Platinum Complexes Bridged by (Diphenylphosphino)cyclopentadienyl Ligands. Reactions with *tert*-Butyl Isocyanide or Phosphorus Ligands

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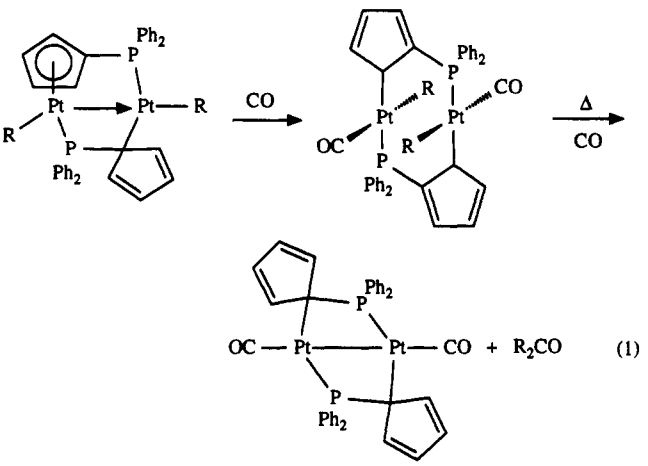
The complexes $[Pt_2R_2(\mu\text{-}C_5H_4PPh_2)_2]$ (1) react with 2 equiv of $CNBu^t$ to form the face-to-face dimers $[Pt_2R_2(CNBu^t)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]$ (2), in which the cyclopentadienyl rings of the bridging dppc ligands are 1,2-substituted by Pt and P. Addition of further $CNBu^t$ produces *cis*- and *trans*-$[PtR(CNBu^t)_2(C_5H_4PPh_2\text{-}P)]$ (3), in which the dppc ligands are coordinated through the P atom only. Reactions of $[Pt_2R_2(\mu\text{-}C_5H_4PPh_2)_2]$ with phosphorus ligands proceed either to form complexes of the type $[PtR(PR'_3)_2(C_5H_4PPh_2\text{-}P)]$ or (by reductive elimination of the appropriate alkane) to produce the platinum(I) dimers $[Pt_2(PR_3)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]$, the course of the reaction being dependent on the nature of the ligand and the solvent. Platinum(I) species of the type $[Pt_2(PR_3)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]$ may be prepared alternatively by displacement of carbon monoxide from $[Pt_2(CO)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]$. The NMR spectra of the platinum(I) compounds are discussed.

Introduction

The (diphenylphosphino)cyclopentadienyl (dppc) ligand has been used to prepare a number of bimetallic complexes, in which the five-membered ring functions as an η^5 ligand.[1,2] We have shown that diplatinum species of the type $[Pt_2R_2(\mu\text{-}C_5H_4PPh_2)_2]$ (**1a–e**; R = CH_3 (Me), C_2H_5 (Et), $CH_2C(CH_3)_3$ (neo-Pe), C_6H_5 (Ph), $CH_2C_6H_5$ (Bz)), adopt both symmetrical and unsymmetrical structures. The latter, in which one of the cyclopentadienyl rings is bound in an η^1 fashion, predominate in solution.[2] Recently, we have described the reactions of these complexes with carbon monoxide.[3] The initial reaction involves coordination of CO and rearrangement of the cyclopentadienyl rings to produce two η^1-bound ligands, 1,2-substituted by platinum and phosphorus. At suitable temperatures these complexes undergo carbonyl insertion and, ultimately, reductive elimination of a ketone from the bimetallic unit to produce the platinum(I) dimer $[Pt_2(CO)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]$ (eq 1). In this paper we report the reactions of $[Pt_2R_2(\mu\text{-}C_5H_4PPh_2)_2]$ and $[Pt_2(CO)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]$ with *tert*-butyl isocyanide and a number of phosphorus ligands.



(1)

Results and Discussion

When a benzene solution of $[Pt_2Me_2(\mu\text{-}C_5H_4PPh_2)_2]$ (**1a**) was treated with 2 equiv of $CNBu^t$, the face-to-face dimeric complex $[Pt_2Me_2(CNBu^t)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]$ (**2a**), containing two 1,2-substituted cyclopentadienyl moieties and a *trans* arrangement of the methyl and isocyanide ligands, was isolated in nearly quantitative yield. The product exhibits methyl, cyclopentadienyl, and ^{31}P resonances in its NMR spectra which are comparable to those found for $[Pt_2Me_2(CO)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]$,[3] indicating that it has a related structure. The analogous reaction of $[Pt_2Ph_2(\mu\text{-}C_5H_4PPh_2)_2]$ (**1d**) produced $[Pt_2Ph_2(CNBu^t)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]$ (**2d**; δ(P) 13.1, ^1J(Pt,P) = 3162 Hz) initially, but this species existed in solution for less than 30 min. After this solution stood, a white solid separated, which was insoluble in common organic solvents. We observed similar behavior in the reaction of **1d** with CO,[3] and in each case we assume that some oligomeric species is formed.

Addition of excess $CNBu^t$ to a CH_2Cl_2 solution of $[Pt_2Me_2(\mu\text{-}C_5H_4PPh_2)_2]$ (**1a**) resulted in cleavage of the platinum–cyclopentadienyl linkage and generation of a monomeric complex of the form *trans*-$[PtMe(CNBu^t)_2(C_5H_4PPh_2\text{-}P)]$ (*trans*-**3a**) (eq 2). The *trans* geometry follows from the small ^1J(Pt,P) coupling constant (Table 1) and the equivalence of the $C(CH_3)_3$ groups. The ^1H NMR spectrum exhibits only two signals for the C_5H_4 group, which remain unchanged on cooling to −50 °C. These results suggest that the cyclopentadienyl group is not fluxional but is uncoordinated, a conclusion that is supported by the observation of three doublets in the $^{13}C\{^1H\}$ NMR spectrum for the C_5H_4 moiety. The reaction of **1d** proceeded analogously to give *trans*-$[PtPh(CNBu^t)_2(C_5H_4PPh_2\text{-}P)]$ (*trans*-**3d**).

We propose zwitterionic structures for the monomeric species, as shown in eq 2. The molecular structure of $Ph_3PC_5H_5$ has been shown to exhibit approximately equal

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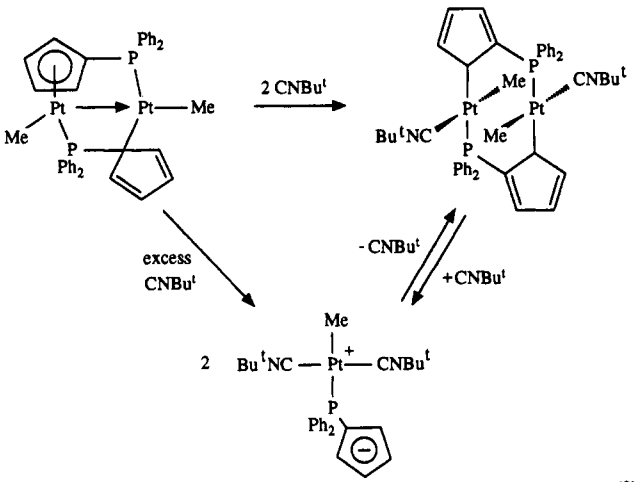
Table 1. $^{31}P\{^1H\}$ NMR Parameters for Complexes of the Type *cis*- or *trans*-$[PtRL_2(C_5H_4PPh_2\text{-}P)]^a$

			dppc		L		
	R	L	δ(P)	^1J(Pt,P)	δ(P)	^1J(Pt,P)	^2J(P,P′)
trans-**3a**	CH_3	$CNBu^t$	2.6	1569			
trans-**3b**	C_2H_5	$CNBu^t$	2.2	1396			
cis-**3b**			4.0	3193			
trans-**3c**	$CH_2C(CH_3)_3$	$CNBu^t$	−0.1	1432			
cis-**3c**			1.9	3144			
trans-**3d**	C_6H_5	$CNBu^t$	−2.1	1488			
trans-**13**	CH_3	PPh_3	3.0 t	1996	27.9 d	3019	22
cis-**13**			14.5 d	2890	30.5 d	2592	375, 21, 18
					22.5 d	1928	
trans-**14**	CH_3	$P(C_6H_4F\text{-}p)_3$	3.5 t	1870	27.3 d	3050	22
cis-**14**			13.8 d	2973	27.4 d	2543	378, 21, 18
					21.0 d	1990	
cis-**15**	CH_3	$P(OPh)_3$	12.6 d	2757	100.1 d	4275	554, 42, 34
					111.7 d	3177	

[a] In $CDCl_3$ solution. Coupling constants are in hertz.

