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THE SYNTHESIS OF SOME BIDENTATE LIGANDS CONTAINING BOTH PHOSPHINE AND NITRILE GROUPS

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Summary

Both $(C_6H_5)_2P(CH_2)_3CN$ and $(C_6H_5)_2P(CH_2)_4CN$ have been obtained from the reaction of $Br(CH_2)_nCN$ ($n = 3,4$) with $(C_6H_5)_2POCH_3$ followed by reduction with $(C_6H_5)_2SiH_2$. These phosphine-nitrile ligands form L_2PdCl_2 complexes which are shown by IR measurements to have *trans* geometries with the phosphine portions of the ligands coordinated. Reactions of o-BrC_6H_4CN with $CH_3(CH_2)_3Li$ followed by R_2PCl ($R = C_6H_5$ or $(CH_3)_2N$) have been used to provide good yields of the corresponding R_2P-*o*-C_6H_4CN products.

Introduction

Mixed donor phosphines are potentially important ligands for homogeneous catalysts and polymer-bound or anchored catalysts. Both Roundhill [1] and Rauchfuss [2], for example, have explored the chemistry of catalytically active metal centers with phosphine-amines and phosphine-ethers including $Ph_2P(CH_2)_nNMe_2$ ($n = 2, 3$) and $Ph_2P(C_6H_4OCH_3$-*o*). For these and related mixed-donor ligands, the phosphine donors are expected to stabilize the complexes, while the weakly coordinating oxygen or nitrogen donors readily dissociate providing vacant coordination sites for the incoming substrates. [1,2] Further, Whitesides [3] and Meek [4] have demonstrated that the amine groups in $HN(CH_2CH_2PPh_2)_2$ and $H_2N(CH_2)_3P(CH_2CH_2PPh_2)_2$, respectively, can be bound to a wide variety of supports.

Complexes of several phosphine-nitrile ligands have also been reported [5]. In addition to providing potentially interesting complexes, such ligands could, through the diverse reactivity patterns of the nitrile group, serve as versatile starting materials for other mixed-donor phosphines. Reduction, for example, produces phosphine-amines as reported by Meek for $NC(CH_2)_2P(CH_2CH_2PPh_2)_2$ [4].

Herein we report the synthesis and some derivatives of three new phosphine-nitriles ($Ph_2P(CH_2)_3CN$, $Ph_2P(CH_2)_4CN$, $(Me_2N)_2P(C_6H_4CN\text{-}o)$) and an improved synthesis of the previously reported $Ph_2P(C_6H_4CN\text{-}o)$ [6]. The procedures used to obtain $Ph_2P(CH_2)_nCN$ (n = 3,4) are based on those reported by Dahl for the synthesis of $R_nP(CH_2CN)_{3-n}$ (R = alkyl or aryl group) [7—9].

Experimental

All reactions and manipulations were carried out in a nitrogen atmosphere. Butyllithium (1.6 *M* in hexane), tris(dimethylamino)phosphine, diphenylsilane, *o*-bromobenzoic acid, 4-bromobutyronitrile, and 5-bromovaleronitrile were purchased from Aldrich Chemical Co., Inc., and used as received. Palladium chloride and sulfur were purchased from Fisher Scientific Co. and used as received. Chlorodiphenylphosphine (Aldrich Chemical Co., Inc.) and phosphorus trichloride (Fisher Scientific Co.) were distilled before use. Diethyl ether was distilled from $LiAlH_4$ immediately before use. Anhydrous methanol was prepared by a published method [10]. Benzene was dried over 4A molecular sieves. Chlorobis(dimethylamino)phosphine [11] (from tris(dimethylamino)phosphine and phosphorus trichloride) and *o*-bromobenzamide [12] were prepared as previously described. *o*-Bromobenzonitrile was obtained in 82% yield by dehydrating *o*-bromobenzamide at 225° C with phosphorus pentoxide.

IR and NMR spectra were recorded using Beckman 4250 and Varian T-60 instruments, respectively. Analytical data were determined by Integral Microanalytical Laboratories, Inc. Raleigh, NC. Analytical and selected spectroscopic data are presented in Table 1.

3-Cyanopropyl(diphenyl)phosphine. 4-Bromobutyronitrile (6.52 g, 0.044 mol) was heated to 140° C and vigorously agitated with a magnetic stirring bar and stream of nitrogen from a gas inlet tube. Methoxy(diphenyl)phosphine (4.76 g, 0.022 mol) was then added dropwise over a 2 h period and the heating and stirring were continued for an additional hour. The excess 4-bromobutyronitrile was removed by vacuum distillation (1.0 mmHg), and, upon cooling to room temperature, a tan-colored solid was obtained in the reaction flask. Diphenylsilane (4.04 g, 0.022 mol) was added to the reaction flask and the mixture maintained at 190° C for 3 h. The product was isolated by vacuum distillation, and the fraction boiling from 195—205°C (1.0 mmHg) was collected to provide 3.39 g (61%) of product.

