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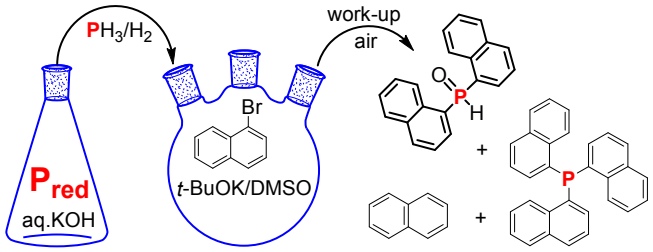

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ABSTRACT

The phosphine, generated together with hydrogen from red phosphorus and aqueous KOH, reacts with 1-bromonaphthalene in the *t*-BuOK/DMSO system under mild conditions (70 °C, atmospheric pressure) to give di(1-naphthyl)phosphine, which is easily oxidized in the presence of air to afford di(1-naphthyl)phosphine oxide in 45% preparative yield. Tri(1-naphthyl)phosphine and naphthalene are also formed in the reaction in 23 and 27% yield, respectively. According to ESR and UV data, the studied phosphination of 1-bromonaphthalene involves a single electron transfer process.

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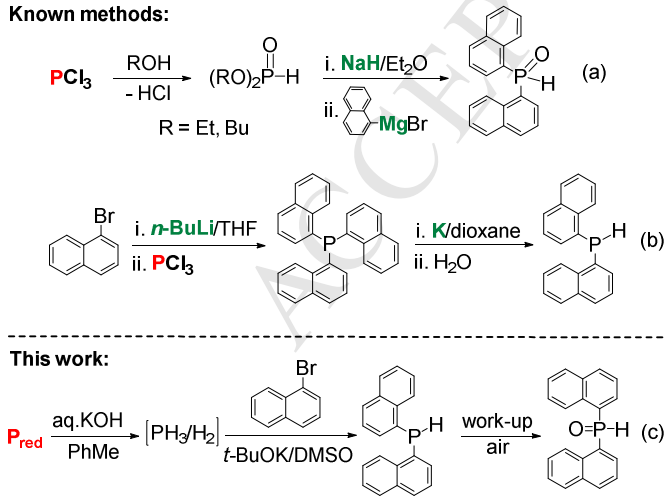
1. Introduction

Organic phosphines and phosphine oxides, bearing sterically hindered substituents, for instance, naphthyl moieties, are excellent ligands for metal complex catalysts inducing many types of transformations.[1] So, di(1-naphthyl)phosphine and its oxide are of special importance as a building block for the construction of luminescent materials,[2] bidentate,[3] asymmetric[4] and special tripod-ligands.[5] The latter are used as catalysts and co-catalysts for asymmetric hydrogenation,[6] hydroformylation,[7] alkylation,[8] Diels-Adler[5b] reaction as well as for alkene polymerization.[9] In addition, di(1-naphthyl)phosphine oxide was claimed as a stabilizer of nanoparticles.[10] Tri(1-naphthyl)phosphine, in its turn, was employed for the preparation of complexes[11] showing high catalytic activity in the cross-coupling reactions,[12] synthesis of diaryl ketones[13] and alcohols,[14] hydrogenation,[15] cyclization,[16] and reduction reaction[17] as well as the complexes having intense long-lived luminescence and photoluminescence.[11a,f]

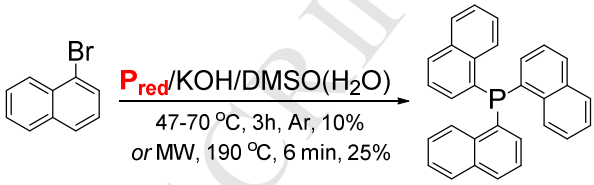
However, the traditional syntheses of bulky naphthylphosphines, including di(1-naphthyl)phosphine and its oxide, are multistep, laborious and require highly aggressive phosphorus halogenides and flammable organometallic reactants.[4c,7,18] For example, these reactions typically involve either PCl_3/*n*-BuLi (or Grignard) reagents (Scheme 1a,b) or cleavage of tri(1-naphthyl)phosphine by alkali metals (Scheme 1b). Herein, we describe the convenient synthesis of di(1-naphthyl)phosphine and its oxide from 1-bromonaphthalene and phosphine in the *t*-BuOK/DMSO system (Scheme 1c). Phosphine is an industrial tail gas[19] and can serve as a cheap source of P, thus search for its utilization is highly desirable. In this work, phosphine is generated together with hydrogen from red phosphorus and aqueous KOH (60%) and used further without isolation and purification. It is worth emphasizing that PH_3/H_2 mixture proved to be easily handled by using a common glass flask placed under a fume hood. Important, that PH_3/H_2 is generated and directed to the reaction mixture only on demand, i.e. in a dosed flow, which is immediately stopped after the reaction completion that warrants sufficient safety (see Supporting information Scheme S1 and Pic. 1).



