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2-Halopyridines in a triple reaction in the P_n/KOH/DMSO system to form tri(2-pyridyl)phosphine: experimental and quantum-chemical dissimilarities

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General remarks

The microanalyses were performed on a Flash EA 1112 Series elemental analyzer. Fourier transform IR spectra were run on a Bruker Vertex 70 instrument. The ^{1}H, ^{13}C, ^{31}P and ^{15}N NMR spectra were recorded on a Bruker AV-400 spectrometer (400.13, 100.61 and 161.98 MHz, respectively) and referenced to H_3PO_4 (^{31}P NMR) as external standards. Chemical shifts (δ) are given in ppm downfield from HMDS as internal standards. 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. Red phosphorus "KSAN Sia", 2-chloropyridine, 2-bromopyridine (Alfa Aesar), KOH and DMSO were used as purchased. All experiments were carried out under argon atmosphere, except for work-up procedures.

1. Experimental section

CAUTION: *White phosphorus is highly toxic and burns spontaneously when exposed to air. It should be handled with extreme care. All the reactions and handling of white phosphorus should be carried out under an inert atmosphere in a well ventilated hood.*

Procedure for the preparation of tri(2-pyridyl)phosphine 2 from 2-chloropyridine 1a and red phosphorus.

A mixture of 2-chloropyridine **1a** (5.68 g, 50 mmol), red phosphorus (3.10 g, 100 mmol), powdered KOH·0.5·H_2O (15.00 g, 230 mmol), DMSO (50 ml), and H_2O (2 ml) was stirred for 1 h at 125°C under argon. The mixture was cooled to room temperature, diluted with H_2O (60 ml)

and extracted with $CHCl_3$ (3 × 20 ml). The combined extract was washed with H_2O (3 × 15 ml) and dried over K_2CO_3. The solvent was removed under reduced pressure and unreacted **1a** (1.2 g, conversion 79%) was distilled of *in vacuo* (1 Torr). The residue was washed with diethyl ester and dried (1 Torr) to furnish 2.41 g (69%) of phosphine **2** as a microcrystalline powder, mp. 115°C (*i*-PrOH).

Reaction of white phosphorus with 2-chloropyridine 1a

A mixture of 2-chloropyridine **1a** (5.68 g, 50 mmol), white phosphorus (3.10 g, 100 mmol), powdered $KOH·0.5·H_2O$ (10.00 g, 154 mmol), DMSO (50 ml), and H_2O (2 ml) was stirred for 3 h at 100°C under argon. The mixture was cooled to room temperature, diluted with H_2O (60 ml) and extracted with $CHCl_3$ (3 × 20 ml). The combined extract was washed with H_2O (3 × 15 ml) and dried over K_2CO_3. The solvent was removed under reduced pressure and unreacted **1a** (1.99 g, conversion 65%) was distilled off *in vacuo* (1 Torr). The residue was washed with diethyl ester and dried (1 Torr) to give 0.94 g (21%) mixture of phosphine **2** with its oxide **3**. In the ^{31}P NMR spectrum of the reaction mixture, the following signals were observed: -1.9 and 15.0 ppm. According to the ^{31}P NMR data, the content of tri(2-pyridyl)phosphine oxide **3** can reach ~ 50 mol %. It should be noted, that extraction of the reaction mixture with $CHCl_3$ selectively gives only phosphine **2** (0.44 g, yield 10%), whereas oxide **3** remains completely in the aqueous layer (according to ^{31}P NMR data) and can be isolated by extraction with $CHCl_3$ after acidification of the aqueous layer.

