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A CONVENIENT SYNTHESIS OF BIS(TRI-t-BUTYLPHOSPHINE)PLATINUM(0) AND ITS OXIDATIVE ADDITION AND LIGAND EXCHANGE REACTIONS *

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Summary

$Pt[P(t\text{-}Bu)_3]_2$ (I) is prepared in high yield from a facile reaction of $P(t\text{-}Bu)_3$ with K_2PtCl_4. Its oxidative addition reactions with $CHCl_3$, CH_2Cl_2, MeI, and I_2, and substitution reactions with CO, $M(CO)_6$ (M = Cr, Mo, W), and t-BuNC have been investigated. Reaction with $CHCl_3$ affords *trans*-$PtHCl[P(t\text{-}Bu)_3]_2$ (II) and $[\overline{Pt(\mu\text{-}Cl)\{P(t\text{-}Bu)_2CMe_2C}H_2\}]_2$ (III), and reaction with CH_2Cl_2 yields $\overline{PtCl\{P(t\text{-}Bu)_2CMe_2C}H_2\}P(t\text{-}Bu)_3$ (IV). $Pt_2Me_2(\mu\text{-}I)_2[P(t\text{-}Bu)_3]_2$ (VI) and $P(t\text{-}Bu)_3$-MeI are formed in the reaction of I with MeI. VI undergoes intramolecular metalation to give $[\overline{Pt(\mu\text{-}I)\{P(t\text{-}Bu)_2CMe_2C}H_2\}]_2$ (V), and CH_4. Reaction of I with I_2 results in the formation of V, *trans*-$PtHI[P(t\text{-}Bu)_3]_2$ (VII) and $P(t\text{-}Bu)_3I_2$. CO readily displaces one phosphine from I to give $Pt_3[P(t\text{-}Bu)_3]_3(CO)_3$ (VIII). I reacts with $M(CO)_6$ to afford VIII and $M(CO)_5P(t\text{-}Bu)_3$. t-BuNC replaces both the phosphines from I to give $Pt_3(t\text{-}BuNC)_3(\mu\text{-}t\text{-}BuNC)_3$ (IX).

Introduction

Several two-coordinate platinum(0) complexes, PtL_2, where L = a bulky tertiary phosphine such as $P(t\text{-}Bu)_3$, $PPh(t\text{-}Bu)_2$, $P(c\text{-}C_6H_{11})_3$ or $P(i\text{-}Pr)_3$ have been reported [1] recently. Reactions [2] of these novel complexes with the exception of the tri-tert-butylphosphine complex have also been investigated. The tri-tert-butylphosphine complex (I), unlike other platinum(0) phosphine complexes, is unaffected by molecular oxygen and as such it has been described [2] as inert and its chemistry has hitherto remained unexplored.

The reported synthesis of I involves reaction of the phosphine with $Pt(COD)_2$

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[3] (COD = 1,5-cyclooctadiene) which is not easily accessible. In the course of our investigations on the reactions of tri-tert-butylphosphine with platinum metals [4,5], it was discovered that I can be prepared in high yield from the reaction of the phosphine with the commercially available potassium tetrachloroplatinate. Furthermore, measurements of its ^{1}H NMR spectrum in chloroform and dichloromethane showed that it slowly reacts with both solvents at room temperature. Therefore, oxidative addition as well as substitution reactions of I were examined. Reactions of I with protic acids providing convenient synthetic routes for the hydrido complexes, *trans*-$PtHX[P(t\text{-}Bu)_3]_2$ and *trans*-$PtH_2[P(t\text{-}Bu)_3]_2$ have been reported [6]. Oxidative addition reactions with chloroform, dichloromethane, methyl iodide and iodine and substitution reactions with carbon monoxide, Group VI metal hexacarbonyls and tri-tert-butylisocyanide are reported herein.

Results and discussion

Reaction of $P(t\text{-}Bu)_3$ with an alcoholic solution of K_2PtCl_4 and KOH afforded I in over 80% yield. Its ^{1}H NMR spectrum in benzene was identical to that reported by Otsuka and coworkers [1] and its ^{31}P NMR spectrum in the same solvent showed a main peak at δ 99.5 ppm and two satellite peaks due to ^{195}Pt—P spin coupling [^1J(Pt—P) = 4420 Hz)].

Addition reactions

$Pt[P(t\text{-}Bu)_3]_2$ dissolves in chloroform to give a dark greenish solution and the ^{1}H NMR of a freshly prepared solution consists of a 1 : 2 : 1 triplet due to the t-Bu protons of I. Within a few hours the solution became yellow and its ^{1}H NMR spectrum, in the t-butyl region, showed an additional triplet due to *trans*-$PtHCl[P(t\text{-}Bu)_3]_2$ (II) [6]. The intensity of the triplet due to I decreased with time with a concomitant increase in the intensity of the triplet due to II. After one week, the solution became colourless and its ^{1}H and ^{31}P NMR spectra were identical to those of an authentic sample of II [6]. Removal of chloroform and recrystallization of the solid from hexane afforded II as the sole platinum containing species in 90% yield. When a freshly prepared solution of I in $CHCl_3$ was refluxed for an hour, a colourless solution was obtained, and the ^{31}P and ^{1}H NMR spectral measurements showed it to contain II and the chloro-bridged dinuclear metalated complex $[\overline{Pt(\mu\text{-}Cl)\{P(t\text{-}Bu)_2CMe_2C}H_2\}]_2$ (III) (Fig. 1, X = Cl) [7].

