A Study of the Reactivity of Secondary Phosphanes with Radical Sources: A New Dehydrocoupling Reaction

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The reactions of secondary phosphanes with radical sources have been investigated. A stoichiometric dehydrocoupling of Ph_2PH with 1,1′-azobis[cyclohexane-1-carbonitrile] (*VAZO® 88*) affords tetraphenyldiphosphane in good yields, whilst reduction of the nitrosyl function was observed upon using 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO). Dialkylphosphane–borane adducts also undergo a dehydrocoupling reaction in the presence of *VAZO® 88* to form R_4P_2.

Introduction. – The syntheses of molecules featuring P–P bonds are effectively accomplished *via* stoichiometric and catalytic processes [1]. Of the former, the two main synthetic methodologies are either *via* a *Würtz* type reduction of the phosphane halides or *via* a dehydrohalogenation of R_2PX and R_2PH. The stoichiometric reduction using alkali metals is commonly used, although P–C bond cleavage of aryl phosphanes has been observed [2]. The catalytic dehydrocoupling reaction to form R_2P-PR_2, RHP–PHR, or *cyclo*-$(PR)_n$ ($n = 5, 6$) is gaining in prominence using a Ti- [3], Zr- [4], and Rh-based [5] catalysis, whilst *Manners* and co-workers have extensively published [6] on the use of Rh catalysis for the hetero-dehydrocoupling of phosphane–borane adducts to form P–B containing rings, chains, and polymers from phenyl [7], ^{t}Bu [8], and fluorous phosphanes [9], along with mechanistic studies [10]. The use of $B(C_6F_5)_3$ as a catalyst has also been reported to dehydrocouple $H_3P \cdot BH_3$ and $PhPH_2 \cdot BH_3$ with low catalyst loadings [11].

We have been investigating new methods towards the preparation of phosphane-substituted tetramethylcyclopentadienes as precursors of unusual actinide complexes. Whilst a number of synthetic methodologies have been reported, there are difficulties concerning low yields or long reaction times with all [12]. One method we tried was *via* the radical initiated hydrophosphination [13][14] of the pendent C=C bond in 1-allyl-2,3,4,5-tetramethylcyclopentadiene, and surprisingly none of the expected tertiary phosphane has been observed. Herein, we report on the unusual reaction chemistry of dialkyl- and diarylphosphanes, and their borane adducts with radical sources.

Experimental. – All manipulations were carried out using standard *Schlenk* and glove-box techniques under an atmosphere of high-purity N_2. Toluene, hexane, and THF were distilled over K, whilst Et_2O was distilled over Na/K. The secondary phosphane–borane adducts were prepared according to the procedure described in [15], whilst all other reagents were obtained from commercial sources and used as received. IR Spectra: *Perkin Elmer Spectrum One* spectrometer with attenuated total reflectance (ATR) accessory. ^{1}H-, ^{11}B-, ^{13}C{^{1}H}-, and ^{31}P-NMR spectra: *Bruker AV400* spectrometer

operating at 400.13 (^{1}H), 128.40 (^{11}B), 100.65 (^{13}C), and 162.01 MHz (^{31}P), resp., and were referenced to the residual ^{1}H or ^{13}C resonances of the solvent used, or external $BF_3(OEt_2)$ (^{11}B) or H_3PO_4 (^{31}P).

Reaction of Ph_2PH with VAZO® 88. To a soln. of Ph_2PH (0.20 g, 1.07 mmol) in toluene (5 cm^3) was added *1,1′-azobis[cyclohexane-1-carbonitrile]* (*VAZO® 88*; 0.52 g, 2.17 mmol), and the mixture was heated to 110° for 36 h. The solvent was removed *in vacuo*, and the residue was extracted with hexane (3×10 cm^3). Placement at −30° overnight yielded a white microcrystalline solid (0.34 g, 88%). Spectroscopic data are consistent with literature data [16].