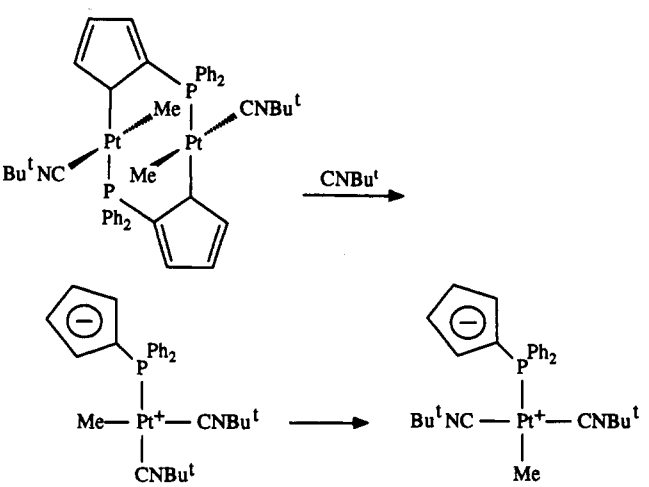


(2)

C–C bond distances, as expected for an aromatic C_5 ring, and it is best described as a phosphonium cyclopentadienide.[4] The NMR resonance for the ring carbons (particularly C_β and C_γ) found here are consistent with those for $Ph_3PC_5H_5$.[5,6] Perhaps more convincingly, the ^{13}C resonances for $[TlAu(C_5H_4PPh_2)_2]_2$, in which the P atom is coordinated to gold and the delocalized ring is only weakly bound to thallium, are strikingly similar to those observed here.[7]

The monomeric complexes *trans*-$[PtR(CNBu^t)_2(C_5H_4PPh_2\text{-}P)]$ (R = Me, Ph) decompose in solution over several days, even when kept at low temperature and under an atmosphere of argon. Thus, attempts to grow single crystals have been unsuccessful. The phenyl derivative has been isolated in analytically pure form, but the methyl compound loses $CNBu^t$ too readily. There is a dynamic equilibrium in solution between $[PtMe(CNBu^t)_2(C_5H_4PPh_2\text{-}P)]$ (**3a**), $[Pt_2Me_2(CNBu^t)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]$ (**2a**), and free $CNBu^t$. Thus, when **1a** was treated with 2 equiv of $CNBu^t$, the dimeric complex $[Pt_2Me_2(CNBu^t)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]$ was formed exclusively, but with 4 equiv of $CNBu^t$ an approximately 1:1 mixture of $[Pt_2Me_2(CNBu^t)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]$ and *trans*-$[PtMe(CNBu^t)_2(C_5H_4PPh_2\text{-}P)]$ was obtained, as evidenced by ^{31}P NMR spectroscopy. Only with 8 equiv of $CNBu^t$ was the monomeric species observed as the sole phosphorus-containing product. Attempts to isolate *trans*-$[PtMe(CNBu^t)_2(C_5H_4PPh_2\text{-}P)]$ by removal of solvent and free isocyanide resulted, therefore, in mixtures of the two isocyanide complexes.

When the reaction of **1a** with $CNBu^t$ was monitored by ^{31}P NMR spectroscopy over a period of *ca.* 1 h, it was found to be quite complicated. No reaction occurred when 4 equiv of $CNBu^t$ was added to a CH_2Cl_2 solution of **1a** at −50 °C. Warming to 25 °C for 10 min, however, resulted in several new species being formed. The predominant species initially was $[Pt_2Me_2(CNBu^t)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]$, although five other singlet resonances, each with ^{195}Pt satellites, were detected. Within a few minutes three of these resonances disappeared, leaving that due to *trans*-$[PtMe(CNBu^t)_2(C_5H_4PPh_2\text{-}P)]$ and a signal at δ(P) 3.2 (^1J(Pt,P) = 3084 Hz), which we assign to *cis*-$[PtMe(CNBu^t)_2(C_5H_4PPh_2\text{-}P)]$ (*cis*-**3a**). Finally, the latter isomerized to the *trans* form (eq 3). If displacement of



(3)

the cyclopentadienyl moiety from platinum in **2a** occurred in a stereospecific manner, as would be expected, then the *cis* isomer would indeed be formed first, although the *trans* isomer is apparently more stable thermodynamically.

The reactions of $[Pt_2R_2(\mu\text{-}C_5H_4PPh_2)_2]$ (R = Et, neo-Pe; **1b,c**) with $CNBu^t$ were also monitored by ^{31}P NMR spectroscopy. The ethyl derivative was treated with 1 equiv of $CNBu^t$ in CD_2Cl_2 solution at ambient temperature and allowed to react for a few minutes, then the solution was cooled to −40 °C. This process was repeated until a total of 4 equiv (2 equiv per platinum) had been added. During the early stages of the reaction a large number of

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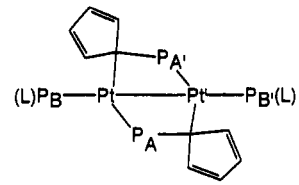
Table 2. $^{31}P\{^1H\}$ NMR Parameters for Complexes of the Type $[Pt_2L_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]^a$

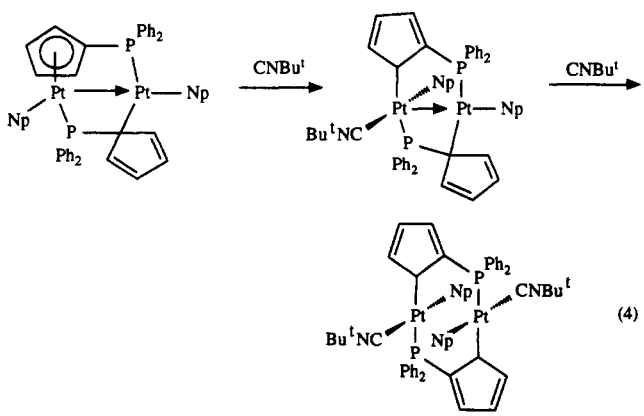


	L	$\delta(P_A)$	$^1J(P_A,Pt)$	$^2J(P_A,Pt')$	$^3J(P_A,P_{A'})$	$\delta(P_B)$	$^1J(P_B,Pt)$	$^2J(P_B,Pt')$	$^3J(P_B,P_{B'})$
4	$CNBu^t$	−1.2	3674	326	27				
	CO[d]	−1.1	3085	287	24				
5	PEt_3	−2.8	3747	288	30	11.6	3100	216	173
6	PMe_2Ph	−1.0	3591	274	30	−13.6	3150	262	190
7	PPh_3	−5.5	3450	309	30	21.1	3159	361	187
8	$P(CH_2CH_2CN)_3$	−5.2	3480	315	29	12.4	3035	326	195
9	PBz_3[b]	−6.4	3527	330	nr	−3.9	2950	320	207
10	PBu^i_3[b]	−3.5	3742	331	32	−1.0	2991	223	180
11	PCy_3[b]	−2.8	3749	335	31	26.8	2951	233	176
12	$P(OPh)_3$[b]	−7.7 t[c]	3118	339	26	107.8 t[c]	5070	588	511

[a] In $CDCl_3$ solution unless stated otherwise. Coupling constants are in hertz. nr = not resolved. [b] In C_6D_6 solution. [c] $J(P_A,P_B)$ 8 Hz. [d] Reference 3.

