between methyl groups of the ligand and the coordination sphere of Ti(III)). Activation parameters are consistent with this interpretation.

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Registry No. Ru(fpd), 76790-97-1; Ti, 7440-32-6; Hpd, 123-54-6.

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Metal-Assisted, Facile Syntheses of Chelating Triphosphine Ligands on Platinum(II)[1]

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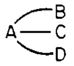
Chelated unsymmetrical triphosphine ligands of the type $R_2PCH_2CH_2CH_2P(Ph)CH_2CH_2PR'_2$ and $R_2PCH_2CH_2CH_2P(Ph)CH_2CH_2CH_2PR'_2$ ($R = R' = C_6H_5$; $R = R' = C_6H_{11}$; $R = C_6H_{11}$, $R' = C_6H_5$) can be synthesized rapidly on platinum by Et_3N-catalyzed condensation of simpler phosphine units onto a coordinated secondary phosphine. The resulting [PtCl(triphos)]X ($X = Cl$, AsF_6) complexes are characterized by elemental analyses and by ^1H, ^{31}P, and ^{195}Pt NMR spectroscopy. For those complexes that contain a five-membered chelate ring, the ^{195}Pt δ values are shifted to higher fields, whereas the ^{31}P δ values are shifted to lower fields, when compared with analogous phosphino groups in six-membered chelate rings.

Introduction

During the past 20 years, tremendous interest and research activity has been expanded on transition-metal complexes of polydentate ligands. Particularly, the syntheses of the tetradentate "tripod-like" ligands of the type



by the research groups of Venanzi,[2] Meek,[3] and Sacconi[4] in the 60s and early 70s depended on Grignard or alkali-metal organophosphide reagents. However, complete variation of the donor groups A, B, C, and D, as well as the length of the connecting chain, was limited by the availability and stability of the appropriate organic halides. During the 70s the research groups of King[5] and Meek[6] developed two valuable alternatives for general syntheses of polydentate ligands containing ethylene chains, i.e., the base- and radical-catalyzed addition of P–H, As–H, and S–H across the double bond of a vinyl group. Thus, by choosing the appropriate route and reagents, one can now "tailor-make" polydentate ligands to incorporate just about any electronic and/or steric effect desired.[7] However, the practical problem of purification of the ligand, often a high-boiling oil, still exists, particularly if the ligand has been constructed from 3–4 fragments.

Triphosphine ligands that contain trimethylene chains are valuable chelating ligands with the larger transition-metal ions (e.g., Rh, Pt, Ir, Ru),[8] and such ligands are becoming increasingly important in the areas of catalysis, asymmetric synthesis, and organometallic stereochemistry.[7,9] In an effort to develop easier routes to a wide variety of $R_2P(CH_2)_n(R')P(CH_2)_mPR''_2$ ligands ($n = 1$–4, $m = 2,3$), we have examined metal-assisted coupling of vinyl-, allyl-, and (3-chloropropyl)phosphine units to coordinated secondary phosphines.[10] This report describes the successful, high-yield syntheses of five triphosphine ligands, including two new ones, on platinum.

Results and Discussion

Symmetric triphosphine ligands such as $PhP(CH_2CH_2CH_2PPh_2)_2$ (ttp) and $PhP(CH_2CH_2PPh_2)_2$ (etp),[11] which have been used by our research group for several years, have previously been synthesized via coupling reactions between alkali-metal phosphides (e.g., Li_2PPh) and chloroalkylphosphines or by the radical addition of a P–H bond

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(11) The ligand abbreviations ttp and etp were derived from the lengths of the alkyl chains connecting the phosphorus atoms, i.e., trimethylene- and ethylenetriphosphine, respectively. The nonsymmetric triphosphine $Ph_2PCH_2CH_2P(Ph)CH_2CH_2CH_2PPh_2$ is then abbreviated eptp. The secondary diphosphine $(C_6H_5)_2PCH_2CH_2CH_2P(Ph)H$ is abbreviated ppH; analogously, $(C_6H_{11})_2PCH_2CH_2CH_2P(Ph)H$ is labeled cyppH. The other unsymmetrical triphosphine ligands are shown by the formulas that specify the length of the connecting chain in abbreviated form, i.e., PC_3P and $PC_2P = (CH_2)_3$ and $(CH_2)_2$ connectors, respectively.