The products formed in the reaction of I with $CHCl_3$ can be rationalized in terms of reactions represented by eq. 1 to 4.

$$Pt[P(t\text{-}Bu)_3]_2 + CHCl_3 \rightarrow trans\text{-}PtH(CCl_3)[P(t\text{-}Bu)_3]_2 \quad (1)$$

$$trans\text{-}PtH(CCl_3)[P(t\text{-}Bu)_3]_2 \rightarrow trans\text{-}PtHCl[P(t\text{-}Bu)_3]_2 + (CCl_2) \quad (2)$$

$$trans\text{-}PtHCl[P(t\text{-}Bu)_3]_2 \rightarrow trans\text{-}\overline{PtCl[P(t\text{-}Bu)_2CMe_2C}H_2]P(t\text{-}Bu)_3 + H_2 \quad (3)$$

$$2\ trans\text{-}\overline{PtCl[P(t\text{-}Bu)_2CMe_2C}H_2]P(t\text{-}Bu)_3 \rightarrow [\overline{Pt(\mu\text{-}Cl)\{P(t\text{-}Bu)_2CMe_2C}H_2\}]_2 + 2\ P(t\text{-}Bu)_3 \quad (4)$$

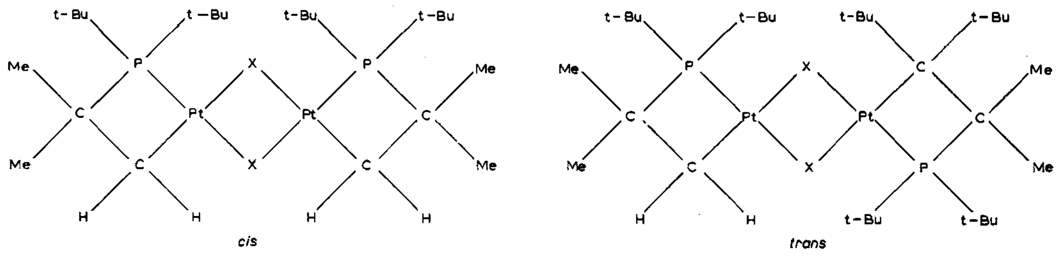


Fig. 1. Structures of complexes III and V.

Evidence for reactions 3 and 4 is provided by independent studies [6,7] on the solution behaviour of *trans*-$PtHCl[P(t\text{-}Bu)_3]_2$ and *trans*-$\overline{PtCl[P(t\text{-}Bu)_2CMe_2CH_2]}$-$P(t\text{-}Bu)_3$ (IV).

The ^1H NMR spectrum of I in CH_2Cl_2 (Table 1) showed, after 24 h, additional peaks in the t-butyl region. After three weeks the ^1H and ^{31}P NMR spectra of the solution indicated complete conversion of I into the metalated complex IV [4] which was recovered from the solution in almost quantitative yield. These results indicate that I reacts slowly with CH_2Cl_2 according to eq. 5 and the resulting product is rapidly converted into IV as represented by eq. 6.

$$Pt[P(t\text{-}Bu)_3]_2 + CH_2Cl_2 \rightarrow trans\text{-}PtCl(CH_2Cl)[P(t\text{-}Bu)_3]_2 \quad (5)$$

$$trans\text{-}PtCl(CH_2Cl)[P(t\text{-}Bu)_3]_2 \rightarrow trans\text{-}\overline{PtCl[P(t\text{-}Bu)_2CMe_2CH_2]}P(t\text{-}Bu)_3 + CH_3Cl \quad (6)$$

No reaction occurred upon mixing equimolar amounts of I and methyl

TABLE 1

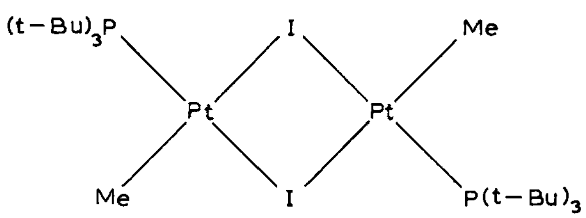
^1H AND ^{31}P-{^1H}NMR SPECTRAL DATA

Complexes	Solvent	^1H NMR		^{31}P-{^1H} NMR	
		δ (ppm)	^3J(P—H) (Hz)	δ (ppm)	J(Pt—P) (Hz)
$Pt[P(t\text{-}Bu)_3]_2$ [a, b]	C_6D_6	t-Bu, 1.47(t)	11.2 [c]	99.5(s)	4420
$P(t\text{-}Bu)_3MeI$	CH_2Cl_2	t-Bu, 1.62(d)	14.5	50.6(s)	
		Me, 2.00(d)	11.0		
$[\overline{Pt(\mu\text{-}I)\{P(t\text{-}Bu)_2CMe_2CH_2\}}]_2$	C_6D_6	t-Bu, 1.31(d)	13.7	−11.9(s)	3560
		CMe_2, 1.26(d)	11.0	−10.9(s)	3560
		CH_2, 1.20(d)	11.7		
$[Pt(\mu\text{-}I)\{P(t\text{-}Bu)_3\}Me]_2$	C_6D_6	t-Bu, 1.02(d)	12.5	44.8(s)	4180
		Me, 2.22(d) [d]	3.0		
$P(t\text{-}Bu)_3I_2$	CH_2Cl_2	t-Bu, 1.70(d)	16.0	81.4(s)	
$Pt_3[P(t\text{-}Bu)_3]_3(CO)_3$	C_6D_6	t-Bu, 1.55(d)	11.2	[e]	
$Pt_3[t\text{-}BuNC]_3[\mu\text{-}t\text{-}BuNC]_3$	C_6D_6	t-Bu, 1.82(s)			
		t-Bu, 1.36(s)			

Abbreviations: s, singlet; d, 1 : 1 doublet; t, 1 : 2 : 1 triplet. [a] In $CHCl_3$: δ = 5.77(t) ppm upfield from $CHCl_3$ [^3J(P—H) + ^5J(P—H) = 11.6 Hz]. [b] In CH_2Cl_2: δ = 3.81(t) ppm upfield from CH_2Cl_2 [^3J(P—H) + ^5J(P—H) = 11.5 Hz]. [c] ^3J(P—H) + ^5J(P—H). [d] ^2J(Pt—CH_3) = 104 Hz. [e] See text.