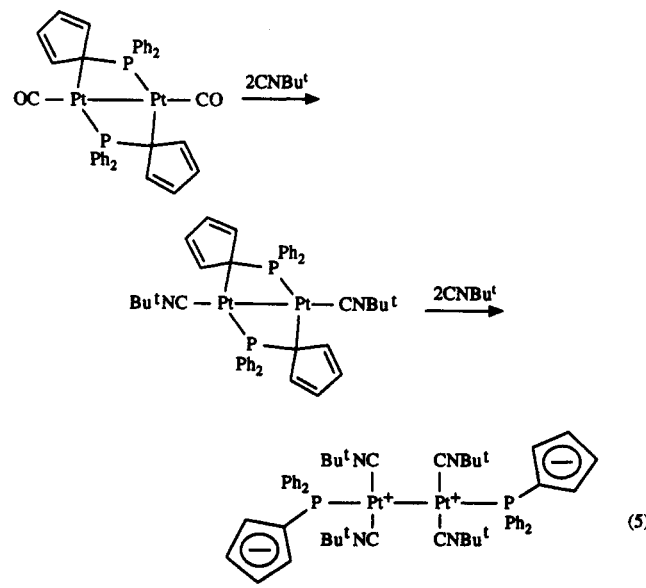
species were formed, the most abundant being $[Pt_2Et_2(CNBu^t)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]$ (**2b**; $\delta(P)$ 12.1, $^1J(Pt,P)$ = 3278 Hz) and *cis*-$[PtEt(CNBu^t)_2(C_5H_4PPh_2\text{-}P)]$ (*cis*-**2b**; $\delta(P)$ 4.0, $^1J(Pt,P)$ = 3193 Hz). On further $CNBu^t$ addition the signals associated with the monomeric complex increased in intensity, and when the complex stood, it isomerized to *trans*-**3b** (Table 1), which was the final product of the reaction.

When a d_8-toluene solution of the neopentyl derivative was treated in analogous fashion, two major species were detected after addition of only 1 equiv of isocyanide. One of these was *trans*-$[Pt(neo\text{-}Pe)(CNBu^t)_2(C_5H_4PPh_2\text{-}P)]$ (*trans*-**3c**) (Table 1), formed in this case at a much earlier stage in the reaction. The second was an unsymmetrical dimeric complex, which exhibited the following ^{31}P NMR parameters: $\delta(P)$ 17.7 d, $^1J(Pt,P)$ = 2844 Hz, $^2J(Pt,P)$ = 51 Hz, $^3J(P,P)$ = 23 Hz; $\delta(P)$ 30.0 d, $^1J(Pt,P)$ = 1942 Hz, $^2J(Pt,P)$ = 389 Hz, $^3J(P,P)$ = 23 Hz. The similarity of the NMR parameters to those found for $[(neo\text{-}Pe)(CO)Pt(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2Pt(CO\text{-}neo\text{-}Pe)]$[3] suggests that this complex has a related structure, and we propose that it is the product of addition of one $CNBu^t$ molecule to the dimeric unit, namely, $[(neo\text{-}Pe)(CNBu^t)Pt(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2Pt(neo\text{-}Pe)]$, in which one of the cyclopentadienyl groups is 1,1-substituted and the other is 1,2-substituted by Pt and P (eq 4; neo-Pe is denoted Np in this equation). Resonances



due to $[Pt_2(neo\text{-}Pe)_2(CNBu^t)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]$ (**2c**; $\delta(P)$ 14.0, $^1J(Pt,P)$ = 3380 Hz) and *cis*-$[Pt(neo\text{-}Pe)(CNBu^t)_2(C_5H_4PPh_2\text{-}P)]$ (*cis*-**3c**; $\delta(P)$ 1.9, $^1J(Pt,P)$ = 3144 Hz) were observed during the reaction sequence, but *trans*-**3c** was the major species present throughout, and it remained as the final product.

In contrast to the reactions with carbon monoxide,[3] there is no evidence for insertion into the platinum–alkyl bonds, and reductive elimination to form a platinum(I) dimer does not occur. Thus, $[Pt_2(CNBu^t)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]$ is not formed by addition of $CNBu^t$ to $[Pt_2R_2(\mu\text{-}C_5H_4PPh_2)_2]$, but it has been prepared by substitution of the terminal CO ligands in $[Pt_2(CO)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]$. The $^{31}P\{^1H\}$ NMR spectrum of $[Pt_2(CNBu^t)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]$ (**4**) is very similar to that of its carbonyl analogue, exhibiting short-range and long-range Pt–P couplings (Table 2). Addition of a further 2 equiv of $CNBu^t$ to $[Pt_2(CNBu^t)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]$ in CD_2Cl_2 solution produced an unstable species, which we have assigned as $[Pt_2(CNBu^t)_4(C_5H_4\text{-}PPh_2\text{-}P)_2]$ ($\delta(P)$ 18.7, $^1J(Pt,P)$ = 2124 Hz, $^2J(Pt,P)$ = 340 Hz, $^3J(P,P)$ = 124 Hz) (eq 5). The large $^3J(P,P)$ value is



indicative of a linear P–Pt–Pt–P unit, and the structure is related to the well-known platinum(I) isocyanide complexes of the type $[Pt_2(CNR)_6]^{2+}$.[8] Two multiplets are observed for the C_5H_4 hydrogens in the ^1H NMR spectrum ($\delta(H)$ 6.40 and 6.47), consistent with an uncoordinated cyclopentadienyl ring. $[Pt_2(CNBu^t)_4(C_5H_4\text{-}$

PPh_2-*P*)$_2$] decomposed readily in solution, however, and could not be isolated.

The course of the reaction between [$Pt_2Me_2(\mu$-$C_5H_4PPh_2)_2$] (**1a**) and a tertiary phosphine or phosphite ligand was found to be dependent on the nature of the ligand and on the solvent employed. In each of the reactions of **1a** with the small, strongly nucleophilic phosphines PEt_3, PBu^n_3, and PMe_2Ph a large number of products was formed. In contrast, the bulky trialkylphosphines PBz_3, PBu^i_3, and PCy_3 were found to react quite cleanly in C_6D_6 solution to generate the platinum(I) dimers [$Pt_2(PR_3)_2(\mu$-η^1-$C_5H_4PPh_2)_2$] (Table 2). Complexes of this type with PEt_3 or PMe_2Ph could be obtained, however, by displacement of CO from [$Pt_2(CO)_2(\mu$-η^1-$C_5H_4PPh_2)_2$] (*vide infra*).

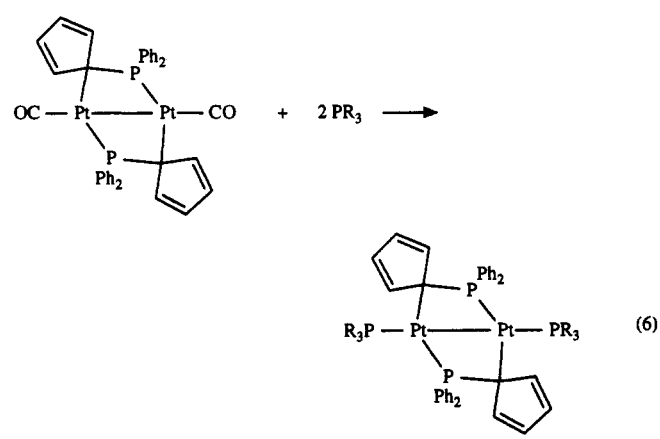
The reaction of **1a** with PPh_3 was studied in some detail. Addition of 2 equiv of PPh_3 in either $CDCl_3$ or C_6D_6 solution produced a mixture of *cis*- and *trans*-[PtMe(PPh_3)$_2$(C_5H_4-PPh_2-*P*)] (**13**) initially. $^{31}P\{^1H\}$ NMR data for these complexes are presented in Table 1. In $CDCl_3$ solution *cis*- and *trans*-[PtMe(PPh_3)$_2$($C_5H_4PPh_2$-*P*)] were gradually converted to *trans*-[PtClMe(PPh_3)$_2$] by chloride abstraction from the solvent. In C_6D_6 solvent, however, over a period of 7 days, signals due to [$Pt_2(PPh_3)_2(\mu$-η^1-$C_5H_4PPh_2)_2$] (**7**) (Table 2) appeared and grew in intensity. Similarly, reaction of **1a** with $P(C_6H_4F$-*p*$)_3$ in $CDCl_3$ solution produced *cis*- and *trans*-[PtMe{$P(C_6H_4F$-*p*$)_3$}$_2$-($C_5H_4PPh_2$-*P*)] (**14**) (Table 1), as well as *trans*-[PtClMe-{$P(C_6H_4F$-*p*$)_3$] (δ(P) 29.0, ^1J(Pt,P) = 2962 Hz), whereas in d_6-acetone only *cis*- and *trans*-[PtMe{$P(C_6H_4F$-*p*$)_3$}$_2$(C_5H_4-PPh_2-*P*)] were observed. When **1a** was treated with 2 equiv of $P(OPh)_3$ in $CDCl_3$ solution, the only product observed was *cis*-[PtMe{$P(OPh)_3$}$_2$($C_5H_4PPh_2$-*P*)] (**15**) (Table 1). When this reaction was carried out in C_6D_6 solution, a mixture of *cis*-[PtMe{$P(OPh)_3$}$_2$($C_5H_4PPh_2$-*P*)] and [Pt_2\{$P(OPh)_3$\}$_2(\mu$-η^1-$C_5H_4PPh_2)_2$] (**12**) (Table 2) was obtained.

