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Reactions[1] of Tri-*tert*-butylphosphine with Platinum(II) and Palladium(II). Facile Intramolecular Metalation of Tri-*tert*-butylphosphine

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Reaction of $P(t\text{-}Bu)_3$ with $PtCl_2$ results in the formation of $(P(t\text{-}Bu)_3H)_2PtCl_4$ (**1**) and the internally metalated complex *trans*-$PtCl(C_4H_8P(t\text{-}Bu)_2)P(t\text{-}Bu)_3$ (**2**). $P(t\text{-}Bu)_3$ also reacts with $PtCl_2(C_6H_5CN)_2$ or with Na_2PtCl_4 to form **1** and **2** but under similar conditions it does not react with $PtCl_2(COD)$. $PdCl_2(C_6H_5CN)_2$, $PdCl_2(COD)$, and Na_2PdCl_4 react with $P(t\text{-}Bu)_3$ to give *trans*-$PdCl_2(P(t\text{-}Bu)_3)_2$ (**3**) which is converted at room temperature into the metalated complex *trans*-$PdCl(C_4H_8P(t\text{-}Bu)_2)P(t\text{-}Bu)_3$ (**4**). Compounds **3**, **4**, and $(P(t\text{-}Bu)_3H)_2PdCl_4$ (**5**) are obtained from the reaction of $P(t\text{-}Bu)_3$ with $PdCl_2$. The products have been characterized by analytical data, molecular weight, and conductance measurements and by ^1H and ^{31}P NMR, infrared, and electronic spectral studies.

Introduction

Intramolecular metalation[3,4] of aromatic carbon atoms in coordinated phosphine and phosphite ligands has been extensively studied during the last 5 years. It is now well recognized that complexes of many transition metals containing arylphosphine[5,7] and aryl phosphite[8,9] ligands undergo ortho metalation. There are also many examples of intramolecular metalation of[10-13] alkyl and alkoxy groups attached to an aromatic ring. There are, however, only a few examples known of intramolecular metalation of a purely aliphatic carbon. Intramolecular metalation of alkyl groups has been postulated[14,15] in the reactions

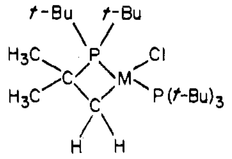
$$Cl_2Pt[P(C_2H_5)_3]_2 + Li(Carb\text{-}R) \rightarrow LiCl + HCl + [(C_2H_5)_2PCH_2CH_2]Pt(Carb\text{-}R)P(C_2H_5)_3 \quad (1)$$

$$[(CH_3)_2PCH_2CH_2P(CH_3)_2]_2Ru \rightleftharpoons [(CH_3)_2PCH_2CH_2P(CH_3)_2]Ru[CH_2(CH_3)PCH_2CH_2P(CH_3)_2]H \quad (2)$$

Shaw and co-workers have reported[10] that the *n*-propyl group in the complexes *trans*-$[PtCl_2(P(t\text{-}Bu)(n\text{-}Pr)_2)_2]$ and *trans*-$[PtCl_2\{P(t\text{-}Bu)_2(n\text{-}Pr)\}_2]$ is metalated when the complexes are heated for several hours. However, it is not known whether the metalation occurs at the C-2 or the C-3 position. It has been suggested[11] that internal metalation is promoted by the presence of bulky substituents on phosphorus and by the formation of five-membered rings on metalation. Kiffen and co-workers[16] have shown that chloro-bridged diplatinum(II) complexes of the type $Pt_2Cl_4L_2$, where L = $P(n\text{-}Bu)_3$, $P(n\text{-}Pr)_3$, PPr_2Ph, and $PPrPh_2$, undergo hydrogen–deuterium exchange at the C-3 position of the *n*-butyl or the *n*-propyl group. The rate of such exchange is markedly higher for the complex $Pt_2Cl_4(P(n\text{-}Pr)(t\text{-}Bu)_2)_2$ which also undergoes slow hydrogen–deuterium exchange at the C-2 position as well at the *tert*-butyl groups. These results suggest that the exchange reaction proceeds via internal metalation of the coordinated phosphine. However, no internally metalated intermediates could be isolated. In continuation of our investigations[17,18] on the reactions of tri-*tert*-butylphosphine with transition metals, we have found that tri-*tert*-butylphosphine undergoes a facile reaction with platinum(II) or palladium(II) chloride to form stable internally metalated complexes containing four-membered rings. Herein we report on the preparation and characterization of these complexes. While this work was in progress, Shaw and co-workers reported[19a] the C-metalated iridium(III) complexes $[Ir\{P(t\text{-}Bu)_2(C_6H_4O)\}\{P(t\text{-}Bu)(C_6H_4O)(CMe_2CH_2)\}]$ and $[Ir(CO)\{P(t\text{-}Bu)_2(C_6H_4O)\}\{P(t\text{-}Bu)(C_6H_4O)(CMe_2CH_2)\}]$. After the completion of this work, the metalation of di-*tert*-butylneopentylphosphine by platinum(II) has been reported.[19b]

