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Addition of diphenylphosphine to Michael-type olefins: the preparation of phosphine-nitrile and phosphine-ester ligands

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Abstract

The reactions of five Michael-type olefins with diphenylphosphine have been carried out. 1-Cyanocyclopentene, 1-cyanocyclohexene, and 4-t-butyl-1-cyanocyclohexene all provide the corresponding 2-diphenylphosphino-1-cyanocycloalkanes, and both methyl acrylate and ethyl methacrylate yield the corresponding 2-diphenylphosphinopropionates. For the products from 1-cyanocyclopentene and 1-cyanocyclohexene, ^{13}C and ^{31}P NMR data are consistent with the formation of both *trans* (Ph_2P equatorial and CN axial) and *cis* (both Ph_2P and CN equatorial) isomers. The morpholine amide of 3-diphenylphosphinopropionic acid has been obtained by treatment of methyl-3-diphenylphosphinopropionate with the dimethylaluminum adduct of morpholine. This phosphine, $Ph_2Pmorph$, has been isolated as its palladium(II) complex, $(Ph_2Pmorph)_2PdCl_2$. A phosphine-benzaldimine, $Ph_2P(CH_2)_3NC(H)C_6H_5$, has been obtained by reacting $Ph_2P(CH_2)_3NH_2$, from the reduction of $PhP(CH_2)_2CN$, with benzaldehyde in the presence of molecular sieves.

Introduction

There continues to be considerable interest in transition metal complexes which contain both hard and soft, formally neutral ligands. Although a range of approaches for obtaining such complexes are known, one strategy involves the use of ligands which incorporate both types of donors suitably placed to promote chelation. Several recent reports have described the diverse chemical properties of complexes containing, for example, phosphines that also contain oxygen or nitrogen donors. Included in the many systems studied are examples of the following types, o-$Ph_2PC_6H_4NHR$ [1], $Ph_2PCH_2CO_2R$ [2], $Ph_2PCH_2C(O)Ph$ [3], and $[Ph_2PCHC(O)Ph]^-$ [3,4], which serve to emphasize the wide range of reactivity and structural patterns which such ligands can impart to metal complexes. To illustrate, studies of complexes containing ligands of the first type (R = alkyl or acyl groups) have yielded considerable new information concerning metal insertions into N–H bonds [1]. In regard to the phosphine-oxygen ligands, nickel group complexes of the last-mentioned ligand have provided effective olefin polymerization catalysts [4] and information about C–C bond-formation reactions promoted by neighboring metals [3a].

Earlier work by Mann established the fact that secondary phosphines add to Michael-type olefines such as acrylonitrile or methyl acrylate to provide hybrid ligands [5]. For olefins of this type, both hydrolysis, if any water is present, and polymerization reactions compete with those which yield product. For both convenience and yield considerations, the approach we have used with success, for acrylonitrile and methacrylonitrile with Ph_2PH, is to utilize an aqueous base as a catalyst in conjunction with mild conditions [6]. For some time we have been interested in using this type of reaction to obtain new types of phosphine-nitrile and phosphine-ester hybrid ligands since both the CN and the CO_2R groups can serve not only as donors but also as precursors to a wide variety of other functional groups including imines, amines and amides. In this paper we describe the preparation, via Michael-type reactions, and selected properties of several new phosphine-nitrile and phosphine-ester ligands. To further outline the general synthetic utility of these functional groups, we also report the conversion of a phosphine-nitrile and a phosphine ester, $Ph_2P(CH_2)_2CN$ and $Ph_2P(CH_2)_2CO_2Me$, into the corresponding benzaldimine and morpholine amide, respectively. The emphasis, however, is on the preparation and properties of the new phosphine-nitrile ligands which are obtained from 1-cyanocyclopentene, 1-cyanocyclohexene and 4-t-butyl-1-cyanocyclohexene. As we describe, these cyclic olefins readily provide some of the few examples of potentially bidentate ligands with the donors positioned on cycloalkanes [7].