Scheme 1. Synthesis of di(1-naphthyl)phosphine and its oxide

Also, J.-L. Montchamp and co-workers have synthesized organophosphorus derivatives of naphthalene without PCl_3 from available reagents (anilinium hypophosphite and BrNp or TfONp) via palladium-catalyzed cross-coupling.[20] Recently, we have reported[21] a simple and straightforward synthesis of tri(1-naphthyl)phosphine by the direct phosphination of 1-bromonaphthalene with red phosphorus in a KOH/DMSO suspension (Scheme 2). No formation of di(1-naphthyl)phosphine has been observed under the studied condition.

The data on the reaction of 1-bromonaphthalene with phosphine are lacking in the literature. Meanhile, 1-bromonaphthalene is known to react with *t*-BuOK/DMSO to give naphthalene, 1- and 2-methylnaphthalenes, 1,2-dimethylnaphthalene, 1- and 2-*tert*-butoxynaphthalenes, dinaphthalenes, dinaphthyl ethers, naphthols, methylmercaptonaphthols.[22]

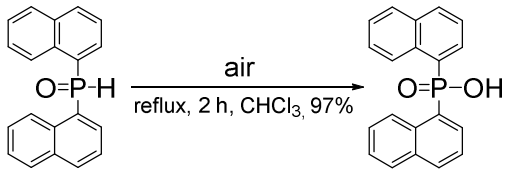


Scheme 2. Synthesis of tri(1-naphthyl)phosphine from red phosphorus and 1-bromonaphthalene

2. RESULTS AND DISCUSSION

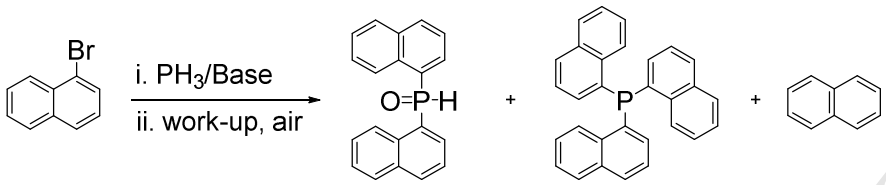
Our experiments have showed that phosphine reacts with 1-bromonaphthalene (BrNp) under the action of the superbase catalytic system such as *t*-BuOK/DMSO, *t*-BuONa/DMSO and KOH/DMSO at heating (60–80 °C, 2.5–6 h, argon blanket) to afford di(1-naphthyl)phosphine 1-Np_2PH, which is selectively oxidized in the process of its isolation on air to produce di(1-naphthyl)phosphine oxide, 1-$Np_2P(O)H$. Under the studied conditions, tri(1-naphthyl)phosphine 1-Np_3P and naphthalene NpH are also formed (Table 1). It is worthwhile to note that BrNp is slowly added dropwise to the PH_3/*t*-BuOK/DMSO system to avoid exhaustive phosphine arylation. Moderate yields of 1-Np_2PH (up to 45%) are attained using the superbase system *t*-BuOK/DMSO and heating of the reagents at 60–70 °C for 2.5–4 h (Table 1, entries 1-3). In these experiments, 1-naphthylphosphine oxide 1-$NpP(O)H_2$, 1,2-dinaphthylphosphine 1,2-Np_2PH and 1,1,2-trinaphthylphosphine 1,1,2-Np_3P are detected in small amounts (NMR data, see Supporting information, Scheme S2). At a higher temperature (80 °C), the yield of phosphines 1,2-Np_2PH, 1,1,2-Np_3P and 1,2,2-Np_3P slightly increases (~5-10%). Under these conditions, the formation of polynaphthalenes are also observed (Table 1, entry 4, see also Supporting information). The latters are also formed when the superbase *t*-BuONa/DMSO system is used (Table 1, entries 5, 6).

Notably, the target 1-$Np_2P(O)H$ is easily oxidized with oxygen (air) at heating (50–70 °C) in organic solvents to afford practically quantitatively di(1-naphthyl)phosphinic acid, an effective ligand and building block in organic chemistry[4f,h,8b,23] (Scheme 3).



Scheme 3. Oxidation of di(1-naphthyl)phosphine oxide

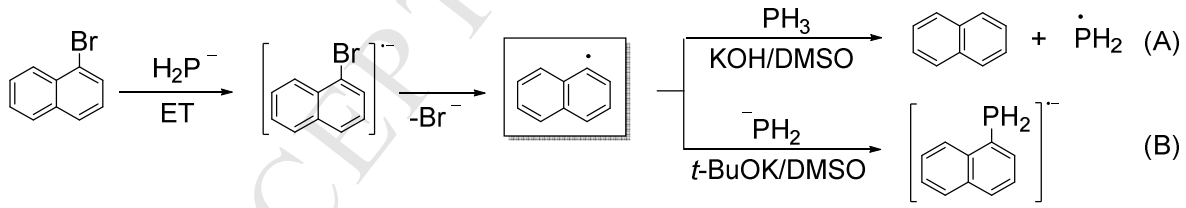
Table 1
Optimization of the reaction conditions.[a]



