Transfer of Tertiary Phosphine between Rhodium and either Platinum or Palladium

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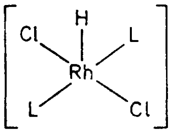
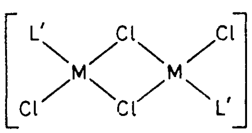
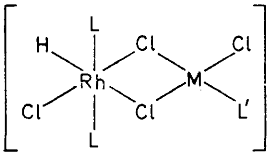
Biheterometallic chloro-bridged hydrido-species of type $[L_2HClRh(\mu-Cl)_2MClL']$ (L = PBu^tPr_2 or $PPrBu^t_2$, M = Pd or Pt, L′ = PEt_3, PBu_3, or PPr_2Bu^t) are formed on mixing toluene solutions of square-pyramidal $[RhHCl_2L_2]$ (L = PPr_2Bu^t or $PPrBu^t_2$) and a chloro-bridged dimeric palladium or platinum complex, $[M_2Cl_4L'_2]$ (M = Pt, L′ = PEt_3, PBu_3, or PPr_2Bu^t; M = Pd, L′ = PBu_3). On standing, in solution, at ambient temperature these biheterometallic complexes decompose, giving rise to mixed tertiary-phosphine complexes of type *trans*-$[MCl_2LL']$. The rate of this reaction is strongly dependent on the nature of both M and L. The ^1H and ^{31}P n.m.r. data of the complexes are reported.

ALTHOUGH the transfer of ionic ligands, *e.g.* halogen, alkyl, or hydride, between two different transition-metal complexes is a well established reaction,[1–5] the transfer of tertiary-phosphine ligands, in the absence of added free tertiary phosphine, is less well documented. In view of our interest [3,5–7] in biheterometallic complexes we have investigated the reaction between co-ordinatively unsaturated rhodium hydrido-species of type (I;


(I)


(II)

L = PPr_2Bu^t or $PPrBu^t_2$), and palladium or platinum chloro-bridged species of type (II; L′ = PEt_3, PBu_3, or PPr_2Bu^t, and M = Pt; L′ = PBu_3 and M = Pd) in an attempt to prepare biheterometallic hydrido-species of type (III).


(III)

RESULTS

With $[RhHCl_2(PPr_2Bu^t)_2]$, *Configuration* (I).—Mixing solutions, in $C_6D_5CD_3$, of $[RhHCl_2(PPr_2Bu^t)_2]$, (I; L = PPr_2Bu^t) (2 molar equivalents), and $[Pt_2Cl_4L'_2]$, (II; L′ = PEt_3, PBu_3, or PPr_2Bu^t (1 molar equivalent), at room temperature resulted in the slow disappearance (over *ca.* 30 min), in the ^1H n.m.r. spectrum, of the hydrido-signal of (I; L = PPr_2Bu^t) and the concurrent appearance of a new hydrido-signal *ca.* 8.5 p.p.m. downfield of the original signal. This new signal was assigned to the hydrido-ligand in (III; L = PPr_2Bu^t, L′ = PEt_3, PBu_3, or PPr_2Bu^t, and M = Pt).* Similarly, in the ^{31}P n.m.r. spectrum of the

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* An analogous decrease in hydrido-chemical shift was observed when the vacant co-ordination site in (I; L = PPr_2Bu^t) was filled by neutral ligands, *i.e.* MeNC, MeCN, or pyridine.[8]

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mixture we observed the disappearance of the signals assigned to the original two complexes and the appearance of a new set of signals assigned to (III). Whereas in the ^{31}P n.m.r. spectrum of the original platinum dimers we observed $^{3}J(^{195}\mathrm{Pt}-^{31}\mathrm{P})$ coupling, this was absent in the new set of signals, indicating that we have destroyed the chloro-bridge in (II). We detected no $^{3}J(^{103}\mathrm{Rh}-^{31}\mathrm{P})$ or $^{3}J(^{195}\mathrm{Pt}-^{31}\mathrm{P})$ coupling in the ^{31}P n.m.r. spectrum of (III); however, this was not unexpected as (*a*) ^{103}Rh–^{31}P couplings are generally over an order of magnitude smaller than the analogous ^{195}Pt–^{31}P couplings, and (*b*) *cis* couplings, *i.e.* $^{3}J(^{195}\mathrm{Pt}-^{31}\mathrm{P})$ in (III), are much smaller than similar *trans* couplings.

TABLE 1

Phosphorus-31 (36.43 MHz) and ^{1}H (90 MHz) n.m.r. data, recorded in $C_6D_5CD_3$ at 30 °C, of complexes of type $[(\mathrm{Bu^tPr_2P})_2\mathrm{HClRh}(\mu\text{-Cl})_2\mathrm{MClL}]$

		^{1}H					^{31}P			
		t-Butyl resonance		Hydride resonance			$\mathrm{PBu^tPr_2}$		L	
L	M	δ [a]	$\lvert ^{3}J(\mathrm{P-H}) + ^{5}J(\mathrm{P-H})\rvert$ [b]	δ [a]	$^{1}J(\mathrm{Rh-H})$ [b]	$J(\mathrm{P-H})$ [b]	δ [c]	$J(^{103}\mathrm{Rh}-^{31}\mathrm{P})$ [d]	δ [c]	$J(^{195}\mathrm{Pt}-^{31}\mathrm{P})$ [d]
$\mathrm{PEt_3}$	Pt	1.31	12.9	−22.67	14.7	11.8	26.5	95.6	4.9	3 821
$\mathrm{PPr_2Bu^t}$ [e]	Pt	1.28	12.9	−22.72	14.9	12.2	27.4	95.6	17.6	3 933
$\mathrm{PBu_3}$	Pt	1.32	12.9	−22.68	15.0	12.1	27.3	95.3	−3.0	3 862
$\mathrm{PBu_3}$	Pd	1.35	12.9	−22.64	14.7	12.1	27.6	95.3	32.4	

