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REDISTRIBUTION REACTIONS OF PLATINUM(II) AND PALLADIUM(II) PHOSPHINE COMPLEXES

JEFFREY A. RAHN, MARK S. HOLT and JOHN H. NELSON*
Department of Chemistry, University of Nevada, Reno, NV 89557-0020, U.S.A.

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Abstract—Anion redistribution equilibria of the type $(R_3P)_2MX_2+(R_3P)_2MY_2 \leftrightharpoons 2(R_3P)_2MXY$ (X, Y = Cl, Br, I, CN, N_3; $R_3P = Me_2PhP$, $MePh_2P$, $(Bzl)_3P$, $(CH_2{=}CH)_2PhP$, $(CH_2{=}CH)Ph_2P$ and 1-phenyl-3,4-dimethylphosphole; M = Pd, Pt) have been studied by $^{31}P\{^1H\}$ and in some cases $^{195}Pt\{^1H\}$ NMR spectroscopy. It was found that except for the two cases when $R_3P = MePh_2P$, M = Pd, X = Cl, Y = Br and $R_3P = Me_2PhP$, M = Pd, X = Cl, Y = Br, redistribution was in general instantaneous. The $(R_3P)_2PdCl_2+(R_3P)_2Pd(CN)_2$ reactions were slow but proceeded to completion. In contrast, when one of the anions is CN^- no anion redistribution was observed for the platinum complexes even after a month. The thermodynamic stabilities of the mixed anion species relative to the symmetric species is anion dependent showing that these are not random processes. The $(R_3P)_2PdXY$ complexes possess the *trans* geometry. The $(R_3P)_2PtXY$ complexes are generally *cis* but in some cases both the *cis* and *trans* isomers are present in solution. A mechanism is proposed for these reactions. Phosphine redistribution of the type $(R_3P)_2MX_2+(R'_3P)_2MX_2 \leftrightharpoons 2(R_3P)(R'_3P)_2MX_2$ is general for palladium. It did not occur for platinum unless one or more of the R and R′ groups on each phosphine was unsaturated (allyl, vinyl or the butadiene moiety of a phosphole). In most of these cases the $(R_3P)(R'_3P)MX_2$ complexes underwent intramolecular [4+2] Diels–Alder cycloaddition reactions.

Ligand redistribution reactions [eq. (1)] are common for typical element compounds.[1]

$$MA+M'B \rightleftharpoons MB+M'A. \qquad (1)$$

The theoretical aspects,[1,2] experimental methods for their study[1–4] and the various systems which undergo this class of reaction have been reviewed.[1–4] Redistribution reactions of transition metal complexes, although less studied,[4] may not be less common. We reported earlier[5,6] that neutral ligand redistribution is a general reaction for palladium(II) complexes. In this paper we extend that study to analogous platinum(II) complexes and consider as well, anionic ligand redistribution for both palladium(II) and platinum(II) phosphine complexes. This type of reaction is of fundamental importance to our understanding of the solution chemistry of "inert" transition metal complexes.

EXPERIMENTAL

Reagents and physical measurements

All chemicals used were reagent grade and were used as received or synthesized as described below. All solvents, when necessary, were dried by standard procedures and stored over Linde 4 Å molecular sieves. All reactions involving phosphines were conducted under a nitrogen atmosphere.

The $^{31}P\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR spectra were recorded at 40.26 and 21.28 MHz, respectively, on a JEOL FX-100 spectrometer in the FT mode. Phosphorus chemical shifts were relative to external 85% H_3PO_4, with a positive value being downfield of the reference. ^{195}Pt chemical shifts are referenced to a standard frequency of 21.4 MHz relative to the proton resonance of TMS at 100 MHz.[7,8] Concentration values for calculating "k_{eq}" were obtained by integration of the areas of the ^{31}P res-

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* Author to whom correspondence should be addressed.

onances, or by measurement of the peak heights. When both methods could be used, the "k_{eq}" values were within 5% of each other.

Synthesis

Most $(R_3P)_2MCl_2$ complexes were prepared by reacting 2 equivalents of the phosphine or phosphole with one equivalent of the $(PhCN)_2MCl_2$ complex in CH_2Cl_2 under a nitrogen atmosphere as reported previously.[9] When R_3P was Bu_3P or Et_3P, 2 equivalents of the phosphine were reacted with 1 equivalent of K_2PtCl_4 as described previously.[10] The bromide,[11] iodide,[11] cyanide[12] and azide[13] complexes were prepared by metathesis of the chloride complexes in a CH_2Cl_2–CH_3OH–H_2O solvent mixture for 1 to 7 days for the palladium and platinum complexes, respectively. Except for cyanide, a 4 : 1 molar ratio of NaX to chloride complex was employed. For the cyanide complexes, a 2 : 1 molar ratio of NaCN to chloride complex was employed. The $^{31}P\{^1H\}$ NMR data for the palladium and platinum complexes is contained in Tables 1 and 2, respectively. The physical properties of all complexes agreed with the literature data.[9–26]

Redistribution reactions

These were performed by dissolving a 1 : 1 molar ratio of the two complexes, 20–60 mg each, in approximately 3 cm^3 of $CDCl_3$. The resultant solution was then placed in a 10 mm NMR tube and spectra were recorded immediately at 300 K, after 2 and 48 h, then again after a week or more.