Entry	Base	Temp (°C)	Time (h)	Products (yield %)[b]			Conversion of BrNp (%)
				1-$Np_2P(O)H$	1-Np_3P	NpH	
1	*t*-BuOK/DMSO	70	4	45	23	27	91
2	*t*-BuOK/DMSO	60	4	35	9.3	19	86
3[c]	*t*-BuOK/DMSO	65–70	2.5	39	4	32	90
4[de]	*t*-BuOK/DMSO	80	4	19	26	23	99
5[e]	*t*-BuONa/DMSO	60	6	38	16	9.2	99
6[e]	*t*-BuONa/DMSO	70	2.5	35	8.4	28	88
7	KOH/DMSO	65–70	4	4	2.5	28	53
8	KOH/DMSO	60	5	0	1.5	23	30
9[f]	*t*-BuOK/DMSO	60	2.5	7	7	27	86

[a] The reaction conditions for entries 1-6, 9: BrNp (48.3 mmol), *t*-BuOK or *t*-BuONa (72.5 mmol), DMSO (80 mL); for 7 and 8 entries: BrNp (48.3 mmol), KOH (178.5 mmol), DMSO (40-50 mL).
[b] The yield was calculated on the basis of BrNp consumed.
[c] 120 mL DMSO was used.
[d] The structural isomers of phosphines were also formed.
[e] The large amounts of insoluble polynaphthalenes were formed.
[f] TEMPO (10 mol%) was added.

The system PH_3/KOH/DMSO appears to be ineffective for phosphination of BrNp, the other conditions being the same (entries 7 and 8). This is likely due to extremely poor solubility of KOH in DMSO (13 mg/100 mL DMSO)[24] that leads to low concentration of phosphide-anion ($^-PH_2$). Therefore, the reaction of PH_3 with naphthalene radical furnishes naphthalene owing to abstraction of hydrogen atom. In that case, naphthalene becomes the major reaction product (Scheme 4, path A).



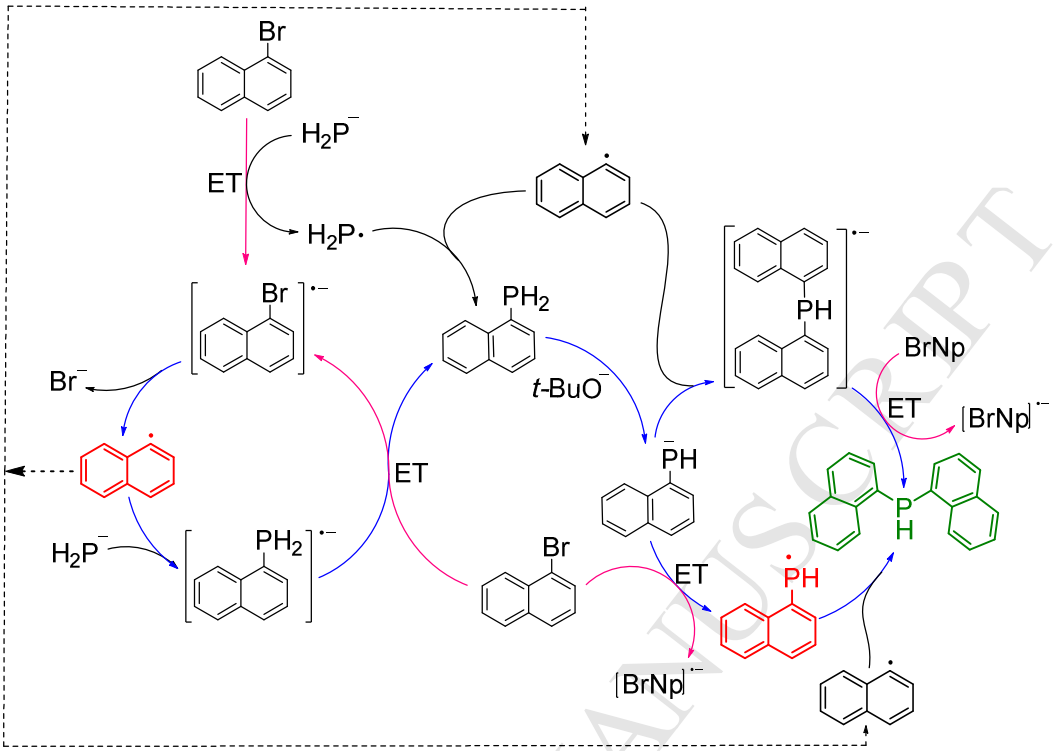
Scheme 4 Two ways of interactions naphthalene radical with PH_3 in different superbasic systems.

In the case of homogeneous system *t*-BuOK/DMSO (entries 1-6), phosphine (PH_3) is almost completely ionized to the phosphide anion ($^-PH_2$), which is able to add to more electrophilic 1-naphthyl radical to furnish the anion-radical of 1-naphthylphosphine (Scheme 4, path B). Abstraction of hydrogen atom from the solvent by 1-naphthyl radicals gives the reduction product, naphthalene. At a lower temperature (60 °C, entry 2), the yield of Np_2PH notably drops, although at a higher temperature (80 °C) Np_3P starts to be prevalent (entry 4). The prolonged process time does not provide higher yields of the target products. Comparison of the three reaction conditions indicates that the new procedure (*t*-BuOK/DMSO) is far superior to the method involving KOH or *t*-BuONa/DMSO in terms of the application scope and the product yield. Then we have found that the reaction is inhibited by the addition (10 mol%) of the radical scavenger TEMPO (entry 9), as well as does not occurs in the absence of a base. These facts suggest ion-radical mechanism of the reaction. This assumption is also confirmed by ESR and UV spectra of the reaction mixture (*vide infra*).