Experimental

General information

Palladium chloride, 4 Å molecular sieves, sodium bisulfite, potassium cyanide and benzaldehyde were used as obtained from Fisher Scientific. Diphenylphosphine, peracetic acid, cyclohexanone, cyclopentanone, 4-t-butylclohexanone, dimethylamine, trimethylaluminum (2 *M* in hexane), methyl acrylate and ethyl methacryate were used as received from Aldrich Chemical Co. Diethyl ether (Fisher Scientific) was distilled from $LiAlH_4$ (Aldrich Chemical Co.) prior to use. Benzene (Fisher Scientific) was distilled from calcium hydride (Aldrich Chemical Co.) while maintaining an argon atmosphere. Morpholine (Aldrich Chemical Co.) was distilled under argon. 3-Diphenylphosphinopropionitrile, $Ph_2P(CH_2)_2CN$, and Na_2PdCl_4 were obtained as described previously [6,8].

Infrared spectra were recorded on either a Beckman 4250 or a Nicolet 5ZDX instrument. Except where noted, NMR data were recorded with a Varian FT-80A instrument. Solution molecular weights (Table 1) were obtained by using a Hitatchi Perkin Elmer 115 molecular weight apparatus. Mass spectra were recorded on a Hewlett Packard 5980A instrument fitted with a Vacumetrics solid inlet probe. Elemental analyses (Table 1) were carried out by Midwest Microlab Ltd., Indianapolis, IN.

Table 1

Analytical and molecular weight data

Compound	Analyses (Found (calcd.) (%))			Mol. wt. [a] (g/mol)
	C	H	N	
$Ph_2PC_5H_8CN$	76.96	6.48	4.75	290 *
	(77.40)	(6.50)	(5.01)	(279)
$Ph_2PC_6H_{10}CN$	77.72	6.83	4.70	290 *
	(77.79)	(6.87)	(4.77)	(293)
$Ph_2PC_{10}H_{18}CN$	78.28	7.86	3.91	349
	(79.05)	(8.08)	(4.01)	(349)
$Ph_2P(CH_2)_2CO_2Me$	70.74	6.21		272
	(70.58)	(6.29)		272
$Ph_2PCH_2CH(Me)CO_2Et$	71.73	7.11		300
	(71.98)	(7.05)		300
$[Ph_2Pmorph]_2PdCl_2 \cdot 0.25CH_2Cl_2$ [b]	53.74	5.22	3.06	-
	(53.84)	(5.26)	(3.28)	-
$Ph_2P(CH_2)_3NC(H)Ph$	79.87	6.77	4.42	330
	(79.74)	(6.69)	(4.23)	(331)

[a] Values marked with an * were obtained by osmometry, others by mass spectroscopy. [b] $Ph_2Pmorph$ is the morpholine amide of $Ph_2P(CH_2)_2CO_2H$. Dichloromethane was also detected by NMR measurements.

Syntheses

1-Cyanocyclopentene. Cyclopentanone (33.7 g, 0.40 mol) was added to a rapidly stirred solution of sodium bisulfite (41.6 g, 0.40 mol) contained in 300 ml of water. After stirring at ambient conditions for 30 min, potassium cyanide (26.1 g, 0.40 mol) in 65 ml of water was added all in one portion, and the mixture was stirred for an additional 2 h. At this point, the cyanohydrin was present as an oil on top of the water. With stirring, dimethylamine (45.1 g 40% solution, 0.40 mol) was then added dropwise, and the mixture stirred under ambient conditions for another 2 h. Dichloromethane (200 ml) was added to the mixture, and the nonaqueous phase was collected. Peracetic acid (95.1 g of 32% solution) was added dropwise to the dichloromethane solution which was maintained at −25 °C. Following the addition, the mixture was stirred overnight at ambient conditions. The acetic acid present was neutralized with a saturated, aqueous potassium hydroxide solution while maintaining the temperature below 25 °C. The nonaqueous phase was collected, and the aqueous phase was extracted with 6 × 150 ml portions of dichloromethane. The nonaqueous portions were combined, dried over magnesium sulfate, and then the dichloromethane was removed by using a rotary evaporator. The resulting amine oxide (treated with a few drops of water if solid) was added dropwise over a period of 3 h to hot silicone oil (100 ml at 250 °C) contained in a vacuum distillation apparatus which was constructed with a 150 mm Vigreux column between the pot and condenser and a cooled receiver, all of which was maintained at ca. 30 mmHg by water aspirator. The crude product, 1-cyanocyclopentene, was purified by distillation (15 mmHg, 65–70 °C) providing 20.7 g (55.6%) of product which had properties that matched those reported [9].

