_{36}Fe_2N_2O_4$	2.17, 2.20 (all s, 6 H each)	3.30 and 4.02, 3.36 and 4.02 (both AB system, 2 H each, *J* = 12.1)	4.12, 4.15 (both s, 5 H each)	4.33 (br.s, 2 H); 4.49, 4.52, 4.86, 4.90 (all s, 1 H each)	7.29 (br.s, 4 H)	648
4b	64.78 64.65	6.37 5.72	4.29 4.08	$C_{34}H_{36}Fe_2N_2O_4 \cdot \cdot 0.5\ C_6H_6$	2.22 (s, 12 H)	3.28, 4.09 (AB system, 4 H, *J* = 12.64)	4.22 (s, 10 H)	4.44, 4.53, 4.94 (all s, 6 H each)	7.08 (d, 2 H); 7.33 (s, 1 H); 7.43 (t, 1 H)	649 $[M + H]^+$
4c	62.97 62.99	5.78 5.60	4.41 4.32	$C_{34}H_{36}Fe_2N_2O_4$	2.27 (s, 12 H)	3.33, 4.14 (AB system, 4 H, *J* = 12.08)	4.26 (s, 10 H)	4.48, 4.58, 4.99 (all s, 6 H each)	7.25 (s, 4 H)	648

plains the duplication of signals in the ^{1}H NMR spectra in some cases.

Experimental

^{1}H NMR spectra were recorded on Bruker WP-200 SY and Bruker 400 HX instruments in $CDCl_3$. Mass spectra (EI) were obtained on a Kratos-MS-890 instrument. Solvents were purified according to standard procedures.

A carbon monoxide flow was passed for 6 h through a suspension of compound **1** (1.1 g, 1.45 mmol) and diatomic phenol **2a—c** (0.16 g, 1.43 mmol) in a mixture of acetone (10 mL) and benzene (50 mL). The reaction mixture was left to stay for ~14 h. A precipitate was filtered off, washed with a $CHCl_3$—Et_3N (4 : 1) mixture, and the liquid phase was concentrated by evaporation. Benzene was added to the residue, and the resulting mixture was treated with a saturated aqueous solution of Na_2CO_3. The organic layer was separated, dried with $MgSO_4$, and concentrated. Chromatography was first carried out on a column with SiO_2 and then on SiO_2 plates, using benzene—Et_3N (10 : 1) mixture as an eluent. The yields and ratios of the obtained products are presented in Scheme 1. The elemental analysis data, mass spectra, and ^{1}H NMR spectra are given in Table 1.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 02-03-33355).

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Received July 23, 2004