Actually, as shown in[21], the reaction proceeds through radical nucleophilic substitution (S_{RN}1-mechanism[25]). The proposed base-promoted S_{RN}1-mechanism is a chain process involving radicals and radical anions as intermediates (Scheme 5). The initiation step is an electron transfer (SET) from H_2P^- anion to BrNp to yield an $[BrNp]^{\cdot-}$ radical anion, which then fragments to produce a naphthyl radical $[Np]^{\cdot}$ and an bromine ion (Br^-). The $[Np]^{\cdot}$ formed is able of coupling with H_2P^- anion to give radical anion $[NpPH_2]^{\cdot-}$, which reacts as an electron transfer reagent to give the primary phosphine $NpPH_2$, coupling product after ET to

the radical precursor, and these cycles repeats again one or two times to eventually give Np_2PH or Np_3P.

It is interesting to note that recombination of the radicals does not lead to the reaction quenching, since the ET process proceeds with participation of 1-naphthylphosphide anion ($NpHP^-$) giving radical $NpHP^{\cdot}$, which is detected by ESR with spin-trapping technique, together with naphthyl radical (depicted in Scheme 5 in red).



Scheme 5. Proposed mechanism of Np_2PH synthesis (depicted in green)

The reaction was studied by ESR techniques both in KOH/DMSO and *t*-BuOK/DMSO media (see ESI). An attempt to directly detect phosphorus-centered and free naphthalene radicals in the reaction mixture using ESR method failed due to their extremely low stability.[26] Therefore, the reaction was carried out in the presence of spin trap, C-phenyl-N-*tert*-butylnitrone (PBN)[27], directly in resonator of the ESR spectrometer. The recorded spectrum (Fig. 1a, top left) was simulated (Fig. 1b, bottom left) to demonstrate that it contains the overlapped signals of three spin adducts **I-III** (Fig. 2), two doublet triplets with an intensity ratio of ~ 10:1: **I**) g = 2.0077, a_N = 14.58 G, a_H = 4.23 G; **II**) g = 2.0077, a_N =15.80 G, a_H = 2.30 G and **III)** weak nitrogen triplet (a_N =14.60 G) split into 3 doublets with the following constants a_P = 15.00 G, a_H = 4.8 G, a_H = 2.6 G with g = 2.0080. The latter signal disappears by the end of the reaction, and the spectrum contains only two the above doublet triplets. Noteworthy, the initial ratio of these signals changes and becomes approximately equals, while the total intensity decreases (Fig. 1c top right). The first two signals are assigned to spin adducts of naphthalene carbon-centered radicals, which differ by constants of hyperfine coupling (HFC), and third signal is attributed to spin adducts of the trap with phosphorus-centered radical $NpHP^{\cdot}$ (see Scheme 5).

It should be emphasized that usually $S_{RN}1$ mechanism is triggered by photo- or electrochemical activation,[25b,c,d] but in our case the thermally initiated $S_{RN}1$ reaction is observed since it occurs even in the dark[27]. Curiously enough, the expected intermediate primary phosphine in the reaction mixture is detected in about 1-5%, probably because of easy dissociation of 1-naphthylphosphine to the corresponding anion and it participation in SET to the BrNp.

Surprisingly, the competitive C-H arylation of BrNp with naphthyl radical, known as BHAS (base-promoted homolytic aromatic substitution) reaction, typical for unactivated aromatic rings[25e,28] (Scheme S3), represents a minor process. The direct cross-coupling products BrNpNp or binaphthyls have been detected in the reaction mixtures in an amount of 5-7% (identified in the reaction mixture by MS).

Following this mechanism the naphthalene radical turns out to react with 1-halonaphthalene to furnish 4-halo-1,1'-binaphthalene.[28c] To suppress this process, one should dilute the reaction mixture to increase concentration of the phosphide-anions (H_2P^-) and to slow the addition of BrNp. However, it is worth noting that a larger amount of DMSO gives lower yields due to H-abstraction (Table 1, entry 4). ·