RESULTS AND DISCUSSION

Anion redistribution

Reaction of complexes containing two different anions, X and Y [eq. (2)], was generally very rapid.

Table 1. ^{31}P NMR data for reactions of the type $(R_3P)_2PdX_2 + (R_3P)_2PY_2 \rightleftharpoons 2(R_3P)_2PdXY$

	$(MePh_2P)_2PdX_2$ $\delta^{31}P^a$			$(MePh_2P)_2PdY_2$ $\delta^{31}P^a$			
X	*cis*	*trans*	Y	*cis*	*trans*	$\delta^{31}P^a$ XY	K_{eq}
Cl	18.0(B)[b]	6.9	Br	5.9	4.2	—	—
Cl	18.0	6.9	I	—	−5.7	3.5	4.2
Cl	—	—	CN	—	—	7.1	∞
Cl	17.9	6.9	N_3	16.6	7.3	7.6	0.3
Br	5.9	4.2	I	3.5	−5.7	0.3	4.7
Br	6.0	4.2	CN	7.2	6.8	5.7	21.2
Br	5.8	4.1	N_3	7.2	—	6.4	—
I	—	−5.7	CN	—	6.8	2.4	21.9
I	—	−5.7	N_3	16.3	7.3	4.9	1.7
CN	—	6.9	N_3	16.4	7.3	7.7	79.1
	$(Me_2PhP)_2PdX_2$ $\delta^{31}P^a$			$(Me_2PhP)_2PdY_2$ $\delta^{31}P^a$			
X	*cis*	*trans*	Y	*cis*	*trans*	$\delta^{31}P$ XY	K_{eq}
Cl	4.7	−6.0	Br	7.8	−10.1	—	—
Cl	5.0	−6.0	I	—	−20.4	−10.9	3.2
Cl	—	—	CN	—	—	−5.5	∞
Cl	4.6(B)[b]	−5.9	N_3	4.6(B)	−3.7	−4.5	—
Br	−7.7	−10.1	I	−10.8	−20.4	−14.3	4.0
Br	—	−10.1	CN	—	−5.5	−7.5	490
Br	−7.7	−10.1	N_3	−3.5	−3.8	−5.7	0.1
I	—	−20.4	CN	—	−5.7	−11.2	29.9
I	—	−20.4	N_3	2.9	−3.7	−7.7	0.3
CN	—	−5.7	N_3	3.7	—	−4.2	112

[a] In ppm in $CDCl_3$ at 300 K.
[b] B = broad.

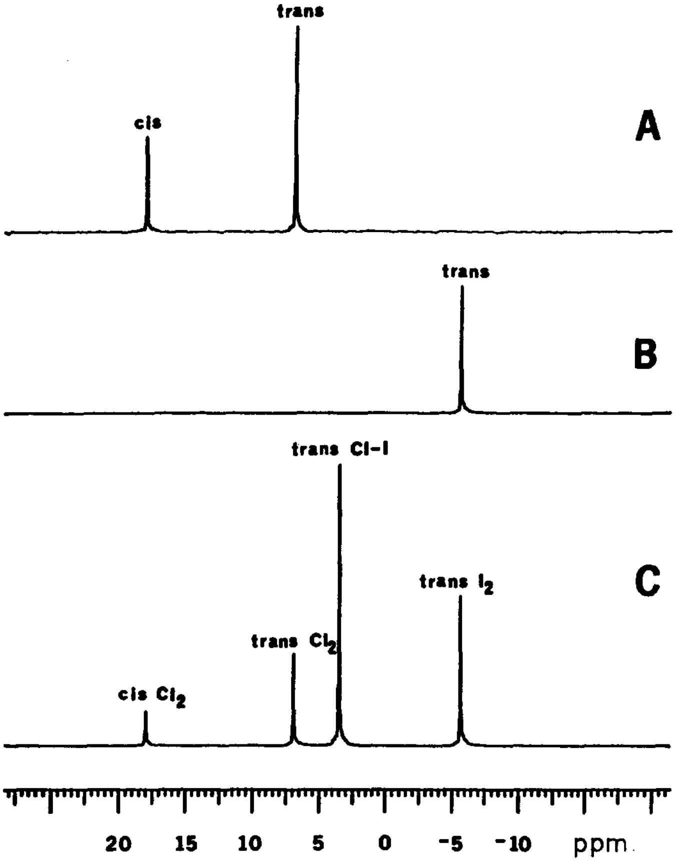


Fig. 1. 40.26 MHz $^{31}P\{^1H\}$ NMR spectra of (A) $(MePh_2P)_2PdCl_2$, (B) $(MePh_2P)_2PdI_2$ and (C) a 1 : 1 molar mixture of the two (all) in $CDCl_3$ at 300 K.