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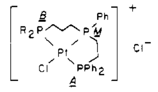
Table I. $^{31}P\{^1H\}$ Spectral Parameters for Three Pt(II)-Triphosphine Complexes Prepared by Et_3N-Catalyzed Condensations[a,b]

complex	δP_A	δP_M	δP_B	$^2J_{P_A\text{-}P_M}$	$^2J_{P_A\text{-}P_B}$	$^2J_{P_B\text{-}P_M}$	$^1J_{Pt\text{-}P_A}$	$^1J_{Pt\text{-}P_M}$	$^1J_{Pt\text{-}P_B}$
$[PtCl\{Ph_2PC_3P(Ph)C_2PPh_2\}]AsF_6$[c]	50.6	32.1	4.2	6.0	376	27.0	2349	3118	2246
$[PtCl\{Ph_2PC_3P(Ph)C_2PPh_2\}]Cl$	49.8	32.5	4.05	6.0	379	26.6	2347	3066	2241
$[PtCl\{(C_6H_{11})_2PC_3P(Ph)C_2PPh_2\}]Cl$	49.5	33.2	9.12	5.0	349	23.6	2260	3140	2219

[a] Spin label assignment for $[PtCl(eptp)]^+$, **1** and [PtCl(cyppep)]Cl, **2**: $R = C_6H_5$ for eptp; $R = C_6H_{11}$ for cyppep



[b] The chemical shift values (δ) are in ppm relative to 85% H_3PO_4 with positive values downfield from the standard; the coupling constants (*J*) are in Hz. [c] See ref 12b.

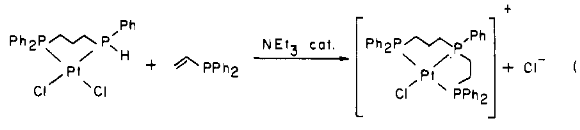
Table II. $^{31}P\{^1H\}$ Spectral Data for Pt(II)-Triphosphine Complexes Prepared from the Coupling Reaction[a]

complex	δP_1	δP_2	δP_3	$^2J_{P_1\text{-}P_2}$	$^2J_{P_2\text{-}P_3}$	$^2J_{P_1\text{-}P_3}$	$^1J_{Pt\text{-}P_1}$	$^1J_{Pt\text{-}P_2}$	$^1J_{Pt\text{-}P_3}$
[PtCl(ttp)]Cl[b,c]	−3.7	−20.7	−3.7	27			2229	3134	
[PtCl(ttp)]Cl[d]	−3.9	−20.6	−3.9	26.5			2221	3076	
$[PtCl\{((C_6H_{11})_2PCH_2CH_2CH_2)_2PPh\}]Cl$[c]	−4.0	−20.4	−4.0	23.6			2152	3236	
$[PtCl\{(C_6H_{11})_2PC_3P(Ph)C_3PPh_2\}]Cl$[d]	−3.1	−16.3	4.8	25.6	23.6	344	2110	3158	2164

[a] The chemical shift values (δ) are in ppm relative to 85% H_3PO_4 with positive values downfield from the standard; the coupling constants (*J*) are in Hz. [b] Solvent = ~20% CD_3NO_2 in CH_3NO_2. [c] P_1 and P_3 are equivalent terminal phosphorus atoms in $PhP(CH_2CH_2CH_2PR_2)_2$ molecules. [d] $P_1 = Ph_2P$ and $P_3 = (C_6H_{11})_2P$ in the ligand $Ph_2PCH_2CH_2CH_2P(Ph)CH_2CH_2CH_2P(C_6H_{11})_2$.

across an appropriate vinyl or allyl substituent.[6,12a] These synthetic routes typically required a few days for completion of the synthesis steps, isolation, and purification of a ligand, many of which were heavy oils.

In the present study, we have developed rapid, high-yield syntheses of triphosphine ligands on platinum by base-catalyzed condensation of simpler phosphine units onto a coordinated secondary phosphine. For example, the known complex [PtCl(eptp)]Cl was prepared in less than 30 min by the triethylamine-catalyzed addition of diphenylvinylphosphine to the P-H bond of coordinated $Ph_2PCH_2CH_2CH_2P(Ph)H$. The reaction is illustrated by eq 1. The $^{31}P\{^1H\}$ NMR parameters for the platinum-assisted reaction product agree very well with an authentic sample of [PtCl(eptp)]Cl that had been prepared by Tau from $PtCl_2(COD)$ (COD = 1,5-cyclooctadiene) and the free triphosphine ligand $Ph_2PCH_2CH_2P(Ph)CH_2CH_2CH_2PPh_2$.[12b] The reaction is virtually quantitative, since the only platinum-phosphine complex in the reaction mixture detectable by $^{31}P\{^1H\}$ NMR is the desired [PtCl(eptp)]Cl. Further indications that P-H addition occurs to the C=C bond of $Ph_2PCH{=}CH_2$ are found from the infrared and ^{31}P NMR spectra. In particular, the $^{31}P\{^1H\}$ NMR spectrum is important (Figure 1), since the chemical shifts of phosphorus nuclei incorporated into a five-membered ring experience large (20–30 ppm) downfield shifts compared to similar monodentate phosphines or to similar phosphorus groups contained in six-membered rings.[13] Comparison of the chemical shifts for nuclei P_A and P_M in the complexes in Table I with the corresponding data for those complexes that do not contain a phosphorus atom in a five-membered chelate ring (Table II) show that nucleus P_A is deshielded significantly compared to PPh_2 groups in the ligands $Ph_2PCH_2CH_2CH_2P(Ph)CH_2CH_2CH_2PPh_2$ and $(C_6H_{11})_2PCH_2CH_2CH_2P(Ph)CH_2CH_2CH_2PPh_2$, in which the PPh_2 group is part of a six-membered ring. In addition, the $^2J_{P_A\text{-}P_M}$ coupling constant is 6 Hz; such a small value is typical of platinum-coordinated cis phosphines that are connected by a $-CH_2CH_2-$ linkage (e.g., $^2J_{PP}$ in PtClEt(dppe) = <2 Hz).[14] In contrast, the values of $^2J_{PP}$ couplings between phosphorus nuclei that are connected via $-CH_2CH_2CH_2-$ linkages are in the range normally observed for platinum(II)–cis-PR_3 complexes, i.e., ~20–25 Hz.[15]