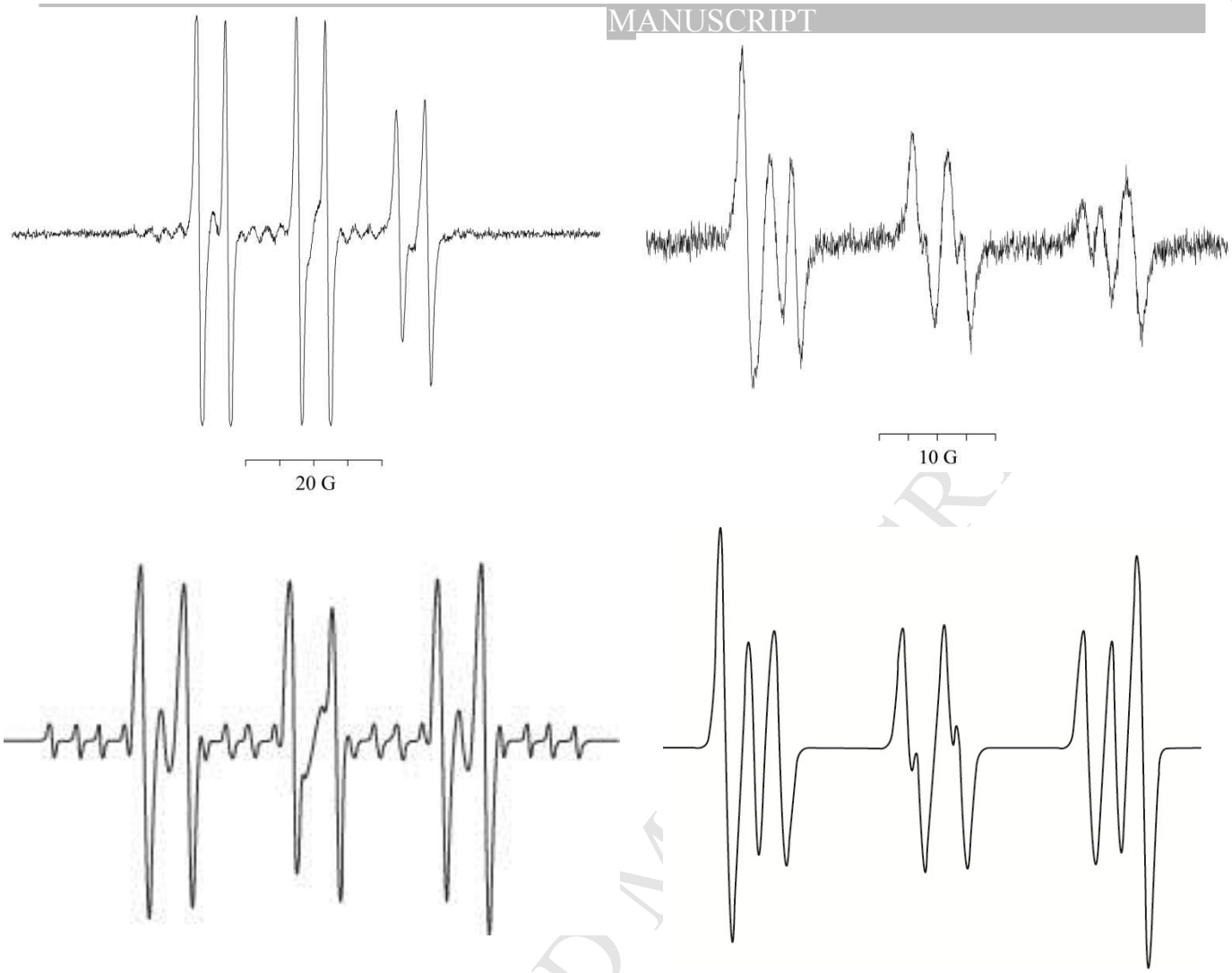


Figure 1. ESR spectra of the reaction mixture PH_3/KOH/DMSO/ PBN: left – experimental (top) – in 30 min after the reaction beginning, simulated (bottom); right – experimental (top) - in 2 h, simulated (bottom).

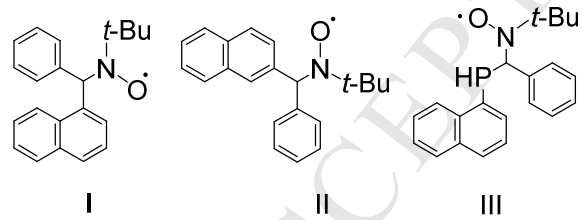


Figure 2. Spin adducts

To shed a further light on the possible reaction mechanism, we have recorded the UV-Vis spectra of the reaction mixture under an Ar atmosphere. We have revealed that *t*-BuOK is dissolved in DMSO forming a pale-yellowish solution, a band being observed at 307 nm (Fig.3). Coloring of the solution likely indicates the generation of solvate-separated ionic pair of the type $K^+ \cdots O \rightarrow S\ Me_2 \cdots {}^-O$*t*-Bu. The addition of phosphine (PH_3) to this mixture results in a new band at 364 nm, which could be assigned to complexes involving phosphide-anion. The introduction of 1-bromonaphthalene leads to deep dark-purple coloring and appearance of the bands at 408 and 540 nm, which evidences the formation of charger transfer (CT) complexes of the presumed kind $[NpPH_2^{\cdot +}\ t\text{-}BuO^{\cdot}]K^+$ (408 nm) or $[Np_2PH^{\cdot +}\ t\text{-}BuO^{\cdot}]K^+$, solvated by DMSO (Scheme 6). The band at 408 nm rather quickly disappears (for 1-2 min), whereas the band at 540 nm is stable for a long time (1-4 h in Ar atmosphere, more details see ESI). In our earlier works,[29] in the reaction of primary or secondary phosphines with acetylenes we have observed charge-transfer absorption band at 412 and 454 nm, attributed to some radical species formed via SET.