4-Cyanobutyl(diphenyl)phosphine. This was synthesized from 5-bromovaleronitrile and methoxy(diphenyl)phosphine using the general procedures described above for the 3-cyanopropyl analog. The addition of methoxy(diphenyl)phosphine to 5-bromovaleronitrile was carried out at 190° C, however, and the fraction boiling from 200—205°C (0.1 mmHg) was collected to provide a 46% yield.

trans-Dichlorobis[3-cyanopropyl(diphenyl)phosphine]palladium and trans-dichlorobis[4-cyanobutyl(diphenyl)phosphine]palladium. Palladium(II) chloride (0.307 g, 1.73 mmol) was dissolved in 4 ml of warm, concentrated hydrochloric acid. The resulting solution was diluted with 50 ml of absolute ethanol and filtered. Under ambient conditions, the filtrate was added to $Ph_2P(CH_2)_3CN$ or $Ph_2P(CH_2)_4CN$ (3.60 mmol) dissolved in 50 ml of absolute ethanol. The mixture was stirred at room temperature for 4 h which produced quantitative yields

TABLE 1

ANALYTICAL AND SELECTED SPECTROSCOPIC DATA

	Analysis (Found (calcd) (%))				IR (cm^{-1})		NMR ^{e} (δ)	
	C	H	N	Cl	ν(CN)	ν(PdCl)	Ph ^{f}	alkyl
$Ph_2P(CH_2)_3CN$	75.66	6.46	5.46	—	2250 ^{a}	—	7.1	1.4—2.3 ^{g}
	(75.87)	(6.37)	(5.53)	—				
$Ph_2P(CH_2)_4CN$	76.78	6.55	5.10	—	2245 ^{b}	—	7.1	1.4—2.4 ^{g}
	(76.38)	(6.79)	(5.24)	—				
$PdCl_2[Ph_2P(CH_2)_3CN]_2$	56.12	4.60	4.00	—	2250 ^{c}	355 ^{d}	—	—
	(56.20)	(4.72)	(4.10)	—				
$PdCl_2[Ph_2P(CH_2)_4CN]_2 \cdot \frac{1}{16} CH_2Cl_2$	56.94	5.07	3.72	10.55	2245 ^{c}	352 ^{d}	—	—
	(57.04)	(5.08)	(3.91)	(10.50)				
$(Me_2N)_2P(C_6H_4CN\text{-}o)$	59.58	7.34	18.91	—	2218 ^{a}	—	7.3	2.68
	(59.72)	(7.29)	(18.99)	—				^{3}J(PH) 8.9 Hz
$(Me_2N)_2P(S)(C_6H_4CN\text{-}o)$	52.11	6.36	16.43	—	2225 ^{b}	—	7.4	2.60
	(52.16)	(6.37)	(16.59)	—				^{3}J(PH) 11.8 Hz

[a] Neat on NaCl. [b] Melt on NaCl. [c] Nujol mull on NaCl. [d] Nujol mull on polyethylene. [e] Recorded in $CDCl_3$. [f] Center of multiplet. [g] Complex multiplet.

of the products as yellow precipitates. The products were collected on a filter and subsequently crystallized from a mixture of dichloromethane and hexane.

Bis(dimethylamino)(o-cyanophenyl)phosphine. A solution of 1.6 *M* butyllithium in hexane (55.7 ml, 89.1 mmol) and 40 ml of diethyl ether was added dropwise over 25 min to a stirred, Dry-Ice-cooled solution of *o*-bromobenzonitrile (16.2 g, 89.0 mmol) dissolved in 110 ml diethyl ether. After the addition, the mixture was stirred for an additional 2.5 h while maintaining the cooling. Bis(dimethylamino)chlorophosphine (13.8 g, 89.3 mmol) in 25 ml of diethyl ether was added dropwise over a period of 15 min to the cold solution, and the mixture was then allowed to stir for an additional hour. The cooling bath was then removed and the reaction mixture stirred at room temperature for 4 h. At the end of this period, the mixture was poured into a vigorously stirred mixture consisting of 500 ml of deoxygenated 1.5 *M* aq. NaOH and 200 ml of diethyl ether. The resulting mixture was stirred for 5 min at room temperature. The diethyl ether layer was separated and the aqueous layer extracted with an additional 100 ml of diethyl ether. The combined ether extracts were dried over anhydrous potassium carbonate for 12 h. The mixture was filtered and the solvent removed. The product was separated by distillation; the fraction which boiled from 105—110°C at 10 mmHg, was collected. The yield was 12.18 g (62%).