The phosphorus ligand that was found to react most cleanly with [$Pt_2R_2(\mu$-$C_5H_4PPh_2)_2$] to produce a platinum(I) dimer of the type [$Pt_2(PR_3)_2(\mu$-η^1-$C_5H_4PPh_2)_2$] was tris(2-cyanoethyl)phosphine, $P(CH_2CH_2CN)_3$; therefore, we used this ligand to carry out a more detailed study of this reaction. Addition of 2 equiv of $P(CH_2CH_2CN)_3$ to a C_6D_6 solution of [$Pt_2Me_2(\mu$-$C_5H_4PPh_2)_2$] under an atmosphere of argon resulted in quantitative conversion to [Pt_2\{$P(CH_2CH_2CN)_3$\}$_2(\mu$-η^1-$C_5H_4PPh_2)_2$] (**8**) (Table 2). This was accompanied by reductive elimination of ethane, which was identified by a signal at 0.84 ppm in the ^1H NMR spectrum and by GC–MS analysis of the gas phase.[9] Analogous reactions of [$Pt_2R_2(\mu$-$C_5H_4PPh_2)_2$] (R = Et, neo-Pe, Bz) with $P(CH_2CH_2CN)_3$ in C_6D_6 solution also produced **8**, along with butane (identified by GC–MS), 2,2,5,5-tetramethylhexane (δ(H) 1.1 s, 18H, CH_3; δ(H) 2.7 s, 4H, CH_2), or 1,2-diphenylethane (δ(H) 2.9 s, 4H, CH_2; δ(H) 6.8–7.8 m, 10H, C_6H_5), respectively.

In order to investigate the mechanism of the reductive-elimination process, a benzene solution containing a 1:1 mixture of [$Pt_2(CH_3)_2(\mu$-$C_5H_4PPh_2)_2$] and [$Pt_2(CD_3)_2(\mu$-$C_5H_4PPh_2)_2$] was treated with 2 equiv of $P(CH_2CH_2CN)_3$ in a sealed, argon-filled vessel at 25 °C. After 2 h, the components of the gas phase were analyzed by GC–MS. The analytical data showed that only d_0- and d_6-ethane were produced (if any d_3-ethane was produced, its concentration was below the detection limit of *ca.* 10%). An analogous study of the reaction of a 1:1 mixture of [$Pt_2(C_2H_5)_2(\mu$-$C_5H_4PPh_2)_2$] and [$Pt_2(C_2D_5)_2(\mu$-$C_5H_4PPh_2)_2$] with 2 equiv of $P(CH_2CH_2CN)_3$ produced d_0- and d_{10}-butane only. Thus, the reductive-elimination takes place by an intramolecular pathway.

As indicated above, the reaction of [$Pt_2R_2(\mu$-C_5H_4-$PPh_2)_2$] with $P(CH_2CH_2CN)_3$ produced [Pt_2\{$P(CH_2CH_2$-$CN)_3$\}$_2(\mu$-η^1-$C_5H_4PPh_2)_2$] as the sole phosphorus-containing product, but many of the corresponding reactions with other tertiary phosphines resulted in mixtures of compounds. We believe the reactions with $P(CH_2CH_2CN)_3$ proceed very cleanly due to two factors. One of these is the poor nucleophilicity of the $P(CH_2CH_2CN)_3$ ligand, which results in greater discrimination between potential reaction pathways. The second factor is the low solubility of the ligand, which effectively causes a slow release of the phosphine into the solution. Thus, unlike the reactions with other ligands, there is always a significant excess of the platinum complex in the solution, which will inhibit formation of the bis(phosphine) species.

It was also pointed out earlier that we were able to prepare [$Pt_2(CNBu^t)_2(\mu$-η^1-$C_5H_4PPh_2)_2$] (**4**) by substitution of the terminal carbonyl ligands in [$Pt_2(CO)_2(\mu$-η^1-$C_5H_4PPh_2)_2$]. We have extended this approach to tertiary phosphine ligands (eq 6) and have prepared and isolated



(6)

PR_3 = PEt_3, PMe_2Ph, PPh_3, $P(CH_2CH_2CN)_3$

representative complexes of the type [$Pt_2(PR_3)_2(\mu$-η^1-C_5H_4-$PPh_2)_2$] (**5–8**; PR_3 = PEt_3, PMe_2Ph, PPh_3, $P(CH_2CH_2$-$CN)_3$). ^{31}P NMR data for these compounds are given in Table 2, and the $^{31}P\{^1H\}$ NMR spectrum of [Pt_2\{$P(CH_2$-$CH_2CN)_3$\}$_2(\mu$-η^1-$C_5H_4PPh_2)_2$] (**8**) is shown in Figure 1.

For each complex of the type [$Pt_2(PR_3)_2(\mu$-η^1-C_5H_4-$PPh_2)_2$] (**5–12**) the $^{31}P\{^1H\}$ NMR spectrum consists of two resonances, each of which exhibits short-range and long-range coupling to ^{195}Pt. The central resonances, due to the isotopomer containing no ^{195}Pt, are singlets. In the isotopomer containing one ^{195}Pt atom, an AA'BB'X pattern is observed. No coupling is observed between the chemically different phosphorus atoms P_A and P_B,[10] but each set of ^{195}Pt satellites is split into a doublet due to a three-

(8) Boehm, J. R.; Doonan, D. J.; Balch, A. L. *J. Am. Chem. Soc.* **1976**, *98*, 4845.

(9) In $CDCl_3$ solution the reaction was complicated by formation of *trans*-[PtClMe{$P(CH_2CH_2CN)_3$}$_2$] (δ(P) 16.3, ^1J(Pt,P) = 2953 Hz), identified by comparison of its NMR spectrum with that of a sample prepared from [PtClMe(COD)] and 2 equiv of $P(CH_2CH_2CN)_3$, and a species containing mutually *trans*, nonequivalent P atoms (δ(P) −0.6 d, ^1J(Pt,P) = 2914 Hz, ^2J(P,P) = 401 Hz; δ(P) 20.1 d, ^1J(Pt,P) = 2598 Hz), which we assume to be either *trans*-[PtClMe{$P(CH_2CH_2CN)_3$}($C_5H_4PPh_2$-*P*)]$^-$ or the protonated form *trans*-[PtClMe{$P(CH_2CH_2CN)_3$}($C_5H_5PPh_2$-*P*)].

(10) A coupling of 8 Hz between the dppc and $P(OPh)_3$ phosphorus atoms was observed for [Pt_2\{$P(OPh)_3$\}$_2(\mu$-η^1-$C_5H_4PPh_2)_2$] only.