$$(R_3P)_2MX_2 + (R_3P)_2MY_2 \rightleftharpoons 2(R_3P)_2MXY. \quad (2)$$

In most cases, an equilibrium mixture of starting materials and either a *cis* or *trans* (in some cases both) mixed anion complex was formed. Equilibrium constants for eq. (2) were calculated from the equation:

$$K_{eq} = \frac{[(R_3P)_2MXY]^2_{total}}{[(R_3P)_2MX_2][(R_3P)_2MY_2]}$$

where $[(R_3P)_2MXY]_{total}$ is the total concentration of the *cis* and *trans* isomers of the mixed anion products.

Palladium reactions. The $(R_3P)_2PdX_2$ complexes generally exist as temperature dependent equilibrium mixtures of *cis* and *trans* isomers in solution.[11,14–20] Their $^{31}P\{^1H\}$ NMR spectra contain two resonances, one for each isomer, with that of the *trans* isomer generally being upfield of that for the *cis* isomer. The $^{31}P\{^1H\}$ NMR spectrum of a typical reaction mixture is shown in Fig. 1(C). The spectrum of the mixture contains, in addition to the resonances expected for the starting materials, a new singlet whose chemical shift lies between those of the *trans*-Cl_2 and *trans*-I_2 complexes. This resonance is assigned to the *trans*-$(MePh_2P)_2PdClI$ complex since the *cis* isomer should show two ^{31}P chemical shifts (*vide infra*). Similar spectra were observed for the 20 reactions listed in Table 1. The *trans* mixed anion complex formed in every case studied, except for the two Cl/Br combinations where only the two starting materials were present in solution after several days.

In several cases where the redistribution occurred, the K_{eq} values differ substantially from the statistical value of four, indicating that these equilibrium constants are influenced by the strengths of the Pd—X bonds[4] and are not random processes.

The reactions between the $(R_3P)_2PdCl_2$ and $(R_3P)_2Pd(CN)_2$ complexes were slower, but proceeded to completion. The *trans*-$(R_3P)_2Pd(CN)Cl$ complex was the only species present in solution after 1 week. Exchanges between the cyanide complexes and the complexes of other anions (Br, I, and N_3) all had equilibrium constants (K_{eq} = 21.1–490) that are much greater than for the non-cyanide containing exchanges. Reaction of the

Table 2. ^{31}P NMR data on exchange reactions of the type $(R_3P)_2PtX_2 + (R_3P)_2PtY_2 \rightleftharpoons 2(R_3P)_2PtXY$

Number	R_3P	X	$\delta^{31}P^a$	$J(Pt—P)^b$	Y	$\delta^{31}P$	$J(Pt—P)$	$\delta^{31}P$ mixed X	$\delta^{31}P$ mixed Y	$J(Pt—P)$ mixed X	$J(Pt—P)$ mixed Y	$J(PP)^b$	K_{eq}
1	Me_2PhP	Cl	−16.0	3547	Br	−16.0	3500	−14.0	−18.0	3519	3524	17	2.6
2	Me_2PhP	Cl	−16.0	3546	I	−23.3	3364	−13.3	−16.3	3359	3520	15	
						−18.1	2316	−14.5		2375		—	0.9
3	Me_2PhP	Cl	−16.0	3547	CN	−13.8	2192	—	—	—	—	—	—
4	Me_2PhP	Cl	−16.0	3546	N_3	−16.9	3370	−13.0	−19.2	3748	3218	24	13.7
5	Me_2PhP	Br	−16.1	3500	I	−18.1	3364	−15.3	−18.7	3348	3503	12	
						−23.3	2316	−18.0		2346		—	1.9
6	Me_2PhP	Br	−16.0	3499	CN	−13.8	2190	—	—	—	—	—	—
7	Me_2PhP	Br	−16.0	3501	N_3	−16.9	3370	−11.9	−21.2	3724	3204	23	16.7
8	Me_2PhP	I	−18.2	3364									
			−23.3	2314	CN	−13.8	2190	—	—	—	—	—	—
9	Me_2PhP	I	−18.1	3364	N_3	−16.9	3370	−12.9	−23.9	3567	3203		
								−10.6		2483		21	5.4
10	Me_2PhP	CN	−13.8	2190	N_3	−16.9	3369	—	—	—	—	—	—
11	$MePh_2P$	Cl	−1.8	3623	Br	−2.2	3572	−0.4	−3.7	3589	3602	16	3.7
12	$MePh_2P$	Cl	−1.8	3623	I	−4.8	3423						
						−7.5	2397	−0.5	−6.3	3414	3604	12	0.064
13	$MePh_2P$	Br	−2.2	3572	I	−4.8	3423	−2.3	−4.8	3401	3579	12	1.8
						−7.5	2397	−2.7		2429		0	
14	$MePh_2P$	Cl	−1.7	3624	N_3	−3.5	3440	0.1	−4.4	3818	3300	23	14.6
15	$MePh_2P$	Br	−2.3	3572	N_3	−3.8	3440	0.2	−6.4	3787	3293	22	28.4