Results and Discussion

Tri-*tert*-butylphosphine reacts with platinum(II) chloride, at room temperature, to form tri-*tert*-butylphosphonium tetrachloroplatinate(II) (**1**) and the internally metalated phosphine complex *trans*-chloro[2-methyl-2-(di-*tert*-butylphosphino)propyl]tri-*tert*-butylphosphineplatinum(II) (**2**).



2, M = Pt
4, M = Pd

The identities of the products were established by analytical data, by conductance and molecular weight measurements, and by ^{31}P and ^1H NMR, infrared, and electronic spectral measurements. Analytical, conductance, and molecular weight data are given in Table I. The NMR data are given in Table II.

Formulation of **1** as $((t\text{-}Bu)_3PH)_2PtCl_4$ is confirmed by analytical, conductance, and spectral data. Conductance data show it to be a 2:1 electrolyte[20] in nitromethane. Its ^1H NMR spectrum consists of two doublets in the 1:27 ratio. The low-field doublet (^1J(P–H) = 464 Hz) can be assigned to the proton directly bonded to the phosphorus and the upfield doublet (^3J(P–H) = 14.8 Hz) to the *tert*-butyl protons. As shown in Table II, the ^1H and the proton decoupled ^{31}P NMR data for **1** are in excellent agreement with those for $((t\text{-}Bu)_3PH)Cl$ and $((t\text{-}Bu)_3PH)[ZnCl_3(P(t\text{-}Bu)_3)]$. The ^1J(P–H) values for the $(t\text{-}Bu)_3PH^+$ cation compare well with the ^1J(P–H) values reported[21,22] for the R_3PH^+ cations. The infrared spectrum of **1** in the 4000–200-cm^{-1} region showed bands similar to those observed for $P(t\text{-}Bu)_3$ as well as additional bands at 2382, 885, and 323 cm^{-1}. The 2382- and 885-cm^{-1} bands can be assigned respectively to the P–H stretching and P–H bending frequencies[23] of the $((t\text{-}Bu)_3PH)^+$ cation, and the 323-cm^{-1} band can be assigned to the antisymmetric Pt–Cl stretching frequency[24] of the $PtCl_4^{2-}$ anion. The P–H stretching frequency for $((t\text{-}Bu)_3PH)Cl$ and $((t\text{-}Bu)_3PH)[ZnCl_3(P(t\text{-}Bu)_3)]$ was observed at 2410 and 2394 cm^{-1}, respectively; the P–H bending frequency was observed at 900 and 868 cm^{-1}, respectively. The UV–visible spectrum of **1**, in dichloromethane, showed absorptions at 20 703 cm^{-1} (ϵ 20), 24 894 cm^{-1} (ϵ 38.6), and 31 113 cm^{-1} (ϵ 100), which are in accord with the reported spectrum[25] for the $PtCl_4^{2-}$ anion.

Table I. Analytical, Conductance, and Molecular Weight Data

Compd	Mp, °C	% C		% H		% Cl		Mol wt[a]		Conductance[b]
		Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	
$((t\text{-Bu})_3PH)_2PtCl_4$[c,d]	170 dec	38.75	38.76	7.60	7.83	19.06	18.33			132
$PtCl(C_4H_8P(t\text{-Bu})_2)(P(t\text{-Bu})_3)$[e]	239 dec	45.44	45.53	8.43	8.52	5.58	6.03	634	601	10
$PdCl_2(P(t\text{-Bu})_3)_2$	209 dec	49.51	49.78	9.36	9.47	12.18	12.35	580	528	20
$PdCl(C_4H_8P(t\text{-Bu})_2)(P(t\text{-Bu})_3)$	142 dec	52.82	52.74	9.81	9.96	6.49	6.39	545	510	10
$((t\text{-Bu})_3PH)_2PdCl_4$	100 dec	44.01	44.26	8.56	8.73	21.70	21.59			112

[a] In benzene; concentration range 10^{-2} to 10^{-3} M. [b] In Ω^{-1} cm^2 mol^{-1}; 10^{-3} M solution in nitromethane. [c] % Pt: calcd, 26.23; found, 25.75. [d] % P: calcd, 8.33; found, 8.16. [e] % Pt: calcd, 30.75; found 30.80.