iodide in benzene or hexane at room temperature. When a benzene or hexane solution containing I and methyl iodide, in 1 : 2 mole ratio, was stirred for 36 h, $P(t\text{-}Bu)_3MeI$ precipitated and the iodo-bridged dinuclear metalated complex $[\overline{Pt(\mu\text{-}I)\{P(t\text{-}Bu)_2CMe_2C}H_2\}]_2$ (V) was recovered from the filtrate as the sole platinum-containing species. $P(t\text{-}Bu)_3MeI$ is an air-stable white solid which is soluble in polar solvents such as dichloromethane. Its ^1H and $^{31}P\text{-}\{^1H\}$ NMR spectral data in dichloromethane are given in Table 1. V is also an air-stable white solid which is soluble in benzene. Its molecular weight in benzene was in excellent agreement with the proposed formulation which is also supported by the ^1H and ^{31}P NMR and the infrared spectral data. Its ^1H NMR spectrum in benzene (Table 1) showed a pattern typical [6,7] of an internally metalated tri-t-butylphosphine group. The ^{31}P NMR spectrum of V in the same solvent showed two main resonances close to each other and with the same value of ^1J(Pt—P), which is in accord with the presence of both the *cis* and *trans* isomers of the dinuclear metalated complex V, (Fig. 1, X = I). The infrared spectrum of V showed a strong band at ca. 135 cm^{-1} attributable to the stretching involving the Pt—I bridge bonds [8].

Addition of methyl iodide to a benzene solution of I, in 2 : 1 mole ratio, gave a white suspension of $P(t\text{-}Bu)_3MeI$ in an orange solution which was found by ^1H NMR spectral measurement to contain some unreacted I and methyl iodide, and a new species subsequently characterized to be a novel dinuclear methylplatinum(II) complex VI (Fig. 2). ^1H NMR spectral measurements at 30 minute intervals for the next 4 hours showed a gradual increase in the intensity of the signals due to VI with concomitant decrease in the intensity of the triplet due to I. After 24 hours, the triplet due to I disappeared, the resonances due to VI became much more intense and additional weak signals attributable to V (Fig. 1, X = I) appeared. Examination of the ^1H NMR spectrum of the solution after another day showed resonances due to only V in the $P(t\text{-}Bu)_3$ region and a singlet at —0.47 ppm relative to external TMS, found to be due to methane. Addition of a benzene solution of methyl iodide to a benzene solution of I in 5 : 1 mole ratio resulted in rapid precipitation of $P(t\text{-}Bu)_3MeI$. The mother liquor afforded a mixture of VI and unreacted I which were separated by treatment with cold hexane. The molecular weight of VI in benzene was in good agreement with the proposed dinuclear formulation. The ^1H and $^{31}P\text{-}\{^1H\}$ NMR spectral data for VI are listed in Table 1. The ^1H NMR shifts for the methyl groups bonded to platinum in complexes of the



(VI)

Fig. 2. Structure of complex VI.

types $PtMeXL_2$ or $PtMe_2L_2$, where L = a tertiary phosphine or a similar ligand, usually occur [9] near or even upfield from TMS. The downfield shift observed for VI (δ = 2.22 ppm) is explicable in terms of electron deficiency at the platinum. Interestingly, the observed ^1J(Pt—P) value for VI is one of the largest ^1J(Pt—P) values reported [10] for a platinum(II) complex. The infrared spectrum of VI, in the solid state, showed a medium-strong band at 520 cm^{-1} attributable to the Pt—CH_3 stretching frequency [11] and a strong band at 165 cm^{-1} due to the bridging Pt—I stretching frequency [8]. Thus, the molecular weight data together with the ^1H and ^{31}P NMR and the infrared spectral data for VI provide convincing evidence for the proposed dinuclear structure (Fig. 2). The observation of a single resonance in the ^{31}P NMR spectrum and the appearance of only one Pt—CH_3 stretching frequency in the infrared appear to indicate the presence of only the *trans* isomer.

VI undergoes intramolecular metalation in the solid state as well as in solution to give methane and the iodobridged dinuclear metalated complex, V. Elemental analysis of an analytically and spectroscopically pure sample of VI changed upon storing at room temperature for about a week, and the ^{31}P NMR spectrum of a freshly prepared solution of the stored sample showed resonances due to both V and VI. Metalation occurred much more rapidly in solution. A freshly prepared and spectroscopically pure solution of VI in benzene, after being stirred for about 5 hours at room temperature, was found to contain about 80% VI and 20% V as shown by ^{31}P NMR spectral measurement. The spectral measurement after 48 hours showed complete conversion of VI into V.

The conversion of VI into V and methane was also confirmed by ^1H NMR spectral measurements. The ^1H NMR spectrum of a freshly prepared sample of VI in deuterated benzene showed characteristic doublets due to $P(t\text{-}Bu)_3$ and the methyl group bonded to platinum. When the solution was allowed to stand for 24 hours, at room temperature, the doublet in the t-butyl region was replaced by three doublets characteristic of V, the doublet and the accompanying satellite peaks due to the methyl group bonded to platinum disappeared, and a strong peak at —0.47 ppm (relative to external TMS) due to methane appeared.

Thus, the overall reaction of I with methyl iodide seems to involve reactions represented by eq. 7 to 9 and can be represented by eq. 10.

$$2\ Pt[P(t\text{-}Bu)_3]_2 + 2\ MeI \rightarrow 2\ trans\text{-}PtMeI[P(t\text{-}Bu)_3]_2 \quad (7)$$

$$2\ trans\text{-}PtMeI[P(t\text{-}Bu)_3]_2 + 2\ MeI \rightarrow Pt_2Me_2(\mu\text{-}I)_2[P(t\text{-}Bu)_3]_2 + 2\ P(t\text{-}Bu)_3MeI \quad (8)$$

$$Pt_2Me_2(\mu\text{-}I)_2[P(t\text{-}Bu)_3]_2 \rightarrow [\overline{Pt(\mu\text{-}I)\{P(t\text{-}Bu)_2CMe_2C}H_2\}]_2 + 2\ CH_4 \quad (9)$$

$$2\ Pt[P(t\text{-}Bu)_3]_2 + 4\ MeI \rightarrow \overline{Pt(\mu\text{-}I)\{P(t\text{-}Bu)_2CMe_2C}H_2\}]_2 + 2\ P(t\text{-}Bu)_3MeI + 2\ CH_4 \quad (10)$$