16	$MePh_2P$	I	−4.7	3424									
			−7.3	2396	N_3	−3.5	3440	−2.2	−8.9	3610	3295	20	8.1
17	$PhVy_2P$[c]	Cl	−5.4	3573	Br	−6.0	3520	−4.6	−6.8	3540	3552	15	4.6
						−7.8	2408						
18	$PhVy_2P$	Cl	−5.1	3573	I	−8.3	3369	−5.2	−8.3	3362	3553	13	1.5
						−7.9	2408						
19	$PhVy_2P$	Br	−5.8	3522	I	−8.4	3369	−6.5	−7.5	3348	3534	12	2.9
20	DMPP[d]	Cl	7.7	3348	Br	7.4	3285	5.7	9.4	3317	3315	17	3.8
21	DMPP	Cl	7.7	3345	I	5.1	3120						
						4.7	2336	10.4	2.9	3144	3301	15	—
22	DMPP	Br	7.5	3286	I	5.2	3120						
						4.8	2336	8.5	4.6	3120	3276	15	4.1
23	Bzl_3P	Cl	5.1	2461	Br	−1.4	2393	−2.0		2424		0	3.7
24	Bzl_3P	Cl	5.1	2461	I	−10.5	2339	−1.8		2385		0	4.9
25	Bzl_3P	Br	−1.4	2393	I	−10.5	2339	−5.6		2361		0	3.4
26	Ph_2VyP	Cl	2.7	3633	Br	2.2	3583	3.2	1.6	3591	3620	15	4.1
27	Ph_2VyP	Cl	2.8	3632	I	0.6	2452	2.0	0.3	3405	3634	12	1.9
						−0.1	3434						
28	Ph_2VyP	Br	2.4	3583	I	0.6	2452	1.08	1.07	3401	3614	11	1.8
						−0.1	3434						

[a] In ppm in $CDCl_3$ at 300 K.

[b] In Hz.

[c] Vy = $CH{=\!=}CH_2$.

[d] DMPP = 1-phenyl-3,4-dimethylphosphole.

azide complexes with the chloride, bromide and iodide complexes, except for the $(MePh_2P)_2PdI_2 + (MePh_2P)_2Pd(N_3)_2$ reaction ($K_{eq} = 1.7$), all had equilibrium constants which were less than one. The equilibrium constants for the chloride with iodide and bromide with iodide reactions were near the statistical value, ranging from 3.2 to 4.2. It should also be noted that the nature of the phosphine affects the value of the equilibrium constant, but that there is no regular trend that is easily discernible relating to either the size or the basicity of the phosphine.

Platinum reactions. The geometry of the $(R_3P)_2PtX_2$ complexes may be easily determined from the magnitude of the platinum–phosphorus coupling constant. For *cis* complexes $^1J(Pt—P)$ is generally greater than 3000 MHz, while for *trans* compounds $^1J(Pt—P)$ is generally less than 2500 Hz.[21,27–29] The $(R_3P)_2PtI_2$ complexes exist as temperature-dependent equilibrium mixtures of *cis* and *trans* isomers in solution. The chloride, bromide and azide complexes are wholly *cis* and the cyanide complexes wholly *trans* in solution.

The $^{31}P\{^1H\}$ NMR spectrum of a typical reaction mixture is shown in Fig. 2. This spectrum contains an AB quartet, in addition to the resonances expected for the starting materials. This AB pattern is assigned to the *cis*-$(R_3P)_2PtXY$ complex. The magnitudes of the two $^1J(Pt—P)$s and $^2J(PP)$[30,31] are all consistent with the *cis* geometry. In all cases, when both the symmetric complexes were *cis*, the mixed anion complex was also *cis*. If both the symmetric complexes were *trans*, then the mixed anion complex which formed was also *trans* [reactions (23), (24), (25)]. In some cases, when one of the symmetric complexes was an iodide complex, a mixture of *cis* and *trans* isomers of $(R_3P)_2PtXI$ [reactions (2), (5), (9), (13)] was formed, with the major species being the *cis* isomer. A similar study[32] with *cis*-$(MePh_2P)_2Pt(NO_3)_2$ and *cis*-$(MePh_2P)_2Pt(CH_3)_2$ showed that the *cis*-$(MePh_2P)_2Pt(NO_3)(CH_3)$ isomer was formed first and that it slowly isomerized to the *trans* isomer.

Most of the equilibrium constants for the anion redistribution reactions of the platinum complexes do not differ markedly from the statistical value of four. The redistribution occurs to the greatest extent when one of the anions is the pseudo-halide N_3^-. Anion redistribution does not occur when one of the anions is cyanide (even after a month) which is in stark contrast to the results of the palladium reactions where the cyanide reactions occurred to the greatest extent. Also, redistribution between chloride and bromide complexes occurred for platinum but not for palladium. Clearly, the metal has an influence on K_{eq}.