Table II. ^{1}H and ^{31}P NMR Data

Compd	^{1}H NMR data				^{31}P NMR data		
	δ(C–H)[a]	δ(P–H)[a]	J(P–C–C–H)[d]	J(P–H)[d]	δ[f]	J(Pt–P)[d]	J(P–P)[d]
$P(t\text{-Bu})_3$	−1.26[b]		10.0		−60.9		
$((t\text{-Bu})_3PH)Cl$	−1.72[b]	−7.3[b]	15.0	464	−46.3		
$((t\text{-Bu})_3PH)_2(PtCl_4)$	−1.80[b]	−7.4[b]	14.8	464	−40.0		
$((t\text{-Bu})_3PH)_2(PdCl_4)$	−1.72[b]	−8.4[b]	15.0	476	−43.2		
$PtCl(C_4H_8P(t\text{-Bu})_2)P(t\text{-Bu})_3$	−1.62[b]		12.4		−66.8[b]	2680	383
	−1.56[b]		11.5		+12.8[b]	2360	382
	−1.48[b]		12.7				
$PdCl(C_4H_8P(t\text{-Bu})_2)(P(t\text{-Bu})_3)$	−1.35[b]		13.6		−61.8		
	−1.21[b]		12.0		+11.8		
	−1.17[b]		14.0				
$PdCl_2(P(t\text{-Bu})_3)_2$	−1.53[c]		12.6[e]		−83.6		
$((t\text{-Bu})_3PH)[ZnCl_3(P(t\text{-Bu})_3)]$	−1.72[b]	−6.93[b]	15.0	474	−44.6		
	−1.59[b]		12.5		−37.4		

[a] In ppm relative to $Me_4Si = 0$; benzene solutions for nonionic compounds; CH_2Cl_2 solutions for ionic compounds. [b] A 1:1 doublet. [c] A 1:2:1 triplet. [d] In Hz. [e] ^3J(P–H) + ^5J(P–H). [f] In ppm relative to 85% $H_3PO_4 = 0$; benzene solutions for nonionic compounds; CH_2Cl_2 solutions for ionic compounds.

The analytical data and the measured molecular weight of **2** agree well with the proposed formulation. The conductance data show it to be a nonelectrolyte in nitromethane. Proton-decoupled ^{31}P NMR spectrum of **2** unequivocally establishes the presence of two nonequivalent phosphorus nuclei, each showing coupling with each other as well as with the ^{195}Pt nucleus. The downfield doublet is assigned to the unmetalated phosphine on the basis of the chemical shift of the free phosphine, and the upfield doublet to the metalated phosphine which is expected to experience an increase in electron density from the methylene group bonded to the metal. ^1J(Pt–P) and ^2J(P–P′) values observed for **2** are in accord with the values reported[10,11] for other internally metalated phosphine complexes of platinum(II). The large value of ^2J(P–P′) shows that the two phosphorus nuclei are trans[26,27] to each other.

The proton NMR spectrum of **2** is also consistent with the proposed formulation. The spectrum exhibits 3 distinct sets of doublets in the ratio of 18:27:6. These doublets are assigned, respectively, to the two *tert*-butyl protons on the metalated phosphine, to the *tert*-butyl group of the unmetalated phosphine, and to the two methyl groups attached to the third tertiary carbon of the metalated phosphine. In addition to these doublets, a few other very low intensity peaks are also evident in the spectrum which may be assigned to the methylene protons which are nonequivalent and can experience additional coupling with the ^{195}Pt nucleus. The infrared spectrum of **2** showed a medium intensity band at 248 cm^{-1} which can be assigned to the stretching frequency of the Pt–Cl bond trans to a Pt–C bond. The low value of the Pt–Cl stretching frequency in **2** is in accord with the reported Pt–Cl stretching frequencies[10,11] in compounds containing a Pt–Cl bond trans to the Pt–C bond.