Reaction of Ph_2PH with TEMPO. To a soln. of Ph_2PH (0.20 g, 1.07 mmol) in toluene (5 cm^3) was added TEMPO (2,2,6,6-tetramethylpiperidin-1-oxyl; 0.33 g, 2.15 mmol), and the mixture was heated to 110° for 36 h. The solvent was removed *in vacuo*, and the residue was extracted with CH_2Cl_2 (10 cm^3). Addition of hexane precipitated a white solid, which was recrystallized from MeOH to give white needles (0.07 g, 37%). M.p. 249–251°. IR (ATR): 2934 (NH), 2580, 1625, 1434 (P=O), 1368, 1168, 1118, 1044, 1023, 755, 711. ^{1}H-NMR (CD_3OD): 1.43 (*s*, 4 Me); 1.67 (*m*, 2 CH_2); 1.81 (*m*, CH_2); 7.37 (6 arom. H); 7.78 (4 arom. H). ^{13}C-NMR (CD_3OD): 15.7 (CH_2); 26.3 (Me); 34.7 (CH_2); 56.3 (C); 127.3 (*d*, ^3J(P,C) = 11), 129.4 (*d*, ^4J(P,C) = 2); 130.9 (*d*, ^2J(P,C) = 8); 138.84 (*d*, ^1J(P,C) = 134). ^{31}P{^{1}H}-NMR (CD_3OD): 20.7. ESI-MS: 360 (100, $[M+H]^+$). Anal. calc. for $C_{21}H_{30}NO_2P$ (359.20): C 70.17, H 8.41, N 3.89; found: C 69.84, H 8.49, N 3.74.

Reaction of $R_2PH \cdot BH_3$ with VAZO® 88. To a soln. of $R_2PH \cdot BH_3$ (0.75 mmol) in toluene (5 cm^3) was added *VAZO® 88* (0.33 g, 1.51 mmol), and the mixture was heated to 110° for 36 h. The solvent was removed *in vacuo*, and the residue was extracted with hexane (3×10 cm^3). Removal of the solvent *in vacuo* afforded the diphosphane as a solid or oil. Yields are given in the *Table*. All spectroscopic data for $^i Pr_4P_2$ [17], $^t Bu_4P_2$ [18], and $(cyclopentyl)_4P_2$ [5a] are consistent with literature data.

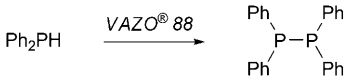
Table. *Yields of the Reaction of $R_2PH \cdot BH_3$ with* VAZO® 88

R	Yield [%]	R	Yield [%]
Ph	92	^{t}Bu	62[a])
^{i}Pr	84	Cyclopentyl	86

[a]) From NMR analysis.

Results and Discussion. – Our initial attempts at hydrophosphination of the pendent alkene 1-allyl-2,3,4,5-tetramethylcyclopentadiene using Ph_2PH and the radical source *VAZO® 88* did not yield the expected tertiary phosphane, rather we were able to identify tetraphenyldiphosphane, Ph_2P-PPh_2, as one of the products in the ^{31}P{^{1}H}-NMR spectrum. When the reaction of Ph_2PH and *VAZO® 88* (1,1′-azobis[cyclohexane-1-carbonitrile]) was examined in toluene, the only P-containing product observed by NMR spectroscopy was Ph_2P-PPh_2 (*Scheme 1*). No H_2 evolution was observed, and the by-product cyclohexanecarbonitrile was identified in the ^{1}H- and ^{13}C-NMR spectrum. Using deuterated Ph_2P-D, the presence of (1-D)cyclohexanecarbonitrile is clearly evidenced (δ(C) = 27.15 ppm, ^1J(C,D) = 20.3 Hz). Isolation of the diphosphane was readily achieved by evaporation of the solvent and extraction into hexane to afford Ph_4P_2 as a pure white solid after recrystallisation. The spectroscopic data are identical to those of authentic diphosphane. We have examined the scope of the reaction with dialkylphosphanes but no reaction was observed, even after prolonged reflux. This can be explained by the more effective inductive effect from the alkyl group which reduces the polarity of the P–H bond and thus reducing the reactivity. Notably, using AIBN as the radical source, a number of peaks in the ^{31}P-NMR spectrum was observed, and no pure products could be isolated.

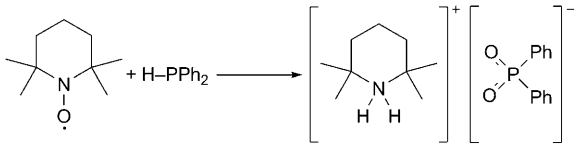
Scheme 1



These observations are pertinent to the mechanism of the hydrophosphination reaction. It is known that the first step is the formation of a phosphinyl radical that reacts with an alkene to form a C-atom-centred radical that undergoes intermolecular hydrogen abstraction from another molecule of the phosphane. If there is no alkene present, then presumably two phosphinyl radicals can combine to form the observed diphosphane. The observation of cyclohexanecarbonitrile also indicates that the *VAZO® 88* abstracts a hydrogen from Ph_2PH. Of note is that the only other report in the literature of a diphosphane observed under these conditions has been from the sterically very bulky $(Me_3Si)_2P-H$ [14].

