values calculated (15 and 30 $M^{-1}\ s^{-1}$) by assuming electron transfer through ammonia, it is tempting to infer that the actual path of electron transfer is largely through ammonia. On the basis of the insensitivity of the rates of ferrocyanide reduction of substituted pyridine pentaamminecobalt(III) complexes to the nature of the substituent in the pyridine ring,[28,29] we suggested previously[8] that electron transfer in these systems involves approach of the $Fe(CN)_6^{4-}$ to the ammonia side of the cobalt(III) complexes. However, calculations based on the Marcus cross relation corrected for electrostatics of rate constants for the $Fe(CN)_6^{4-}$–$Ru(NH_3)_5py^{3+}$ reaction were taken[8] to indicate that, in this system, the actual path of electron transfer is through the pyridine ligand. The different mechanism suggested for the $Fe(CN)_6^{4-}$–$Ru(NH_3)_5py^{3+}$ reaction on the one hand and the $Fe(CN)_6^{4-}$–$Co(NH_3)_5py^{3+}$ and $CoEDTA^{2-}$–$Ru(NH_3)_5py^{3+}$ reactions on the other can be rationalized on the basis of orbital symmetry considerations.[8,30] For the former system, acceptor and donor orbitals are of π symmetry and, therefore, a π carrier orbital in the pyridine ligand apparently provides an efficient path for electron transfer. In contrast, for the Fe–Co or Co–Ru systems, donor and acceptor orbitals are of π and σ or σ and π symmetry, respectively. This symmetry mismatch may render the path via pyridine inoperative, and the reactions then proceed with the reductant approaching the oxidant on the ammonia side. We are planning to study the reductions of $Ru(NH_3)_5py^{3+}$ and $Co(NH_3)_5py^{3+}$ by $FeEDTA^{2-}$, a π-donor reducing agent, to inquire into the validity of the orbital symmetry considerations.

Registry No. $Ru(NH_3)_5bpy^{3+}$, 54714-03-3; $Ru(NH_3)_5bpy^{2+}$, 54714-01-1; $CoEDTA^{2-}$, 14931-83-0; $CoEDTA^{-}$, 15136-66-0; $Ru(NH_3)_5py^{3+}$, 33291-25-7; $Ru(NH_3)_5py^{2+}$, 21360-09-8.

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(28) For example, the rate constants at 25 °C and ionic strength 0.10 M for the $Co(NH_3)_5py^{3+}$–$Fe(CN)_6^{4-}$ and $Co(NH_3)_5bpy^{3+}$–$Fe(CN)_6^{4-}$ reactions are 36.2 and 58.3 $M^{-1}\ s^{-1}$, respectively.[29]

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Design and Synthesis of New Polydentate Phosphine and Mixed-Donor Phosphine Ligands

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Received January 26, 1979

By using available vinyl phosphines, allyl compounds, and tertiary phosphines that contain a chloroalkyl group and matching up a synthesis route from among the radical-chain, base-catalyzed, or coupling methods, one can now synthesize a very large number of polydentate phosphine ligands that contain mixed-donor groups, specific types of donors at selected structural sites, and connecting alkyl chains of varying length. Such combinations are illustrated in this paper by the preparations of 16 polydentate ligands, 12 of which are new. The other four ligands or intermediates are made by superior routes compared to the present literature methods. These relatively simple, high-yield-synthesis routes lead to ligands either with a variety of substituents on phosphorus or with a variety of group 5A and 6A donor atoms in the same ligand.

Introduction

The number and diversity of tertiary phosphines used to prepare new coordination and organometallic compounds has increased rapidly during the past 20 years.[1] Compared to monodentate ligands with comparable donor groups, a properly designed polydentate ligand can simultaneously provide (1) more control on the coordination number,[2] stereochemistry,[3] and magnetic properties[4] of the resulting complex, (2) increased basicity (or nucleophilicity) at the metal,[5] and (3) higher optical yields in catalytic asymmetric synthesis.[6,7] Incorporation of other group 5 and/or group 6 donor atoms to form a "mixed" phosphine readily facilitates controlled variation of the steric and electronic properties of the ligands.

The ability to vary the chelate chain length is an important consideration in the design of polydentate ligands, as important structural differences have been observed in coordination compounds simply by changing the length of the chelate chain. For example, the open-chain triphosphine ligands $PhP(CH_2CH_2PPh_2)_2$, etp, and $PhP(CH_2CH_2CH_2PPh_2)_2$, ttp, differ by only one methylene unit in the flexible connecting chains; however, the structures of the five-coordinate cations $[Co(etp)L_2]^+$ (L = $P(OMe)_3$, PR_3, CO) and $[Co(ttp)L_2]^+$ are trigonal bipyramidal and square pyramidal, respectively.[3,8]

Meek and Li[9] prepared a series of palladium thiocyanate complexes containing the homologous series of chelating diphosphine ligands $Ph_2P(CH_2)_nPPh_2$ (n = 1, 2, 3). All three ligands contain equivalent donor groups, but remarkable control on the mode of thiocyanate bonding was observed in the structures; namely, both thiocyanate groups were S bonded for n = 1, one was S bonded and one was N bonded for n =

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2, and both were N bonded for $n = 3$.[9,10] This regular change in the mode of bonding by the thiocyanate group is explicable in terms of the steric requirement of S- and N-bonded thiocyanate and the P–Pd–P angles within the chelate rings, which are 73, 86, and 91° respectively for $n = 1$, 2, and 3. Increasing the chain length to $n > 4$ in some diphosphine ligands can result in the ligand forming a polymeric complex or "trans spanning" of the metallic ion instead of producing the normal cis chelate.[11]

The most widely used polydentate ligands contain ethylene ($-CH_2CH_2-$) connecting chains between donor atoms. Three methods of synthesis are generally used: nucleophilic attack on an ethylene dihalide and, more recently, King's "base-catalyzed" and Meek's "radical-chain" addition of P—H, As—H, and S—H groups across C=C bonds.[12,13] These methods of constructing ethylene polydentate ligands are very useful; however, the base-catalyzed method cannot be used for alkyl-chain lengths greater than $n = 2$, and the free-radical method is limited to specific cases when $n > 2$. By utilization of the above methods along with Grim's general synthesis of $Cl(CH_2)_nPR_2$ compounds[14] and Issleib's coupling reactions,[15] a very large number of polydentate ligands can be designed and synthesized that incorporate mixed-donor groups and specific donors at selected structural sites. In this paper we demonstrate relatively simple, high-yield routes to several such combinations of new polydentate ligands.

Experimental Section

Reagents. Diphenylphosphine, phenylphosphine, dicyclohexylphosphine, and 2-cyanoethylphosphine were obtained from either Strem Chemical Co. or Pressure Chemical Co. and were used as obtained. Phenyldivinylphosphine and diphenylvinylphosphine from either Strem Chemical Co. or Pressure Chemical Co. were vacuum distilled (<0.1 torr) prior to use. The authentic nature of these reagents was checked by ^1H and ^{31}P NMR. All organic starting materials were reagent grade and were distilled under N_2 prior to use to ensure maximum purity. All reagent grade solvents used were dried according to recommended methods and degassed prior to use.