1-Cyanocyclohexene and 4-t-butyl-1-cyanocyclohexene. These were obtained in 38 and 24% yields, respectively, by using the procedure described immediately above. Both were purified by distillation at ca. 15 mmHg. The former and latter were collected at 88–95 °C and 140–145 °C, respectively. The products were identified by comparing their properties to those reported [9,10].

2-Diphenylphosphino-1-cyanocyclopentane. 1-Cyanocyclopentene (10 ml, ca. 0.09 mol) was added dropwise over a 20 min period to a stirred mixture of diphenylphosphine (8.00 g, 0.043 mol) and 0.5 ml of concentrated, aqueous hydroxide in 25 ml of acetonitrile which was maintained at 60 °C and under a blanket of nitrogen. The reaction was continued until an IR spectrum indicated that the ν(PH) band had disappeared. Following the reaction, 50 ml of dichloromethane were added, and the resulting mixture extracted with 3 × 10 ml of saturated, aqueous sodium chloride. The nonaqueous portion was dried over anhydrous magnesium sulfate. The product (8.2 g, 68%, m.p. 89–91 °C) was obtained by distillation (0.1 mmHg, 155–165 °C). The product could be crystallized from 2-propanol.

2-Diphenylphosphino-1-cyanocyclohexane and 2-diphenylphosphino-4-t-butyl-1-cyanocyclohexane. These were obtained in 57 and 32% yields, respectively, by the procedure described immediately above for 2-diphenylphosphino-1-cyanocyclopentane. However, the latter compound was not distilled; rather it was crystallized from 2-propanol. The melting points of the mixtures were 135–138 and 174–176 °C, respectively.

Methyl 3-diphenylphosphinopropionate, $Ph_2P(CH_2)_2CO_2Me$. Diphenylphosphine (5.35 g, 28.7 mmol), methyl acrylate (9.17 g, 107 mmol) and 3 drops of hydrated tetraethylammonium hydroxide were placed in 50 ml of deoxygenated acetonitrile. The mixture was stirred at ambient conditions under argon for 1 h at which time an IR spectrum indicated the absence of a ν(PH) band. Deoxygenated dichloromethane and water (75 and 15 ml, respectively) were added to the mixture, the organic portion separated, and fractionated. The portion boiling from 140–145 °C at 0.05 mmHg was collected providing 6.80 g (87%) of a colorless oil.

Ethyl 3-diphenylphosphino-2-methylpropionate, $Ph_2PCH_2CH(CH_3)CO_2Et$. This compound was prepared from ethyl methacrylate by using the procedure described immediately above. The compound was obtained in 91% yield as a colorless oil (b.p. 145–150 °C, 0.05 mmHg).