Addition of an equimolar amount of I_2 to a solution of I in benzene or hexane resulted in the precipitation of $P(t\text{-}Bu)_3I_2$ which was isolated and characterized. Its ^1H and $^{31}P\text{-}\{^1H\}$ NMR spectral data are given in Table 1. The filtrate was found to contain the iodo-bridged dinuclear metalated complex V (Fig. 1, X = I) and the hydrido complex, *trans*-$PtHI[P(t\text{-}Bu)_3]_2$, VII, which were separated and characterized unequivocally by the analytical, molecular weight and the spectral data. The ^{1}H and ^{31}P NMR and infrared spectral data for V have been discussed earlier; the spectral data for VII were identical to those for an authentic sample of *trans*-$PtHI[P(t\text{-}Bu)_3]_2$ prepared from the reaction of I with HI [6]. The molecular weights for both V and VII, in benzene, were also in excellent agreement with the proposed formulations. From these results it is apparent that the following reactions are involved in the reaction of I with I_2.

$$Pt[P(t\text{-}Bu)_3]_2 + I_2 \rightarrow trans\text{-}PtI_2[P(t\text{-}Bu)_3]_2 \quad (11)$$

$$trans\text{-}PtI_2[P(t\text{-}Bu)_3]_2 \rightarrow trans\text{-}\overline{PtI[P(t\text{-}Bu)_2CMe_2C}H_2]P(t\text{-}Bu)_3 + HI \quad (12)$$

$$Pt[P(t\text{-}Bu)_3]_2 + HI \rightarrow trans\text{-}PtHI[P(t\text{-}Bu)_3]_2 \quad (13)$$

$$trans\text{-}PtHI[P(t\text{-}Bu)_3]_2 \rightarrow trans\text{-}\overline{PtI[P(t\text{-}Bu)_2CMe_2C}H_2]P(t\text{-}Bu)_3 + H_2 \quad (14)$$

$$2\ trans\text{-}\overline{PtI[P(t\text{-}Bu)_2CMe_2C}H_2]P(t\text{-}Bu)_3 \rightarrow [\overline{Pt(\mu\text{-}I)\{P(t\text{-}Bu)_2CMe_2C}H_2\}]_2 + 2\ P(t\text{-}Bu)_3 \quad (15)$$

$$P(t\text{-}Bu)_3 + I_2 \rightarrow P(t\text{-}Bu)_2I_2 \quad (16)$$

Evidence for reactions 14 and 15 is available from independent studies on the intramolecular metalation of the hydrido complexes, *trans*-$PtHX[P(t\text{-}Bu)_3]_2$ [6].

Substitution reactions

Carbon monoxide readily reacts with I according to eq. 17 to give the orange-red trinuclear cluster, $Pt_3[P(t\text{-}Bu)_3]_3(CO)_3$, (VIII) (Fig. 3, R = t-Bu)

$$3\ Pt[P(t\text{-}Bu)_3]_3 + 3\ CO \rightarrow Pt_3[P(t\text{-}Bu)_3]_3(CO)_3 + 3\ P(t\text{-}Bu)_3 \quad (17)$$

quantitatively. The trimeric formulation of VIII was confirmed by the molecular weight measurement in benzene.

Trinuclear clusters, $Pt_3(PR_3)_3(CO)_3$, containing other tertiary phosphine have been reported by other workers [2,12]. After the completion of this work, a brief report on VIII has also appeared [12d]. A structure of D_{3h} skeletal symmetry similar to that shown in Fig. 3 has been proposed for such complexes on the basis of the NMR and infrared spectral data [2,12]. Unfortunately, the structural conclusions are based either on erroneous reasonings * or contradictory observations **. Fast ligand exchange on the NMR time scale as reported for some such complexes [12a,12c] can create problems in the interpretation of the NMR data, and distortions from the idealized symmetry as found in the case of $Pt_3[P(c\text{-}C_6H_{11})_3(CO)_3$ [12a] can invalidate structural conclusions based on the CO stretching frequencies. The infrared spectrum of VIII, in the CO stretching region, shows two strong bands at ca.

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* The conclusion of previous workers [2,12d] that the observation of two CO stretching frequencies in the infrared is consistent with structure of D_{3h} skeletal symmetry is contrary to the group theoretical prediction of only one infrared CO stretching frequency.

** For example, Otsuka and coworkers [2] have reported two infrared frequencies in the bridging CO stretching region for $Pt_3[P(t\text{-}Bu)_2Ph]_3(CO)_3$ whereas Clark and coworkers [12c] report only one such frequency for $Pt_3(PR_3)_3(CO)_3$.

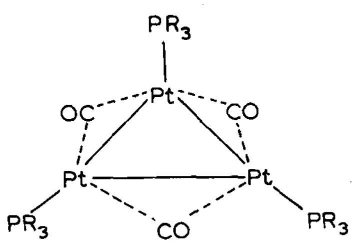


Fig. 3. Proposed structure of complex VIII.