Spectral Characterization. Infrared spectra of the solids were measured on a Perkin-Elmer 337 grating spectrophotometer from 400 to 4000 cm^{-1} as Nujol mulls and/or KBr pellets. Mass spectra were collected on an AEI MS-902 mass spectrometer operating at 70 eV. Proton magnetic resonance spectra were collected on a Varian A60A or an EM360 spectrometer with Me_4Si as an internal standard at ambient temperature (~30 °C). Fourier-mode, proton-noise-decoupled phosphorus-31 NMR spectra were collected at ambient temperature (~30 °C) on a Bruker HX-90 spectrometer operating at 36.43 MHz. Ten-millimeter tubes with concentric 5-mm inserts (containing the deuterium lock and trimethyl phosphate as a secondary standard) were used for the ^{31}P spectra; the chemical shifts are reported relative to 85% H_3PO_4 and are reproducible to ±0.05 ppm. Positive chemical shifts are *downfield* from 85% H_3PO_4. A Rayonet RPR-100 photochemical reactor containing 16 × 350 nm bulbs was used for all photolysis experiments. Standard techniques for the manipulation of air-sensitive compounds were used for the preparation of all trivalent phosphorus compounds and their metal complexes. High-purity nitrogen provided an inert atmosphere, and solvents were degassed by purging them with nitrogen for 0.5 h prior to use. All transfers were completed by using (i) syringes which were flushed with N_2 before use, (ii) stainless-steel transfer tubes, rubber septa, and positive N_2 pressure, or (iii) a bent glass tube containing a Teflon stopcock and positive N_2 pressure.

Combustion analyses were performed by MHW Laboratories, Phoenix, Ariz.

Synthesis of Phosphorus Compounds

1. $Ph_2PCH_2CH_2CH_2Cl$.

$$Ph_2PH + n\text{-}BuLi \rightarrow Ph_2PLi + n\text{-}BuH$$

$$Ph_2PLi + ClCH_2CH_2CH_2Cl \rightarrow Ph_2PCH_2CH_2CH_2Cl + LiCl$$

A solution of 70.2 mL of *n*-BuLi (0.1613 mol in hexane) was added slowly to a solution containing 30.0 g of diphenylphosphine (0.161 mol) dissolved in 800 mL of THF. After this solution was stirred for 0.5 h, it was transferred via a stainless-steel tube into a pressure-equalizing dropping funnel. This solution was then added dropwise (over a period of 6 h) into a cooled (0 °C) 2-L, three-neck flask containing 200 mL of 1,3-dichloropropane (10-fold excess) dissolved in 300 mL of ether. The red color of the solution dissipated upon addition to the dichloropropane. After this solution was stirred overnight, 50 mL of water was added, the reaction was stirred for 0.5 h, and all solvents were removed in vacuo (<0.1 torr). Water (150 mL) and ether (300 mL) were added to the flask, and the product was extracted from the aqueous layer with ether (3 × 225 mL). All the extracts were transferred to a Schlenk flask, and the ether was removed in vacuo. The pale yellow product was finally heated to 65 °C in vacuo for 1 h to remove any remaining volatile material. The yield based on Ph_2PH was 99%. The spectroscopic data (^1H, ^{31}P NMR) matched those of an authentic sample.[14]

2. $(C_6H_{11})_2PCH_2CH_2CH_2Cl$.

$$(C_6H_{11})_2PH + n\text{-}BuLi \rightarrow (C_6H_{11})_2PLi + n\text{-}BuH$$

$$(C_6H_{11})_2PLi + ClCH_2CH_2CH_2Cl \rightarrow (C_6H_{11})_2PCH_2CH_2CH_2Cl + LiCl$$

A solution containing 14.0 mL of $(C_6H_{11})_2PH$ (14.0 g, 0.071 mol) and 50 mL of ether was added dropwise with stirring over a 30-min period to a solution containing 50 mL of 1.6 M *n*-BuLi (0.08 mol in hexane) and 100 mL of ether via a pressure-equalizing dropping funnel. Gas evolution was observed and a yellow solid separated. After the mixture was stirred for 3 h at 0 °C, it was allowed to warm to room temperature. The resulting slurry was then added to a solution (0 °C) containing 30 mL of 1,3-dichloropropane (35 g, 0.310 mol) and 50 mL of ether over a 1-h period via a bent glass tube containing a Teflon stopcock. The addition caused both the evolution of heat and the formation of a heavy white precipitate. The resulting mixture was then refluxed overnight and hydrolyzed with 175 mL of H_2O. The pale yellow organic layer was separated, and the remaining solution was then extracted with ether (3 × 25 mL). The combined organic portions were then dried over anhydrous sodium sulfate. The resulting clear solution was heated to 60 °C under vacuum to remove solvents and excess 1,3-dichloropropane. A pale yellow oil resulted; yield 17.3 g, 89% (based on $(C_6H_{11})_2PH$).

The oxide was prepared by treating a portion of the oil with 20% H_2O_2. The mass spectrum of the oxide shows strong parent-ion peaks at *m/e* 290 and 292 in the correct isotopic ratio (3:1) for ^{35}Cl and ^{37}Cl for one chlorine atom, as required for $(C_6H_{11})_2P(O)CH_2CH_2CH_2Cl$.

3. $Ph_2PCH_2CH_2CH_2P(H)Ph$, PPH.

$$PhPH_2 + Na \xrightarrow[NH_3]{\text{liquid}} NaP(H)Ph + {}^1/{}_2H_2$$

$$NaP(H)Ph + ClCH_2CH_2CH_2PPh_2 \rightarrow PhP(H)CH_2CH_2CH_2PPh_2$$

A cooled (−78 °C) 2-L, three-neck flask equipped with a mechanical stirrer, a dropping funnel with a gas inlet, and a dry-ice condenser was charged with 1 L of liquid ammonia. Sodium (4.10 g, 0.178 mol) was slowly added to the ammonia, creating a blue color. Dropwise addition of $PhPH_2$ (20.4 mL, 0.186 mol) over a 5-min period caused the solution to turn orange after 15 min. After the solution was stirred for 1 h, 42.3 g (0.161 mol) of $Ph_2PCH_2CH_2CH_2Cl$ in 300 mL of ether was added dropwise over a 1-h period. The solution was stirred for 1.5 h, the dry-ice bath was removed, and the ammonia was slowly allowed to evaporate into a hood with constant stirring under a flow of nitrogen. The solution was then hydrolyzed with 150 mL of H_2O and extracted with ether (3 × 225 mL), and the extracts were placed in a Schlenk flask. The solvents were removed in vacuo (room temperature), and the remaining clear oil was heated to 80 °C in vacuo for 2 h to remove any remaining volatile compounds; yield 99% (based

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on ($(C_6H_5)_2PCH_2CH_2CH_2Cl$). The mass spectrum of this compound gave a parent-ion peak at the expected *m/e* value of 336.