Benzaldimine of $PhP_2(CH_2)_2NH_2$, $Ph_2P(CH_2)_3NC(H)C_6H_5$. A mixture of $Ph_2P(CH_2)_2CN$ (4.00 g 16.7 mmol) in 200 ml of dry diethyl ether was added dropwise over 1 h to a stirred mixture of lithium aluminum hydride (6.30 g, 166 mmol) in 150 ml of diethyl ether which was maintained at 0 °C and under a blanket of argon. Following the addition, the mixture was stirred at ambient conditions for an additional 60 h. The mixture was cooled to 0 °C, and, then in sequence, 6.6 ml of deoxygenated water, 6.6 ml of 10% aqueous sodium hydroxide, and 2 ml of deoxygenated water were added. The resulting mixture was filtered under argon and the solvent evaporated to dryness. The resulting oil was dissolved in 250 ml of benzene, and benzaldehyde (1.77 g, 16.7 mmol) and 4 Å molecular sieves (50 g) were added. The mixture was stirred at ambient conditions for 48 h and then at 50 °C for 2 h while maintaining a blanket of argon. The mixture was filtered under argon and evaporated to dryness providing a white solid which was crystallized from a mixture of benzene and hexane to provide 2.15 g (39%) of colorless product (m.p. 80–81 °C).

Morpholine amide of $Ph_2P(CH_2)_2CO_2H$, $Ph_2P(CH_2)_2C(O)N(CH_2)_4O$ *(*Ph_2P*-morph).* Benzene (100 ml) and trimethylaluminum (6.6 g of 20% solution, 18 mmol) were cooled to −10 °C. Morpholine (1.6 g, 18 mmol) was added dropwise via syringe to the cold mixture which was stirred and maintained under argon.

Following the addition, the resulting solution was stirred at −10 °C for 30 min, and then the mixture was warmed, during a 45 min period, to room temperature. $Ph_2P(CH_2)_2CO_2CH_3$, (5.0 g, 18 mmol) was added and the mixture was refluxed for 20 h. Deoxygenated, aqueous hydrochloric acid (27.5 ml, 0.7 *M*), water (10 ml) and dichloromethane (50 ml) were added, and the nonaqueous layer was collected, dried over magnesium sulfate, and evaporated to dryness to provide 6.5 g of an oil.

Palladium(II) derivative of $Ph_2Pmorph$ *(*$PdCl_2(Ph_2Pmorph)_2$*).* A 2.00 g portion of the oil from the reaction described above was dissolved in 25 ml of deoxygenated ethanol and mixed with Na_2PdCl_4 (0.87 g, 2.96 mmol), dissolved in 6 ml of deoxygenated water. The mixture was stirred at ambient conditions for 4 h. The yellow precipitate which formed was collected on a filter, dried and crystallized from a mixture of dichloromethane, ethanol and heptane. The yield was 1.85 g of yellow colored crystals (dec. 203–208 °C).

Results and discussion

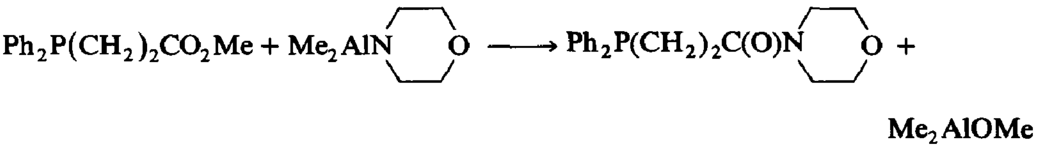
Reactions of Ph_2PH with Michael-type olefins can potentially provide a high yield, convenient starting point for a variety of functionalized phosphines. To further our understanding of this type of reaction and resulting products, we have elected to carry out syntheses of the types summarized below.

$$Ph_2PH + HC{=}C(CH_2)_nCN \longrightarrow Ph_2PCH(CH_2)_nCHCN$$

$$Ph_2P(CH_2)_2CN \xrightarrow{LiAlH_4} Ph_2(CH_2)_3NH_2 \xrightarrow[-H_2O]{C_6H_5CHO} Ph_2P(CH_2)_3N{=}C(H)C_6H_5$$