The $(Bzl_3P)_2PtX_2$ (X = Cl, Br and I) complexes are each *trans* isomers, probably because of the

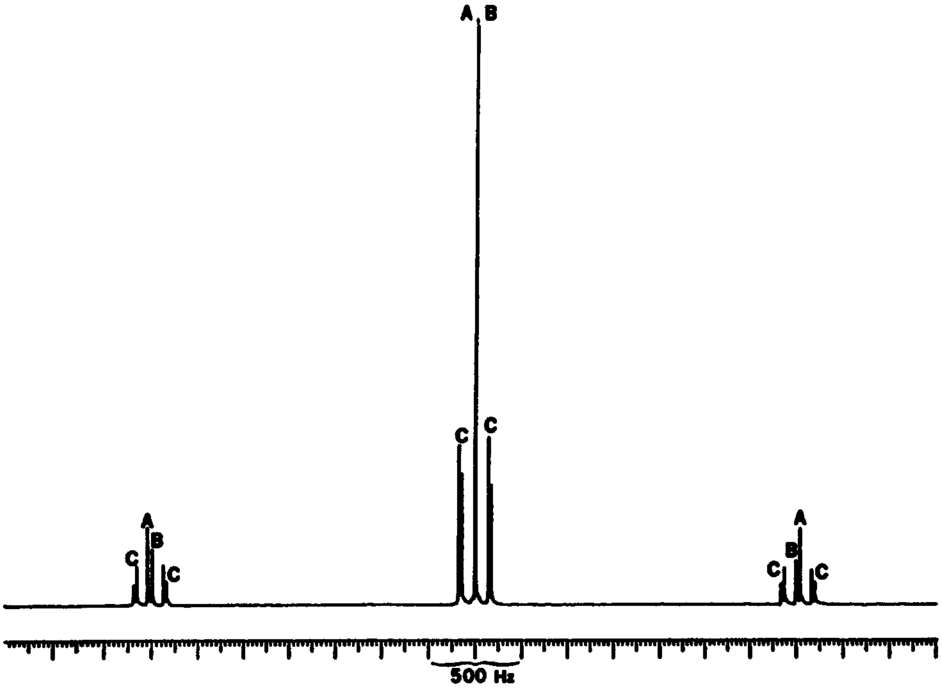


Fig. 2. 40.26 MHz $^{31}P\{^1H\}$ NMR spectrum of an equilibrium mixture of (A) $(Me_2PhP)_2PtCl_2$, (B) $(Me_2PhP)_2PtBr_2$ and (C) $(Me_2PhP)_2PtClBr$ in $CDCl_3$ at 300 K.

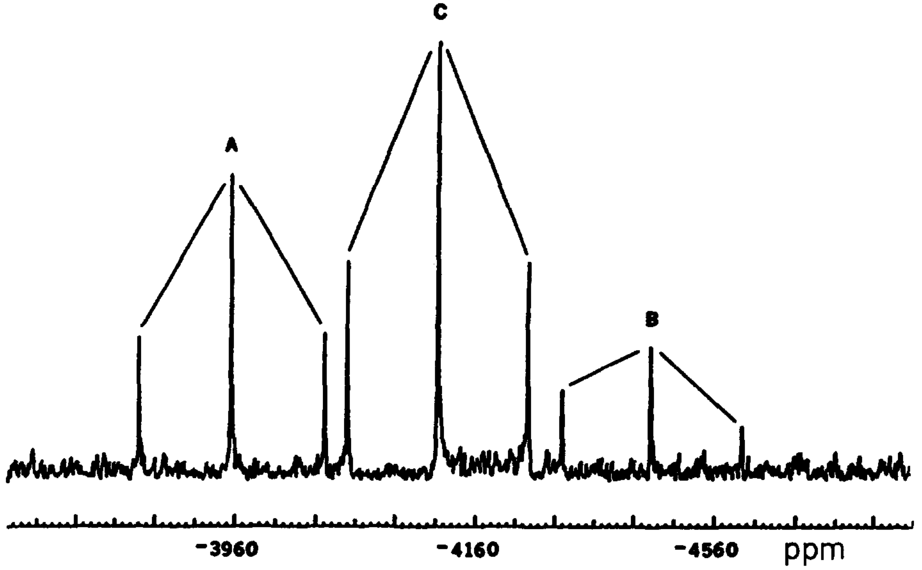


Fig. 3. 21.28 MHz ^{195}Pt{^{1}H} NMR spectrum of an equilibrium mixture of (A) $(Bzl_3P)_2PtCl_2$, (B) $(Bzl_3P)_2PtBr_2$ and (C) $(Bzl_3P)_2PtBrCl$ in $CDCl_3$ at 300 K.