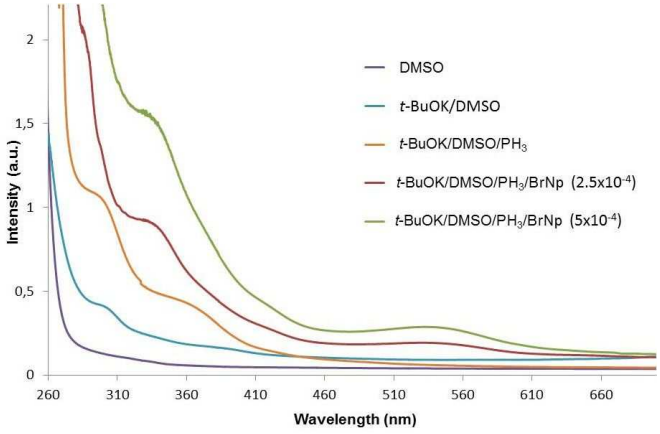
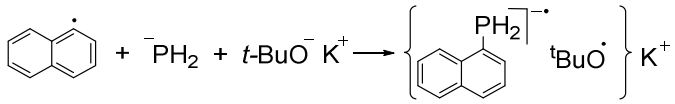


Figure 3. UV-Vis spectra of the reaction mixture *t*-BuOK/DMSO to which PH_3 and BrNp were added stepwise and when necessary

The data implies that phosphide-anion reacts with naphthyl radical to give radical anion $[NpPH_2]^{\bullet-}$, which further undergoes electron transfer to the next molecule of BrNp to form at the beginning primary phosphine $NpPH_2$ and then secondary- and tertiary phosphines.



Scheme 6. Probable CT complex formation

3. Conclusion

In summary, the PCl_3-free convenient phosphination of 1-bromonaphthalene with PH_3 in the superbasic system *t*-BuOK/DMSO (70 °C) leading to di(1-naphthyl)phosphine and its oxide has been developed. Reactivity of phosphide-anion toward 1-bromonaphthalene is demonstrated and it is found the reaction proceeds through base-promoted radical nucleophilic substitution ($S_{RN}1$-type chemistry).

4. Experimental section

4.1. General

The monitoring was carried out by $^{31}P\{^1H\}$ NMR spectroscopy of the reaction mixtures. To correctly evaluate the content of the reaction products basing on relative integral intensity of signals in the ^{31}P NMR spectrum, we used pulse sequence «zg30» (BRUKER standard pulse program) and time of relaxation delay d1 = 5 s. The ^1H, ^{13}C and ^{31}P NMR spectra were recorded using a Bruker AV-400 spectrometer at 400.13, 100.62 and 161.98 MHz, respectively. The ^1H NMR chemical shifts are expressed with respect to residual protonated $CDCl_3$ (7.27 ppm), which served as an internal standard. The ^{13}C NMR shifts are expressed with respect to the $CDCl_3$ (77.0 ppm). 85% H_3PO_4/D_2O was used as external standards for ^{31}P NMR. The FTIR spectra were recorded on a Bruker Vertex 70 spectrometer. The C, H microanalyses were performed on a Flash EA 1112 SHNS-O/MAS analyzer, while the P contents were determined by combustion method. Melting points were established using a Kofler micro hot stage.

CW EPR spectra were recorded with FT X-band Brüker ELEXSYS E 580 spectrometer (X-wave range 9.7 GHz). Precision of the measurement of g-factor was ± 0.0002. CW EPR-spectra were recorded at the following conditions: amplitude modulation 0.5-1.0 G, receiver gain 60–90 dB, time constant 0.02 s, conversion time 0.04 s, microwave power 0.6325 mW. The monitoring of the reaction was carried out at 65–85 °C temperature in ampoules of 1.5 mm diameter directly in the resonator of EPR spectrometer. The simulated spectra were obtained using the WINEPR SimFonia 1.25 Program (Bruker Inc. 1996). Concentration of PBN was 10-1-10-2 M/l. UV–Vis spectra were recorded on a Perkin Elmer Lambda 35 spectrometer at 25-70 °C). UV−Vis spectra of reaction mixture (BrNp/*t*-BuOK ($2.5\times10^{-3} \div 5\times10^{-4}$ mmol/L) measured in DMSO using a 1 cm cuvette at rt under Ar atmosphere. FT-IR spectra were recorded on a Bruker Vertex 70 spectrometer at ambient temperature.

Controlled generation of phosphine together with hydrogen was rendered in a separate reactor by the addition of warm aqueous solution of KOH (60%) to a suspension of red phosphorus in toluene at 20–50 °C.[30] Unused outlet PH_3 was absorbed by sol. 20% DMSO/aq.$CuSO_4$ (or aq. $Cu(OAc)_2$). DMSO was dried over Al_2O_3 (2–3 days) and distilled under KOH in vacuum and stored over molecular sieves (4 Å) under N_2. Red phosphorus (KSAN' SIA, China), *t*-BuOK (Aldrich), *t*-BuONa were all commercial samples which were used without further purification. Liquid 1-bromonaphthalene (Alfa Aesar, 97%) was freshly distilled before their utilization. All reaction glassware and equipment were thoroughly cleaned and dried prior to use. All experiments were carried out under Ar atmosphere, except for work-up procedures.