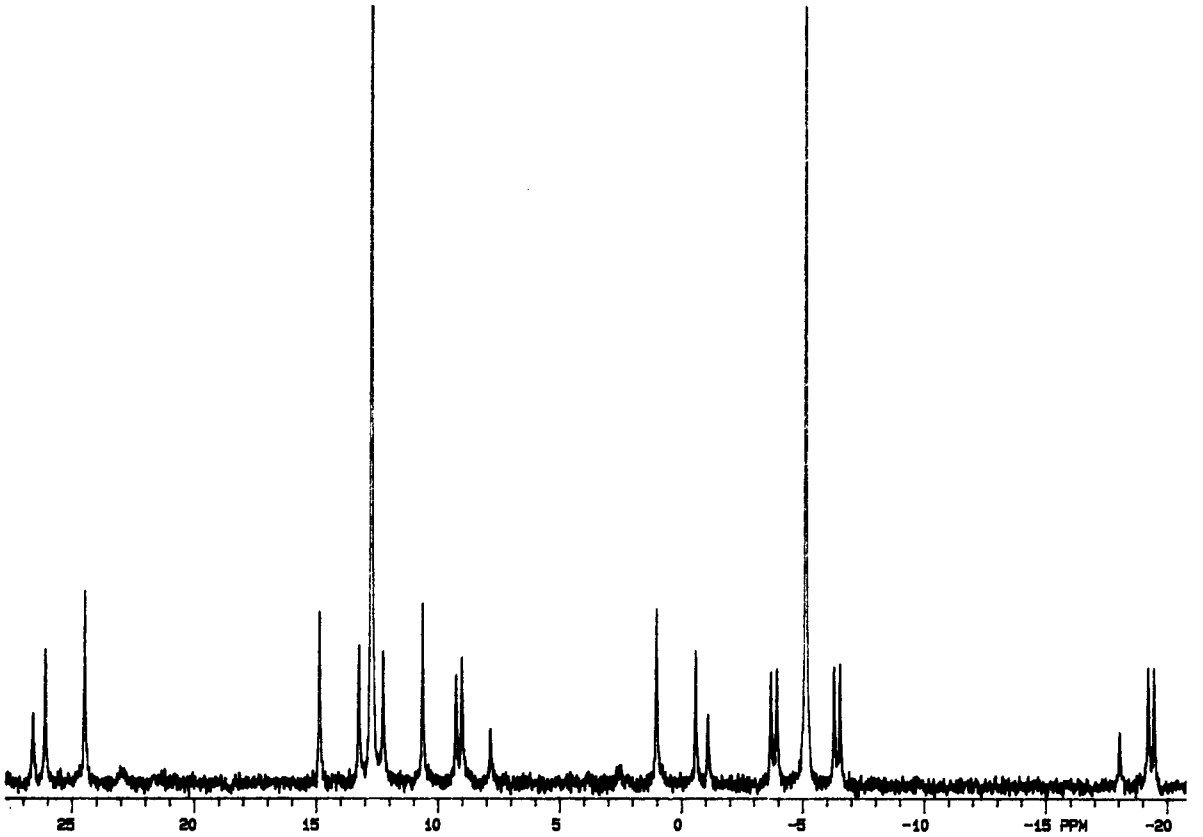


Figure 1. $^{31}P\{^1H\}$ NMR spectrum of $[Pt_2\{P(CH_2CH_2CN)_3\}_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]$ (8), recorded in $CDCl_3$ solution.

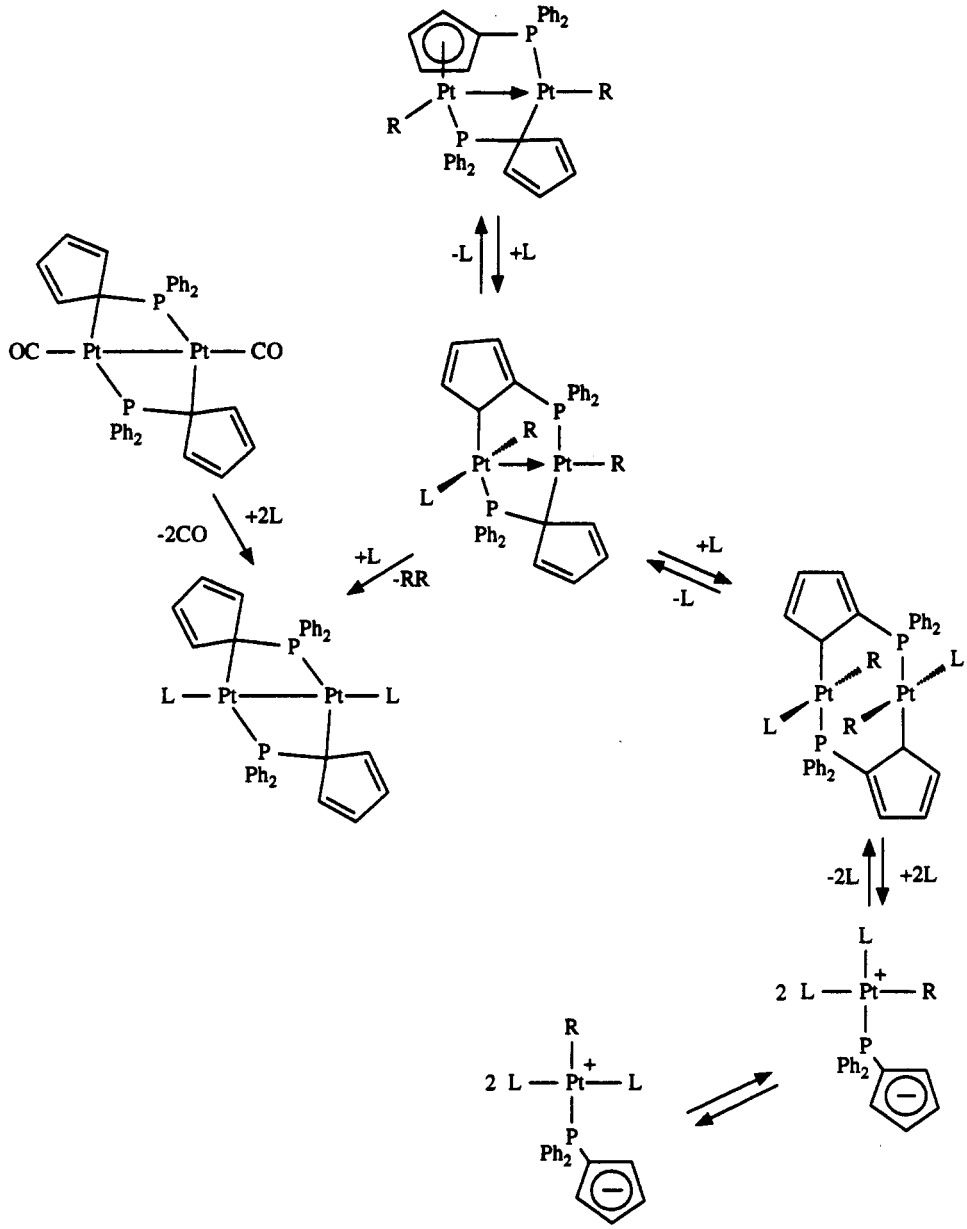
bond coupling between the chemically identical but magnetically nonequivalent P atoms. The $^3J(P,P)$ coupling between the dppc P atoms is *ca.* 30 Hz, whereas there is a significantly larger three-bond coupling (*ca.* 200 Hz) between the two terminal P atoms, due to the linear P–Pt–Pt–P backbone of the complex. The dppc P atom has a $^1J(Pt,P)$ value of 3500–3700 Hz, whereas the terminal P atom shows a somewhat smaller one-bond coupling constant, and each type of P atom exhibits a $^2J(Pt,P)$ value of *ca.* 300 Hz. The $^{195}Pt_2$ isotopomer gives rise to a doublet whose separation corresponds to $|^1J(Pt,P) + {}^2J(Pt,P)|$,[11] which allows the relative signs of the two coupling constants to be determined. In the case of the dppc P atom, the lines of this doublet lie inside the outer doublets due to $^1J(Pt,P)$, indicating that the one-bond and two-bond couplings are of opposite sign. Since $^1J(Pt,P)$ coupling constants are taken to be positive,[12] this implies that $^2J(Pt,P)$ is negative. On the other hand, for the terminal P atom, the lines of the doublet lie outside the doublets due to $^1J(Pt,P)$, indicating that the sign of $^2J(Pt,P)$ is positive in this instance. Negative $^2J(Pt,P)$ couplings have been found in dppm-bridged platinum complexes where the P atom lies *cis* to a Pt–Pt bond.[13–15]