steric bulk of Bzl_3P. Formation of *trans*-$(Bzl_3P)_2PtXY$ would then be expected. The ^{195}Pt{^{1}H} NMR spectrum for the reaction of $(Bzl_3P)_2PtCl_2$ with $(Bzl_3P)_2PtBr_2$ is shown in Fig. 3. For *trans*-$(Bzl_3P)_2PtCl_2$, $\delta^{195}Pt = -3954$ ppm and for *trans*-$(Bzl_3P)_2PtBr_2$, $\delta^{195}Pt = -4478$ ppm. The ^{195}Pt chemical shift of *trans*-$(Bzl_3P)_2PtBrCl$ is, as anticipated[33] due to the rough additivity of the halide influence on $\delta^{195}Pt$, intermediate between these two values ($\delta^{195}Pt = -4210$ ppm). Figure 4 shows the ^{195}Pt{^{1}H} NMR spectrum for the reaction of $(MePh_2P)_2PtBr_2$ with $(MePh_2P)_2PtI_2$ which displays the presence of both *cis*- ($\delta = -4931$ ppm) and *trans*- ($\delta = -5120$ ppm) $(MePh_2P)_2PtBrI$.

An unexpected trend was noted concerning the platinum–phosphorus coupling constants for the *cis* mixed halide complexes produced in reactions involving the chloride, bromide and iodide

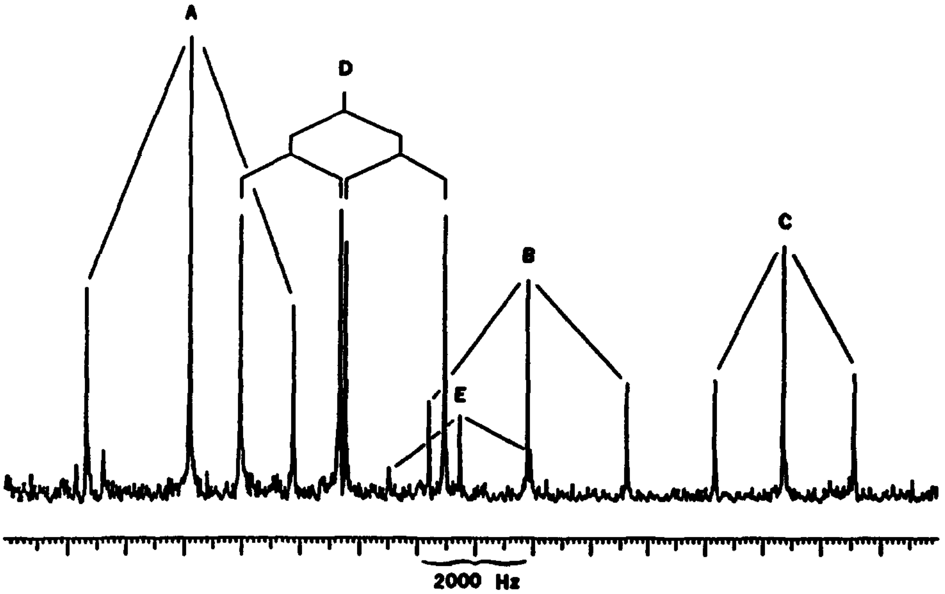
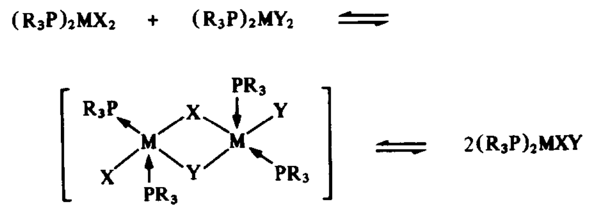


Fig. 4. 21.28 MHz ^{195}Pt{^{1}H} NMR spectrum of an equilibrium mixture of (A) *cis*-$(MePh_2P)_2PtBr_2$ ($\delta = -4685$ ppm), (B) *cis*-$(MePh_2P)_2PtI_2$ ($\delta = -5230$ ppm), (C) *trans*-$(MePh_2P)_2PtI_2$ ($\delta = -5648$ ppm), (D) *cis*-$(MePh_2P)_2PrBrI$ ($\delta = -4931$ ppm) and (E) *trans*-$(MePh_2P)_2PtBrI$ ($\delta = -5120$ ppm) in $CDCl_3$ at 300 K.

complexes. In most cases, there is a reversal in the magnitude of *J*(Pt—P). Reaction (5) is a typical example. For *cis*-$(Me_2Ph)_2PtBr_2$ and *cis*-$(Me_2PhP)_2PtI_2$, ^1J(Pt—P) is, respectively, 3500 and 3364 Hz. For the *cis*-$(Me_2PhP)_2PtBrI$ complex, the resonance assigned to the phosphorus *trans* to bromide has ^1J(Pt—P) of 3348 Hz and that assigned to the phosphorus *trans* to iodide has ^1J(Pt—P) of 3503 Hz. This is just opposite to our expectations. A reversal in the assignment of the phosphorus resonances for the *cis*-$(R_3P)_2PtXY$ complexes would give ^1J(Pt—P) coupling constants that are consistent with expectations, but then the chemical shifts would be difficult to explain.[34] Hence, the exact assignment of the chemical shifts in these cases is uncertain but the conclusions regarding the reactions remain the same, independent of the assignment.