Synthesis of di(1-naphthyl)phosphine oxide

To a solution of *t*-BuOK (8.14 g, 72.5 mmol) in anhydrous and degassed DMSO (73 mL), blown with argon and saturated with dry phosphine, a solution of 1-bromonaphthalene (10.01 g, 48.3 mmol) in anhydrous DMSO (7 mL) was added dropwise at 70 °C for 1 h under stirring and continuous bubbling of the phosphine. The reaction mixture was heated (70 °C) for 0.5 h in the flow of phosphine, the phosphine feeding was stopped, but the mixture was continuously stirred for 1.5 h (70 °C). In the ^{31}P NMR spectrum of the reaction mixture, the following signals were observed: -62.03 (d, $^1J_{PH}$ 227 Hz) for 1-Np_2PH, -33.37 (s) for 1-Np_3P and -2.49 (t, $^1J_{PH}$ 463 Hz) for 1-$NpP(O)H_2$ in a ratio of ~ 5:1.5:0.1. Trace amounts of 1,2-Np_2PH (-49.78 ppm) and 1,1,2-Np_3P (-22.70 ppm) were also formed. Then the mixture was blown with argon, cooled and diluted with cold water (80 mL) to give a white precipitate (1.15 g). The latter was filtered off, washed with water (5×30 mL) and Et_2O (3×25 mL), dried on the air to get 1-Np_3P (0.68 g). The filtrate was sequentially extracted with Et_2O (50 mL) and CH_2Cl_2 (2×50 mL).

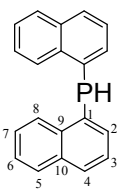
(a) Ether extract was washed with cold water (3×20 mL), dried over K_2CO_3, the solvent was removed under reduced pressure to give a white wax-like crude product (5.01 g), which was heated under 1 Torr (100–150 °C, sand bath) to sublimate naphthalene (1.37 g) and to distill unreacted BrNp (0.95 g, conversion 91%). The residue was dissolved in EtOH (22 mL), white precipitate was filtered off, washed with EtOH (10×5 mL) and dried *in vacuo* to give a creamy solid (0.62 g, 1-Np_3P).

Secondary phosphine oxide 1-$Np_2P(O)H$ (2.30 g) was isolated from alcoholic extract after removing the solvent and drying in vacuum.

(b) CH_2Cl_2 extract was washed with brine (10% aq. sol. KCl), orange precipitate was filtered off, dried over K_2CO_3 and the solvent was removed to give white wax-like product (1.21 g). The latter was heated under 1 Torr (100-150 °C, sand bath) to sublimate naphthalene (0.17 g), the residue was washed with EtOH (3×20 mL), the 1-Np_3P (0.08 g) was filtered off, EtOH was removed to afford 1-$Np_2P(O)H$ (0.65 g).

Total yield of 1-$Np_2P(O)H$ is 2.95 g (45%). Total yield of 1-Np_3P is 1.38 g (23%). Yield of naphthalene is 1.54 g (27%).

Di(1-naphthyl)phosphine, Np_2PH, the compound was identified by ^1H NMR, ^{31}P NMR, and these data were consistent with literature values.[7]



^1H NMR ($CDCl_3$): 8.24 (m, 2H, H^8), 7.92-7.79 (m, 6H, H^{3-5}), 7.50 (d, 1H, J_{PH} 227 Hz, PH), 7.48-7.44 (m, 4H, $H^{6,7}$), 7.30 (dd, 2H, *J* 7.5 Hz, H^2). ^{31}P NMR ($CDCl_3$): -61.76 ppm (J_{PH} 227 Hz). Found: C, 83.41; H, 5.26. Anal. Calcd for $C_{20}H_{15}P$: C, 83.90; H, 5.28.

Di(1-naphthyl)phosphine oxide, 1-$Np_2P(O)H$, white powder, mp 168–169 °C. FTIR (neat), cm^{-1}: 449, 664, 674, 757, 773, 944, 993, 1164, 1179, 1215, 1376, 1459, 1506, 1570, 1590, 1620, 2316, 2851, 2923, 2957, 3056. ^1H NMR ($CDCl_3$): 8.90 (d, *J* 481 Hz, 1H, PH); 8.35 (m, 2H, H^8), 8.05 (d, *J* 8.3 Hz, 2H, H^4), 7.97 (d, *J* 7.2 Hz, 2H, H^2), 7.92 (m, 4H, $H^{3,5}$), 7.52 (m, 4H, $H^{6,7}$).