For characterization of the compound, several coordination complexes have been isolated and characterized as containing either the neutral PPH ligand [e.g., $PtCl_2(PPH)$] or its anionic form PP^- (e.g., $[PtCl(PP)]_2$ and $[Pt(CH_3)(PP)]_2$, proved by an X-ray structure termination).[16,17] In addition, the liquid ligand PPH was oxidized to the waxy trioxide derivative $Ph_2P(O)CH_2CH_2CH_2PPh(O)OH$, which gave the correct parent-ion peak at *m/e* 384.

4. $PhP(CH_2CH_2CH_2NH_2)_2$, PN_2.

$$PhPH_2 + 2CH_2{=}CHCH_2NH_2 \xrightarrow{h\nu} PPh(CH_2CH_2CH_2NH_2)_2$$

A Pyrex Schlenk flask containing 7.0 g (0.064 mol) of $PhPH_2$ and 9.1 g (0.16 mol) of freshly distilled allylamine was irradiated (350 nm) for 12 h with constant stirring. The crude product was then vacuum distilled at 130 °C (<0.1 torr) to give 13.5 g of a colorless oil (95% yield). This compound has been prepared and characterized previously;[18] the spectroscopic data matched those reported previously.

5. $PhHPCH_2CH_2CH_2NH_2$, PHN.

$$PhPH_2 + CH_2{=}CHCH_2NH_2 \xrightarrow{h\nu} PhHPCH_2CH_2CH_2NH_2$$

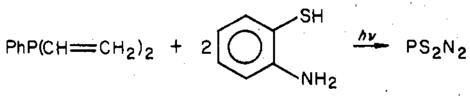
A Pyrex Schlenk flask containing 11.0 g of $PhPH_2$ (0.1 mol), 5.7 g of allylamine (0.1 mol), and 100 mg of AIBN [2,2′-azobis(isobutyronitrile)] was irradiated (350 nm) for 12 h with constant stirring. The crude product was vacuum distilled, and 11.2 g (65%) of a fraction boiling at 110 °C (1.5 torr) was collected as the product. The mass spectrum of the liquid gave a parent-ion peak at *m/e* 167, which is the expected value for PHN.

6. $Ph_2PCH_2CH_2Si(OEt)_3$.

$$Ph_2PH + CH_2{=}CHSi(OC_2H_5)_3 \xrightarrow{h\nu} Ph_2PCH_2CH_2Si(OEt)_3$$

A Schlenk flask containing 5.0 g of Ph_2PH (0.026 mol), 5.1 g of $(EtO)_3SiCH{=}CH_2$, and 100 mg of AIBN was heated for several hours at 110 °C under constant stirring. Vacuum distillation of the resulting solution gave 7.5 g (75% yield) of $Ph_2PCH_2CH_2Si(OEt)_3$ (bp 160–165 °C, <1 torr).

7. Pentadentate Ligand $PhP(CH_2CH_2S(C_6H_4\text{-}o\text{-}NH_2))_2$, PS_2N_2.



A 100-mL Schlenk flask containing 3.0 g of phenyldivinylphosphine (0.0185 mol), 4.8 g of $o\text{-}NH_2C_6H_4SH$ (0.038 mol), and 0.10 g of AIBN was heated to 110 °C for 18 h under constant stirring with 0.01 g of additional AIBN being added after 2- and 4-h intervals. The resulting solution was then heated to 100 °C for 6 h in vacuo to remove any volatile components. The remaining colorless oil corresponded to the ligand (6.9 g, 90% yield).

Several solid coordination complexes have been prepared from a stock solution of the PS_2N_2 ligand; for example, $NiBr_2(PS_2N_2)$ and $CoBr_2(PS_2N_2)$ gave satisfactory elemental analyses for the expected compositions.[19]

8. $N{\equiv}CCH_2CH_2P(CH_2CH_2PPh_2)_2$, etp-CN.

$$N{\equiv}CCH_2CH_2PH_2 + 2CH_2{=}CHPPh_2 \xrightarrow{h\nu} \text{etp-CN}$$

A Pyrex Schlenk flask which contained 6.0 g (0.069 mol) of $H_2PCH_2CH_2C{\equiv}N$, 30.0 g of $Ph_2PCH{=}CH_2$ (0.14 mol), and 100 mg of AIBN was irradiated (350 nm) with stirring for 11.5 h. More diphenylvinylphosphine (1.5 mL) was added and the flask was irradiated for an additional 4-h period. The product was then heated to 90 °C in vacuo to remove any remaining volatile materials; yield 99% (based on (2-cyanoethyl)phosphine).

In addition to the spectroscopic data on etp-CN reported in this paper, several coordination complexes have been characterized by combustion elemental analyses.[19] Two of these analyses are given. Anal. Calcd for RhCl(etp-CN): C, 57.29; H, 4.97; P, 14.30; Cl, 5.45. Found: C, 56.95; H, 4.75; P, 14.57; Cl, 5.18. Calcd for $CoCl_2$(etp-CN): C, 60.99; H, 5.29; N, 2.30; Cl, 11.60. Found: C, 60.57; H, 5.41; N, 2.08; Cl, 11.42.

9. $H_2NCH_2CH_2CH_2P(CH_2CH_2PPh_2)_2$, PP_2N.

$$N{\equiv}CCH_2CH_2P(CH_2CH_2PPh_2)_2 + LiAlH_4 \rightarrow PP_2N$$

A solution containing 3.2 g of etp-CN (6.2 mmol) in 10 mL of benzene was added dropwise into a cooled (0 °C), stirred slurry containing 0.80 g of $LiAlH_4$ and 40 mL of ether. After the foaming subsided, the flask was allowed to warm to room temperature and the mixture was stirred for 24 h. The solution was then carefully hydrolyzed with 0.8 mL of H_2O, with 0.8 mL of 10% NaOH, and finally with 0.24 mL of H_2O. The slurry was filtered through Celite filter aid, and the remaining solid was washed with ether (3 × 30 mL). The solvents were removed from the resulting solution at 80 °C in vacuo to give a viscous oil, yield 81% (based on etp-CN).

10. $Ph_2PCH_2CH_2CH_2P(Ph)CH_2CH_2CH_2N(CH_3)_2$, PPN.

$$Ph_2PCH_2CH_2CH_2PPhH + CH_2{=}CHCH_2N(CH_3)_2 \xrightarrow{h\nu} PPN$$

A photolysis experiment was carried out in a Pyrex vessel containing a benzene solution of 11.85 g of (3-(diphenylphosphino)propyl)phenylphosphine (PPH) (0.035 mol), ~100 mg of AIBN, and 12 mL (excess) of *N,N*-dimethylallylamine. After the solution was irradiated for 36 h at 350 nm, the benzene was removed in vacuo and the remaining oil was heated at 80 °C under a dynamic vacuum (<0.1 torr) for 3 h; yield 12.95 g, 90% (based on PPH).

In addition to the spectral data reported in this paper, the PPN ligand has been characterized in the form of several solid coordination complexes, which give satisfactory elemental analyses. Two of the four-coordinate examples are given. Anal. Calcd for $[PtCl(PPN)]AsF_6$: C, 37.13; H, 3.96; N, 1.67; Cl, 4.22. Found: C, 36.85; H, 3.73; N, 1.50; Cl, 4.50. Calcd for RhCl(PPN): C, 55.77; H, 5.95; P, 11.06; Cl, 6.33. Found: C, 55.93; H, 5.88; P, 11.21; Cl, 6.33.