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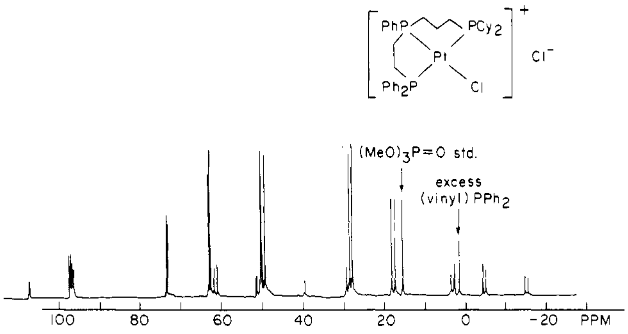

Figure 1. 36.43-MHz $^{31}P\{^1H\}$ NMR spectrum of $[PtCl\{(C_6H_{11})_2PC_3P(Ph)C_2PPh_2\}]Cl$ in CH_2Cl_2 solution.

Treatment of $PtCl_2(cyppH)$ (cyppH = $(C_6H_{11})_2PCH_2CH_2CH_2P(H)C_6H_5$) with diphenylvinylphosphine in ethanol in the presence of Et_3N catalyst also yields a facile condensation to produce the platinum complex of the new triphosphine ligand $Cy_2PCH_2CH_2CH_2P(Ph)CH_2CH_2PPh_2$. In the absence of Et_3N, the condensation in ethanol is slower, requiring 12 h at room temperature. Apparently ethanol is sufficiently basic to generate a small concentration of the phosphido nucleophile, which then attacks the vinyl group to produce the triphosphine ligand.

In an experiment similar to the above vinyldiphenylphosphine reaction, $PtCl_2(cyppH)$ was treated with allyldiphenylphosphine in ethanol but no P-H reaction occurred with the allyl group; after more than 24 h, the exclusive product is $[PtCl(cyppH)(allylPPh_2)]Cl$. In the presence of triethylamine, P-H addition to the allyl group does occur cleanly; the result is a complicated mixture of complexes. This result is similar to the observation that KO-*t*-Bu-catalyzed addition of P-H to the C=C bond of uncoordinated allylphosphines

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Table III. ^{195}Pt{^{1}H} NMR Data for Monomeric Platinum(II)-Phosphine Complexes

no.	complex	δ_{Pt}[a]	$^1J_{Pt-P_1}$[a]	$^1J_{Pt-P_2}$	$^1J_{Pt-P_3}$
1	*cis*-$PtCl_2(PMe_2Ph)_2$[b,c]	−853	3548		
2	*cis*-$PtCl_2(PMePh_2)_2$[b,c]	−886	3622		
3	*cis*-$PtCl_2(P\textit{n}\text{-}Bu_3)_2$[b,c]	−888	3435		
4	*cis*-$PtCl_2(PEt_3)_2$[b,c]	−932	3560		
5	$PtCl_2$(ppH)	−955	3403	3256	
6	$PtCl_2$(dppp)[c]	−963	3410		
7	$PtCl_2$(cyppH)	−993	3303	3390	
8	$PtCl_2$(dpet)	−1062	3557	3662	
9	$[PtCl\{((C_6H_{11})_2PCH_2CH_2CH_2)_2PPh\}]Cl$[d]	−1185	2152	3236	
10	$[PtCl\{(C_6H_{11})_2PC_3P(Ph)C_3PPh_2\}]Cl$	−1234	2110	3158	2164
11	[PtCl(ttp)]Cl[d]	−1240	2221	3076	
12	$[PtCl\{(C_6H_{11})_2PC_3P(Ph)C_2PPh_2\}]Cl$	−1295	2260	3140	2219
13	[PtCl(cptp)]Cl	−1325	2347	3066	2241