In view of the normal synthetic route to complexes of the type *trans*-PtX_2L_2, where L is a tertiary phosphine, the reaction of $P(t\text{-Bu})_3$ and Na_2PtCl_4 was carried out. Surprisingly, no *trans*-$PtCl_2(P(t\text{-Bu})_3)_2$ was isolated. Instead, the internally metalated phosphine complex (structure **2**) and $((t\text{-Bu})_3PH)_2PtCl_4$ were the only products obtained. The reaction of $PtCl_2(C_6H_5CN)_2$ and the phosphine also gave the metalated product **2**. However, $PtCl_2$(COD), COD = cycloocta-1,5-diene, did not undergo any reaction with tri(*tert*-butyl)phosphine. In any of the reactions of $P(t\text{-Bu})_3$ with Pt(II), no evidence was found for the presence of *cis*- or *trans*-$PtCl_2(P(t\text{-Bu})_3)_2$ in the reaction products even when shorter reaction periods were used.

Reaction of $PdCl_2$(COD) with tri-*tert*-butylphosphine afforded a solid which was characterized to be *trans*-$PdCl_2(P(t\text{-Bu})_3)_2$ (**3**) by elemental analyses, molecular weight and conductance measurements, and infrared and NMR measurements. The conductance and molecular weight data show it to be a molecular species. The proton NMR spectrum of **3** consisted of a 1:2:1 triplet characteristic of mutually trans phosphine groups,[10,27,28] with ^3J(P–H) + ^5J(P–H) = 12.6 Hz. The infrared spectrum of **3** showed a single Pd–Cl stretching frequency at 366 cm^{-1} similar to that exhibited by *trans*-PdX_2PR_3 complexes.[29-31] The proton-decoupled ^{31}P NMR spectrum of **3** showed a single peak. In benzene solution, **3** is slowly converted into the internally metalated phosphine complex, *trans*-chloro[2-methyl-2-(di-*tert*-butylphosphino)propyl]tri-*tert*-butylphosphinepalladium(II) (**4**). The identity of the metalated complex was established by analytical and molecular weight data as well as by spectroscopic data. The proton NMR spectrum of **4** is similar to that of the platinated phosphine complex consisting of three distinct sets of doublets in 18:27:6 ratio. Just like the platinum complex, these doublets are assigned to the metalated phosphine *tert*-butyl groups, the unmetalated phosphine, and the methyl groups attached to the third tertiary carbon of the metalated phosphine. Some very low intensity peaks were also observed in the spectrum which can be attributed to the methylene group bonded to the palladium atom. The proton-decoupled ^{31}P NMR spectrum exhibited the presence of two kinds of phosphorus nuclei, consistent with one metalated and one unmetalated phosphine. However, unlike the metalated platinum(II) complex **2**, the palladium(II) complex **4** does not show coupling between the two phosphorus nuclei, which indicates that the coordinated phosphine in the metalated palladium complex is labile. The low $\nu_{(Pd-Cl)}$ value[32] of 250 cm^{-1} observed for **4** is consistent with the proposed trans structure. Reaction of tri-*tert*-butylphosphine with Na_2PdCl_4 or $PdCl_2(C_6H_5CN)_2$ also resulted in the initial isolation of the *trans*-$PdCl_2(P(t\text{-}Bu)_3)_2$ complex, which subsequently underwent internal metalation in benzene, at room temperature, to give **4** and $((t\text{-}Bu)_3PH)_2PdCl_4$ (**5**).

The reaction of $PdCl_2$ and $P(t\text{-}Bu)_3$ yielded a mixture of *trans*-$PdCl_2(P(t\text{-}Bu)_3)_2$ (**3**), the metalated complex *trans*-$PdCl\{C_4H_8P(t\text{-}Bu)_2\}P(t\text{-}Bu)_3$ (**4**), and the ionic compound $((t\text{-}Bu)_3PH)_2PdCl_4$ (**5**). The identity of the tetrachloropalladate salt was established by elemental analyses, conductivity data, and spectral measurements. Its conductance in nitromethane showed that it is a 2:1 electrolyte.[20] Its infrared spectrum showed characteristic bands at 2300, 905, and 349 cm^{-1} due to the P–H stretching,[23] P–H bending,[23] and Pd–Cl stretching[33] frequencies, respectively. The electronic spectrum of **5** in methylene chloride showed bands at 32 260 cm^{-1} (ϵ 2525), 43 700 cm^{-1} (ϵ 8795), and 50 000 cm^{-1} ($\epsilon >$ 10 000) which are very similar to those observed in the electronic spectra of solutions of Na_2PdCl_4 or K_2PdCl_4 in CH_2Cl_2. The proton NMR spectrum showed two doublets in the ratio of 1:27, quite characteristic of the tri-*tert*-butylphosphonium cation. The proton-decoupled ^{31}P NMR spectrum of **5** showed a single resonance at 43 ppm downfield from orthophosphoric acid, consistent with the chemical shifts of $[(t\text{-}Bu)_3PH]Cl$ and $((t\text{-}Bu)_3PH)_2PtCl_4$ which are −46.3 and −40.0 ppm, respectively.