The reactivity of the stable nitroxide radical 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) has been investigated with other main group hydrides and shown to extract a hydrogen from aluminium and gallium hydrides to form a nitroxide group-13 metal hydride species [19], or the reduction of TEMPO to the corresponding 2,2,6,6-tetramethylpiperidin-1-ol and formation of M–M bonded R_3E-ER_3, where E = Sn or Ge [20]. When the reaction of TEMPO and diphenylphosphane in a 2:1 ratio is followed by ^{31}P-NMR spectroscopy, three resonances are observed at *ca.* 30 ppm. After workup, white alcohol-soluble crystals were obtained. These crystals were subjected to X-ray diffraction, and, although the crystals were twinned, atom connectivity could be established and shown to be the salt 2,2,6,6-tetramethylpiperidinium diphenylphosphate (*Scheme 2*). The spectroscopic data confirm this formulation. For instance, the ^{31}P resonance at 20.7 ppm is similar to that found in $[NH_4][Ph_2PO_2]$ (δ(P) 13.3 ppm) [21], whilst the P=O stretch is at 1434 cm^{-1} in the IR spectrum.

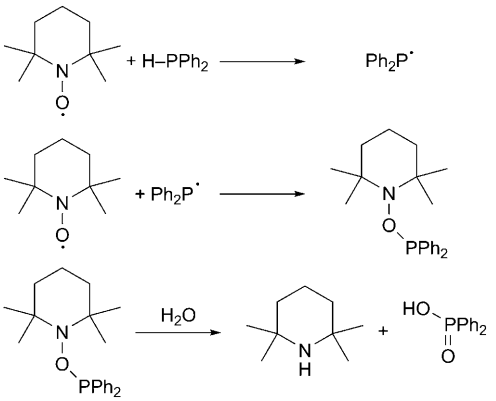
Scheme 2



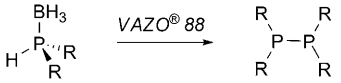
The formation of this species can be rationalised as shown in *Scheme 3*. Given the results obtained above, TEMPO presumably reacts with Ph_2PH *via* a hydride-abstraction reaction to form the phosphane-centred radical which reacts with a second equivalent of TEMPO to form an intermediate phosphinite. Hydrolysis of this phosphinite with adventitious H_2O liberates the amine and diphenylphosphonic acid, which react together to form the observed product. The reduction of TEMPO by R_3SiH forms the amine *via* a similar mechanism [20], whilst EtSH has also been observed to reduce TEMPO to the amine [22]. Diphenylphosphonic acid is well-known to be deprotonated by amines to form the corresponding salts [23].

Given the recent interest in dehydrocoupling of phosphane–borane adducts to form phosphinoborane rings and chains [6], and the use of these adducts in the hydrophosphination of unactivated alkenes [24], we were interested to investigate the

Scheme 3



Scheme 4



reactivity with radical sources. The reaction of $Ph_2PH \cdot BH_3$ with AIBN afforded a number of products that could not be separated. However, using *VAZO® 88* as the radical source, the formation of Ph_2P-PPh_2 was seen as the only P-containing product (*Scheme 4*). As the BH_3 group effectively increases the polarity of the P–H bond, we reasoned that more electron-donating dialkylphosphane-boranes would react, possibly to form the known rings or chains. However, monitoring by ^{31}P-NMR spectroscopy showed that for dicyclopentyl- and diisopropylphosphane–borane, the only observable products were due to R_2PH and R_4P_2. Upon addition of more $BH_3 \cdot THF$ and heating for a longer period of time, all secondary phosphane can be converted to the tetraalkyldiphosphane (*Table*). This implies that the borane adduct is the reactive species, although the mechanism is unclear; monitoring the reaction by ^{11}B-NMR spectroscopy shows only the phosphane–borane adduct, $BH_3 \cdot THF$, and an unidentified peak at -13.5 ppm, which is a *triplet* in the H-coupled ^{11}B spectrum ($^1J(B,H) = 107$ Hz). The reaction with the bulky $^t Bu_2PH \cdot BH_3$ does give some of the $^t Bu_4P_2$ (*ca.* 60% by NMR analysis) along with other unidentified products. The lower yield of this compound is probably due to the extremely sterically bulky diphosphane, whose crystal structure has recently been reported [25]; the dehydrocoupling of $^t Bu_2PH \cdot BH_3$ requires more forcing conditions compared to the diphenyl analogue [9]. We were unable to satisfactorily purify this compound.

In conclusion, we have found that diarylphosphanes can be readily coupled to form tetraaryldiphosphanes in the presence of the radical source *VAZO® 88*, whilst reduction of the nitrosyl group of TEMPO has been observed. Dehydrocoupling of dialkylphosphanes can be achieved using the more reactive phosphane–borane adducts.

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