[a] δ is given relative to *cis*-$PtCl_2(SMe_2)_2$ at 0 ppm; negative values are upfield from the standard,[21b] coupling constants (J) are given in Hz. [b] Data from ref 21b. [c] P_1 and P_2 are equivalent, no P_3. [d] P_1 and P_3 are equivalent.

produces a mixture of products in which phosphorus addition occurs at both the terminal and middle carbon atoms of the allyl group.[5] Although the based-catalyzed route with allyldiphenylphosphine produces a mixture of products, allylphosphines may still be valuable building units, since Arpac and Dahlenburg published a report, after we had completed our study, that a radical-chain process (initiated by AIBN[6a]) does produce triphosphine ligands via condensation with allylphosphines.[16]

The P-H bond of coordinated cyppH in the allyldiphenylphosphine complex $[PtCl(cyppH)(allylPPh_2)]Cl$ is relatively acidic and undergoes exchange with methanol-*d* (CH_3OD). The pseudotriplet originally present in the ^{31}P{^{1}H} NMR spectrum of $[PtCl(cyppH)(allylPPh_2)]Cl$ at −24.1 ppm is split into three triplets of 1:1:1 intensity by the deuterium nucleus ($I = 1$). The $^1J_{PD}$ coupling is 67 Hz; the observed ratio $^1J_{PH}/^1J_{PD}$ (430 Hz/67 Hz = 6.42) is very close to the theoretical ratio (γ_H/γ_D) of 6.51.[17] Although deuterium exchange has been observed previously for phenyl- and diphenylphosphine in CD_3OD,[17] to our knowledge this is the first report of such an exchange in a transition-metal complex of a secondary phosphine under such mild conditions. The protons of $Fe(CO)_4(HPPh_2)_2$ do not exchange with D_2O;[18] however, proton exchange has been reported for $M(CO)_4(PH_3)_2$ complexes (M = Cr, Mo, W) and $Cr(CO)_{6-n}(PH_3)_n$ (n = 1-3) when those complexes were passed through an acidic alumina column that had been deactivated by D_2O or alternatively when they reacted in the presence of Et_3N.[19]

Clean, easy syntheses of chelated triphosphine ligands containing two trimethylene chains were accomplished on platinum by treating the $PtCl_2$(ppH) and $PtCl_2$(cyppH) complexes with either $ClCH_2CH_2CH_2PPh_2$ or $ClCH_2CH_2CH_2PCy_2$ in THF or ethanol in the presence of a stoichiometric quantity of NEt_3. The acidic P-H bond reacts with NEt_3 to produce a metal-phosphido site which then undergoes nucleophilic displacement of chloride from the $ClCH_2CH_2CH_2PR_2$ molecule to form the chelated triphosphine and the amine hydrochloride salt, $[HNEt_3]^+Cl^-$. The ^{31}P{^{1}H} NMR spectral data for an authentic sample of $[PtCl(ttp)]AsF_6$ and for three triphosphine complexes synthesized from $PtCl_2$(ppH) and $PtCl_2$(cyppH) via the platinum-phosphido coupling reaction are presented in Table II. The ^{31}P NMR spectra are A_2MX spin systems (Pt-P coupling due to 33.8% ^{195}Pt), except in the complexes of the unsymmetrical triphosphine ligands (e.g., $[PtCl\{(C_6H_{11})_2PC_3P(Ph)C_3PPh_2\}]Cl$), which display an ABMX spectral pattern (Figure 2). An unambiguous assignment of chemical shifts to the $(C_6H_{11})_2P$ and $(C_6H_5)_2P$ groups in the ^{31}P NMR spectrum of $[PtCl\{(C_6H_{11})_2PC_3P(Ph)C_3PPh_2\}]Cl$ is not possible from the spectrum alone. However, by comparison of the δ_P values with those of other platinum-triphosphine complexes, the resonances at −3.1 and 4.9 ppm are consistent with the resonances of $(C_6H_5)_2P$ and $(C_6H_{11})_2P$ groups, respectively, in other complexes with similar environments. The trans coupling constant, $^2J_{P_1-P_3}$, of $[PtCl\{(C_6H_{11})_2PC_3P(Ph)C_3PPh_2\}]Cl$ is 344 Hz, and it is comparable to the trans coupling observed for [PtCl(eptp)]Cl (374 Hz) and $[PtCl\{(C_6H_{11})_2PC_3P(Ph)C_2PPh_2\}]Cl$ (349 Hz).