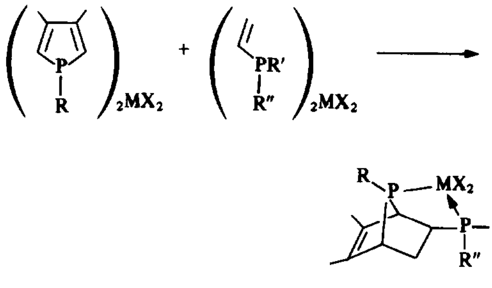
Mechanism of anion redistribution. As with geometrical isomerizations[35] of L_2MX_2 complexes, both associative and dissociative mechanisms are possible for the anion redistribution reactions. We believe that the associative mechanism illustrated in eq. (3), which has been previously proposed,[36–38] is the most likely process. We do not wish to imply anything regarding the coordination geometry of the anion-bridged intermediate (i.e. either square-based pyramidal (SBP) or trigonal-bipyramidal (TBP)), or of the actual location of the ligands not involved in bridging. Based upon the limited amount of structural data[39] on L_3MX_2 complexes the geometry may be distorted between SBP and TBP.



(3)

Phosphine redistribution

Palladium reactions. We have previously reported[5,6] on the neutral ligand redistribution of palladium complexes and found it to be fairly general. Six new reactions, all involving phosphines with unsaturated substituents, were carried out between pairs of palladium(II) phosphine complexes (Table 3). In each case, the $(R_3P)(R'_3P)PdX_2$ complex was in equilibrium with $(R_3P)_2PdX_2$ and $(R'_3P)PdX_2$, but also in each case this mixed ligand complex underwent a subsequent Diels–Alder [4+2] cycloaddition reaction[40] as illustrated in eq. (4). For the chloride complexes, only the *cis* mixed



(4)

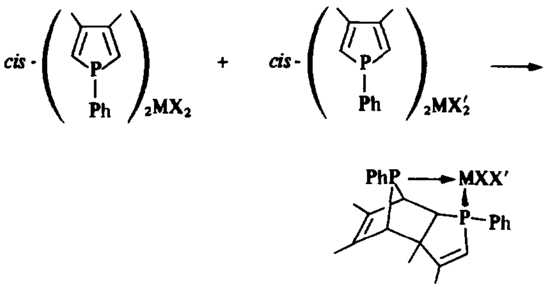
Table 3. ^{31}P NMR data on reactions of the type $(R_3P)_2PdX_2 + (R'_3P)_2PdX_2 \rightleftharpoons 2(R_3P)(R'_3P)PdX_2$, [4+2] cycloaddition product

				$\delta^{31}P^c$			$\delta^{31}P^c$	
Number	X	R_3P^a	R'_3P^b	Mixed ligand	Geometry	$J(PP)^d$	[4+2] product^e	J(PP)
29	Cl	$PhVy_2P$	DMPP	26.9, 15.7	*cis*	4.9	123.8, 35.4	4.9
30	Cl	Ph_2VyP	DMPP	27.4, 23.4	*cis*	0	124, 34.6	7.3
31	Br	$PhVy_2P$	DMPP	24.4, 13.7	*cis*	22	124.5, 35.5	1.5
				17.3, 4.5	*trans* AB	544	—	—
32	Br	Ph_2VyP	DMPP	21.9, 15.2	*cis*	0	123.9, 35.4	0
				14.0	*trans*	0	—	—
33	I	$PhVy_2P$	DMPP	6.5, −1.0	*trans* AB	540	120.7, 33.2	2.3
34	I	Ph_2VyP	DMPP	6.7	*trans*	0	121.4, 34.6	0

[a] Vy = $CH{=}CH_2$.
[b] DMPP = 1-phenyl-3,4-dimethylphosphole.
[c] In PPM in $CDCl_3$ at 300 K.
[d] In Hz.
[e] See ref. 40.

Table 4. Attempted exchange reactions of platinum(II) phosphine complexes of the type $L_2PtX_2 + L'_2PtX_2 \rightleftarrows$ No reaction

L	L′	X
$MePh_2P$	Me_2PhP	Cl
$MePh_2P$	Me_2PhP	Br
$MePh_2P$	Me_2PhP	I
Me_2PhP	Ph_2Vyp	Cl
Me_2PhP	$PhVy_2P$	Cl
Bzl_3P	Bu_3P	Cl
Bzl_3P	Bu_3P	Br
Bzl_3P	Bu_3P	I
cis-Et_3P	Bu_3P	Cl
trans-Et_3P	Bu_3P	Cl



(5)

ligand complex was formed. For the bromide complexes, both the *cis* and *trans* mixed ligand complexes were formed and for the iodide complexes, only the *trans* mixed ligand complex was formed. This is in agreement with previous observations that the *cis* isomer stability decreases with increasing size of the halide.[11] In each case, ligand redistribution was instantaneous and the following Diels–Alder cycloaddition relatively slow. Because of the following Diels–Alder cycloaddition reaction, K_{eq} for the ligand redistribution could not be measured. We also observed slow Diels–Alder [4+2] reactions [eq. (5)] in reactions (20), (21) and (22) of Table 2. Details of these Diels–Alder reactions will be described in subsequent publications.