11. $Ph_2PCH_2CH_2CH_2P(Ph)CH_2CH_2CH_2OPh$, PPO.

$$Ph_2PCH_2CH_2CH_2P(H)Ph + CH_2{=}CHCH_2OPh \xrightarrow{h\nu} PPO$$

A solution of 2.5 mL of PPH (7.5 mmol) and 5 mL of allyl phenyl ether (excess) was photolyzed at 350 nm under a stream of N_2. After 6 h, the excess allyl phenyl ether was removed by vacuum distillation (2 torr, 45 °C). The reaction was judged to be complete due to the absence of the PH peaks in the $P\{^1H\}$ NMR and infrared spectra. The yield was 3.5 g of a colorless oil (99%).

12. $Ph_2PCH_2CH_2CH_2P(Ph)CH_2CH_2CH_2NH_2$, $PPNH_2$.

$$Ph_2PCH_2CH_2CH_2P(H)Ph + CH_2{=}CHCH_2NH_2 \xrightarrow{h\nu} PPNH_2$$

A solution of 7.5 mL of 0.70 M PPH (5.25 mmol) in benzene, 75 mg of AIBN, and 1.5 mL of allylamine was photolyzed at 350 nm under a stream of N_2 for 24 h. The unreacted allylamine and benzene were removed by vacuum distillation (2 mm, 45 °C) to give a colorless oil. The yield was 2.0 g (99%).

13. $CH_2[CH_2P(Ph)CH_2CH_2CH_2NH_2]_2$, P_2N_2.

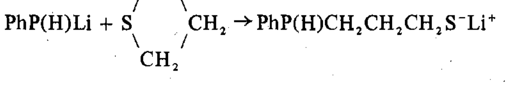
$$PhHPCH_2CH_2CH_2NH_2 + n\text{-BuLi} \rightarrow PhLiPCH_2CH_2CH_2NH_2 + n\text{-BuH}$$

$$2PhLiPCH_2CH_2CH_2NH_2 + BrCH_2CH_2CH_2Br \rightarrow P_2N_2$$

A solution containing 6.25 g of $PhHPCH_2CH_2CH_2NH_2$ (0.0374 mol) and 70 mL of THF was treated dropwise with 23.4 mL (1.6 M) of *n*-BuLi (0.0374 mol) while being stirred; the solution turned yellow. The color lightened after 3.78 g (0.0187 mol) of $BrCH_2CH_2CH_2Br$ was added dropwise, and the resultant solution was refluxed for 2 h. Hydrolysis with 100 mL of H_2O and extraction with ether (150 mL) yielded a colorless organic solution. Removal of solvents in vacuo gave 6.5 g (92%) of the expected product, which is a colorless oil.

14. $CH_2[CH_2SCH_2CH_2CH_2PPhH]_2$, S_2P_2.

$$PhPH_2 + n\text{-BuLi} \rightarrow PhP(H)Li + n\text{-BuH}$$



$$2PhHPCH_2CH_2CH_2SLi + BrCH_2CH_2CH_2Br \rightarrow S_2P_2$$

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Table I. Spectral Data on Compounds Prepared via the Free-Radical Method

	^{31}P NMR parameters^a			^{1}H NMR parameters^b			
compd	δ_{P_1}	δ_{P_2}	J_{PP}, Hz	τ_{Ph}	τ_{CH_2}	τ_{other}	unique IR features, cm^{-1}
$PhP(CH_2CH_2CH_2NH_2)_2$	−25.6			2.6	7.38, 8.42, 7.5	NH_2 8.99	NH_2 3280, 3375
$PhHPCH_2CH_2CH_2NH_2$^{c}	−52.4			2.8	8.35 (m)	NH_2 9.05, PH 4.15 (½ d of t)^c [$^2J_{PH} = 6.5$ Hz]	NH_2 3275, 3350 PH 2270
$Ph_2PCH_2CH_2Si(OEt)_3$	−9.9			2.7	7.86 (m)	OCH_2 6.23 (q), CH_3 8.8 (t) [$^2J_{PH} = 7.0$ Hz]	
$NCCH_2CH_2P(CH_2CH_2PPh_2)_2$	−21.0	−13.9	24.9	2.8	8.25 (m)		CN 2260 w
$H_2N(CH_2)_3P(CH_2CH_2PPh_2)_2$	−22.6	−13.5	25.3	2.8	8.25 (m)	NH_2 9.5 (br)	NH_2 3350
$Ph_2P(CH_2)_3P(Ph)(CH_2)_3OPh$	−27.5	−18.2	<1	2.8	8.2 (m)	OCH_2 6.15, OPh 3.15	
$Ph_2P(CH_2)_3P(Ph)(CH_2)_3NH_2$	−27.2	−18.2	<1	2.8	8.4	NH_2 9.4 (br), CH_2NH_2 5.6 (t)	NH_2 3350
$Ph_2P(CH_2)_3P(Ph)(CH_2)_3N(CH_3)_2$	−27.2	−18.2	<1	2.8	8.38 (m)	$N(CH_3)_2$ 7.88	
$PhP(CH_2CH_2S(C_6H_4\text{-}o\text{-}NH_2))_2$	−27.3			3.6, 2.9	8.25 (m) 7.42 (m)	NH_2 6.15	NH_2 3410, 3510

[a] Phosphorus-31 chemical shifts are in ppm relative to 85% H_3PO_4, with negative values being upfield from the reference; benzene is the solvent. P_2 is the diphenyl-substituted phosphorus atom. [b] Proton chemical shifts are in τ units, relative to Me_4Si. [c] The $^1J_{P-H}$ value is 204 Hz.

A 1-L Grignard flask equipped with a stirring motor, a pressure-equalizing dropping funnel, and gas inlets was charged with 12.43 g of $PhPH_2$ (0.113 mol) and 250 mL of petroleum ether (bp 65–110 °C). Dropwise addition of 100 mL of *n*-BuLi (2.4 M) to the stirred solution resulted in the evolution of heat and the formation of the dark yellow dilithium phenylphosphide, $PhPLi_2$. After this slurry was refluxed for 1 h, the solid was collected on a frit and washed with 100 mL of petroleum ether. The color changed to the characteristic canary yellow of lithium phenylphosphide, PhP(H)Li, when 300 mL of ether and 12.78 g of $PhPH_2$ were added to the solid. After the mixture was stirred overnight, a solution containing 16.76 g of trimethylene sulfide in 100 mL of ether was added; then the mixture was refluxed for 8 h. The resulting light yellow solution was allowed to cool to room temperature, and a solution of 22.3 g of $BrCH_2CH_2CH_2Br$ in 75 mL of ether was added dropwise over a 2-h period. The color changed from yellow to white as the solution was refluxed for several hours. The resulting solution was treated with 100 mL of a 10% NH_4Cl-H_2O solution. The water layer was removed and extracted with ether (3 × 50 mL). The organic layers were combined and dried over anhydrous Na_2SO_4. The solvent was removed at reduced pressure, and the remaining clear solution was heated (150 °C) in vacuo for 8 h to remove any remaining volatile material. The yield of a colorless oil was 39.5 g (86% based on $PhPH_2$).

