

Short Note

Diphenyl(2-propoxyethyl)phosphine

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Abstract: A new 2-(diphenylphosphino)ethyl propyl ether as hemilabile hybrid ether-phosphine ligand [$\text{Ph}_2\text{PCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_3$] was made available. The structure of the titled compound was characterized by elemental analysis, IR, ^{31}P -NMR, ^1H -NMR, ^{13}C -NMR, UV-visible spectroscopy and EI-MS.

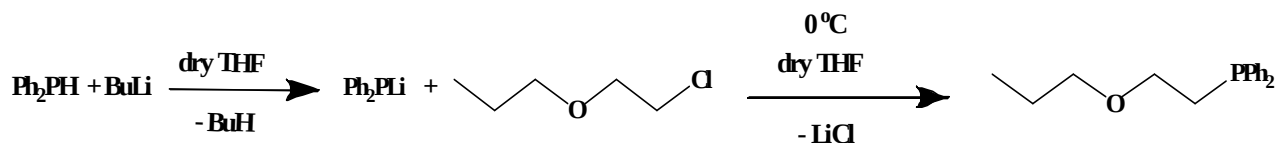
Keywords: ether-phosphine; bifunctional ligand; ^{31}P -NMR

1. Introduction

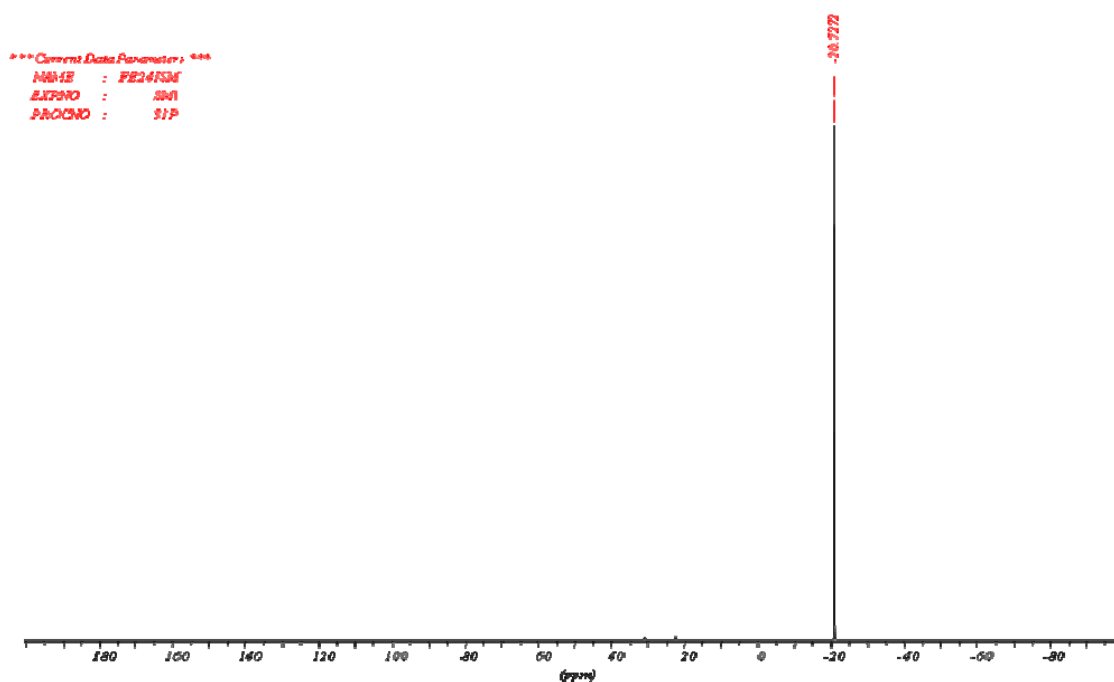
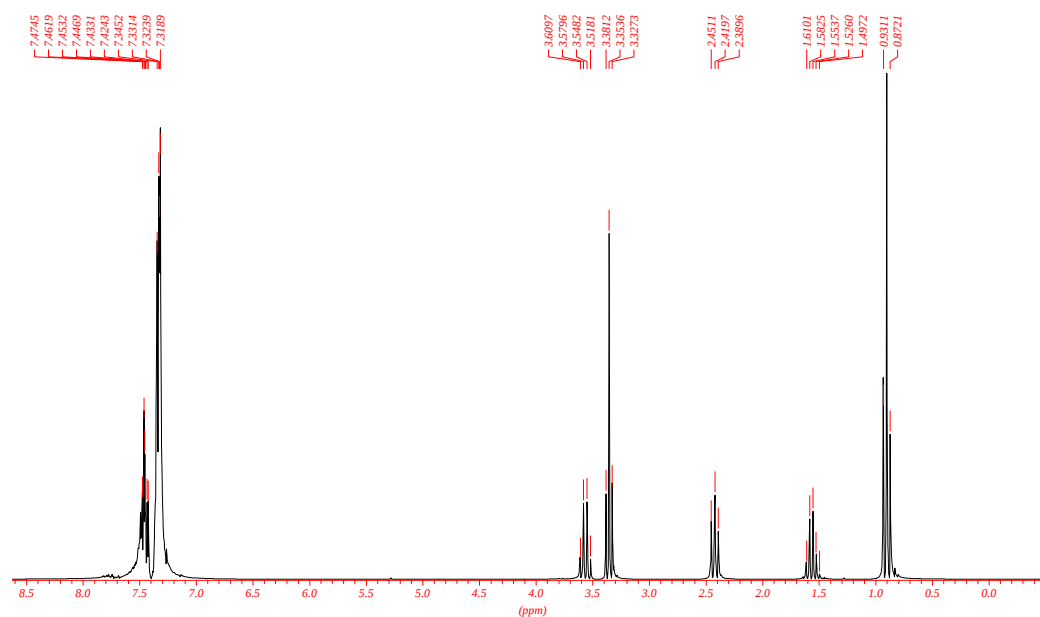
In recent years, there has been a considerable interest in the design and use of so-called hemilabile ligands [1-5]. They contain a soft donor (e.g., phosphorus) closely coordinated to the transition metal with a hard donor (e.g., oxygen) forming only a weak contact to the metal center. Due to this feature, the (ether) oxygen atom can easily be displaced by an incoming substrate. In addition, the oxygen function, which may be regarded as an intramolecular solvent, is able to stabilize a transition-metal fragment after substrate dissociation, and therefore, decomposition is suppressed [4-9]. Thus, ether phosphines are capable of making available and protecting vacant coordination sites and lead to an improvement in both catalytic and stoichiometric reactions [5-9]. The strength of the metal oxygen bond in (ether phosphine)ruthenium complexes depends on the O nucleophilicity of the ether moiety, the ring size of the cyclic ether, the number and position of the oxygen atoms in the ring, and the basicity at the metal.