1785 and 1730 cm^{-1} in the solid state as well as in solution in dichloromethane. These frequencies are similar to those reported by Otsuka and coworkers [2] and indicate a trimeric structure of lower than D_{3h} symmetry similar to that found for $Pt_3[P(c\text{-}C_6H_{11})_3]_3(CO)_3$. Since the CO stretching frequencies in the solid state are almost identical to those in solution, the compound is indicated to have a similar structure in the solid state as well as in solution. The ^1H NMR spectrum of VIII in dichloromethane (Table 1) is not affected by the addition of some free phosphine to the solution. The possibility of phosphine exchange on the NMR time scale can, therefore, be ruled out. The ^{31}P-$\{^1H\}$ NMR spectrum of VIII is shown in Fig. 4. The spectrum can be interpreted [13] by con-

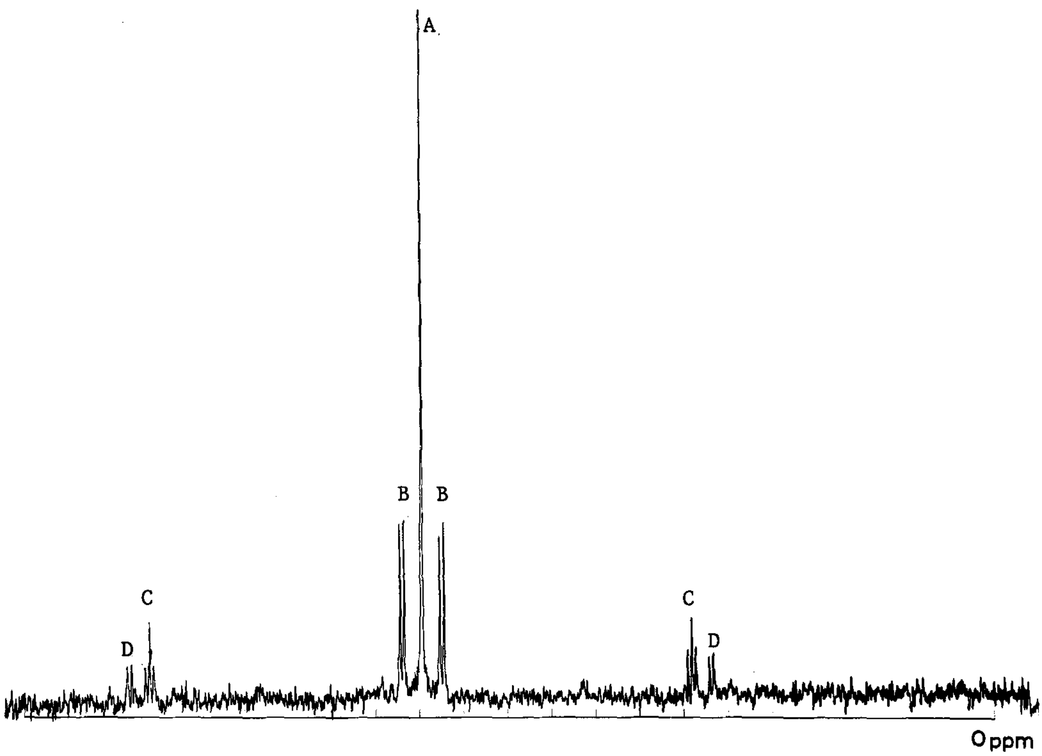
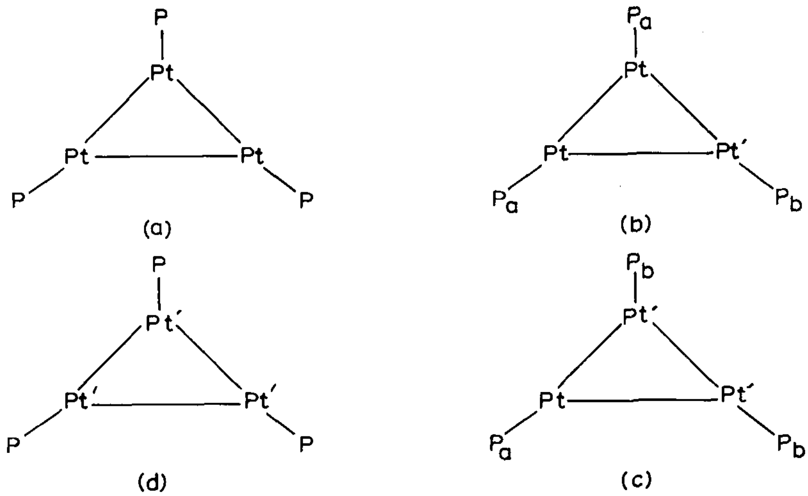


Fig. 4. ^{31}P-$\{^1H\}$ spectrum of $Pt_3[P(t\text{-}Bu)_3]_3(CO)_3$.

sidering that VIII exists as a mixture of four magnetic isomers, (a—d) [Pt and Pt′ represent Pt having I = 0 and 1/2, respectively].



The isomer a, with all three platinum nuclei having I = 0 gives rise to a single line (A in Fig. 4) at 94.8 ppm. Two doublets (B in Fig. 4) centered at 86.9 and 102.5 ppm arise due to P_a nuclei of the isomer b which are coupled to the ^{195}Pt[^2J(Pt—P_a) = 388.5 Hz] as well as to the phosphorus P_b [^3J(P_a—P_b) = 39.1 Hz]. P_b of isomer b appears as two triplets (C in Fig. 4) centred at —12.7 and 202.2 ppm, due to coupling with ^{195}Pt[^1J(Pt—P_b) = 5279.6 Hz] and P_a nuclei [^3J(P_a—P_b) = 39.1 Hz]. The P_b nuclei of isomer c give rise to two doublets (D in Fig. 4), centred at —20.5 and 210.0 ppm, due to coupling with ^{195}Pt[^1J-(Pt—P_b) + ^2J(Pt—P_b) * = 5598.2 Hz] and P_a[^3J(P_b—P_a) = 41.5 Hz]. The expected lines for P_a as well as P nuclei of isomer d are not observed due to their very low relative intensities [<4% in case of isomer d].