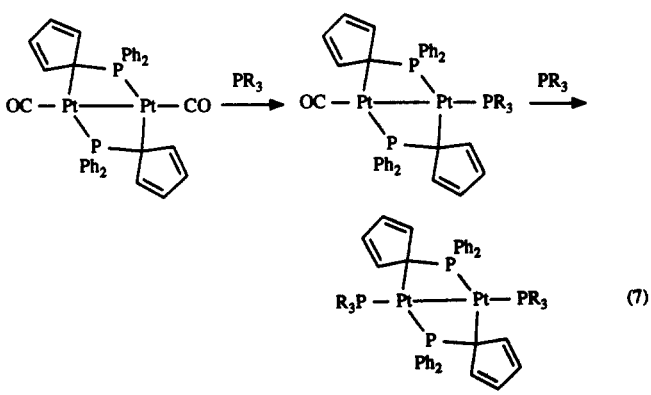
The ^1H NMR spectra of $[Pt_2(PR_3)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]$ are quite straightforward. Their $^{13}C\{^1H\}$ NMR spectra, as well as those of the CO and $CNBu^t$ analogues, however, exhibit complex multiplets owing to the virtual coupling of the P atoms. Nelson has shown[16] that the multiplets observed for the ^{13}C resonances in bis(phosphine) complexes are dependent on the magnitude of $J(P,P)$. When it is large, a 1:2:1 triplet is observed, when it is small (but nonzero), a five-line multiplet results, and when $J(P,P) = 0$, the spectrum appears as a doublet. In the case of $[Pt_2(PEt_3)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]$ (**5**) the carbon atoms of the cyclopentadienyl and phenyl rings that couple to ^{31}P experience the relatively weak $^3J(P,P)$ coupling of 30 Hz associated with the dppc P atoms and appears as five-line multiplets. Conversely, the methylene carbons of the PEt_3 ligands are influenced by the strong $^3J(P,P)$ coupling of 173 Hz and appear as a 1:2:1 triplet. The molecules contain an effective plane of symmetry, composed of the two four-membered Pt_2PC rings and the two terminal P atoms; therefore, the phenyl rings of the dppc ligands are magnetically equivalent. In $[Pt_2(PMe_2Ph)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]$ (**6**) the two methyl groups on each PMe_2Ph ligand are also related by means of this plane of symmetry.

When $[Pt_2(CO)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]$ was treated with 1 equiv of PPh_3 or PEt_3, almost quantitative conversion to an unsymmetrical complex of the type $[(CO)Pt(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2Pt(PR_3)]$ took place, as evidenced by $^{31}P\{^1H\}$ NMR spectroscopy (eq 7). Only traces of the symmetrical complexes $[Pt_2(CO)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]$ and $[Pt_2(PR_3)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]$ were observed in the case of PPh_3, but somewhat larger amounts were present with PEt_3, even when the reaction was performed at −50 °C. ^{31}P NMR data for the unsymmetrical complexes, which were not isolated, are given in Table 3. In these species the P atoms of the dppc ligands are, of course, nonequivalent, and each exhibits short-range and long-range coupling to ^{195}Pt. The assignments of the resonances to the two dppc P atoms were made by comparison with those observed for

(11) Brown, M. P.; Puddephatt, R. J.; Rashidi, M.; Seddon, K. R. *J. Chem. Soc., Dalton Trans.* **1977**, 951.
(12) McFarlane, W. *J. Chem. Soc. A* **1967**, 1922.
(13) Brown, M. P.; Fisher, J. R.; Franklin, S. J.; Puddephatt, R. J.; Seddon, K. R. *J. Organomet. Chem.* **1978**, *161*, C46.
(14) Grossel, M. C.; Batson, J. R.; Moulding, R. P.; Seddon, K. R. *J. Organomet. Chem.* **1986**, *304*, 391.
(15) Anderson, G. K. *Adv. Organomet. Chem.* **1993**, *35*, 1.
(16) Redfield, D. A.; Nelson, J. H.; Cary, L. W. *Inorg. Nucl. Chem. Lett.* **1974**, *10*, 727.

Scheme 1

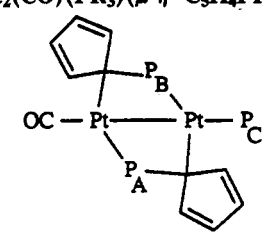




(7)

$[Pt_2(CO)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]$ and $[Pt_2(PR_3)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]$. There is again no $^2J(P,P)$ coupling observed between the cis P atoms, but a small three-bond coupling is detected between the P atom of the tertiary phosphine and the more distant dppc P atom, in addition to the previously observed $^3J(P,P)$ involving the two dppc P atoms. In this case the P–P couplings are found in the central resonances as well as in the ^{195}Pt satellites.

Table 3. $^{31}P\{^1H\}$ NMR Parameters for the Complexes $[Pt_2(CO)(PR_3)(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]^a$



	PR_3			PR_3	
	PPh_3	PEt_3		PPh_3	PEt_3
$\delta(P_A)$	–0.8	–2.9	$^2J(Pt,P_A)$	320	330
$\delta(P_B)$	–6.9	–3.7	$^2J(Pt,P_B)$	290	238
$\delta(P_C)$	21.2	8.5	$^2J(Pt,P_C)$	318	266
$^1J(Pt,P_A)$	3313	3438	$^3J(P_A,P_B)$	28	27
$^1J(Pt,P_B)$	3333	3504	$^3J(P_A,P_C)$	6	7
$^1J(Pt,P_C)$	3169	3098	$^2J(P_B,P_C)$	nr	nr

[a] In $CDCl_3$ solution. Coupling constants are in hertz. nr = not resolved.

A series of reaction pathways that may account for the observed chemistry is shown in Scheme 1. Only in the

reaction of $[Pt_2(neo\text{-}Pe)_2(\mu\text{-}C_5H_4PPh_2)_2]$ with $CNBu^t$ was an intermediate of the type $[R(L)Pt(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2PtR]$ observed, but we believe it is at this point that the pathway diverges toward either reductive-elimination or further ligand addition. In contrast to the reactions with CO or $CNBu^t$, species of the type $[Pt_2R_2(L)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]$, although presumably formed transiently, have not been detected when L is a tertiary phosphine or phosphite. Instead the reaction proceeds rapidly to the monomeric bis(ligand) complex. This pathway is favored in polar solvents, whereas in benzene solution the reductive-elimination pathway is able to compete in the cases of PPh_3, $P(C_6H_4F\text{-}p)_3$, and $P(OPh)_3$. With $P(CH_2CH_2CN)_3$, PBz_3, $PBu^i{}_3$, and PCy_3 the reductive-elimination pathway is followed exclusively. In the case of $P(CH_2CH_2CN)_3$, the only one for which we performed isotopic labeling studies, no crossover products are obtained, indicating that the elimination is an intramolecular process. This implies that, in this case at least, elimination from $[R(R_3P)Pt(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2PtR]$ occurs exclusively, since reversible $[PtR(PR_3)_2(C_5H_4PPh_2\text{-}P)]$ formation would lead to mixing of the alkyl ligands.

A major question remains regarding the actual elimination step. One possibility is that it involves migration of an alkyl group from one platinum to the other, through a transient alkyl-bridged species, and reductive elimination from a single metal center. Such a process has been proposed for dinuclear eliminations from a dppm-bridged palladium system.[17] Alternatively, a concerted dinuclear reductive elimination, involving both metal centers, might occur. Further work is in progress in an attempt to differentiate between these two possible mechanisms.

Experimental Section

NMR spectra were recorded on a Varian XL-300 spectrometer. ^1H and ^{13}C chemical shifts were measured in δ units relative to the residual solvent resonance (TMS at δ 0); ^{31}P shifts were measured relative to external H_3PO_4. Infrared spectra were recorded on a Perkin-Elmer 783 spectrophotometer. GC–MS data were obtained using a Hewlett-Packard HP 5988 instrument. Microanalyses were performed by Atlantic Microanalytical Laboratories, Norcross, GA. The complexes $[Pt_2R_2(\mu\text{-}C_5H_4PPh_2)_2]$ (R = CH_3, CD_3, C_2H_5, C_2D_5, $CH_2C(CH_3)_3$, C_6H_5, $CH_2C_6H_5$) were prepared as described previously.[2,3] The ligands were obtained from commercial suppliers and were used as received. All reactions were carried out under an atmosphere of argon, and the products were worked up in air.