^{13}C NMR ($CDCl_3$): 133.9 (d, *J* 11.5 Hz, C^9), 133.5 (C^7), 133.4 (d, *J* 9.5 Hz, C^{10}), 132.7 (d, *J* 11.5 Hz, C^8), 129.1 (d, *J* 98.0 Hz C^1), 129.1 (C^4), 127.7 (C^5), 126.7 (C^6), 125.0 (d, *J* 14.5 Hz, C^3), 124.9 (d, *J* 20.6 Hz, C^2). ^{31}P NMR ($CDCl_3$): 18.85 (d, *J* 481 Hz, PH); Found: C, 78.98; H, 4.93. Anal. Calcd for $C_{20}H_{15}OP$: C, 79.46; H, 5.00.

Di(1-naphthyl)phosphinic acid, 1-Np$_2$P(O)OH

Solution of di(1-naphthyl)phosphine oxide (0.1 g) in chloroform (5 mL) was refluxed in air for 2 h. Then the solvent was distilled under reduced pressure and residue was dried in vacuum. Di(1-naphthyl)phosphinic acid was prepared in near quantitative yield.

White powder, mp 198-201 ^{o}C, FTIR (KBr): 3055, 3008, 2955, 2922, 2854, 2632, 2289, 1955, 1646, 1619, 1591, 1568, 1505, 1456, 1432, 1382, 1334, 1212, 1178, 1152, 1025, 995, 951, 833, 800, 773, 753, 680, 566, 526, 479. ^{1}H NMR ($CDCl_3$): 9.58 (br, 1H, OH), 8.48 (d, *J* 8.5 Hz, 2H, H^8), 8.16 (dd, *J* 16.3 and 7.2 Hz, 2H, H^2), 7.92 (d, *J* 8.4 Hz, 2H, H^4), 7.79 (d, *J* 8.1 Hz, 2H, H^5), 7.45-7.37 (m, 4H), 7.40-7.36 (m, 4H, $H^{6,7}$), 7.29 (t, *J* 7.7 Hz, 2H, H^3). ^{13}C NMR ($CDCl_3$): 133.5 (d, *J* 11 Hz, C^9), 133.4 (d, *J* 11 Hz, C^8), 133.3 (d, *J* 2 Hz, C^7), 132.7 (d, *J* 11 Hz, C^{10}), 128.9 (d, *J* 137 Hz, C^1), 128.7 (C^4), 127.1 (C^5), 126.6 (d, J 5 Hz, C^3), 126.1 (C^6), 124.5 (d, *J* 15 Hz, C^2). ^{31}P NMR ($CDCl_3$): 37.3 ppm. MS *m/z* calcd for $C_{20}H_{15}O_2P$: MS (M^+ 315).

Tri(1-naphthyl)phosphine, Np$_3$P, white powder, m.p. 265-265.5^{o}C, lit.[31] (263-265^{o}C). FT-IR (KBr, cm^{-1}): 405, 440, 521, 552, 625, 660, 733, 772, 795, 860, 919, 953, 976, 1018, 1057, 1138, 1207, 1254, 1327, 1377, 1454, 1497, 1585, 1620, 1643, 1708, 1829, 1890, 1948, 3005, 3047. ^{1}H NMR ($CDCl_3$): 8.51 (dd, 1H, $^3J_{HH}$ 8.0 Hz, $^4J_{PH}$ 4.5 Hz, H^8), 7.87 (d, 1H, ^3J 7.5 Hz, H^5), 7.82 (d, 1H, $^3J_{HH}$ 8.3 Hz, H^4), 7.52 (dd, 1H, $^3J_{HH}$ 7.7 Hz, $^3J_{HH}$ 7.5 Hz, H^6), 7.44 (dd, 1H, $^3J_{HH}$ 8.2 Hz, $^3J_{HH}$ 7.5 Hz, H^7), 7.23 (dd, 1H, $^3J_{HH}$ 8.3 Hz, $^3J_{HH}$ 7.5 Hz, H^3), 6.93 (dd, 1H, $^3J_{HH}$ 7.5 Hz, $^3J_{HP}$ 5.9 Hz, H^2). ^{13}C NMR ($CDCl_3$): 135.7 (d, ^1J 24 Hz, C^1), 133.5 (d, ^2J 4.8 Hz, C^2), 133.4 (C^9), 132.8 (d, ^3J 11.2 Hz, C^{10}), 129.6 (C^4), 128.6 (C^5), 126.6 (d, ^3J 4.9 Hz, C^8), 126.3 (C^7), 126.0 (C^6), 125.8 (C^3). ^{31}P{^{1}H} NMR ($CDCl_3$): –32.05. Anal. Calcd for $C_{30}H_{21}P$: C, 87.36; H, 5.13; P, 7.51. Found: C, 86.95; H, 5.05. MS *m/z* calcd for $C_{30}H_{21}P$: M^+ 427.

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CAUTION: *Phosphine gas is toxic and explosive. It should be handled with extreme care. All the reactions and handling of phosphine should be carried out under an inert atmosphere in a well ventilated hood.*

Supplementary data

Supplementary data copies of ^{1}H and ^{13}C NMR spectra for all products. Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/

j.tet.2015.08.066. These data include MOL files and InChiKeys of the most important compounds described in this article.

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