The reaction of tri-*tert*-butylphosphine with platinum(II) or palladium(II) chloride can, therefore, be represented as shown below. The fact that *trans*-$PdCl_2(P(t\text{-}Bu)_3)_2$ can be

$$MCl_2 + 2P(t\text{-}Bu)_3 \rightarrow trans\text{-}MCl_2(P(t\text{-}Bu)_3)_2$$

$$trans\text{-}MCl_2(P(t\text{-}Bu)_3)_2 \rightarrow MCl(C_4H_8P(t\text{-}Bu)_2)P(t\text{-}Bu)_3 + HCl$$

$$2HCl + trans\text{-}MCl_2(P(t\text{-}Bu)_3)_2 \rightarrow ((t\text{-}Bu)_3PH)_2MCl_4$$

isolated at room temperature whereas the analogous platinum complex is not isolable under similar conditions implies that the platinum complex undergoes internal metalation at a much faster rate than the palladium complex. In a study of internal metalation of platinum(II) and palladium(II) complexes of the type *trans*-MCl_2L_2, where M = Pt or Pd and L = $P(t\text{-}Bu)(p\text{-}tolyl)_2$, $P(t\text{-}Bu)(n\text{-}Pr)_2$, $P(t\text{-}Bu)_2Ph$, $P(t\text{-}Bu)_2(p\text{-}tolyl)$, or $P(t\text{-}Bu)_2(n\text{-}Pr)$, Shaw and co-workers[10] found that the platinum(II) complexes undergo internal metalation upon heating but the corresponding palladium(II) complexes remain unchanged. Failure of the palladium(II) complexes to undergo internal metalation has been attributed to the reluctance of palladium(II) to undergo oxidative addition to form the palladium(IV) intermediate. Our results on the metalation of tri(*tert*-butyl)phosphine are in accord with this suggestion.

Facile metalation of tri-*tert*-butylphosphine by platinum(II) as well as by palladium(II) is in marked contrast with the stability of platinum(II) and palladium(II) complexes of tri-*o*-tolylphosphine.[34] Tolman[35,36] has introduced the concept of ligand cone angle to measure the steric effects of substituents in phosphorus ligands and he has calculated the cone angles for a large number of phosphorus ligands. According to the cone angle values proposed by Tolman, tri(*tert*-butyl)phosphine is more sterically hindered than the mixed *tert*-butylphosphines used by Shaw and co-workers,[10] but it is less bulky than tri-*o*-tolylphosphine for which a cone angle of 195° has been proposed.[35,36] In view of the marked tendency of tri(*tert*-butyl)phosphine to form internally metalated complexes which contain a four-membered ring we believe that tri-*tert*-butylphosphine has much greater steric requirement than tri-*o*-tolylphosphine. From a crystallographic study of the complex anion $(NiBr_3P(t\text{-}Bu)_3)^-$ the Ni–$P(t\text{-}Bu)_3$ cone angle has been determined to be 180 ± 2°.[17] Thus the cone angle for tri-*o*-tolylphosphine should be significantly smaller than that proposed by Tolman.

Experimental Section

Reagents and Chemicals. Tri-*tert*-butylphosphine was prepared as described previously.[18] All operations involved in the reactions of tri-*tert*-butylphosphine and subsequent handling of the products were carried out either in a glovebox under an atmosphere of oxygen-free dry nitrogen or in a conventional vacuum system. All solvents were dried by standard methods and stored appropriately prior to use. Platinum(II) and palladium(II) salts were obtained from Johnson Matthey and Mallory Ltd. Cycloocta-1,5-diene and benzonitrile complexes of Pt(II) and Pd(II) were prepared by literature methods.[37,38]