15. $PhP(CH_2CH_2CH_2P(C_6H_{11})_2)_2$, Cy-ttp.

$$PhPH_2 + 2n\text{-}BuLi \rightarrow PhPLi_2 + 2n\text{-}BuH$$

$$PhPLi_2 + 2ClCH_2CH_2CH_2P(C_6H_{11})_2 \rightarrow PhP(CH_2CH_2CH_2P(C_6H_{11})_2)_2$$

A solution of 50 mL of *n*-BuLi (1.6 M in hexane, 0.08 mol) was added with constant stirring to a solution of 3.7 g of phenylphosphine (3.7 mL, 0.034 mol) in 50 mL of hexane. The resulting yellow mixture was refluxed for 1 h and then allowed to cool to room temperature. The supernatant was decanted by syringe and discarded. The solid was washed with 50 mL of ether and then added slowly as a slurry (in 60 mL of ether) to a vigorously stirred solution of 17.3 g of (3-chloropropyl)dicyclohexylphosphine (0.067 mol) in 50 mL of ether at 0 °C over a period of 1 h. After the addition was complete, the solution was refluxed overnight, then hydrolyzed with 150 mL of H_2O, and treated similarly to the case of (3-chloropropyl)dicyclohexylphosphine to give a viscous yellow oil. An infrared spectrum of the oil showed a ν_{P-H} at 2270 cm^{-1} so the oil was transferred to a Kugelrohr apparatus and heated at 160 °C for 2 h. A colorless oil was removed, leaving a yellow oily residue. The residue was dissolved in 30 mL of benzene and then chromatographed on a 15-cm column of neutral activated alumina (10% H_2O) by elution with benzene. Approximately 250 mL of eluate was collected and concentrated in vacuo to give 15.5 g of a yellow oil (0.0268 mol, 80% yield). This yellow oil proved to be pure bis(3-(dicyclohexylphosphine)propyl)phenylphosphine by infrared, ^{1}H NMR, and ^{31}P NMR spectra and by characterization of several metal complexes. Overall yield of the triphosphine, based on dicyclohexylphosphine, was 71%.

To obtain a solid derivative of the liquid ligand, we treated it with 20% H_2O_2, which gave the trioxide. The compound melts and liberates water at 120–125 °C, solidifies, and then remelts at 162–165 °C. Anal. Calcd for $C_{36}H_{65}P_3O_5$ (Cy-ttpO$_3$·2H_2O): C, 64.46; H, 9.77; O, 11.92. Found: C, 64.32; H, 9.78; O, 12.15.

16. Bis(3-(diphenylphosphino)propyl)phenylphosphine, ttp.

$$PhPLi_2 + Ph_2PCH_2CH_2CH_2Cl \rightarrow PhP(CH_2CH_2CH_2PPh_2)_2$$

To a solution of $PhPH_2$ (6.4 g, 0.058 mol) in dry petroleum ether (boiling range 65–110 °C, 200 mL) was added 55 mL of 2.4 M *n*-BuLi in hexane (0.132 mol); a yellow precipitate formed immediately. The mixture was refluxed for 1 h and then cooled to room temperature. The solvent was removed by filtration through a frit in the bottom of a Grignard flask, and the yellow solid (Li_2PPh) was washed with hexane (110 mL). Ether (150 mL) was added to this yellow solid, and the resulting mixture was then transferred in portions under nitrogen via a bent glass adapter into a 1-L, three-neck flask containing (3-chloropropyl)diphenylphosphine (29.8 g, 113.4 mmol). The resulting mixture was stirred with a magnetic stirrer for 24 h at room temperature and then refluxed overnight. The resultant yellow mixture was hydrolyzed with ethanol (60 mL) and distilled water (200 mL) in sequence. The ether layer was separated with a syringe, and the aqueous layer was extracted with benzene (600 mL). The ether and benzene solutions were combined and dried over anhydrous sodium sulfate for 3 h. The solution was filtered into a 200-mL Schlenk flask, and then the solvent was removed in vacuo at 40–50 °C (oil-bath temperature). Finally the resultant orange-yellow oil was heated to 130 °C (oil-bath temperature) at 0.15 torr for 12 h; yield 30 g (94%). The ^{1}H NMR, ^{31}P NMR, and infrared spectra of the compound match those of an authentic sample.[5]

17. Photolysis of Diphenylphosphine with Allyl Chloride. A solution of 3.0 g of diphenylphosphine (0.016 mol) and 10.0 mL of allyl chloride (0.123 mol) in 50 mL of degassed 2-propanol was photolyzed (350 nm) in a Pyrex vessel under a slow stream of N_2 for 16 h. At this point a colorless heavy oil had separated as a separate phase. The volatile components were removed by distillation in vacuo overnight at 50 °C. The remaining oil was extracted with 30 mL of ether, but some heavy oil remained. Upon removal of the solvent in vacuo a colorless oil remained. The infrared spectrum of this oil was consistent with that of an authentic sample of (3-chloropropyl)diphenylphosphine except for the presence of an additional sharp absorption at 1650 cm^{-1}. Proton NMR ($CDCl_3$) and $^{31}P\{^1H\}$ NMR ($CDCl_3$) showed the products to be a 3:1 mixture of (3-chloropropyl)- and allyldiphenylphosphines by integrated intensity ratios.

Results and Discussion

Free-Radical-Catalyzed Synthesis. The free-radical addition of P—H, As—H, or S—H groups across the C═C double bond of vinyl or selected allyl compounds is a useful method for synthesizing polydentate ligands.[13] The compounds prepared by this process are illustrated in Scheme I, and their $^{31}P\{^1H\}$ and ^{1}H NMR spectral data are given in Table I. The general reaction is shown in eq 1 and 2. This method has

$$R_2PH + CH_2{=}CHE \rightarrow R_2PCH_2CH_2E \quad (1)$$
$$E = NH_2, NMe_2, PR_2, AsR_2, OPh, SPh$$

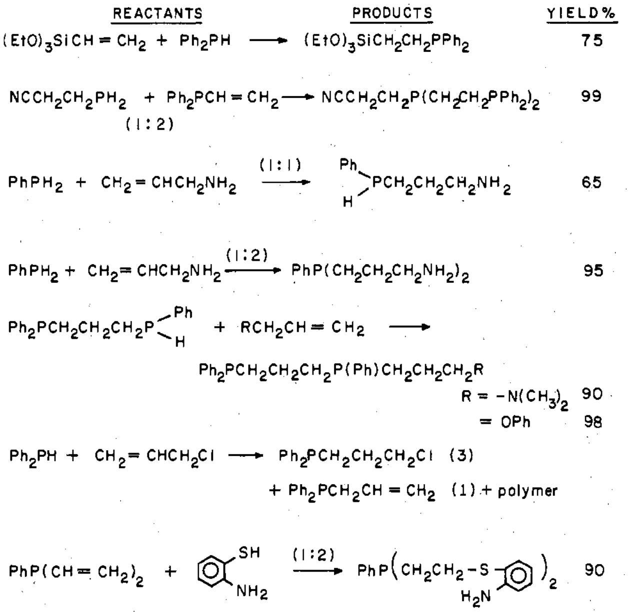
$$R_2PH + CH_2{=}CHCH_2E \rightarrow R_2PCH_2CH_2CH_2E \quad (2)$$
$$E = OPh, OH, NH_2, NMe_2$$