Tri(2-pyridyl)phosphine 2

IR (KBr): 3145, 3036, 2982, 2852, 1653, 1566, 1448, 1418, 1278, 1150, 1087, 1043, 985, 901, 769, 618, 502 cm^{-1}. ^1H NMR (400.13 MHz, $CDCl_3$): δ = 7.19 (dd, $^3J_{56}$ = 4.7 Hz, $^3J_{54}$ = 5.7 Hz, 3H, H-5), 7.39 (d, $^3J_{34}$ = 7.7 Hz, 3H, H-3), 7.59 (tt, $^3J_{43}$ = $^3J_{45}$ 7.7 Hz, $^4J_{46} \approx {}^4J_{4P} \approx$ 1.9 Hz, 3H, H-4), 8.69 (brd, $^3J_{65}$ = 4.7 Hz, 3H, H-6). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 122.70 (C-5), 129.18 (d, $^2J_{PC}$ = 20.0 Hz, C-3), 135.75 (d, $^3J_{PC}$ = 3.9 Hz, C-4), 150.31 (d, $^3J_{PC}$ = 12.0 Hz, C-6), 161.85 (d, $^1J_{PC}$ = 2.6 Hz, C-2). ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = -1.89 ppm. Anal. Calcd for $C_{15}H_{12}N_3P$: C, 67.92; H, 4.56; N, 15.84; P, 11.68. Found: C, 68.03; H, 4.49; N, 15.89; P, 11.98.