2. Result and Discussion

The desired ether-phosphine [2-(diphenylphosphino)ethyl propyl ether, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_3$] hemilabile ligand was made available in a very good yield as displayed in Scheme 1.

Scheme 1. The synthetic route to the title compound.

The structure of the $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_3$ ligand was confirmed by elemental analysis, IR, UV-visible spectroscopy and EI-MS, as well as ^{31}P -NMR, ^1H -NMR, ^{13}C -NMR as shown in Figures 1 and 2.

Figure 1. ^{31}P -NMR of $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_3$ in CDCl_3 .**Figure 2.** ^1H -NMR of $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_3$ in CDCl_3 .

3. Experimental

3.1. Preparation

A solution of n-BuLi in n-hexane (25 mL of a 1.6 M solution, 2.56 g) was added dropwise to a solution of diphenylphosphine (7.44 g, 40.0 mmol) in dry THF (100 mL) at $-5\text{ }^{\circ}\text{C}$ over a period of 5 h. The red solution consisting of Ph_2PLi was stirred for 2 h at ambient temperature. Then a solution of $\text{ClCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_3$ (4.94 g, 40.0 mmol) in dry THF (50 mL) was added dropwise within 30 min, until all the red color disappeared, the reaction temperature was kept constant at $0\text{ }^{\circ}\text{C}$ during the addition. Subsequently, the solution was stirred for another 30 min under reflux to ensure completion of the reaction, then it was cooled to $20\text{ }^{\circ}\text{C}$. To the colorless mixture, a degassed aqueous solution saturated with NH_4Cl (100 mL) was added and the organic layer was separated. The solution was dried with Na_2SO_4 and separated from the solid residue. After evaporation of the volatile materials under vacuum, the crude product was distilled to yield a highly viscous colorless air-sensitive oil.

Boiling point: 374 K (5 mbar).

Yield: 8.93 g (83%).

MS (EI): $m/z = 272.2$ (M^+).

IR (KBr, cm^{-1}): 3180 (ν_{PhH}) and 2970 (ν_{CH}). 1540 ($\nu_{\text{C}=\text{C}}$).

UV-visible absorption: $\lambda_{\text{max}} = 240\text{ nm}$.

$^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ (ppm) -20.7 .

^1H NMR (CDCl_3): δ (ppm) 0.9 (t, $J = 7.2\text{ Hz}$, 3H, CH_3), 1.5 (m, 2H, CH_2CH_3), 2.4 (t, $J = 7.9\text{ Hz}$, 4H, PCH_2), 3.3 (t, 2H, $J = 6.9\text{ Hz}$, $\text{PCH}_2\text{CH}_2\text{O}$), 3.6 (q, $J = 7.5\text{ Hz}$, 2H, $\text{OCH}_2\text{CH}_2\text{CH}_3$), 6.6–7.7 (4 m, 26H, Ph-H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ (ppm) 10.9 (s, 1C, CH_3), 23.2 (s, 1C, CH_2CH_3), 29.1, 29.3 (d, 1C, PCH_2), 68.1, 68.5 (d, 1C, $\text{PCH}_2\text{CH}_2\text{O}$), 72.9 (s, 1C, OCH_2CH_2), 128.7–138.8 (4 m, 12C, Ph).

Elemental analysis: Calculated for $\text{C}_{17}\text{H}_{21}\text{OP}$. C, 74.98; H, 7.77%. Found: C, 74.73; H, 7.65%.

Acknowledgements

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