Table II. Spectral Data on Compounds Prepared via the Coupling Method

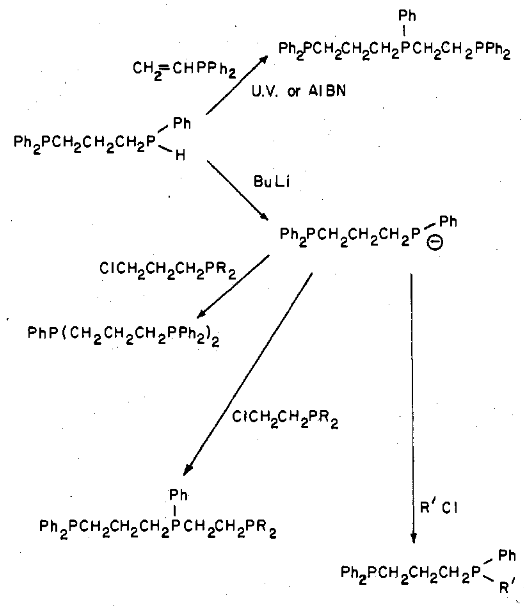
compd	^{31}P NMR parameters[a]			^{1}H NMR parameters[b]			unique IR features, cm^{-1}
	δ_{P_1}	δ_{P_2}	J_{PP}, Hz	τ_{Ph}	τ_{CH_2}	τ_{other}	
$Ph_2PCH_2CH_2CH_2Cl$	−17.9			2.7	7.9 (m)	CH_2Cl 6.48 (t)	
$Cy_2PCH_2CH_2CH_2Cl$	−6.2				δ_{Cy,CH_2} 7.9–9.2 (m)	CH_2Cl 6.49 (t)	
$Ph_2PCH_2CH_2CH_2PPhH$[c]	−54.5	−18.0	<1	2.9	8.3 (m)	PH 6.0 (d of t)	P–H 2290
$CH_2(CH_2P(Ph)(CH_2)_3NH_2)_2$	−25.9			2.8	8.0 (m)	NH_2 9.3 (br)	NH_2 3275, 3340
$CH_2(CH_2S(CH_2)_3PPhH)_2$[d]	−53.4			2.7	7.5 (m) 8.2 (m)	PH 5.86 (d)	P–H 2290
$PhP(CH_2CH_2CH_2PPh_2)_2$	−28.2	−18.1	0.5	2.7	8.2 (m)		
$PhP(CH_2CH_2CH_2PCy_2)_2$	−28.1	−7.8[e]	<1	2.7	$\tau_{CH_2,Cy}$ 8.1–9.1		

[a] Phosphorus-31 chemical shifts are in ppm relative to 85% H_3PO_4 with negative values being upfield from the reference; the solvent is benzene. P_1 and P_2 are the phenyl- and diphenyl-substituted phosphorus atoms, respectively. [b] Proton chemical shifts are in τ units, relative to Me_4Si, in $CDCl_3$. [c] The $^1J_{PH}$ value is 203 Hz. [d] The $^1J_{PH}$ value is 202 Hz. [e] In this case P_2 is the dicyclohexylphosphino group.

Scheme I



Scheme II



tremendous utility for synthesis of ligands containing mixed-donor groups simply by choosing the appropriate vinyl or allyl compound. The method seems to be general for vinyl compounds, and it works well for allyl compounds that have electronegative substituents (e.g., OH, OR, NH_2, NR_2). In the cases of allyl halides, allylphosphines, and allylsulfur compounds, a competing formation of other radicals (e.g., Cl·, RS·) and/or rearrangements lead to a mixture of products.

Mono- or disubstitution on primary phosphines can be controlled by the stoichiometry of the reactants. For example, UV irradiation of a 1:1 mole ratio of phenylphosphine and allylamine in dilute solution produces $PhHPCH_2CH_2CH_2NH_2$ as the major product, whereas greater than a 2:1 mole ratio of reagents produces the disubstituted product $PhP(CH_2CH_2CH_2NH_2)_2$. The latter compound has been studied as a tridentate ligand[18,19] and as a part of a PN_3 macrocyclic ring ligand.[20] The $PhHPCH_2CH_2CH_2NH_2$ compound should be an interesting bidentate ligand in its own right; also, it is an interesting candidate for making mixed tridentate (or higher dentate) ligands.

The mixed tertiary–secondary diphosphine $Ph_2PCH_2CH_2CH_2PPhH$ is proving to be an interesting ligand since it can function either as a neutral diphosphine ligand or as a phosphine–phosphide anionic bidentate ligand.[16] Also, it is a valuable intermediate for synthesizing mixed and unsymmetrical polydentate ligands. For example, the P—H bond can be added across the C=C double bond of vinyl compounds, or the compound can be converted by butyllithium to a phosphide nucleophile and added to an alkyl halide (Scheme II). Valuable chiral ligands for catalytic asymmetric synthesis can be readily envisaged from $Ph_2PCH_2CH_2CH_2PPhH$, since treatment with any RCl will generate a chiral center at the secondary phosphine site and treatment with an optically active halide (e.g., *l*-menthyl chloride) will produce diastereomers.

In order to simplify purification of the product and to favor complete reaction of $Ph_2PCH_2CH_2CH_2Cl$, we prepared $Ph_2PCH_2CH_2CH_2PPhH$ (PPH) by adding the (3-chloropropyl)diphenylphosphine to a solution containing a 10% molar excess of sodium and a 15% excess of phenylphosphine (reactions 3 and 4). After the reaction is complete and hydrolyzed, the excess phenylphosphine can be removed in vacuo.

$$PhPH_2 + Na \xrightarrow[-78\ ^\circ C]{NH_3(l)} PhPH^-Na^+ + {}^1/_2H_2 \qquad (3)$$

$$PhHP^-Na^+ + ClCH_2CH_2CH_2PPh_2 \rightarrow PhHPCH_2CH_2CH_2PPh_2 + NaCl \qquad (4)$$

The spectral data for $Ph_2PCH_2CH_2CH_2PPhH$ are given in Table II. The ^{31}P NMR spectra (proton decoupled and nondecoupled) are shown in Figure 1. Note that the upfield doublet (J_{PH} = 203 Hz) collapses to a singlet (J_{PP} < 1 Hz) upon irradiation and proves that the chemical shift of the -PPhH group is upfield from that of Ph_2P, as expected for the more basic phosphine group. The proton NMR spectrum displays resonances in the phenyl (τ 2.9) and methylene (τ 8.3) regions and a doublet of triplets (τ 6.0; J_{PH} = 203 Hz)

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(20) J. Riker-Nappier and D. W. Meek, *J. Chem. Soc., Chem. Commun.*, 422 (1974).