$$Ph_2PH + H_2C{=}C(R)CO_2R' \longrightarrow Ph_2PCH_2CH(R)CO_2R'$$

$$(R = H,\ R' = Me;\ R = Me,\ R' = Et)$$

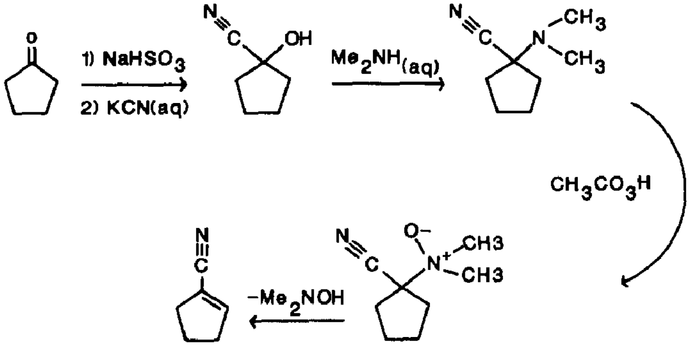


$$Ph_2P(CH_2)_2CO_2Me + Me_2AlN(CH_2CH_2)_2O \longrightarrow Ph_2P(CH_2)_2C(O)N(CH_2CH_2)_2O + Me_2AlOMe$$

Cyclic systems

As a part of our studies involving the cycloalkene nitriles, we elected to determine if the approach summarized in Scheme 1, shown with cyclopentanone as the starting material, could provide useful quantities of the three ene-nitriles shown below. As indicated in the experimental section, all three were readily obtained in moderate yields. Attractive features of this alternative synthesis [9–11] are that it is based entirely on readily available, low cost materials and that water is used as the solvent for the first steps of the reaction. The fact that cyclopentanone provided the highest yield is not surprising in view of the fact that Cope reactions most probably proceed via five-membered ring E_i mechanisms, a situation which provides an especially favorable intermediate in the case of five-membered rings.

Addition of Ph_2PH to these ene-nitriles has been accomplished at 60 °C by using an aqueous base catalyst in acetonitrile. For 1-cyanocyclohexene and 1-cyanocyclopentene, two isomers (each with an enantiomer) are expected of the types shown in Fig. 2. For both starting materials, ^{31}P and ^{13}C spectroscopy clearly indicate the presence of two products. Accordingly, as summarized in Table 2, both



Scheme 1

ene-nitriles provide products which yield two ^{31}P signals in the range expected for phosphines of this general type [12]. Further, both products also provide ^{13}C spectra which clearly display two sets of CN carbon signals (doublets), again consistent with the presence of two isomers. On the other hand, if an equatorial-positioned tert-butyl group is assumed, four sets of enantiomers are expected from the reaction between 4-tert-butyl-1-cyanocyclohexene and Ph_2PH. Our ^{31}P and ^{13}C measurements have, however, indicated the presence of only two isomers.

In Fig. 2 the cyclohexane-based systems have been pictured with the Ph_2P groups in the axial positions with the CN groups either in the axial or equatorial positions. Given the relative sizes of R_2P [13] and CN [14] groups, it is expected that the conformations shown should predominate, especially for cyclohexane-based systems. The fact that the two isomers of 2-diphenylphosphino-1-cyanocyclohexane provide ^{31}P shifts which are similar to each other supports this contention. The *trans* isomer (either diequatorial or diaxial) is expected to be strongly biased toward the diequatorial conformation. Since the second isomer provides a similar ^{31}P shift, it too is predicted to have an equatorial Ph_2P group because phosphorus signals are known to be strongly dependent on steric environment [13a]. However, the phosphorus shift differences observed for the five-membered ring isomers are significantly larger (7.5 vs. 0.9 Hz). This suggests that, compared to the cyclohexane-based system, the Ph_2P groups in the two isomers of $Ph_2PC_5H_8CN$ on the average occupy significantly different steric environments.