Preparation of $[Pt_2Me_2(CNBu^t)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]$ (2a). To a benzene solution (15 mL) of $[Pt_2Me_2(\mu\text{-}C_5H_4PPh_2)_2]$ (0.114 g, 0.115 mmol) was added $CNBu^t$ (26.0 μL, 0.230 mmol) dropwise. The mixture was stirred for 3 h at ambient temperature. The solvent was evaporated *in vacuo*, and the oily residue was dissolved in CH_2Cl_2 (5 mL). Petroleum ether (20 mL) was added, and the solvents were again removed *in vacuo*. The resulting yellow powder was washed with petroleum ether (3 × 5 mL) and dried *in vacuo* (0.125 g, 94%). Anal. Calcd for $C_{46}H_{52}N_2P_2Pt_2$: C, 50.92; H, 4.80; N, 2.58. Found: C, 50.00; H, 4.69; N, 2.53. IR: ν(CN) 2180 cm^{-1}. ^1H NMR ($CDCl_3$): δ(H) 0.52 (d, ^3J(P,H) = 6 Hz, ^2J(Pt,H) = 62 Hz, PtCH_3), 0.88 (s, C(CH_3)$_3$), 5.18 (d, ^3J(P,H) = 12 Hz, ^2J(Pt,H) = 141 Hz), 6.22 (br), 6.40 (br) (C_5H_4 (fourth resonance is obscured by the aromatic signals)), 7.05–7.90 (m, C_6H_5). $^{13}C\{^1H\}$ NMR: δ(C) −1.0 (d, ^2J(P,C) = 7 Hz, ^1J(Pt,C) = 541 Hz, PtCH$_3$), 29.6 (s, ^3J(Pt,C) = 32 Hz, C(CH_3)$_3$), 54.6 (s, C(CH$_3$)$_3$), 62.2 (dd, J(P,C) = 56, 23 Hz), 118.7 (d, J(P,C) = 12 Hz), 131.4 (s), 142.8 (s) (C_5H_4 (fifth carbon resonance not observed)), 127.5 (d, ^3J(P,C) = 10 Hz, C_3), 127.6 (d, ^3J(P,C) = 10 Hz, $C_{3'}$), 128.2 (s, C_4), 129.6 (s, $C_{4'}$), 132.0 (d, ^2J(P,C) = 12 Hz, C_2), 136.0 (d, ^2J(P,C) = 12 Hz, $C_{2'}$), 141.0 (d, ^1J(P,C) = 49 Hz, C_1, C_6H_5) ($C_{1'}$ resonance not observed). $^{31}P\{^1H\}$ NMR: δ(P) 12.6 (s, ^1J(Pt,P) = 3028 Hz).

Preparation of *trans*-$[PtPh(CNBu^t)_2(C_5H_4PPh_2\text{-}P)]$ (*trans*-3d). To a stirred CH_2Cl_2 solution (15 mL) of $[Pt_2Ph_2(\mu\text{-}C_5H_4PPh_2)_2]$ (0.120 g, 0.115 mmol) was added $CNBu^t$ (45.0 μL, 0.400 mmol) dropwise. The mixture was stirred for 30 min and then reduced in volume to *ca.* 3 mL. The resulting brown, oily solution was treated with petroleum ether (25 mL), yielding a yellow precipitate. The solid was filtered, washed with petroleum ether (3 × 5 mL), and dried *in vacuo* to leave the product as a pale yellow solid (0.124 g, 89%). Anal. Calcd for $C_{33}H_{37}N_2PPt$: C, 57.64; H, 5.38; N, 4.07. Found: C, 57.17; H, 5.38; N, 4.40. IR: ν(CN) 2215 cm^{-1}. ^1H NMR ($CDCl_3$): δ(H) 1.10 (s, C(CH_3)$_3$), 6.40 (br), 6.47 (br) (C_5H_4), 7.00–7.78 (m, C_6H_5). $^{13}C\{^1H\}$ NMR: δ(C) 29.1 (s, C(CH$_3$)$_3$), 58.4 (s, C(CH$_3$)$_3$), 90.5 (d, ^1J(P,C) = 74 Hz, ^2J(Pt,C) not observed, C_α), 110.4 (d, ^3J(P,C) = 16 Hz, ^4J(Pt,C) = 8 Hz, C_γ), 116.3 (d, ^2J(P,C) = 17 Hz, ^3J(Pt,C) = 17 Hz, C_β) (C_5H_4), 124.5 (s, C_4), 128.2 (d, ^3J(P,C) = 7 Hz, ^2J(Pt,C) = 48 Hz, C_2), 139.0 (s, ^3J(Pt,C) = 41 Hz, C_3), 144.9 (d, ^2J(P,C) = 90 Hz, ^1J(Pt,C) not observed, C_1) (PtC_6H_5), 127.5 (d, ^3J(P,C) = 10 Hz, C_3), 129.1 (s, C_4), 133.1 (d, ^2J(P,C) = 11 Hz, ^3J(Pt,C) = 11 Hz, C_2), 138.5 (d, ^1J(P,C) = 55 Hz, ^2J(Pt,C) not observed, C_1) ($P(C_6H_5)_2$). $^{31}P\{^1H\}$ NMR: δ(P) −2.1 (s, ^1J(Pt,P) = 1488 Hz).

Preparation of *trans*-$[PtMe(CNBu^t)_2(C_5H_4PPh_2\text{-}P)]$ (*trans*-3a). This complex was prepared as above and was obtained as a pale yellow powder in 94% yield. Attempts to obtain this in analytically pure form resulted in loss of $CNBu^t$. ^1H NMR ($CDCl_3$): δ(H) 0.63 (d, ^3J(P,H) = 6 Hz, ^2J(Pt,H) = 58 Hz, PtCH_3), 1.10 (s, C(CH_3)$_3$), 6.32 (s), 6.34 (s) (C_5H_4), 7.21–7.35 (m), 7.58–7.62 (m), (C_6H_5). $^{13}C\{^1H\}$ NMR: δ(C) −12.5 (d, ^2J(P,C) = 70 Hz, ^1J(Pt,C) = 391 Hz, PtCH$_3$), 29.5 (s, C(CH_3)$_3$), 58.2 (s, C(CH$_3$)$_3$), 92.4 (d, ^1J(P,C) = 74 Hz, ^2J(Pt,C) not observed, C_α), 110.0 (d, ^3J(P,C) = 15 Hz, ^4J(Pt,C) = 20 Hz, C_γ), 116.0 (d, ^2J(P,C) = 17 Hz, ^3J(Pt,C) = 17 Hz, C_β) (C_5H_4), 127.5 (d, ^3J(P,C) = 11 Hz, C_3), 128.8 (s, C_4), 133.0 (d, ^2J(P,C) = 11 Hz, ^3J(Pt,C) = 12 Hz, C_2), 139.2 (d, ^1J(P,C) = 52 Hz, ^2J(Pt,C) not observed, C_1) (C_6H_5). $^{31}P\{^1H\}$ NMR: δ(P) 2.6 (s, ^1J(Pt,P) = 1569 Hz).

Preparation of $[Pt_2(PEt_3)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]$ (5). To a CH_2Cl_2 solution (10 mL) of $[Pt_2(CO)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]$ (0.120 g, 0.127 mmol) was added PEt_3 (37.7 μL, 0.254 mmol) dropwise. The solution was stirred for 30 min; then the volume was reduced to *ca.* 1 mL and petroleum ether (10 mL) was added. A yellow precipitate formed immediately. The solid was filtered, washed with petroleum ether (3 × 5 mL), and dried *in vacuo* to leave the product as a pale yellow powder (0.076 g, 53%). Anal. Calcd for $C_{46}H_{58}P_4Pt_2$: C, 49.11; H, 5.16. Found: C, 49.38; H, 5.24. ^1H NMR ($CDCl_3$): δ(H) 0.48 (dt, ^3J(H,H) = 8 Hz, ^3J(P,H) = 16 Hz, CH_3), 0.92 (m, CH_2), 6.40 (m), 7.80 (m) (C_5H_4), 7.12–7.38 (m), 7.45–7.58 (m) (C_6H_5). $^{13}C\{^1H\}$ NMR: δ(C) 7.9 (s, ^3J(Pt,C) = 22 Hz, CH_3), 16.4 (t, J(P,C) = 25 Hz, ^2J(Pt,C) = 25 Hz, CH_2), 121.1 (five-line m, J(P,C) = 11 Hz, C_β), 130.6 (br, C_γ) (C_5H_4 (*ipso* carbon not observed)), 127.0 (five-line m, J(P,C) = 10 Hz, C_3), 128.8 (s, C_4), 133.2 (five-line m, J(P,C) = 12 Hz, C_2), 138.7 (m, C_1) (C_6H_5).