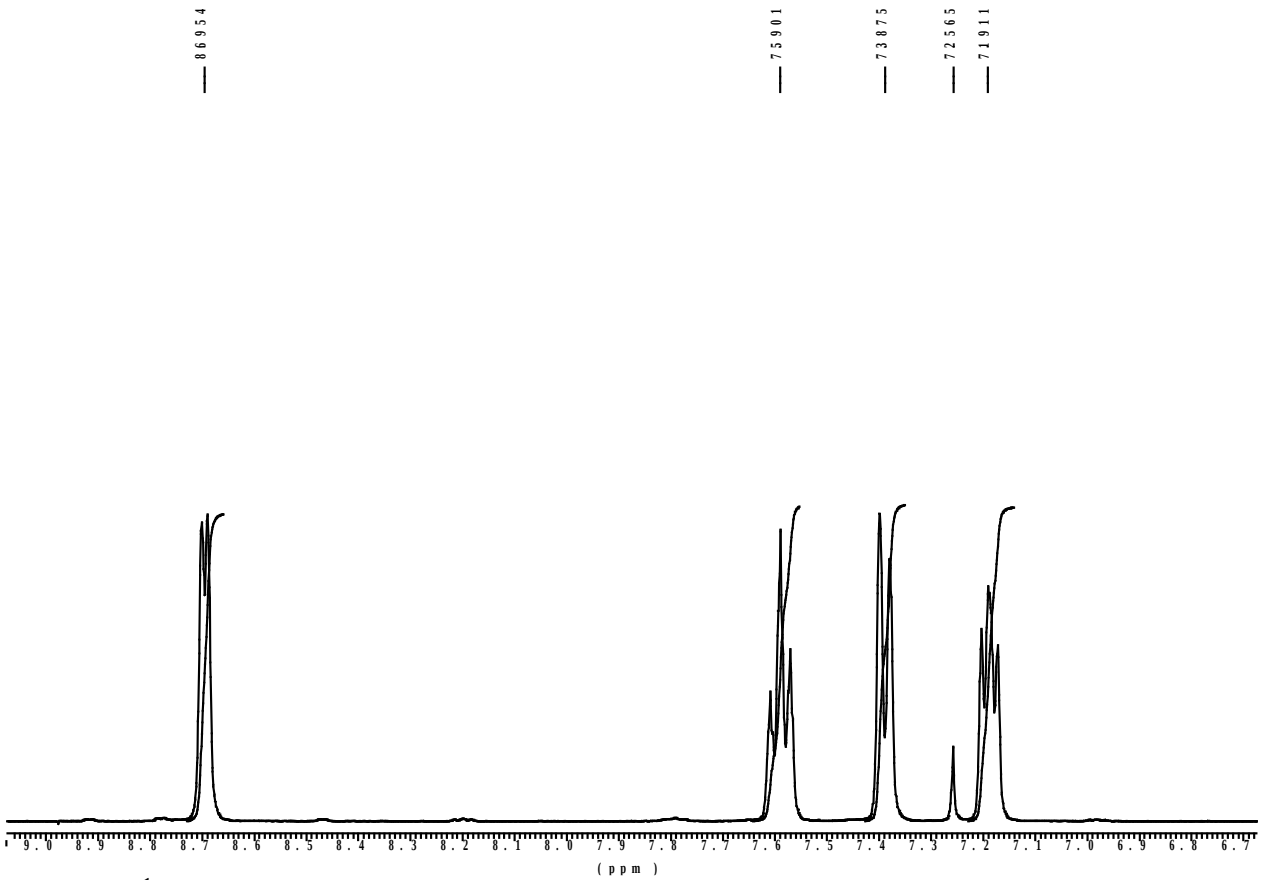

Figure S1. ^{1}H NMR spectrum ($CDCl_3$) of tri(2-pyridyl)phosphine **2**

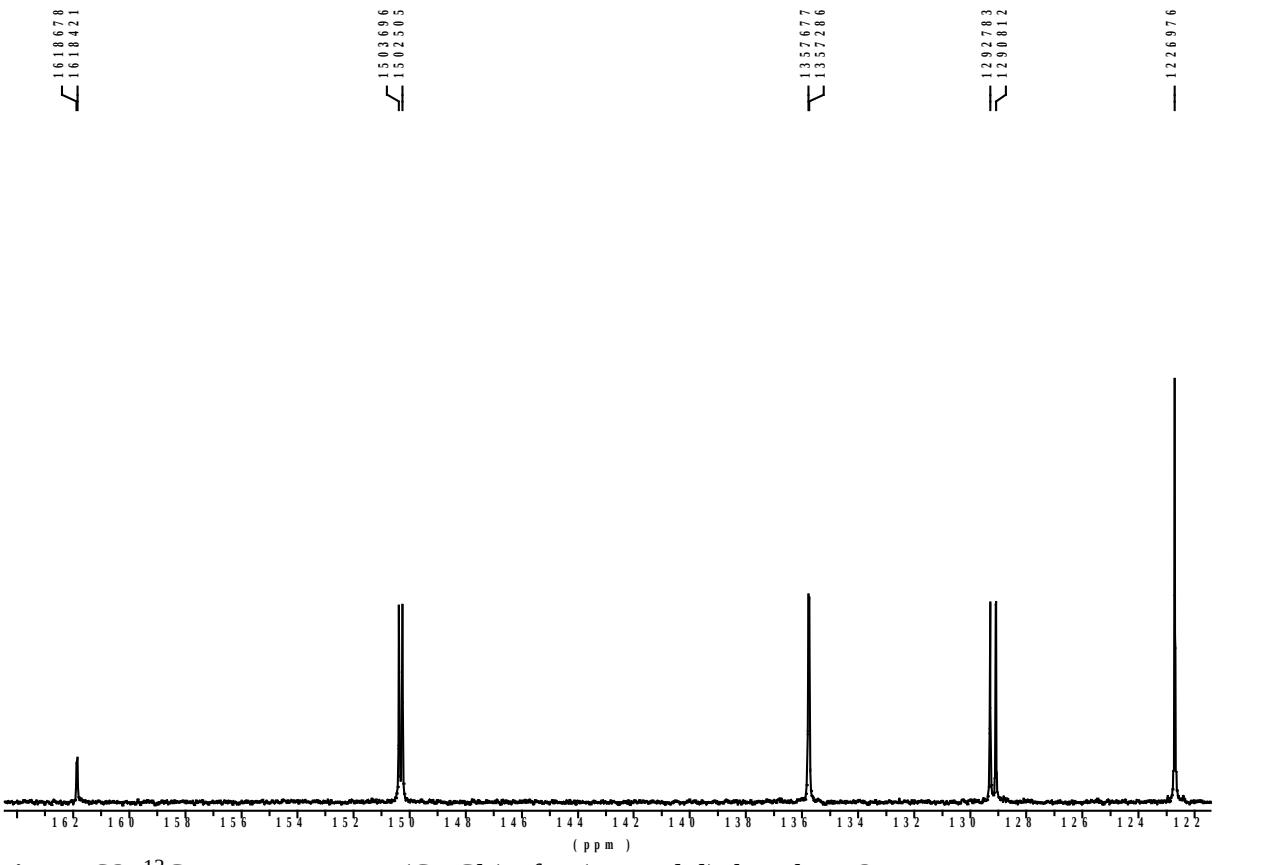

Figure S2. ^{13}C NMR spectrum ($CDCl_3$) of tri(2-pyridyl)phosphine **2**

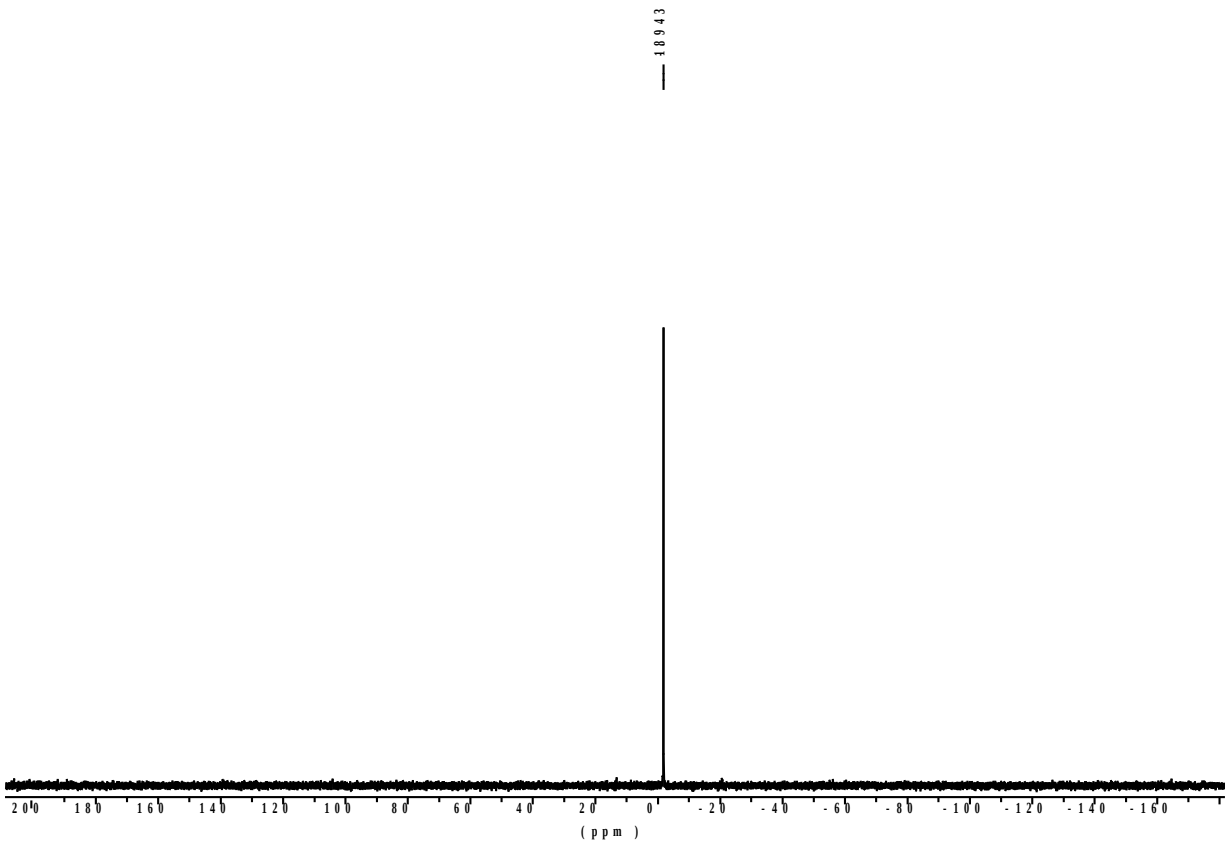

Figure S3. ^{31}P NMR spectrum ($CDCl_3$) of tri(2-pyridyl)phosphine **2**

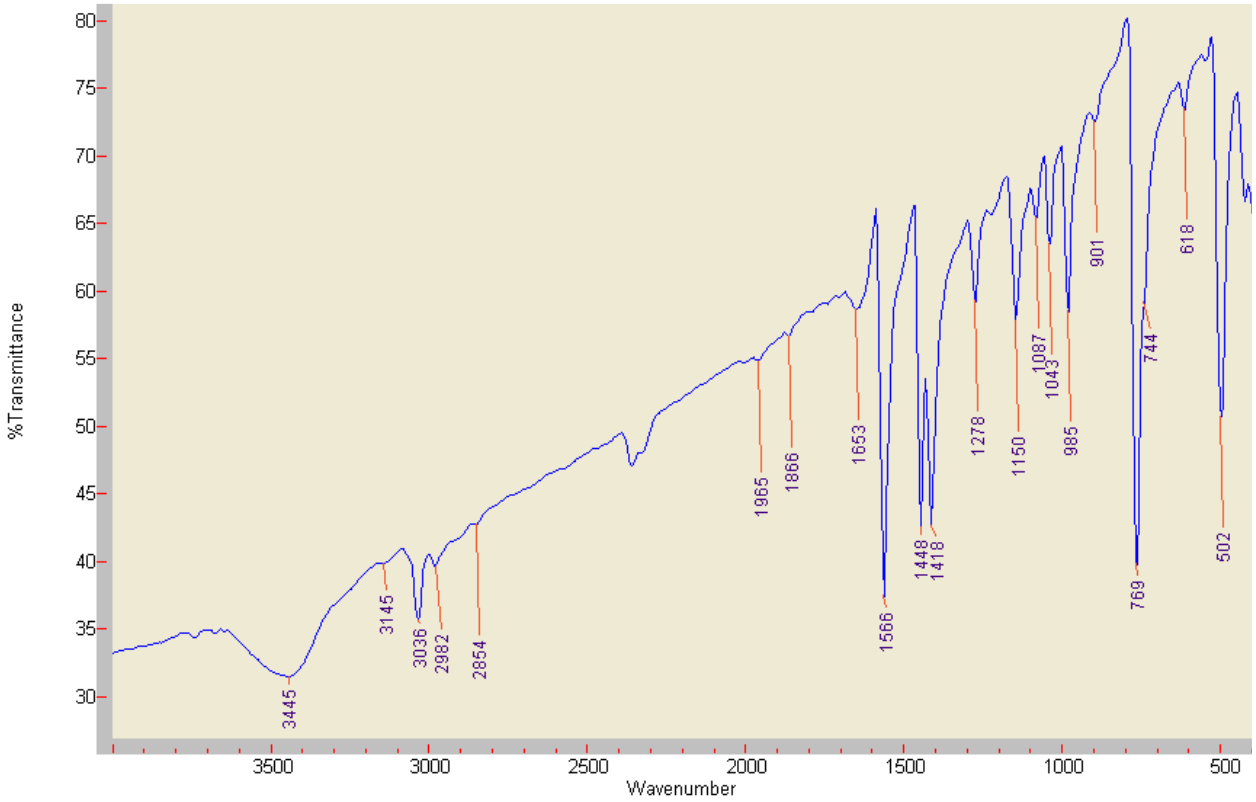

Figure S4. FT-IR spectrum (KBr) of tri(2-pyridyl)phosphine **2**

Quantum-chemical evaluation

The ground-state geometrical parameters of 2-chloropyridine, 2-bromopyridine, H_2P^-, and $H_2P(O)^-$ anions were obtained through a full geometry optimization using second-order Møller-Plesset perturbation theory (MP2) together with the cc-pVTZ basis sets [S1,S2]. The MP2 calculations were carried out using the Gaussian package of programs [S3]. According to our calculations, the $H_2P(O)^-$ anion (which can also be represented by $[H_2P{=}O]^-$ structural formula), has a non-planar structure characterized by C_s point group symmetry. This is confirmed by our computations of harmonic vibrations, which show no imaginary frequencies. The optimized structures of 2-chloropyridine, 2-bromopyridine, and H_2P^- were verified in the same way.