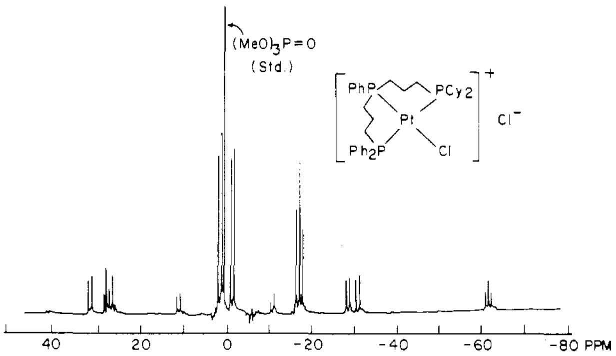

Figure 2. 36.43-MHz ^{31}P{^{1}H} NMR spectrum of $[PtCl\{(C_6H_{11})_2PC_3P(Ph)C_3PPh_2\}]Cl$ in CH_2Cl_2 solution.

Platinum-195 NMR Spectra of the Complexes. The shielding term, σ, for platinum-195 is dominated by the paramagnetic contribution, σ_p. Although at least three factors affect the chemical shifts of ^{195}Pt, some empirical trends have emerged: (a) replacement of an alkyl group by an aryl group on a coordinated phosphorus or arsenic ligand causes an increased chemical shift for platinum; (b) a decrease in the electronegativity of the ligands bonded to platinum causes an increased shielding of platinum; (c) increased covalent bonding between a platinum atom and its ligands withdraws electron density from the metal and leads to more positive (i.e., downfield) chemical shifts.[20] Examination of the δ_{Pt} values for complexes **1**-**8** in Table III (i.e., $PtCl_2$(L-L) and *cis*-$PtCl_2L_2$ complexes) is consistent with trend a above. In this series of chloride complexes, the effects of variations in trends b and c are minimized. The chemical shift values of $PtCl_2$(ppH) and $PtCl_2$(cyppH) are reversed from that expected from trend a; this effect may result from the large disparity in size between the Cy_2P and Ph(H)P groups of cyppH. A decrease

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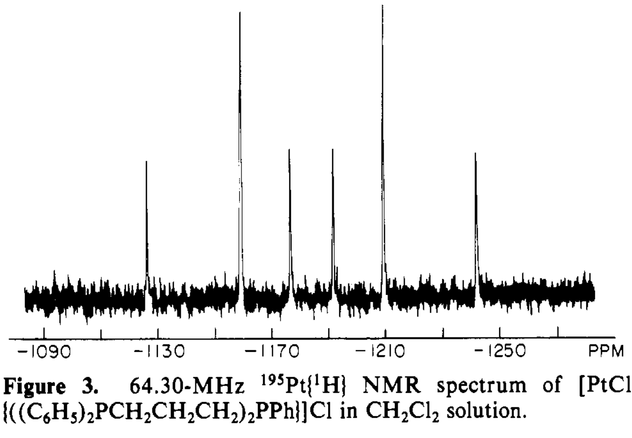

Figure 3. 64.30-MHz ^{195}Pt{^{1}H} NMR spectrum of [PtCl{$((C_6H_5)_2PCH_2CH_2CH_2)_2PPh$}]Cl in CH_2Cl_2 solution.

in δ_{Pt} has been observed previously on substitution of $P(C_6H_{11})_3$ for $P(i\text{-}C_3H_7)_3$ in Pt(0)–carbonyl clusters of the type $Pt_3(\mu_2\text{-}CO)_3(PR_3)_3$.[21a,b]

The chemical shift of $PtCl_2$(dpet) (−1062 ppm) is upfield from those of $PtCl_2$(ppH), $PtCl_2$(cyppH), and $PtCl_2$(dppp).[22] A major difference between $PtCl_2$(dpet) and the other three compounds is the five-membered chelate ring in $PtCl_2$(dpet), whereas six-membered chelate rings are present in the other compounds. A five-membered chelate ring effect (i.e., a shift of δ_{Pt} values to higher field) also has been observed in platinum(II)–cycloalkane, platinum(II)–thiolato, and platinum(IV)–phosphino complexes.[21c] In the case of platinum(II)–phosphino complexes, a small effect has been reported previously between $Pt(CH_3)_2$(dppp) and $Pt(CH_3)_2$(dppe). However, the authors of that paper did not believe that the effect (14 ppm) was significant when compared to the large range of ^{195}Pt chemical shifts.[23] As previously stated, when a phosphorus atom is part of a five-membered ring, the ^{31}P resonance appears significantly downfield (20–30 ppm) from that of a comparable nonchelated phosphine.[13] Thus, these *low-field* ^{31}P chemical shifts are apparently concomitant with *high-field* shifts in the ^{195}Pt NMR spectra.