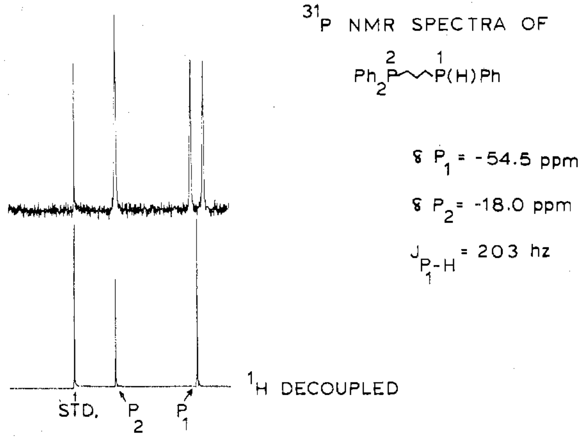
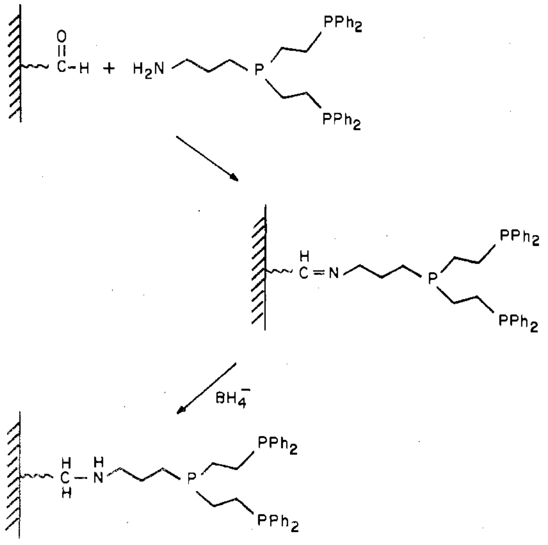


Figure 1. (Top) The $^{31}P\{^1H\}$ NMR spectrum of (3-(diphenylphosphine)propyl)phenylphosphine. (Bottom) The $^{31}P\{^1H\}$ NMR spectrum of the same sample using broad-band proton decoupling.

Scheme III

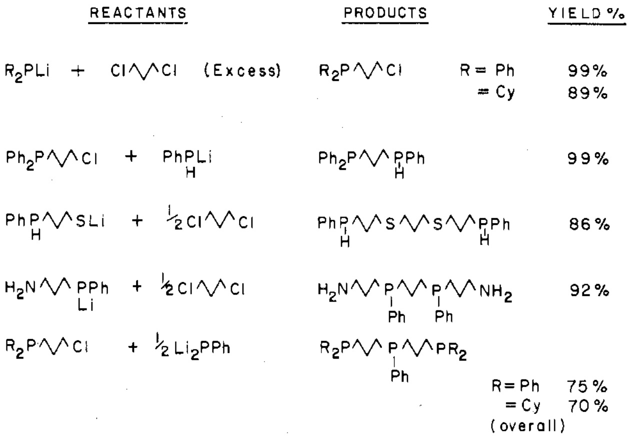


which is assigned to the proton directly attached to the phosphorus atom. The mass spectrum of this compound gave a parent-ion peak at m/e 336, as expected for PPH.

Three ligands, $(EtO)_3SiCH_2CH_2PPh_2$, $H_2NCH_2CH_2CH_2P(Ph)CH_2CH_2CH_2PPh_2$, and $H_2NCH_2CH_2CH_2P(CH_2CH_2PPh_2)_2$, were prepared to demonstrate that the radical-chain process could lead to several ligands that would have interesting applications in the area of supported phosphine catalysts. The spectral data are given in Table I. The silicon–phosphine ligand can be attached directly to a solid support by displacement of the ethoxy groups, and the $H_2NCH_2CH_2CH_2P(CH_2CH_2PPh_2)_2$ ligand can be attached via the amino group (e.g., Scheme III.)[19]

Diphosphines containing an additional donor group that could bond weakly to the metal and function as tridentate ligands have interesting possibilities as potential catalysts. Therefore, the three compounds, $Ph_2PCH_2CH_2CH_2PPhCH_2CH_2CH_2E$ (E = $N(CH_3)_2$, NH_2, OPh), were prepared by treating $Ph_2PCH_2CH_2CH_2PPhH$ with the corresponding allyl compounds. NMR and infrared spectral data on the compounds are presented in Table I. The proton NMR spectrum clearly shows a sharp dimethylamine CH_3 resonance at τ 8.22. This resonance serves as a useful probe as it shifts ~0.7 ppm downfield when the nitrogen bonds to a transition metal.[19] Initial studies with the iridium(I) chloride complex of $Ph_2PCH_2CH_2CH_2P(Ph)CH_2CH_2CH_2N(CH_3)_2$ have shown that it hydrogenates 1-octene very rapidly (with no isomerization) at ambient conditions.[19]

Scheme IV



As an alternate means of synthesis of the (3-chloropropyl)diphenylphosphine intermediates, photolysis of diphenylphosphine and allyl chloride was investigated. The goal was to add the phosphine group to the terminal carbon of allyl chloride in an anti-Markownikoff fashion as is observed with the vinyl compound; however, elimination of HCl accompanied the addition in alcohol solvents or in a neat mixture. The ratio of addition product to elimination product was invariant with solvent at ~3:1.

Coupling Method of Synthesis. The so-called coupling method has been used to make a variety of useful phosphine ligands.[16,21c] Heretofore, the utility of the method often has been limited by the availability of the appropriate organic halides. Since useful intermediates of this type are now more accessible, this route offers useful preparations of new types of polyphosphines, especially when combined with the free-radical route. The spectral data for the phosphines prepared by the coupling method are given in Table II, and Scheme IV gives the details of the syntheses.

The improved synthesis of bis(3-(diphenylphosphino)propyl)phenylphosphine, ttp, serves as an instructive example. The reaction of dilithium phenylphosphide with 2 equiv of (3-chloropropyl)diphenylphosphine (eq 5; R = Ph) gives an

$$PhPLi_2 + 2Cl(CH_2)_3PR_2 \rightarrow PhP[(CH_2)_3PR_2]_2 \quad (5)$$
$$R = Ph, Cy$$

excellent yield of the triphosphine. The overall yield of ttp by the new method (two separate synthetic steps, 77%) is a considerable improvement over the published procedure (five synthetic steps, 55%).[5] Substitution of phenyl by cyclohexyl groups in the intermediate halide does not reduce the yield significantly (71%), but the resulting triphosphine ligand shows marked differences in chemical behavior upon complexation with a transition metal.