The atomic Mulliken populations in the highest molecular orbitals of 2-chloropyridine, 2-bromopyridine, H_2P^-, and $H_2P(O)^-$ anions computed using cc-pVTZ basis set are shown in Tables S1-S4 and can be used to analyze the character of these MOs. For 2-chloropyridine and 2-bromopyridine, analogous analysis was performed also for the highest unoccupied MOs to quantify their localization properties (an appropriately modified version of the GAMESS program [S4,S5] has been used). The results are shown in Tables S1 and S2. The atomic charges were obtained from the natural bond orbital (NBO) [S6-S9] analysis of the Hartree–Fock wavefunctions computed using cc-pVTZ basis set (Tables S5 and S6). The energies of the highest occupied and lowest unoccupied MOs were computed using the outer-valence Green's functions (OVGF) method [S10-S12] as implemented in the GAUSSIAN program [S3]. The respective values are listed in Table S7.

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Table S1. Mulliken atomic populations in HOMOs (units are electrons) and LUMOs atomic character (molecular orbital fraction localized on atoms) for 2-chloropyridine

Atom	HOMO-4	HOMO-3	HOMO-2	HOMO-1	HOMO	LUMO	LUMO+1
N	0.05	0.02	1.19	0.59	0.02	0.20	0.02
C2	0.05	0.03	0.15	0.05	0.37	0.07	0.26
C3	0.01	0.03	0.12	0.37	0.42	0.13	0.19
C4	0.12	0.02	0.03	0.62	0.03	0.35	0.03
C5	0.22	0.00	0.13	0.17	0.51	0.06	0.25
C6	0.18	0.01	0.17	0.14	0.35	0.16	0.20
Cl	1.36	1.88	0.09	0.04	0.28	0.01	0.03

Table S2. Mulliken atomic populations in HOMOs (units are electrons) and LUMOs atomic character (molecular orbital fraction localized on atoms) for 2-bromopyridine

Atom	HOMO-4	HOMO-3	HOMO-2	HOMO-1	HOMO	LUMO	LUMO+1
N	0.00	1.08	0.05	0.57	0.03	0.21	0.02
C2	0.13	0.18	0.01	0.04	0.32	0.09	0.24
C3	0.01	0.12	0.01	0.40	0.38	0.11	0.21
C4	0.14	0.04	0.01	0.57	0.03	0.35	0.02
C5	0.28	0.11	0.00	0.12	0.46	0.07	0.24
C6	0.14	0.15	0.01	0.17	0.30	0.14	0.22
Br	1.29	0.20	1.91	0.09	0.47	0.01	0.03

Table S3. Mulliken atomic populations in HOMOs (units are electrons) for H_2P^-

Atom	HOMO-3	HOMO-2	HOMO-1	HOMO
P	1.37	0.86	1.57	1.98
H	0.32	0.57	0.22	0.01
H	0.32	0.57	0.22	0.01

Table S4. Mulliken atomic populations in HOMOs (units are electrons) for $[H_2P{=}O]^-$

Atom	HOMO-6	HOMO-5	HOMO-4	HOMO-3	HOMO-2	HOMO-1	HOMO
O	1.57	0.29	0.51	1.25	1.39	1.24	0.58
P	0.42	1.10	0.77	0.49	0.60	0.22	1.12
H	0.01	0.30	0.35	0.14	0.01	0.27	0.15
H	0.01	0.30	0.37	0.12	0.01	0.27	0.15

Table S5. Atomic NBO charges (a.u.) for 2-chloropyridine and for 2-bromopyridine

Molecule 2-X-pyridine	N	C2	C3	C4	C5	C6	X
X=Cl	-0.50	0.25	-0.29	-0.11	-0.28	0.11	-0.01
X=Br	-0.51	0.19	-0.29	-0.11	-0.28	0.11	0.06

Table S6. Atomic NBO charges (a.u.) for H_2P^- and $[H_2P{=}O]^-$

Anion	O	P	H	H
H_2P^-		-0.78	-0.11	-0.11
$[H_2P{=}O]^-$	-1.28	0.79	-0.26	-0.26

Table S7. Orbital energies computed using OVGF method (eV)

System	HOMO-2	HOMO-1	HOMO	LUMO	LUMO+1
2-chloropyridine	-10.25	-10.63	-9.48	1.23	1.63
2-bromopyridine	-10.73	-10.59	-9.35	1.17	1.54
H_2P^-	-6.10	-3.55	-0.70	9.05	
$[H_2P{=}O]^-$	-5.49	-3.64	-1.94	8.77	