The five platinum(II)–triphosphine complexes in Table III obey empirical observation a above; the ^{195}Pt chemical shifts of the complexes that contain alkyl-substituted phosphines appear at lower field than do analogous complexes of the aryl-substituted phosphines. The ^{195}Pt resonance of the triphosphine complexes is upfield relative to the diphosphine complexes; this shift is due to replacement of an electronegative chloride ligand with a PR_3 ligand. The high-field shift has also been rationalized as being due to a decrease in the transition energies between the ground and excited states of the platinum 5d and 6s electrons on formation of the cationic complexes.[21b] As noted above for the $PtCl_2$–diphosphine complexes that contain a five-membered chelate ring, the ^{195}Pt chemical shifts for those [PtCl(triphos)]Cl complexes that contain a five-membered chelate ring (eptp and $(C_6H_{11})_2PC_3P(Ph)C_2PPh_2$ ligands) also appear at higher fields than those for platinum nuclei involved in six-membered rings with otherwise comparable phosphino groups. The ^{195}Pt{^{1}H} NMR spectrum of [PtCl{$PhP(CH_2CH_2CH_2Pcy_2)_2$}]Cl is presented in Figure 3; it corresponds to the X portion of an A_2MX spin system, and the $^1J_{PtP}$ couplings, which are easily extracted by direct measurement, agree with those obtained from the ^{31}P spectrum.

Experimental Section

Reagents and Chemicals. The chemicals used in this research were reagent grade and were used without further purification unless otherwise stated. Diphenylphosphine, phenylphosphine, and dicyclohexylphosphine were purchased from Pressure Chemical Co., Pittsburgh. Allyldiphenylphosphine and vinyldiphenylphosphine were purchased from Strem Chemical Co., Newburyport, MA. Triphenylphosphine, and 1,3-dichloropropane were obtained from Aldrich Chemical Co., Milwaukee, WI. The diphosphine ligand 1-(diphenylphosphino)-2-(phenylethylphosphino)ethane (dpet) was supplied by Professor S. O. Grim, University of Maryland, College Park, MD. The tertiary–secondary diphosphine 1-(diphenylphosphino)-3-(phenylphosphino)propane (ppH) was prepared by Uriarte's modification[6b] of Tau's method.[12b] Potassium tetrachloroplatinate (K_2PtCl_4) was prepared from platinum metal foil.[24]

All solvents were reagent grade and were distilled under N_2 from appropriate drying agents,[25] except for absolute ethanol, anhydrous diethyl ether, and hexane, which were used as received.

Instrumentation. Infrared spectra were recorded on either a Perkin-Elmer 337 or a Perkin-Elmer 283B grating spectrophotometer from 4000 to 400 (P.E. 337) or 200 (P.E. 283B) cm^{-1}. The samples were examined as pressed KBr pellet or Nujol mulls between KBr plates. Spectra were calibrated against sharp peaks (1601.4 and 1028.0 cm^{-1}) of polystyrene film.

Continuous-wave 60-MHz proton NMR spectra were collected on samples in 5-mm tubes on a Varian EM-360 spectrometer and Fourier-mode proton spectra were obtained on either a Bruker HX-90 spectrometer operating at 90 MHz or a Bruker WM-300 at 300 MHz. Phosphorus-31 NMR spectra were run on samples in 10-mm tubes using nondeuterated solvents on the Bruker HX-90 operating at 36.43 MHz in the Fourier mode. Spectra were calibrated through the use of coaxial insert tubes that contained trimethyl phosphate (δ = 1.59 relative to 85% H_3PO_4) and a deuterated solvent (e.g., acetone-d_6 or toluene-d_8). Spectra were often recorded both in the ^{1}H-coupled and broad-band-noise-^{1}H-decoupled modes.

Broad-band-noise-^{1}H-decoupled ^{195}Pt NMR spectra were obtained in 10-mm tubes at 64.30 MHz on a Bruker WM-300 spectrometer equipped with an Aspect 2000 data system. Spectra were referenced to an external saturated aqueous solution of K_2PtCl_4 (+1927 ppm relative to *cis*-$PtCl_2(S(CH_3)_2)_2$.[26] Chemical shifts thus determined are reproducible to ±2.0 ppm.

General Experimental Procedures. All reactions were carried out under an atmosphere of high-purity nitrogen by the use of standard Schlenk techniques. Solutions of air-sensitive reagents were transferred between reaction vessels using stainless-steel or Teflon transfer tubes or syringes flushed with nitrogen. Air-sensitive solids were transferred in either a glovebag or a Vacuum Atmospheres HE43 drybox equipped with an MO-40 catalyst system. Solvents were purged with purified nitrogen for 30 min immediately before use.