Recent advances in the synthesis of phosphorus-containing macrocycles has provided routes to an entire new area of phosphorus chemistry.[21] The synthesis (and future perturbations) of tetradentate ligands capable of cyclization should lead to many different types of macrocyclic ligands. The tetradentate $CH_2[CH_2P(Ph)CH_2CH_2CH_2NH_2]_2$ was prepared by the reactions in eq 6 and 7. The synthesis of a tetradentate

$$PhHP(CH_2)_3NH_2 + n\text{-}BuLi \rightarrow PhP(Li)(CH_2)_3NH_2 + n\text{-}BuH\uparrow \quad (6)$$

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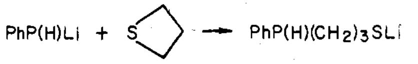
[21] (a) L. Horner, H. Kunz, and P. Walach, *Phosphorus*, **6**, 63 (1975); (b) T. A. DelDonno and W. Rosen, *J. Am. Chem. Soc.*, **99**, 8051 (1977); (c) E. P. Kyba, C. W. Hudson, M. J. McPhaul, and A. M. John, *ibid.*, **99**, 8052 (1977).

$$2PhP(Li)(CH_2)_3NH_2 + Br(CH_2)_3Br \rightarrow H_2N(CH_2)_3(Ph)P(CH_2)_3P(Ph)(CH_2)_3NH_2 + 2LiBr \quad (7)$$

ligand containing the S_2P_2 donor sets is an example of the versatility of the coupling method. Nucleophilic attack on trimethylene sulfide by lithium phenylphosphide produces an intermediate which can be easily coupled to form the S_2P_2 donor set (eq 8 and 9). Proton NMR studies have previously



(8)

$$2PhP(H)(CH_2)_3SLi + Br(CH_2)_3Br \rightarrow PhP(H)(CH_2)_3S(CH_2)_3S(CH_2)_3P(H)Ph + 2LiBr \quad (9)$$

shown that the S–H bond is is the most acidic bond in $PhHPCH_2CH_2CH_2SH$;[18] therefore, the mercaptide end functions as the nucleophile and the secondary phosphine assumes the terminal position in the coupling reaction.

Registry No. $Ph_2PCH_2CH_2CH_2Cl$, 57137-55-0; $Cy_2PCH_2CH_2CH_2Cl$, 71734-57-1; $Cy_2P(O)CH_2CH_2CH_2Cl$, 71734-58-2; PPH, 57322-05-1; $Ph_2P(O)CH_2CH_2CH_2PPh(O)OH$, 71734-59-3; PN_2, 6775-01-5; PHN, 13822-50-9; $Ph_2PCH_2CH_2Si(OEt)_3$, 18586-39-5; PS_2N_2, 71734-60-6; etp-CN, 71734-61-7; PP_2N, 71734-62-8; PPN, 71734-63-9; PPO, 71734-64-0; $PPNH_2$, 71734-65-1; P_2N_2, 71734-66-2; S_2P_2, 71734-67-3; Cy-ttp, 70786-89-9; $PhP(O)(CH_2CH_2CH_2P(O)Cy_2)_2$, 71734-68-4; ttp, 34989-06-5; Ph_2PLi, 4541-02-0; $ClCH_2CH_2CH_2Cl$, 142-28-9; Cy_2PLi, 19966-81-5; NaP(H)Ph, 51918-31-1; $PhPH_2$, 638-21-1; $CH_2{=}CHCH_2NH_2$, 107-11-9; $CH_2{=}CHSi(OEt)_3$, 78-08-0; $PhP(CH{=}CH_2)_2$, 26681-88-9; o-$NH_2C_6H_4SH$, 137-07-5; $NCCH_2CH_2PH_2$, 6783-71-7; $CH_2{=}CHPPh_2$, 2155-96-6; $CH_2{=}CHCH_2N(CH_3)_2$, 2155-94-4; $CH_2{=}CHCH_2OPh$, 1746-13-0; $PhLiPCH_2CH_2CH_2NH_2$, 71766-70-6; $BrCH_2CH_2CH_2Br$, 109-64-8; trimethylene sulfide, 287-27-4; $PhHPCH_2CH_2CH_2SLi$, 71734-69-5; $PhPLi_2$, 13595-56-7; RhCl(etp-CN), 71733-88-5; $CoCl_2$(etp-CN), 71733-89-6; [PtCl(PPN)]AsF_6, 71733-91-0; RhCl(PPN), 71733-92-1.

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Phosphorus-31 NMR Study of Rhodium Poly(phosphine) Nitrosyl Complexes. An Attempt To Prepare the Elusive Example of a Planar $\{MNO\}^{10}$ Complex Containing a Bent Nitrosyl Ligand

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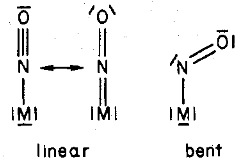
Received April 25, 1979

Displacement of triphenylphosphine from $Rh(PPh_3)_3NO$ by chelating bis(phosphine), tris(phosphine), and tetrakis(phosphine) ligands produces a series of new complexes of formulation $RhL_n(PPh_3)_{3-n}NO$, where L_n corresponds to a poly(phosphine) ligand containing n phosphine groups. On the basis of phosphorus-31 NMR spectroscopy, all of these complexes have a pseudotetrahedral inner coordination sphere around rhodium. They appear to have nearly linear Rh–N–O linkages. The potentially tridentate ligand $Ph_2PCH_2CH_2CH_2P(Ph)CH_2CH_2CH_2NMe_2$ displaces only two triphenylphosphine ligands from $Rh(PPh_3)_3NO$, as the $-NMe_2$ group remains nonbonded in solution. At −40 °C the potentially tetradentate ligand $P(CH_2CH_2PPh_2)_3$ functions as a tridentate in which one of the terminal $-PPh_2$ groups is nonbonded. However, at higher temperatures, all three terminal diphenylphosphino groups undergo exchange. A line-shape analysis of the ^{31}P NMR spectra gives $\Delta G^{\ddagger} = 8.6$ kcal/mol and $\Delta S^{\ddagger} = -17.2$ eu which indicates that the exchange occurs via an associative mechanism and suggests the transient formation of the "supersaturated" 20-electron, five-coordinate complex $Rh(PP_3)NO$. Complexes of the type $Rh(R_2P(CH_2)_nPRR')(PPh_3)NO$ are chiral at the rhodium atom. Use of a diphosphine ligand containing a chiral substituent on one phosphorus atom (i.e., (2-(diphenylphosphino)ethyl)neomenthylphenylphosphine) shows that the phosphorus resonance is affected more by the chiral carbon substituent than by the chiral nature of the rhodium atom. Trends among the phosphorus–rhodium and phosphorus–phosphorus coupling constants are discussed in relation to the oxidation state of rhodium and the number and size of any chelate rings in the $RhL_n(PPh_3)_{3-n}NO$ complexes.

Introduction

Judging by the number of articles and reviews[1] that have appeared in recent years concerning the coordination chemistry of nitric oxide, it is one of the most vigorous research areas. Catalytic reduction of nitrogen oxides (NO, NO_2, etc.) by homogeneous systems[1d] appears to be promising. The potential role of the nitrosyl moiety (NO) as an electron sink comparable to the $\pi \rightleftarrows \sigma$ interconversion of allyl ligands has also been recognized as being pertinent to various catalytic cycles.[2] Moreover, theoretical questions about the structure, bonding, and reactivity of the metal–nitrosyl linkage continue to create controversy.

The bonding of NO to a metal complex spans a range of M–N–O angles from 120 to 180°.



Interconversion between these extreme geometries is believed to be necessary for activation of the nitrosyl group in the catalytic reduction by CO,[3] but unequivocal evidence for conversion of linear into bent NO is known for only two reactions,[4] both of which involve coordination of an additional

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0020-1669/80/1319-0085$01.00/0