As indicated above, four pairs of enantiomers are possible from the reaction involving the 4-t-butyl-1-cyanocyclohexene, but only two ^{31}P and CN carbon signals have been observed. Clearly, as observed for the cyclohexane-based system, both provide ^{31}P shifts which are similar, the result expected if both Ph_2P groups have similar steric environments. Considering steric interactions, it is reasonable to propose that the two isomers are those with both the $C(CH_3)_3$ and Ph_2P groups equatorial and the CN groups either axial or equatorial. However, neither the ^{13}C

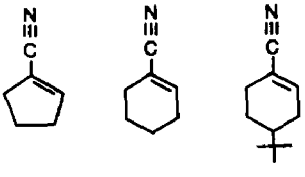
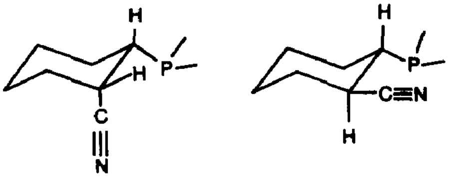


Fig. 1. Michael-type olefins prepared and reacted with diphenylphosphine.



cis
(R,R and S,S)

trans
(R,S and S,R)

Fig. 2. Proposed conformations of *cis*- and *trans*-$Ph_2PC_6H_{10}CN$.

(vide infra) nor the ^{31}P data presented in Table 2 strongly support this conclusion. First, the ^{31}P chemical shifts are both upfield of those from the cyclohexane-based compounds, a situation which could arise either because the the Ph_2P groups are axial [13a] or equatorial and influenced by the $C(CH_3)_3$ groups. Another possibility, of course, is that the cyclohexane ring is distorted from the usual chair conformation.

Table 2
Selected spectroscopic data

Compound	NMR[a], chemical shifts, δ (ppm) (*J*(PC), (Hz))					IR[b] (cm^{-1}) ν(CX)[f]
	δ(P)[c]	δ(C^1)[d]	δ(C^2)	δ(C^3)	δ(C)[e]	
$Ph_2PC_5H_8CN$[g,h]	−3.8 80%	–	–	–	122.6 (7.0)	2230
	−11.3 20%	–	–	–	120.9 (5.0)	2230
$Ph_2PC_6H_{10}CN$[g,h]	−10.0 75%	–	–	–	120.3 (2.5)	2232
	−10.9 25%	–	–	–	122.3 (8.0)	2232
$Ph_2PC_{10}H_{18}CN$[g,h]	−16.7 40%	–	–	–	122.3 (11.8)	2235
	−17.3 60%	–	–	–	121.4 (2.1)	2235
$Ph_2P(CH_2)_2CO_2Me$[i]	−15.7	23.2 (12.1)	30.8 (19.5)	–	174.2 (15.1)	1738
$Ph_2PCH_2CH(Me)CO_2Et$[j]	−19.5	32.9 (13.7)	37.5 (17.2)	18.9 (10.5)	176.7 (6.9)	1738
$Ph_2Pmorph$[k]	−15.3	23.2 (11.0)	29.4 (20.4)		171.4 (14.6)	1646
$[Ph_2Pmorph]_2PdCl_2$[h,k]	17.6 90%	–	–		–	1639
	28.6 10%	–	–		–	
$Ph_2P(CH_2)_3NC(H)Ph$	−14.6	25.8 (11.8)	27.6 (16.5)	62.5 (13.1)	161.4 (n.o.)	1645

[a] All data were obtained by using $CDCl_3$ solutions. [b] Solids and liquids were recorded as KBr pellets and neat samples on NaCl plates, respectively. [c] Relative amounts were estimated from ^{31}P data. [d] Carbons 1–3 are α–γ to the phosphorus, respectively. [e] Nonaromatic *sp* or *sp*^{2} carbons. [f] X = N or O. [g] Samples enriched in one component by fractional crystallization have been obtained for each of the three product mixtures. As a result, there is correspondence between the ^{31}P and ^{13}C data. [h] Mixtures of isomers with complex patterns which have not been completely assigned. [i] A Me-C signal was observed at 51.8 ppm. [j] Et-carbon signals were observed at 14.4 (CH_3) and 60.8 (CH_2) ppm. [k] Ph_{2morph} is the morpholine amide of $Ph_2P(CH_2)_2CO_2H$.