The Tertiary–Secondary Diphosphine Ligand $(C_6H_{11})_2PCH_2CH_2CH_2P(H)C_6H_5$, cyppH. To a Pyrex Schlenk flask containing 25.0 g (0.126 mol) of $(C_6H_{11})_2PH$ dissolved in 300 mL of THF and cooled to 0 °C was added 155 mL of a 1.2 M (1.1 equiv.) methyllithium–diethyl ether solution. The clear solution became dark red immediately and evolved a large quantity of methane gas. A finely divided yellow suspension of $LiPCy_2$ appeared in the reaction vessel as it was allowed to warm to room temperature. This suspension was transferred slowly via a glass tube equipped with a Teflon stopcock to a second flask containing a solution of 100 g of 1,3-dichloropropane (0.89 mol) in 200 mL of diethyl ether. The solution in the second flask was stirred vigorously during the addition. The first reaction flask was rinsed with 100 mL of diethyl ether after the transfer was completed, and this rinse solution was added to the contents of the second flask.

After the solution was stirred overnight, the reaction solvents were evaporated under reduced pressure to give a cloudy oil which was treated with 60 mL of ethanol and 150 mL of water before being extracted three times with 150-mL portions of diethyl ether. The extracts were transferred to a flask containing anhydrous $MgSO_4$ and charcoal and allowed to stand overnight. This solution was filtered and transferred to a clean flask; the solvent was then evaporated at

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(22) The ligand abbreviations dpet, dppp, and dppe are for $Ph_2PCH_2CH_2P(Ph)Et$, $Ph_2PCH_2CH_2CH_2PPh_2$, and $Ph_2PCH_2CH_2PPh_2$, respectively.

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Table IV. Elemental Analyses of Platinum(II)–Polyphosphine Complexes[a]

complex	calcd (found) % C	% H	% Cl	% F
$PtCl_2(ppH)$	41.87 (41.94)	3.68 (3.73)	11.77 (11.84)	10.28 (10.61)[b]
$PtCl_2(cyppH)$	41.05 (41.36)	5.58 (5.71)	11.54 (11.29)	
$[PtCl(eptp)]AsF_6$	43.42 (42.52)	3.64 (3.77)	3.66 (3.94)	11.78 (12.32)
$[PtCl\{((C_6H_{11})_2PCH_2CH_2CH_2)_2PPh\}]AsF_6$	42.97 (42.78)	6.11 (6.32)	3.52 (3.34)	11.33 (11.57)
$[PtCl\{(C_6H_{11})_2PC_3P(Ph)C_3PPh_2\}]AsF_6$	47.34 (47.07)	6.73 (7.00)	3.89 (3.64)	12.48 (12.31)
$[PtCl\{(C_6H_{11})_2PC_3P(Ph)C_2PPh_2\}]AsF_6$	42.89 (42.06)	4.83 (5.00)	3.62 (3.44)	11.63 (11.91)

[a] Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ. [b] % P in this case, instead of % F.

40 °C to yield 29.4 g of a yellowish oil. The yield of $(C_6H_{11})_2PCH_2CH_2CH_2Cl$ was 84.9% based on $(C_6H_{11})_2PH$.

A solution containing 22.6 g of $(C_6H_{11})_2PCH_2CH_2CH_2Cl$ in 100 mL of toluene was added dropwise from a pressure-equalizing funnel to a mechanically stirred solution of liquid ammonia at −78 °C which contained 2.0 g of sodium metal, 9.5 g of phenylphosphine, $PhPH_2$, and 100 mL of diethyl ether. After addition was completed, the ammonia was allowed to evaporate overnight. The resulting residue in the flask was treated with 200 mL of a saturated aqueous solution of NH_4Cl, and then the organic portion was extracted with diethyl ether, dried over $MgSO_4$, and isolated by removal of all volatile materials at 50 °C and 0.1 torr. The diphosphine cyppH was generally sufficiently pure to use as a ligand; however, purer material could be obtained by vacuum fractional distillation on a Kugelrohr apparatus. The fraction collected at 130–160 °C (0.1 torr) was identified as cyppH on the basis of its infrared, ^1H NMR, and ^{31}P NMR spectra; yield 38.5 g (65%, based on $(C_6H_{11})_2PH$).

Platinum(II) Complexes. $PtCl_2(ppH)$. A slurry of 0.2230 g (0.62 mmol) of $PtCl_2(COD)$ in 20 mL of benzene was treated with 1.5 mL of a toluene solution of ppH (0.41 M, 0.62 mmol). When the reagents were combined, the solid $PtCl_2(COD)$ rapidly dissolved and then a white finely divided solid of $PtCl_2(ppH)$ separated. After the mixture was filtered, additional product was obtained by reducing the filtrate volume to 1–2 mL in a stream of N_2 and adding 40 mL of diethyl ether. The total amount of product was collected on a filter, washed with 2 × 10 mL of diethyl ether, and recrystallized from CH_3NO_2; yield 0.31 g (83%); mp 220 °C dec. The elemental analyses for this and the other platinum complexes are reported in Table IV.