I also reacts with chromium(0), tungsten(0) and molybdenum(0) hexacarbonyls, $M(CO)_6$ in THF according to eq. 18:

$$3\ Pt[P(t\text{-}Bu)_3]_2 + 3\ M(CO)_6 \rightarrow VIII + 3\ M(CO)_5P(t\text{-}Bu)_3 \qquad (18)$$

Reactions with $Cr(CO)_6$ and $W(CO)_6$ are, however, very sluggish. When equimolar amounts of I and $Cr(CO)_6$ or $W(CO)_6$ were allowed to react in refluxing THF for ~15 hours, the product was found (by IR and ^{1}H NMR) to be a mixture containing VIII, $M(CO)_5P$(t-Bu)$_3$ and about 60% unreacted I and the hexacarbonyl (see Experimental). Separation of individual components proved difficult. Reaction with $Mo(CO)_6$ was complete in ~20 h at 25—30°C. The IR and ^{1}H NMR spectra of the product showed it to be a 1 : 1 mixture of VIII and $Mo(CO)_5P$(t-Bu)$_3$. Repeated washing of the mixture with hexane and acetone afforded ~90% pure VIII. Concentration of the washings and sublimation of the resulting solid gave pure $Mo(CO)_5P$(t-Bu)$_3$. The complexes $M(CO)_5P$(t-Bu)$_3$ have been previously prepared by the irradiation of a mixture

* Due to magnetically inequivalent $Pt^{1/2}$ nuclei [cf. ref. 13] of c.

of $M(CO)_6$ and $P(t\text{-}Bu)_3$ [14]. The infrared spectra for the three $M(CO)_5P$-(t-Bu)$_3$ complexes were identical to those reported [14] by previous workers.

Treatment of I with an excess tert-butyl isocyanide afforded an orange-red solid found to be the trinuclear complex, $Pt_3(t\text{-}BuNC)_3(\mu\text{-}t\text{-}BuNC)_3$, IX, previously prepared by Stone and coworkers [16] by the reaction of t-BuNC with $Pt(COD)_2$. The infrared spectrum of IX in the region 1700—2200 cm^{-1} was identical to that reported by Stone and coworkers [15]. The ^1H NMR spectrum of IX in deuterated benzene showed two singlets at δ 1.82 and 1.36 ppm in 1 : 1 intensity ratio. The former may be assigned to bridging t-BuNC as the protons are expected to be more shielded due to comparatively larger $Pt\rightarrow L$ back bonding. The latter singlet is assigned to the terminal t-BuNC group.

When I and t-BuNC were allowed to react in equimolar quantities only IX was isolated along with unreacted I. This shows that isocyanides are stronger bases towards Pt^0 than tertiary phosphines or carbon monoxide.

In summary, results reported herein clearly show that I undergoes oxidative addition as well as substitution reactions with a variety of substrates. Although I is not as reactive as platinum(0) complexes of less bulky phosphines, it appears to have an interesting chemistry as shown by the formation of unexpected and often novel products in its reactions.

Experimental section

General

All operations involved in the preparation of tri-tert-butylphosphine and its complexes and subsequent reactions of these complexes were carried out under an atmosphere of oxygen-free dry argon using a glove-box (Vacuum Atmospheres Corporation) and standard vacuum techniques.

Physical measurements

Elemental analyses were performed either by M.H.W. Laboratories, Phoenix, Arizona, or by Guelph Chemical Laboratory, Guelph, Ontario. Melting points were determined with a Gallenkamp melting point apparatus and are uncorrected. Infrared spectra were determined with a Perkin-Elmer 180 double beam spectrophotometer using sealed KBr liquid cells or KBr, KRS-5 and polyethylene demountable cells. Spectra in the solid state were obtained with samples prepared as mulls in Nujol and halocarbon oil. ^1H NMR spectra were recorded either on a Varian A60 or a Varian EMK39 or a Bruker WP60 FT spectrometer; the reported chemical shifts, δ, are in ppm with reference to internal TMS; positive values are downfield from TMS. $^{31}P\text{-}\{^1H\}$ spectra were measured with a Bruker WP60 FT spectrometer using 85% H_3PO_4 as external reference; the positive δ values are downfield from 85% H_3PO_4. Molecular weights were determined either in benzene or 1,2-dichloroethane with a Hitachi-Perkin-Elmer 115 osmometer.

Materials

Tri-tert-butylphosphine was prepared as described previously [16]. Platinum sponge was supplied by Johnson Mathey and Mallory Limited and was converted into potassium tetrachloroplatinate(II) by a reported method [17].

Pentane and benzene were dried over sodium wire and distilled. Chloroform and dichloromethane were stored over molecular sieves prior to use. Carbon monoxide from Matheson was purified by passing through a column of KOH pellets. Other chemicals were used as received.

Preparation of $Pt[P(t\text{-}Bu)_3]_2$, I

Tri-tert-butylphosphine (4.1 mmol) and potassium tetrachloroplatinate (2 mmol) were successively added to deoxygenated absolute ethanol (25 ml) containing KOH (3 mmol). The reaction mixture was stirred at 35—40°C for ~48 h. The solvent was removed under vacuum and the residue extracted with hexane (~30 ml). The extract was concentrated to ~5 ml and cooled to give colourless crystals of $Pt[P(t\text{-}Bu)_3]_2$ in ~80% yield. M.p. 237°C (dec) [lit [1], M.p. 234—238°C (dec)]. Anal. Found: C, 48.38; H, 9.16. Calcd. for $PtC_{24}H_{54}P_2$: C, 48.05; H, 9.07%.

Reactions of I with chloroform and dichloromethane

(a) In a typical experiment 0.1 mmol I was dissolved in $CHCl_3$ or CH_2Cl_2 (ca. 1.5 ml) and the ^1H NMR spectra of the solutions were recorded immediately. The solutions were allowed to stand at room temperature, and their ^1H NMR spectra were recorded periodically until completion of the reaction.

(b) A solution of 0.4 mmol I in $CHCl_3$ (30 ml) was stirred for a week at room temperature. The $CHCl_3$ was then removed under reduced pressure and the residue extracted with hexane (~35 ml). Concentration of the extract to about 2 ml and cooling gave colourless crystalline *trans*-$PtHCl[P(t\text{-}Bu)_3]_2$, II, in 80% yield, m.p. 215°C. Anal. Found: C, 44.9; H, 8.62; Cl, 5.31; Mol. wt. 620 (benzene). Calcd. for $PtC_{24}H_{55}P_2Cl$: C, 45.2; H, 8.65; Cl, 5.59%; Mol. wt. 635. ^1H NMR (C_6H_6): $P(t\text{-}Bu)_3$, 1.55 (t) [^3J(P—H) + ^5J(P—H) = 12.6 Hz]; (Pt—H), —18.4 ppm (t) [^1J(Pt—H) = 1072 Hz]. ^{31}P-{H} NMR (C_6H_6): 75.0 ppm [^1J-(Pt—P) = 2959 Hz]. IR: ν(Pt—H), 2382 cm^{-1}.