The CN carbon shifts and ^3J(PC) values provide another potential source of information regarding the conformations of these phosphine-nitriles. It is well-established, for example, that axial CN carbons in compounds like *cis*- and *trans*-4-t-butyl-1-cyanocyclohexene give signals which are upfield from the equatorial group signals [15]. In our hands, the two isomers of this locked cyclohexane system gave CN group signals at δ 122.7 (*cis*) and 123.4 ppm (*trans*). This trend, axial upfield of equatorial, also follows that observed for the CH_3 group in methylcyclohexane [16]. If this trend holds for the compounds reported here, the isomer of 2-diphenylphosphino-1-cyanocyclohexane with the ^{31}P shift of δ -10.0 ppm would be predicted to be the *cis* isomer, and, for the five-membered ring analog, the isomer with the ^{31}P signal at δ -11.3 is predicted to have the CN group in the more axial-like position.

The ^3J(PC) values (PCCCN) are yet another source of information which could potentially provide information about these compounds. For both six-membered ring systems, one isomer gives a coupling constant of about 2 Hz which is consistent with a dihedral angle of about 60° [13b]. But, the values of the other two isomers, 8.0 and 11.8 Hz, may be larger than expected for a similar dihedral angle. In fact, the larger of these values is consistent with a dihedral angle of about 180°, a situation which would arise if the Ph_2P and CN groups were both axial. It has been noted previously, however, that ^3J(PC) coupling in compounds with trivalent phosphorus atoms does not always follow a Karplus-type relationship [17], and ^3J(PC) of about 8 Hz have been reported previously for systems with dihedral angles of about 60° [13b,d]. Clearly, the complete characterization of these phosphine-nitriles must await either more complete spectroscopic studies and/or X-ray analysis.

Acyclic systems

The use of Michael-like reactions to obtain phosphine-ester ligands of the type $R_2P(CH_2)_2CO_2R$ has apparently not been investigated extensively. The only reference to the topic we found was that which pertained to the reaction between *m*-$MeOC_6H_4(C_6H_5)PH$ and ethyl acrylate [5b]. Given our interest in these types of ligands, we elected to explore the possibility of using mild conditions to effect the reaction between Ph_2PH and methyl acrylate and ethyl methacrylate. Excellent yields of pure products (air sensitive oils) were obtained at room temperature by mixing an excess of the acrylates with Ph_2PH in the presence of a small amount of aqueous base. In fact, NMR scale experiments have indicated that the addition reaction takes place rapidly at room temperature, even in the absence of catalyst. However, for larger scale reactions, complete addition of all the Ph_2PH present was always achieved only when a small amount of base was used. Further, polymer formation was not a problem, likely because of the mild conditions employed, and, since the acrylates were not distilled, the presence of polymerization inhibitor. Although we purified both compounds by distillation, products which are pure by NMR standards can simply be obtained by removing, with a rotary evaporator, the excess acrylate and dichloromethane.

To further emphasize the potential usefulness of these easy-to-prepare functionalized phosphines [20], we have been establishing reaction conditions which can convert nitrile and ester functionalities into other metal- or substrate-binding groups. In particular, we have been interested in phosphines containing either amides or secondary amines. In regard to obtaining the former, one synthetic approach for preparing amides involves the reaction of an ester with the Me_2AlNR_2