Physical Measurements. Elemental analyses were performed by M.H.W. Laboratories, Garden City, Mich., by Galbraith Laboratories, Knoxville, Tenn., or by Alfred Bernhardt Microanalysis Laboratorium, West Germany. Infrared spectra were recorded either on a Beckman IR-12 or on a Perkin-Elmer 180 spectrophotometer. Spectra of the complexes were measured in the solid state. Samples were prepared either as KBr or CsI disks or as mulls in Nujol or halocarbon oil. ^{31}P NMR spectra were obtained with a Bruker HFX-90 Fourier transform spectrometer and ^1H NMR spectra were recorded on Varian A-60 and HA-100 spectrometers. All spectral measurements were carried out at ambient temperatures. Electronic spectra were recorded on a Cary 118 spectrophotometer. Conductance measurements were made on a Yellow Springs Instrument Model 31 conductivity bridge using a conductivity cell with platinized platinum electrodes. Molecular weights were measured with a Hitachi Perkin-Elmer 115 osmometer. Melting points were determined with a Gallenkamp melting point apparatus in glass capillary tubes and are uncorrected.

Reaction of Tri-*tert*-butylphosphine with Platinum(II) Chloride. (a) A yellowish solution with some suspended solid was formed when a mixture of $P(t\text{-}Bu)_3$ (2 mmol) and $PtCl_2$ (1 mmol) in 25 mL of benzene was stirred for 3 days. Filtration gave a light orange solid and a light yellow solution. The solid was washed with benzene and dissolved in dichloromethane. Upon adding hexane or petroleum ether to this solution, a very light orange solid was obtained which was characterized as $((t\text{-}Bu)_3PH)_2PtCl_4$, yield 90%. The light yellow filtrate was evaporated to give a pale yellow solid which was recrystallized from hexane to give a pale white solid which was found to be $PtCl(C_4H_8P(t\text{-}Bu)_2)P(t\text{-}Bu)_3$, yield 70%.

(b) When the above reaction was carried out in dichloromethane, an orange-red solution containing some dark solid was formed. After filtration and evaporation of the filtrate, a cream colored solid was obtained which was dissolved in dichloromethane. Upon adding hexane to the solution, $((t\text{-}Bu)_3PH)_2PtCl_4$ was obtained as a pale orange precipitate, yield 85%. Concentration of the filtrate gave $PtCl(C_4H_8P(t\text{-}Bu)_2)P(t\text{-}Bu)_3$, yield 70%.

Reaction of Tri-*tert*-butylphosphine with Dichlorodibenzonitrileplatinum(II). A yellow solution was formed when $PtCl_2(C_6H_5CN)_2$ (1 mmol) and $P(t\text{-}Bu)_3$ (2 mmol) were stirred in 25 mL of benzene for 3 h. The solution was filtered and evaporated to give a light yellow solid which was recrystallized from hexane to give $PtCl(C_4H_8P(t\text{-}Bu)_2)P(t\text{-}Bu)_3$.

Attempted Reaction between Tri-*tert*-butylphosphine and Dichlorocycloocta-1,5-dieneplatinum(II). No reaction was observed when $PtCl_2(COD)$ and $P(t\text{-}Bu)_3$ in 1:2 mole ratio were stirred in benzene or in dichloromethane at room temperature for up to 7 days.

Reaction of Tri-*tert*-butylphosphine with Sodium Tetrachloroplatinate(II). $P(t\text{-}Bu)_3$ (2 mmol) and Na_2PtCl_4 (1 mmol) were stirred in 25 mL of methanol to give a red-orange solution. A tan solid was obtained after filtration and evaporation. Extraction of the solid with hexane gave a light yellow solution and an orange-brown solid. The light yellow solution yielded $PtCl\{C_4H_8P(t\text{-}Bu)_2\}P(t\text{-}Bu_3)$. The orange-brown solid was recrystallized from a mixture of dichloromethane and hexane to give $[(t\text{-}Bu)_3PH]_2PtCl_4$. Similar products were obtained from the reaction of $P(t\text{-}Bu)_3$ and K_2PtCl_4.

Reaction of Tri-*tert*-butylphosphine with Dichlorocycloocta-1,5-dienepalladium(II). (a) $P(t\text{-}Bu)_3$ (2 mmol) and $PdCl_2(COD)$ (1 mmol) were stirred in 25 mL of dichloromethane for 2 days to give a red-orange solution. Filtration and subsequent evaporation of the filtrate yielded an orange solid which was recrystallized from hexane to give *trans*-$PdCl_2(P(t\text{-}Bu)_3)_2$, yield 50%.