(c) A solution of 0.33 mmol I in 20 ml $CHCl_3$ was refluxed for ~1 h to give a colourless solution. Upon cooling to room temperature and removing the solvent a sticky solid was obtained which was extracted with benzene. The ^{31}P-{^1H} NMR spectrum of the benzene solution showed characteristic peaks due to *trans*-$PtHCl[P(t\text{-}Bu)_3]_2$ [75.0 ppm (t); ^1J(Pt—P) = 2959 Hz], and [$Pt(\mu\text{-}Cl)$-{$P(t\text{-}Bu)_2CMe_2CH_2$}$]_2$ (III) [—16.38 ppm; ^1J(Pt—P) = 3760 Hz] and —15.98 ppm [^1J(Pt—P) = 3740 Hz].

(d) A solution of I (0.4 mmol) in dichloromethane (20 ml) was refluxed for ~1 h. The ^1H NMR spectrum of the solution showed peaks due to I as well as some additional peaks. The solution was kept at room temperature for three weeks. Removal of the solvent in vacuo and recrystallization of the residue from hexane gave $PtCl[P(t\text{-}Bu)_2CMe_2CH_2]P(t\text{-}Bu)_3$, (IV), (~80% yield), m.p. 239°C. Anal. Found: C, 45.53; H, 8.53; Cl, 6.03; Mol. wt. 640 (benzene). Calcd. for $PtC_{24}H_{53}P_2Cl$: C, 45.4; H, 8.43; Cl, 5.58%; Mol. wt. 633. ^1H NMR (CH_2Cl_2): 1.62 (d) [^3J(P—H) = 12.4 Hz], 1.56 (d) [^3J(P—H) = 11.5 Hz], 1.48 ppm (d) [^3J(P—H) = 12.7 Hz]; integrated intensity ratio, 1.62: 1.56: 1.48 ppm = 27 : 18 : 6. ^{31}P-{^1H} NMR (C_6D_6): 66.8 (d) [^2J(P—P) = 383 Hz, ^1J(Pt—P) = 2680 Hz], —12.8 ppm (d) [^2J(P—P) = 383 Hz, ^1J(Pt—P) = 2360 Hz].

Reaction of I with methyl iodide

(a) To a solution of I (0.33 mmol) in hexane (10 ml) was added, dropwise, with constant stirring, a solution of CH_3I (0.33 mmol) in 5 ml hexane. After stirring the mixture for an hour and subsequent evaporation under vacuum, I was recovered almost quantitatively.

(b) To a solution of I (0.33 mmol) in hexane (10 ml) was added a solution of methyl iodide (0.66 mmol) in hexane (25 ml) and the reaction mixture was stirred for ~36 h. An off-white solid which came out gradually was filtered, washed with hexane (2 × 5 ml) and recrystallized from a mixture of dichloromethane/hexane to give colourless $P(t\text{-}Bu)_3MeI$ (~0.32 mmol); m.p. 220°C, Anal. Found: C, 44.70; H, 8.67; I, 36.5. Calcd. for $C_{13}H_{30}IP$: C, 45.40; H, 8.72; I, 36.9%. The filtrate and washings were combined together and concentrated to give off-white $[\overline{Pt(\mu\text{-}I)\{P(t\text{-}Bu)_2CMe_2CH_2}\}]_2$, V, yield: (0.16 mmol) which was recrystallized from benzene/pentane. M.p. 230°C. Anal. Found: C, 27.80; H, 5.01; I, 24.10; Mol. wt. 1045 (benzene). Calcd. for $Pt_2C_{24}H_{52}P_2I_2$: C, 27.50; H, 4.96; I, 24.00%, Mol. wt. 1056.

(c) To a solution of 2 mmol I in 15 ml benzene was added dropwise with stirring, a solution of 10 mmol methyl iodide in 15 ml benzene. Halfway during the addition of CH_3I a white precipitate appeared and the reaction mixture became intense orange. The reaction mixture was stirred for ~1 h and then filtered. The precipitate was washed with benzene (2 × 4 ml) and recrystallized from dichloromethane/hexane to give $P(t\text{-}Bu)_3MeI$ (~0.20 mmol). The combined filtrate and washings were concentrated and the resulting orange residue was washed with hexane (2 × 5 ml) to remove unreacted I (~0.10 mmol) and then recrystallized from benzene/hexane to give orange VI (~0.1 mmol), m.p. 205°C. Anal. Found: C, 29.02; H, 5.77; I, 23.86; Mol. wt., 1045 (benzene). Calcd. for $C_{26}H_{60}P_2I_2Pt_2$: C, 28.90; H, 5.57; I, 23.60%; Mol. wt, 1078.

Reaction of I with iodine

(a) A solution of I_2 (0.33 mmol) in benzene (50 ml) was added dropwise (~1 h) to a stirred solution of 0.33 mmol I in 20 ml benzene at ~10°C. The iodine colour was discharged with each addition. At the end, an orange reaction mixture was obtained which was filtered to give an off-white solid which was recrystallized from dichloromethane to give ~0.15 mmol pure $P(t\text{-}Bu)_3I_2$; m.p. 152°C. Anal. Found: C, 30.97; H, 5.98; I, 55.90. Calcd. for $C_{12}H_{27}PI_2$: C, 31.7; H, 5.95; I, 55.7%. Removal of the solvent from the filtrate and extraction of the residue with hexane gave V (~0.08 mmol). The hexane extract was freed from the solvent under reduced pressure to give a white solid which was recrystallized from cold hexane to give *trans*-$PtHI[P(t\text{-}Bu)_3]_2$ (~0.15 mmol); m.p. 195°C. Anal. Found: C, 39.80; H, 7.69; I, 17.70%; Mol. wt. 730 (benzene). Calcd. for $C_{24}H_{55}P_2IPt$: C, 39.60; H, 7.55; I, 17.5%; Mol. wt. 727. ^1H NMR (C_6D_6): two triplets centred at 1.50 [$^3J(P-H)$ + $^5J(P-H)$ = 12.0 Hz] and −16.4 ppm [$^1J(Pt-H)$ = 1096 Hz] due to t-Bu and Pt—H protons, respectively. $^{31}P\text{-}\{^1H\}$ NMR (C_6D_6): 76.6 ppm [$^1J(Pt-P)$ = 2903 Hz].