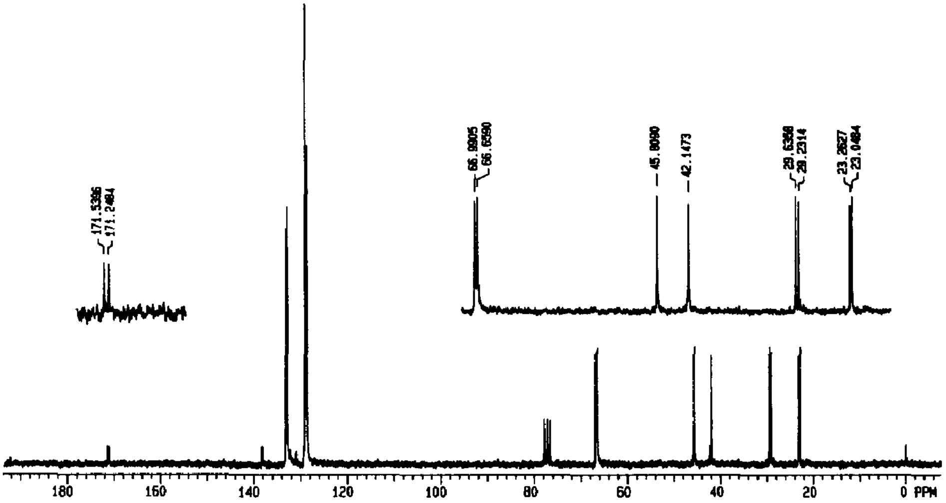


Fig. 3. $^{13}C\{^1H\}$ NMR spectrum (NT-200 instrument) of the morpholine amide of $Ph_2P(CH_2)_2CO_2H$ (Ph_2P_{morp}).

of choice [18]. We have used this method to prepare the morpholine amide of 3-diphenylphosphinopropionic acid, $Ph_2P(CH_2)_2C(O)N(CH_2)_4O$, in good yield. To date, we have not been able to purify this phosphine by standard crystallization-based procedures. Both ^{13}C and ^{31}P measurements on the crude oil, however, have provided substantial proof that the reaction provides the product in the form indicated. As shown in Fig. 3, a ^{13}C spectrum obtained directly from a sample of oil displays only the signals expected for the product as formulated. Specifically, there are four singlets in the δ 40–70 ppm range which arise from the four nonequivalent ring carbons (hindered rotation around the CN bond gives rise to *cis*- and *trans*-isomers) and two doublets at δ 23.2 and 29.4 with J(PC) values of 9.1 and 20.0 Hz, respectively. These results indicates that this route provides a viable alternative to, for example, the procedure reported by McLain for the preparation of similar phosphine-amides from aza crown ethers, $Cl(CH_2)_3CO_2Cl$, and Ph_2P^- [19]. One attractive feature of this phosphine-ester route is that, since many types of ester starting materials are available, a wide variety of phosphine-amide and, with subsequent reduction reactions, phosphine-amine ligands can be envisioned.

To assist with the characterization, a Pd^{II} derivative of this amide ligand has also been prepared. As summarized in the Tables, the data are in accord with the proposed structures. For example, the ^{31}P spectrum of the Pd^{II} product is consistent with the presence of both *cis*- and *trans*-phosphine complexes. That is, the upfield and downfield signals, δ 17.6 and 28.6 ppm, are in the range expected for *trans*- and *cis*-oriented complexes, respectively [6,12]. Also, the upfield signal is more intense, and we estimate that the mixture is 90% *trans* isomer.

For the benzaldimine derivative, $Ph_2P(CH_2)_3NC(H)Ph$, reduction of $PhP(CH_2)_2CN$ with $LiAlH_4$ followed by the reaction of the resulting amine with benzaldehyde provided the product as a colorless solid. Although the yield reported above is modest, it reflects losses during the isolation of the phosphine-amine intermediate and the crystallization processes. In fact, the phosphine-amine has typically been obtained in 80% yield, and, with careful exclusion of water and oxygen, the subsequent reaction is essentially quantitative as judged from spectroscopic data. In addition to the data presented in the Tables, the ^{13}C data in the aliphatic region are also completely consistent with the formula presented. Accordingly, three doublets are observed at δ 25.8, 27.6, and 62.5 ppm with $J(PC)$ values of 11.8, 16.5, and 13.1 Hz, respectively.

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