Preparation of $[Pt_2(PMe_2Ph)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]$ (6). This complex was prepared in a manner similar to that for the PEt_3 species and isolated in 82% yield. Anal. Calcd for $C_{50}H_{50}P_4Pt_2$: C, 51.55; H, 4.30. Found: C, 51.52; H, 4.32. ^1H NMR ($CDCl_3$): δ(H) 0.98 (t, J(P,H) = 4 Hz, ^3J(Pt,H) = 35 Hz, ^4J(Pt,H) = 16 Hz, CH_3), 6.28 (m), 6.75 (m) (C_5H_4), 7.00–7.45 (m, C_6H_5). $^{13}C\{^1H\}$ NMR: δ(C) 15.3 (t, J(P,C) = 27 Hz, CH_3), 121.5 (five-line m, J(P,C) = 12 Hz, C_β), 131.2 (br, C_γ) (C_5H_4 (*ipso* carbon not observed)), 127.2 (five-line m, J(P,C) = 10 Hz, C_3), 128.8 (s, C_4), 132.8 (five-line m, J(P,C) = 12 Hz, C_2), 139.9 (five-line m, J(P,C) = 41 Hz, C_1) (C_6H_5 (dppc)), 127.5 (five-line m, J(P,C) = 10 Hz, C_3), 128.5 (s, C_4), 130.7 (five-line m, J(P,C) = 13 Hz, C_2), 138.0 (five-line m, J(P,C) = 43 Hz, C_1) (C_6H_5 (PMe_2Ph)).

Preparation of $[Pt_2(PPh_3)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]$ (7). This complex was prepared as above and isolated in 61% yield. Anal.

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Calcd for $C_{70}H_{58}P_4Pt_2$: C, 59.50; H, 4.11. Found: C, 58.90; H, 4.38. ^1H NMR ($CDCl_3$): δ(H) 5.65 (m), 6.60 (m) (C_5H_4), 6.85–7.18 (m, C_6H_5). $^{13}C\{^1H\}$ NMR: δ(C) 121.9 (five-line m, J(P,C) = 10 Hz, C_β), 131.4 (br, ^3J(Pt,C) = 39 Hz, C_γ) (C_5H_4 (*ipso* carbon not observed)), 126.9 (five-line m, J(P,C) = 8 Hz, C_3), 128.2 (s, C_4), 132.9 (five-line m, J(P,C) = 12 Hz, C_2) (C_6H_5 (dppc)), 127.0 (five-line m, J(P,C) = 10 Hz, C_3), 128.7 (s, C_4), 134.3 (five-line m, J(P,C) = 13 Hz, C_2) (C_6H_5 (PPh_3)).

Preparation of $[Pt_2\{P(CH_2CH_2CN)_3\}_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]$ (8). This compound was prepared analogously and isolated in 64% yield. Anal. Calcd for $C_{52}H_{52}N_6P_4Pt_2$: C, 48.98; H, 4.08; N, 6.59. Found: C, 48.80; H, 4.13; N, 6.56. ^1H NMR ($CDCl_3$): δ(H) 1.38 (m), 1.98 (m) (CH_2), 6.64 (m), 7.10 (m) (C_5H_4), 7.40–7.65 (m, C_6H_5). $^{13}C\{^1H\}$ NMR: δ(C) 12.5 (t, J(P,C) = 6 Hz, ^3J(Pt,C) = 35 Hz, PCH_2CH_2), 20.7 (t, J(P,C) = 22 Hz, ^2J(Pt,C) = 49 Hz, PCH_2), 118.1 (five-line m, J(P,C) = 14 Hz, C_β), 123.5 (m, C_α), 130.8 (br, C_γ) (C_5H_4), 128.5 (five-line m, J(P,C) = 10 Hz, C_3), 131.1 (s, C_4), 133.2 (five-line m, J(P,C) = 11 Hz, C_2), 136.2 (five-line m, J(P,C) = 46 Hz, C_1) (C_6H_5).

Preparation of $[Pt_2(CNBu^t)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]$ (4). This complex was prepared as above and isolated in 78% yield. Anal. Calcd for $C_{44}H_{46}N_2P_4Pt_2$: C, 50.09; H, 4.36; N, 2.66. Found: C, 49.97; H, 4.29; N, 2.61. ^1H NMR ($CDCl_3$): δ(H) 1.30 (s, $C(CH_3)_3$), 6.42 (m), 6.58 (m, C_5H_4), 7.15–7.38 (m, C_6H_5). $^{13}C\{^1H\}$ NMR: δ(C) 30.2 (s, $C(CH_3)_3$), 55.6 (s, $C(CH_3)_3$), 119.2 (five-line m, J(P,C) = 12 Hz, C_β), 120.9 (dd, J(P,C) = 27, 10 Hz, C_α), 126.4 (five-line m, J(P,C) = 6 Hz, C_γ) (C_5H_4), 127.4 (five-line m, J(P,C) = 11 Hz, C_3), 129.4 (s, C_4), 132.9 (five-line m, J(P,C) = 13 Hz, C_2), 139.2 (five-line m, J(P,C) = 47 Hz, C_1) (C_6H_5).

Reactions of $[Pt_2Me_2(\mu\text{-}C_5H_4PPh_2)_2]$ with PBz_3, PBu^i_3, PCy_3, and $P(OPh)_3$. In each case 2 equiv of the appropriate ligand was added to a C_6D_6 solution (0.5 mL) of $[Pt_2(CH_3)_2(\mu\text{-}C_5H_4PPh_2)_2]$ (*ca.* 30 mg). The complexes **9–12** were characterized in solution by $^{31}P\{^1H\}$ NMR spectroscopy (Table 2).

Reaction of $[Pt_2Me_2(\mu\text{-}C_5H_4PPh_2)_2]$ with PPh_3. $[Pt_2Me_2(\mu\text{-}C_5H_4PPh_2)_2]$ (0.033 g, 0.37 mmol) and PPh_3 (0.019 g, 0.072 mmol) were placed in an NMR tube. The tube was evacuated and then filled with argon, and C_6D_6 (0.5 mL) was introduced by syringe. The reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy, *cis*- and *trans*-$[PtMe(PPh_3)_2(C_5H_4PPh_2\text{-}P)]$ (*cis*-**13** and *trans*-**13**) being formed initially and $[Pt_2(PPh_3)_2(\mu\text{-}\eta^1\text{-}C_5H_4PPh_2)_2]$ (**7**) not being observed until after 7 days.

Reaction of $[Pt_2Me_2(\mu\text{-}C_5H_4PPh_2)_2]$ with $P(C_6H_4F\text{-}p)_3$. $[Pt_2Me_2(\mu\text{-}C_5H_4PPh_2)_2]$ (0.023 g, 0.025 mmol) and $P(C_6H_4F\text{-}p)_3$ (0.017 g, 0.054 mmol) were placed in an NMR tube. The tube was evacuated and filled with argon; then d_6-acetone (0.5 mL) was introduced by syringe. The products were identified as *cis*- and *trans*-$[PtMe\{P(C_6H_4F\text{-}p)_3\}_2(C_5H_4PPh_2\text{-}P)]$ (*cis*-**14** and *trans*-**14**) by $^{31}P\{^1H\}$ NMR spectroscopy.

Crossover Study of the Reaction of $[Pt_2(CH_3)_2(\mu\text{-}C_5H_4PPh_2)_2]$ and $[Pt_2(CD_3)_2(\mu\text{-}C_5H_4PPh_2)_2]$ with $P(CH_2CH_2CN)_3$. $[Pt_2(CH_3)_2(\mu\text{-}C_5H_4PPh_2)_2]$ (20.0 mg) and $[Pt_2(CD_3)_2(\mu\text{-}C_5H_4PPh_2)_2]$ (20.1 mg) were dissolved together in $CHCl_3$ (4 mL) in a 25-mL round-bottomed flask fitted with a rubber septum. The solution was degassed by three freeze–pump–thaw cycles; then argon was admitted to the flask. A solution of $P(CH_2CH_2CN)_3$ (17.0 mg) in $CHCl_3$ (1 mL) was injected into the flask by syringe, and the solution was stirred for 30 min. A 0.1 mL aliquot of the gas phase was removed with a gas syringe and analyzed by GC–MS.

A similar experiment was carried out by allowing a 1:1 mixture of $[Pt_2(C_2H_5)_2(\mu\text{-}C_5H_4PPh_2)_2]$ and $[Pt_2(C_2D_5)_2(\mu\text{-}C_5H_4PPh_2)_2]$ to react with $P(CH_2CH_2CN)_3$.

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