$PtCl_2(cyppH)$. Substitution of the cyppH ligand for ppH in the preceding reaction yields $PtCl_2(cyppH)$ in 86% yield based on $PtCl_2(COD)$.

[PtCl(ttp)]Cl. To a suspension of 0.278 g (0.46 mmol) of $PtCl_2(ppH)$ in 20 mL of THF was added with vigorous stirring 1.0 mL of a diethyl ether solution of $(C_6H_5)_2PCH_2CH_2CH_2Cl$ (0.53 M) followed immediately by 1.0 mL of triethylamine; the solids dissolved. After 1 h, a white precipitate began to appear. The mixture was stirred overnight and the white solid was collected on a filter; it was identified as [PtCl(ttp)]Cl by comparing its $^{31}P\{^1H\}$ NMR data with those of an authentic sample of $[PtCl(ttp)]AsF_6$.[12,15]

$[PtCl\{(C_6H_{11})_2PC_3P(Ph)C_3PPh_2\}]AsF_6$. Addition of 1 equiv of $(C_6H_{11})_2PCH_2CH_2CH_2Cl$ dissolved in toluene to a suspension of 0.30 g (0.50 mmol) of $PtCl_2(ppH)$ in 20 mL of absolute ethanol resulted in dissolution of all of the solid. The resulting solution was treated with 0.5 mL of triethylamine and stirred for 8 h. Removal of solvent at 0.1 torr and treatment with diethyl ether resulted in the precipitation of $[PtCl\{(C_6H_{11})_2PC_3P(Ph)C_3PPh_2\}]Cl$. The solid complex was collected on a filter and washed with 2 × 5 mL of water and 2 × 10 mL of diethyl ether. The compound was dissolved in ethanol and refluxed with 1 equiv of $NaAsF_6$ to give the complex in 80% yield on cooling the solution.

$[PtCl(cyttp)]AsF_6$. Substitution of $PtCl_2(cyppH)$ for $PtCl_2(ppH)$ in the above synthesis resulted in the isolation of $[PtCl(cyttp)]AsF_6$.

$[PtCl(eptp)]AsF_6$. A suspension of 0.30 g (0.50 mmol) of $PtCl_2(ppH)$ in 20 mL of ethanol was treated with 1 equiv of neat vinyldiphenylphosphine, whereupon all of the solid material dissolved. After the solution was stirred for 12 h at room temperature, a white precipitate was obtained by reducing the solvent volume and treatment with diethyl ether. The precipitate was isolated by filtration and characterized as [PtCl(eptp)]Cl by comparison of its $^{31}P\{^1H\}$ NMR spectrum with that of an authentic sample.[12] The chloride salt was then treated with $NaAsF_6$ in boiling ethanol to yield $[PtCl(eptp)]AsF_6$ in 77% yield.

$[PtCl\{(C_6H_{11})_2PC_3P(Ph)C_2PPh_2\}]AsF_6$. Substitution of $PtCl_2(cyppH)$ for $PtCl_2(ppH)$ in the above procedure produced $[PtCl\{(C_6H_{11})_2PC_3P(Ph)C_2PPh_2\}]AsF_6$.

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Registry No. cyppH, 82763-84-6; $PtCl_2(COD)$, 12080-32-9; $PtCl_2(ppH)$, 88496-13-3; $PtCl_2(cyppH)$, 88496-14-4; [PtCl(ttp)]Cl, 71597-21-2; $[PtCl(cypptp)]AsF_6$, 88496-19-9; $[PtCl(cyttp)]AsF_6$, 88496-17-7; [PtCl(eptp)]Cl, 88496-09-7; $[PtCl(eptp)]AsF_6$, 88496-08-6; $PtCl_2(dppp)$, 59329-00-9; $PtCl_2(dpet)$, 88496-15-5; [PtCl(cypptp)]Cl, 88496-12-2; $[PtCl(cyppep)]AsF_6$, 88510-30-9; [PtCl(cyppep)]Cl, 88496-10-0; [PtCl(cyttp)]Cl, 88496-11-1; $(C_6H_{11})_2PH$, 829-84-5; $(C_6H_{11})_2PCH_2CH_2CH_2Cl$, 71734-57-1; $PhPH_2$, 829-85-6; $(C_6H_5)_2PCH_2CH_2CH_2Cl$, 57137-55-0; 1,3-dichloropropane, 142-28-9; vinyldiphenylphosphine, 2155-96-6.