Bis(dimethylamino)(o-cyanophenyl)phosphine sulfide. A solution of bis-(dimethylamino)(*o*-cyanophenyl)phosphine (2.14 g, 9.67 mmol) in 10 ml of dry benzene was added dropwise over a period of 10 min at room temperature to a suspension of elemental sulfur (0.31 g, 9.70 mmol) in 50 ml of dry benzene. After the addition, the mixture was refluxed for 2 h. The solvent was then removed under vacuum. The resulting yellow solid was dissolved in 20 ml of hot pentane and treated with charcoal. Upon cooling, the resulting solution yielded colorless crystals (m.p. 50°C) which weighed 1.21 g (49%).

o-Cyanophenyl(diphenyl)phosphine, $(C_6H_5)_2PC_6H_4CN$. A solution of 1.6 *M* butyllithium in hexane (13.6 ml, 22 mmol) and 10 ml of diethyl ether was added dropwise over 10 min to a stirred, Dry-Ice-cooled solution of *o*-bromobenzonitrile (3.96 g, 21.8 mmol) in 300 ml of diethyl ether. After the addition, the mixture was stirred for 3 h. Chlorodiphenylphosphine (3.90 ml, ca. 4.80 g, 21.7 mmol) was then added dropwise over a period of 45 min to the cold solution and the resulting mixture stirred for an additional 3 h. The reaction mixture was then allowed to warm to room temperature and stirred overnight. The resulting mixture was treated with 50 ml of distilled water and stirred for 10 min. The aqueous layer was separated from the diethyl ether and extracted with an additional 50 ml of diethyl ether. The combined ether solutions were dried over magnesium sulfate. The mixture was filtered and the solvent removed under vacuum yielding 4.23 g (68%) of crude product. The product was dissolved in 50 ml of hot isopropanol, treated with charcoal, filtered and cooled to —5°, which yielded 3.29 g (53%) of crystals that melted at 146—147°C. The properties matched those obtained from a sample synthesized by the previously reported procedure [6].

Results and discussion

The reactions of $Br(CH_2)_nCN$ (n = 3—4) with Ph_2POCH_3 at elevated temperatures followed by reduction with Ph_2SiH_2 yields the corresponding phosphine-

$$\begin{tikzcd}[column sep=small] Ph_2POCH_3 + Br(CH_2)_nCN \arrow[r] & PH_2P(O)(CH_2)_nCN + CH_3Br \arrow[d, "Ph_2SiH_2"] \\ & Ph_2P(CH_2)_nCN \end{tikzcd}$$

nitriles in moderate yields. Both products have been isolated by high-vacuum distillations which provide the butyronitrile derivative ($n = 3$) as a colorless oil and the valeronitrile product ($n = 4$) as a colorless solid that melts at 55°C. The products are slowly oxidized when exposed to air.

The major side product obtained from these reaction is Ph_2PCH_3 which arises from $Ph_2P(O)CH_3$. The amount of this product was decreased by slowly adding Ph_2POCH_3 to a two-fold excess of $Br(CH_2)_nCN$ that was vigorously agitated with stirring and bubbling nitrogen.

The results from several reactions between Ph_2POCH_3 and $Br(CH_2)_nCN$ show that the corresponding oxides for the $n = 3$ and 4 cases are formed in ca. 70—80% and 50—60%, respectively. The reductions with Ph_2SiH_2 in both cases consistently provide 80% yields of the phosphines. We have also used polymethylhydrosiloxane (PMHS) at 300°C for these reductions. In our hands, however, the Ph_2SiH_2 has provided superior yields.

Both phosphine-nitriles react with H_2PdCl_4 to form complexes of the stoichiometry L_2PdCl_2 (see Table 1) which can be obtained as large yellow crystals from mixtures of dichloromethane and hexane. The IR spectra of both complexes display $\nu(CN)$ bands at or near the positions observed for the free ligands, and intense single bands in the $\nu(PdCl)$ region. Thus, both derivatives are, as expected, *trans* complexes with the phosphine portion of the ligands dominating the donor properties.

Reaction of *o*-cyanophenyllithium with R_2PCl (R = Ph, Me_2N) yields the corresponding derivative. For $Ph_2P(C_6H_4CN\text{-}o)$, yields of ca. 50% are obtained,

$$R_2PCl + Li(C_6H_4CN\text{-}o) \rightarrow LiCl + R_2P(C_6H_4CN\text{-}o)$$

which represents a substantial improvement over the previously reported method (23%) which was based on $LiPPh_2$ and $ClC_6H_4CN\text{-}o$ [6]. The dimethylamine product is a light yellow, air-sensitive liquid. The ^1H NMR spectrum displays a doublet at δ 2.68 ppm ($^3J(PH)$ 8.9 Hz) and a multiplet in the phenyl region at δ 7.3 ppm (see Table 1). These NMR values are similar to those reported for $(Me_2N)_2PC_6H_5$ where signals at δ 2.30 ($^3J(PH)$ 8.8 Hz) and 6.89 ppm are observed [13]. The fact that the chemical shift for the methyl protons in $(Me_2N)_2P(C_6H_4CN\text{-}o)$ is at lower field than the phenyl analog is consistent with the expected inductive effect from a nitrile group:

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