(b) Reaction of I_2 with I in hexane also gave $P(t\text{-}Bu)_3I_2$, $[\overline{PtI\{P(t\text{-}Bu)_2CMe_2CH_2}\}]_2$ and *trans*-$PtHI[P(t\text{-}Bu)_3]_2$.

Reaction of I with carbon monoxide

Carbon monoxide was bubbled into a pentane (10 ml) solution of I (0.5

mmol) at room temperature for ~5 min. An orange-red solid which precipitated immediately was filtered, washed with pentane (2 × 5 ml) and dried. It was characterized as $Pt_3[P(t\text{-}Bu)_3]_3(\mu\text{-}CO)_3$, VIII (Yield >90%). Anal. Found: C, 36.69; H, 6.39%; Mol. wt. 1240 (benzene). Calcd. for $C_{39}H_{81}P_3O_3Pt_3$: C, 36.7; H, 6.41%; Mol. wt. 1276. M.p. 155—170°C (gradually turned brown and finally black without melting). The filtrate, on concentration, gave $P(t\text{-}Bu)_3$ which was identified by its ^1H NMR spectrum.

Reactions of I with Group VI metal hexacarbonyls

(a) Molybdenum hexacarbonyl (0.5 mmol) and I (0.5 mmol) were stirred (~15 h) together in THF (10 ml) at room temperature. The reddish reaction mixture was freed from the solvent under reduced pressure to give brown-red residue which, after being washed with pentane (4 × 10 ml) and acetone (3 × 5 ml), was found to be ~90% pure $Pt_3[P(t\text{-}Bu)_3]_3(CO)_3$ (>70% yield) as shown by its IR spectrum. The washings were concentrated to give a brown red residue which was sublimed at 80—100°C/10^{-3} mmHg to give pale yellow $Mo(CO)_5P(t\text{-}Bu)_3$ in ~50% yield. Anal. Found: C, 46.30; H, 6.25. Calcd. for $C_{17}H_{27}PO_5Mo$: C, 46.61; H, 6.16%. M.p. 188—190°C (lit. [5] m.p. 190°C) ^1H NMR (C_6D_6): 1.34 ppm (d) [$^3J(P—H)$ = 11.6 Hz]. $^{31}P\text{-}\{^1H\}$ NMR (C_6D_6): 103.4 ppm.

(b) Treatment of I with $Cr(CO)_6$ or $W(CO)_6$ under similar conditions gave a mixture containing only a small amount of $Pt_3[P(t\text{-}Bu)_3]_3(CO)_3$ and $M(CO)_5P(t\text{-}Bu)_3$ (M = Cr, Mo) and largely unreacted I as shown by ^1H NMR and IR spectra.

(c) An equimolar mixture of $Pt[P(t\text{-}Bu)_3]_2$ and $W(CO)_6$ was stirred (~15 h) in refluxing THF. Volatiles were removed in vacuo to give a dark-brown residue which was extracted with pentane (10 ml) and benzene (5 ml). Removal of the solvent from the extract gave an orange solid which was a mixture of unreacted I, $W(CO)_5P(t\text{-}Bu)_3$ and $Pt_3[P(t\text{-}Bu)_3]_3(CO)_3$ as shown by its ^1H NMR spectrum (C_6H_6). Sublimation of the orange residue at ~80°C/10^{-2} mmHg gave yellow $W(CO)_5P(t\text{-}Bu)_3$ (yield ~20%), m.p. 151°C (lit. [5] m.p. 150°C). Anal. Found: C, 38.62; H, 5.25. Calcd. for $C_{17}H_{27}PO_5W$: C, 38.81; H, 5.13%. ^1H NMR (C_6D_6): 1.33 ppm (d) [$^3J(P—H)$ = 11.8 Hz]. $^{31}P\text{-}\{^1H\}$ NMR (C_6D_6): 90.6 ppm [$^1J(W—P)$ = 231.9 Hz].

Reaction of I with tert-butylisocyanide

To a solution of I (0.5 mmol) in pentane (10 ml) was added dropwise tert-butylisocyanide (1.05 mmol) in the same solvent at room temperature with rapid stirring. An orange-red solid gradually came out which was filtered, washed with pentane (5 ml) containing a trace of the isocyanide followed by pure pentane (2 × 5 ml) and dried. It was characterized as $Pt_3(t\text{-}BuNC)_3(\mu\text{-}t\text{-}BuNC)_3$, IX, (yield ~70%). Anal. Found: C, 33.60; H, 5.00; N, 7.70. Calcd. for $C_{30}H_{54}N_6Pt_3$: C, 33.25; H, 4.98; N, 7.75%. M.p. 125—145°C (gradually turned brown and finally black without melting) IR (Nujol) 2200—1700 cm^{-1} region: 2142vs, 2090(sh), 1728s(sh) and 1705vs cm^{-1}. Filtrate on concentration afforded $P(t\text{-}Bu)_3$ as characterized by its ^1H NMR spectrum.

When I and t-BuNC were allowed to react as above in 1 : 1 molar ratio, IX (~40%) was isolated. The filtrate after concentration under reduced pressure was found to contain $P(t\text{-}Bu)_3$ as well as unreacted I (~50%).

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