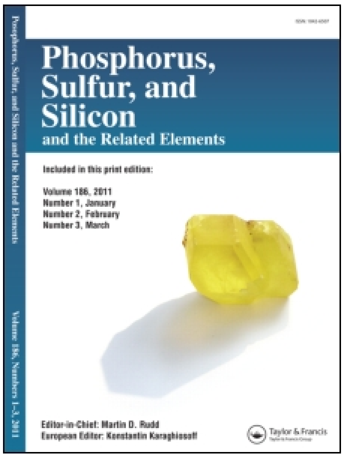

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THE CHELETROPIC REACTION OF COORDINATED o-BENZOQUINONE DIIMINES WITH TRIPHENYLPHOSPHINE

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THE CHELETROPIC REACTION OF COORDINATED *o*-BENZOQUINONE DIIMINES WITH TRIPHENYLPHOSPHINE

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Coordinated *o*-benzoquinone diimine and 4-methyl-*o*-benzoquinone diimine in $[Co(diimine)_3]PF_6$ (**1**) undergo facile cheletropic reaction with triphenylphosphine to give first 2,3-dihydro-1,3,2-λ^5-benzodiazaphospholes (**2**), which on decyclization result in the equilibrium products *N*-(2-aminophenyl)iminotriphenylphosphorane (**3a**) and *N*-(2-amino-4-methylphenyl)iminotriphenylphosphorane (**3b**) respectively in moderate yields.

Key words: 1,4-Cycloaddition; cheletropic reaction; *o*-benzoquinone diimine; iminophosphorane; benzodiazaphosphole.

o-Quinones,[1] *o*-quinone monoimines,[2] and *o*-quinone diimines[3] are well known substrates for various electrocyclic reactions. Trivalent phosphorus compounds react easily in electrocyclic reactions with conjugated dienes and heterodienes to give phosphole derivatives.[4,5] The reactions of *o*-quinones with phosphines and phosphites have been studied thoroughly and reported in the literature.[6] Only a limited number of cases are known for the similar reaction with *o*-quinone monoimines[3] due to the relative instability of the latters, and none of unsubstituted *o*-quinone diimines because of their instability. *o*-Quinone diimines show enhanced stability when they are coordinated to metals and a fair number of *o*-quinone diimine metal complexes could be isolated and characterized.[7]

Since coordinated heterodienes can undergo electrocyclic reactions with dienophiles[8] we looked at the reaction of *o*-benzoquinone diimine complexes with triphenylphosphine in order to obtain 2,3-dihydro-1,3,2-λ^5-benzodiazaphospholes as a result of a cheletropic reaction. As starting *o*-quinone diimine complexes the compounds of the formulae $[Co(diimine)_3]PF_6$ (**1**) have been chosen, which were prepared according to the method by Warren[7] from *o*-phenylenediamines. With 4-nitro- and *N,N'*-diacetyl-*o*-phenylenediamine the corresponding complexes could not be obtained.

Tris(*o*-benzoquinonediimine)cobalt(III) hexafluorophosphate (**1a**) and tris(4-methyl-*o*-benzoquinonediimine)cobalt(III) hexafluorophosphate (**1b**) react with triphenylphosphine in acetonitrile at reflux temperature in a smooth reaction. The coordinated diimine ligands undergo a cheletropic reaction with tri-

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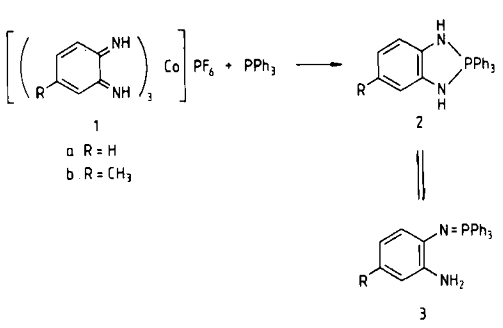
phenylphosphine according to Scheme 1 to give 2,3-dihydro-2,2,2-triphenyl-1,3,2-λ^5-benzodiazaphospholes (**2**) as primary products. The 2,3-dihydrobenzo-diazaphospholes (**2**) show an equilibrium with N-(aminophenyl)iminophosphoranes (**3**) and its state is influenced by the nature of substituents on the nitrogen and phosphorus atom mainly.[9]



SCHEME 1.

In case of **3a** and **3b** the equilibrium is largely shifted to the iminophosphoranes (**3**) as established by ^{31}P NMR (see Table I). In Table II physical constants, yields and elemental analyses of the compounds **3a–b** are given.

The yield of iminophosphoranes is rather low due to the work-up process, since their separation from triphenylphosphine, present in excess, needs several recrystallizations.

TABLE I

IR, MS and ^{31}P NMR data of the compounds **3a–b**

No.	IR Spectra, cm^{-1} ν(NH), nujol	Mol. weight	MS M$^+$	^{31}P NMR (CDCl$_3$),δ (Standard, H_3PO_4)
3a	3326 3446	368.52	368	4.80
3b	3320 3440	382.42	382	4.07

TABLE II

Physical constants, yields and elemental analyses of the compounds **3a–b**

No.	Yield[a] %	Mp °C	Formula	EA	C	H	N
3a	32	140–2	$C_{24}H_{21}N_2P$	Found	78.21	5.74	7.63
				Calcd.	77.58	5.94	7.51
3b	26	129–30	$C_{25}H_{23}N_2P$	Found	78.48	6.05	7.35
				Calcd.	77.92	5.94	7.03

[a] Isolated yields.

EXPERIMENTAL

Methods of Analysis. The ^{31}P NMR spectra were obtained on a Varian CFT 20 spectrometer, the IR spectra were run on a Specord IR-75 spectrophotometer and the MS spectra were recorded on a Jeol MS 01 SG2 mass spectrometer.

Starting Materials. Complex **1a** was prepared according to the literature.[7] **1b** was synthesized by the same method starting from 4-methyl-*o*-phenylenediamine. Yield 73%, IR (nujol): $\nu = 3334\,cm^{-1}$ (NH), $C_{21}H_{24}N_6CoPF_6$ (564.82), Calcd. C 44.71 H 4.27 N 14.94 Found C 44.52 H 4.31 N 14.88.

General Method for Preparation of N-(aminophenyl)iminotriphenylphosphoranes **(3a–b)**. Tris(*o*-benzoquinonediimine)cobalt(III) hexafluorophosphate and triphenylphosphine in acetonitrile were refluxed under argon for 20 h. The solvent was removed in vacuum and the crude product was crystallyzed first from acetonitrile, where the excess of PPh_3 separates, then several times from ether.

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