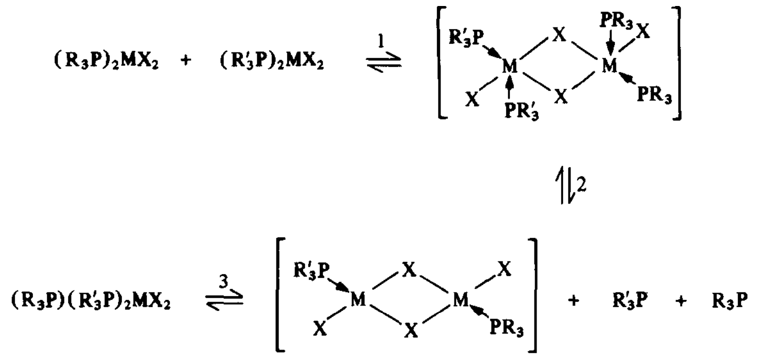
Platinum reactions. For all the platinum reactions listed in Table 4 there was no evidence of phosphine redistribution in $CDCl_3$ over a period of 4 weeks. In contrast, for each of the reactions listed in Table 5, phosphine redistribution not only occurred but did so instantaneously. It should be noted that all of the phosphines which participated in the redistribution reaction bear unsaturated substituents (allyl, vinyl, or the butadiene moiety of the phosphole ring). Most of the $(R_3P)(R'_3P)PtX_2$ complexes have the *cis* geometry. Reactions (39) and possibly (40) (both iodides) showed *trans* mixed ligand species. For reactions (35) and (36), equilibrium constants could be measured. For all other cases, [4+2] Diels–Alder cycloaddition occurred and equilibrium constants could not be measured.

Mechanism of phosphine redistribution. It is tempting to suggest that the mechanism for phos-

Table 5. ^{31}P NMR data on reactions of the type $(R_3P)_2PtX_2 + (R'_3P)_2PtX_2 \rightleftarrows 2(R_3P)(R'_3P)PtX_2 \rightarrow [4+2]$ cycloaddition product

				$\delta^{31}P^b$ (J(Pt—P))^c		[4+2] cycloaddition products				
Number	X	R_3P^a	R'_3P^a	Mixed ligand	$J(PP)^c$	$\delta^{31}P$	J(Pt—P)	$\delta^{31}P$	J(Pt—P)	J(PP)
35[d]	Cl	Ph_2VyP	$PhVy_2P$	3.4(3649), −5.6(3562)	17	—	—	—	—	—
36[e]	Cl	DMPP	$Ph(allyl)_2P$	8.5(3363), −2.8(3584)	17	—	—	—	—	—
37	Cl	$PhVy_2P$	DMPP	8.1(3325), 3.1(3613)	19	96.1	3254	21.4	3420	17
38	Cl	Ph_2VyP	DMPP	8.8(3350), 4.3(3652)	17	96.0	3237	20.7	3474	17
39	I	$PhVy_2P$	DMPP	3.3(2300), −6.1(2446)	450	98.5	2957	23.1	3188	10
40	I	Ph_2VyP	DMPP	2.8[f]	—	99.1	2932	24.5	3274	10

[a] Vy = CH=CH$_2$; DMPP = 1-phenyl-3,4-dimethylphosphole.
[b] In ppm in $CDCl_3$ at 300 K.
[c] In Hz.
[d] $K_{eq} = 5.3$.
[e] $K_{eq} = 57.3$.
[f] Concentration too low to observe additional NMR parameters.



(6)

phine ligand redistribution is similar to that of anion redistribution. We propose the mechanism shown in eq. (6). This is not dissimilar from dimer formation and phosphine dissociation which has been proposed to occur in similar systems.[41,42] Platinum(II) is more inert than palladium(II) and platinum–ligand bond strengths are generally greater than palladium–ligand bond strengths for the same ligands. Hence, one may anticipate the equilibrium constant for equilibrium (2) [eq. (6)] to be smaller for platinum than for palladium and we propose then that neutral ligand redistribution should only occur with platinum for weakly bound ligands. We have shown that redistribution reactions, contrary to our initial expectations, are not only common but unexpectedly rapid for "inert" square-planar palladium(II) and platinum(II) complexes. It seems most likely that they occur by associative processes involving bridged intermediates. The spontaneous *cis–trans* isomerizations which are common[11,14,20] for $(R_3P)_2PdX_2$ complexes, may occur by similar processes.

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