CONCLUSIONS

Two $Ru(bpy)_3^{2+}$–viologen complexes, in which the components are linked by a hydrocarbon chain, were synthesized and characterized by PMR, visible, and UV spectrophotometry.

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SYNTHESIS OF HYDRIDOPHOSPHINES BY THE REDUCTION OF P(III) ISOTHIOCYANATES AND CYANIDES

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In a continuation of studies on the properties of isothiocyanates [1] and cyanides [2, 3] derived from tricoordinated phosphorus acids, we investigated the reaction of these compounds with $LiAlH_4$ and found that these reactions proceed in ether at 20°C to give the corresponding P(III)–H derivatives in yields up to 70%.

$$PhPX_2 \xrightarrow{LiAlH_4} Ph{-}PH_2$$

(I)

X = CN, NCS

$$Ph{-}\underset{\displaystyle R}{\overset{\displaystyle |}{P}}{-}X \xrightarrow{LiAlH_4} Ph{-}\underset{\displaystyle R}{\overset{\displaystyle |}{P}}{-}H$$

(II, III)

R = Ph, X = CN, NCS (II); R = Et, X = CN (III).

Hydridophosphines (I)-(III) were characterized by ^{31}P NMR spectroscopy; their physical indices corresponded to those given in the literature. In addition to the reported methods for the preparation of organic hydridophosphines [4], these reactions may be used for the synthesis of various P(III)–H derivatives.

EXPERIMENTAL

The ^{31}P NMR spectra were taken on a KGU-4 NMR spectrometer at 10.2 MHz relative to 85% H_3PO_4. All the operations were carried out in a dry argon atmosphere.

Phenylphosphine (I). a. A suspension of 4.2 g phenyldicyanophosphine in 20 ml ether was added with stirring over 2 h to a suspension of 1 g $LiAlH_4$ in 25 ml ether. The mixture was heated at reflux for 3 h and 10 ml water and 1 ml hydrochloric acid were added. The ethereal layer was separated from the precipitate. The solvent was evaporated and the residue was distilled in vacuum to give 1.8 g (61%) (I), bp 42°C (15 mm). ^{31}P NMR spectrum (δ, ppm): −122, J_{P-H} = 196 Hz [5].

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b. A solution of 6.7 g phenylisothiocyanatophosphine in 20 ml ether was added dropwise to a suspension of 1 g $LiAlH_4$ in 20 ml ether over 1.5 h. The mixture was treated by analogy to the above procedure to give 1.6 g (58%) (I), bp 42°C (15 mm).

Diphenylphosphine (II). a. By analogy to the above experiment, 2 g $LiAlH_4$ in 50 ml ether and 12.6 g diphenylcyanophosphine in 40 ml ether gave 8.1 g (73%) (II), bp 156-157°C (16 mm). ^{31}P NMR spectrum (δ, ppm): −41, J_{P-H} = 200 Hz [5].

b. By analogy to the above experiment, 2 g $LiAlH_4$ in 50 ml ether and 14.4 g diphenylisothiocyanatophosphine in 40 ml ether gave 6.7 g (60%) (II), bp 156-157°C (16 mm).

Phenylethylphosphine (III). By analogy to the above experiment, 1.2 g $LiAlH_4$ in 25 ml ether and 2.3 g phenylethylcyanophosphine in 20 ml ether gave 1.3 g (69%) (III), bp 131-133°C. ^{31}P NMR spectrum (δ, ppm): −44, J_{P-H} = 200 Hz.

CONCLUSIONS

P(III) isothiocyanates and cyanides are reduced by lithium aluminum hydride to give the corresponding hydridophosphines.

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DIBUTYL CYANOPHOSPHITE AND ITS PROPERTIES

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The reaction of P(III) acid chlorides with trimethylsilylcyanide usually proceeds in the presence of $TiCl_4$ and leads to the corresponding P(III) cyanides [1, 2]. We have found that dibutyl cyanophosphite (I) is formed from dibutyl chlorophosphite and trimethylsilylcyanide in satisfactory yield both in the presence and absence of $TiCl_4$.

$$(BuO)_2PCl + Me_3SiCN \rightarrow \underset{(I)}{(BuO)_2PCN} + Me_2SiCl$$

The reaction of dibutyl cyanophosphite (I) with tributylstannane in THF gives dibutoxyphosphine (II), which is a new variant for the synthesis of organic hydridophosphines [3].

$$(I) + Bu_3Sn{-}H \rightarrow \underset{(II)}{(BuO)_2P{-}H}$$

The end of the reaction is indicated by the disappearance of the IR bands at 1810 cm^{-1} (Sn–H) in the reaction mixture and the appearance of a band at 2210 cm^{-1} and a ^{31}P NMR signal δ_P at 162 ppm, J_{P-H} = 200 Hz, characteristic for the P(III)–H bond [4].

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