(b) A dark red solution was formed when $PdCl_2(COD)$ and $P(t\text{-}Bu)_3$, in 1:2 mole ratio, were stirred in benzene for 24 h. Upon removing the solvent a yellow-orange solid was obtained which was extracted with hexane to give a yellowish orange solution and an orange solid which was characterized to be $((t\text{-Bu})_3PH)_2PdCl_4$. Removal of the solvent from the yellowish orange solution gave a yellow solid which was found to be a mixture of *trans*-$PdCl_2(P(t\text{-Bu})_3)_2$ and $PdCl(C_4H_8P(t\text{-Bu})_2)(P(t\text{-Bu})_3)$ as shown by its ^{31}P NMR. It was dissolved in benzene and the solution was stored at room temperature for 1 week. Removal of the benzene and treatment of the resulting solid with hexane gave a pale yellow solution and a yellowish orange residue. Pale yellow $PdCl(C_4H_8P(t\text{-Bu})_2)(P(t\text{-Bu})_3)$ was isolated by evaporating the hexane solution. The yellowish orange solid was found to be $((t\text{-Bu})_3PH)_2PdCl_4$.

Reaction of Tri-*tert*-butylphosphine with Sodium Tetrachloropalladate(II). $P(t\text{-Bu})_3$ (2 mmol) and Na_2PdCl_4 (1 mmol) were stirred in 25 mL of CH_2Cl_2 for 24 h. A deep red solution was formed initially which later became yellow. Filtration yielded a yellow-orange filtrate from which a yellow solid was obtained upon removing the solvent. The solid was recrystallized from hexane to give a pale yellow solid which was characterized to be *trans*-$PdCl_2(P(t\text{-Bu})_3)_2$, yield 60%. When methanol was used as a solvent, approximately the same yield was obtained at a much shorter reaction period. Reaction of K_2PdCl_4 and $P(t\text{-Bu})_3$, under similar conditions, gave a poor yield of *trans*-$PdCl_2(P(t\text{-Bu})_3)_2$.

Reaction of Tri-*tert*-butylphosphine with Dichlorodibenzonitrilepalladium(II). Reaction of $PdCl_2(C_6H_5CN)_2$ and $P(t\text{-Bu})_3$ in 1:2 mole ratio, in CH_2Cl_2 with stirring for 3 h, gave *trans*-$PdCl_2(P(t\text{-Bu})_3)_2$ in 80% yield.

Reaction of Tri-*tert*-butylphosphine with Palladium(II) Chloride. (a) $P(t\text{-Bu})_3$ (2 mmol) and $PdCl_2$ (1 mmol) were stirred in 25 mL of dichloromethane for 3 days to give a dark-colored solution. Filtration gave a red-brown solution which when stripped of solvent gave a dark brown solid. The solid was extracted with hexane or petroleum ether giving a light yellow filtrate and a brownish orange solid which was found to be $((t\text{-Bu})_3PH)_2PdCl_4$. The light yellow filtrate yielded a pale yellow solid which was found to be a mixture of *trans*-$PdCl_2(P(t\text{-Bu})_3)_2$, and $PdCl(C_4H_8P(t\text{-Bu})_2)P(t\text{-Bu})_3$.

(b) When the above reaction was carried out in benzene, a greenish yellow solution was initially formed. Upon filtering the solution and evaporating the filtrate, a mixture of *trans*-$PdCl_2(P(t\text{-Bu})_3)_2$, $((t\text{-Bu})_3PH)_2PdCl_4$, and $PdCl(C_4H_8P(t\text{-Bu})_2)P(t\text{-Bu})_3$ was obtained.

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Registry No. **1**, 63230-82-0; **2**, 63230-78-4; **3**, 63230-79-5; **4**, 63230-80-8; **5**, 63230-81-9; $PtCl_2(C_6H_5CN)_2$, 14873-63-3; $PdCl_2(C_6H_5CN)_2$, 14220-64-5; Na_2PtCl_4, 10026-00-3; Na_2PdCl_4, 13820-53-6; $PdCl_2(COD)$, 12107-56-1; $PtCl_2$, 10025-65-7; $PdCl_2$, 7647-10-1; $P(t\text{-Bu})_3$, 13716-12-6; $((t\text{-Bu})_3PH)Cl$, 63197-35-3; $((t\text{-Bu})_3PH)[ZnCl_3(P(t\text{-Bu})_3)]$, 62598-25-8.

References and Notes

(1) Presented in part at the Centennial Meeting of the American Chemical Society, New York, N.Y., April 1976.
(2) Postdoctoral Teaching/Research Associate, University of Guelph, 1976.
(3) G. W. Parshall, *Acc. Chem. Res.*, **3**, 139 (1970).
(4) G. W. Parshall, *Acc. Chem. Res.*, **8**, 113 (1975).
(5) M. A. Bennett and D. L. Milner, *J. Am. Chem. Soc.*, **91**, 6983 (1969).
(6) W. Keim *J. Organomet. Chem.*, **14**, 179 (1968).
(7) W. Keim *J. Organomet. Chem.*, **19**, 161 (1969).
(8) R. P. Stewart, Jr., L. R. Isbrandt, J. J. Benedict, and J. G. Palmer, *J. Am. Chem. Soc.*, **98**, 3215 (1976), and references therein.
(9) M. Preece, S. D. Robinson, and J. N. Wingfield, *J. Chem. Soc., Dalton Trans.*, 613 (1976), and references therein.
(10) A. J. Cheney, B. E. Mann, B. L. Shaw, and R. M. Slade, *J. Chem. Soc. A*, 3833 (1971).
(11) A. J. Cheney and B. L. Shaw, *J. Chem. Soc. A*, 754, 860 (1972).
(12) D. F. Gill, B. E. Mann, and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 270 (1973).
(13) C. E. Jones, B. L. Shaw, and B. L. Turtle, *J. Chem. Soc., Dalton Trans.*, 992 (1974).
(14) J. Chatt and J. M. Davidson, *J. Chem. Soc.*, 843 (1965).
(15) S. Bresadola, P. Rigo, and A. Turco, *Chem. Commun.*, 1205 (1968).
(16) A. A. Kiffen, C. Masters, and L. Raynand, *J. Chem. Soc., Dalton Trans.*, 853 (1975).
(17) E. C. Alyea, A. Costin, G. T. Fey, G. Ferguson, R. G. Goel, and R. J. Restivo, *J. Chem. Soc., Dalton Trans.*, 1294 (1975).
(18) E. C. Alyea, G. Fey, and R. G. Goel, *J. Coord. Chem.*, **5**, 143 (1976).
(19) (a) H. D. Empsall, E. M. Hyde, and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1690 (1975); (b) R. Mason, M. Textor, N. Al-Salem, and B. L. Shaw, *J. Chem. Soc., Chem. Commun.*, 292 (1976).
(20) W. J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).
(21) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy", Vol. 2, Pergamon, Oxford, 1966.
(22) V. Mark, C. H. Dungan, M. M. Crutchfield, and J. R. Van Wazer, *Top. Phosphorus Chem.*, **5**, 227 (1967).
(23) D. E. Corbridge, *Top. Phosphorus Chem.*, **6**, 235 (1967).
(24) D. M. Adams and D. C. Newton, *J. Chem. Soc. A*, 2998 (1969).
(25) D. S. Martin, *Adv. Chem. Ser.*, **No. 98** (1971).
(26) *Spectrosc. Prop. Inorg. Organomet. Compd.*, **2**, 19 (1969), and references therein.
(27) A. Pidcock and J. F. Nixon, *Annu. Rev. NMR Spectrosc.*, **2**, 345 (1969).
(28) R. K. Harris, *Can. J. Chem.*, **42**, 2275 (1964).
(29) D. M. Adams, J. Chatt, J. Gerratt, and A. D. Westland, *J. Chem. Soc. A*, 734 (1964).
(30) R. J. Goodfellow, J. G. Evans, R. L. Goggin, and D. A. Duddell, *J. Chem. Soc. A*, 1604 (1968).
(31) K. Shobatake and K. Nakamoto, *J. Am. Chem. Soc.*, **92**, 3332 (1970).
(32) B. Crociani, T. Boschi, R. Pietropaolo, and U. Belluco, *J. Chem. Soc. A*, 531 (1970).
(33) P. J. Hendra, *J. Chem. Soc. A*, 1298 (1967).
(34) M. A. Bennett and P. A. Longstaff, *J. Am. Chem. Soc.*, **91**, 6266 (1969).
(35) C. A. Tolman, *J. Am. Chem. Soc.*, **92**, 2956 (1970).
(36) C. A. Tolman, *Chem. Rev.*, **77**, 313 (1977).
(37) J. R. Doyle, P. E. Slade, and H. B. Jonassen, *Inorg. Synth.*, **6**, 216 (1960).
(38) D. Drew and J. R. Doyle, *Inorg. Synth.*, **13**, 47 (1972).