N.m.r. data measured in CD_2Cl_2, for $[\mathrm{RhHCl_2(PPr_2Bu^t)_2}]$, configuration (I) [f]: ^{1}H δ(Bu^{t}) [a] 1.23 p.p.m., $\lvert ^{3}J(\mathrm{P-H}) + ^{5}J(\mathrm{P-H})\rvert$ [b] 12.9 Hz, δ(hydride) [a] −31.16 p.p.m., $^{1}J(\mathrm{Rh-H})$ [b] 35.6, $J(\mathrm{P-H})$ [b] 13.2 Hz; ^{31}P δ(P) [c] 35.5 p.p.m., $^{1}J(^{103}\mathrm{Rh}-^{31}\mathrm{P})$ [d] 97.5 Hz.

[a] Relative to internal $SiMe_4$ ±0.02 p.p.m. [b] ±0.1 Hz. [c] Relative to 85% phosphoric acid (see Experimental section) with the sign convention that increasing frequency is positive. [d] ±1.0 Hz. [e] Hydrogen-1 n.m.r. data for $\mathrm{PPr_2Bu^t}$ bound to Pt: δ(Bu^{t}) 1.16 p.p.m.; $^{3}J(\mathrm{P-H})$ 14.4 Hz. [f] Previously reported (ref. 8) with CD_2Cl_2 as solvent.

TABLE 2

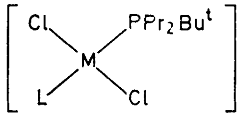
Phosphorus-31 (36.43 MHz) and ^{1}H (90 MHz) n.m.r. data, recorded in $C_6D_5CD_3$ at 30 °C, of complexes of type *trans*-$[\mathrm{MCl_2LL'}]$

			^{1}H			^{31}P					
			t-Butyl resonance								
L	L′	M	δ [a]	$^{3}J(\mathrm{P-H})$ [b]	$^{5}J(\mathrm{P-H})$ [b]	δ_A [c]	δ_B [c]	$\Delta\nu$ [d]	$^{2}J(^{31}\mathrm{P_A}-^{31}\mathrm{P_B})$ [d]	$^{1}J(^{195}\mathrm{Pt}-^{31}\mathrm{P_A})$ [d]	$^{1}J(^{195}\mathrm{Pt}-^{31}\mathrm{P_B})$ [d]
$\mathrm{PPrBu^t_2}$	$\mathrm{PEt_3}$	Pt	1.43	12.0	0.9	33.5	9.5	875	447	2 469	2 430
	$\mathrm{PPr_2Bu^t}$ [e]	Pt	1.43	11.1	1.8	47.9	34.8	477	440	2 462	2 464
	$\mathrm{PBu_3}$	Pt	1.43	12.2	*f*	33.5	1.8	1 155	447	2 471	2 412
	$\mathrm{PBu_3}$	Pd	1.42	12.1	0.9	41.6 [g]	10.1 [g]	1 091	516		
$\mathrm{PPr_2Bu^t}$	$\mathrm{PEt_3}$	Pt	1.25	10.9	2.9	25.3	5.7	356	450	2 406	2 433
	$\mathrm{PBu_3}$	Pt	1.23	12.0	1.5	30.9	−5.5	456	456	2 465	2 418
	$\mathrm{PBu_3}$	Pd	1.23	11.7	1.5	36.8	0.4	662	530		

N.m.r. data for $[\mathrm{RhHCl_2(PPrBu^t_2)_2}]$, configuration (I) [h]: ^{1}H δ(Bu^{t}) 1.41 p.p.m., $\lvert ^{3}J(\mathrm{P-H}) + ^{5}J(\mathrm{P-H})\rvert$ 12.3 Hz, δ(hydride) [a] 31.03 p.p.m.; $^{1}J(\mathrm{Rh-H})$ [b] 32.6, $J(\mathrm{P-H})$ [b] 12.3 Hz; ^{31}P δ(P) [c] 47.5 p.p.m., $^{1}J(\mathrm{Rh-P})$ 97.1 Hz.

[a] Relative to internal $SiMe_4$ ±0.02 p.p.m. [b] ±0.1 Hz. [c] Relative to 85% H_3PO_4 (see Experimental section) with the sign convention that increasing frequency is positive. [d] ±1.0 Hz. [e] Hydrogen n.m.r. data for $\mathrm{PPr_2Bu^t}$: δ(Bu^{t}) 1.22 p.p.m.; $^{3}J(\mathrm{P-H})$ 11.5, $^{5}J(\mathrm{P-H})$ 1.8 Hz. [f] $^{5}J(\mathrm{P-H})$ not resolved <0.5 Hz. [g] In the absence of white-noise decoupling; A identified as $\mathrm{PBu_3}$ and B as $\mathrm{PPrBu^t_2}$. [h] Previously reported (ref. 8) with CD_2Cl_2 as solvent.

On allowing the reaction solution to stand for several hours at ambient temperature further changes were observed in both the ^{1}H and the ^{31}P n.m.r. spectrum of the mixture. In the ^{1}H n.m.r. spectrum the hydrido-signal disappeared completely and the ' triplet ' arising from the virtual coupling of the two $\mathrm{PPr_2Bu^t}$ ligands in (III) was replaced by a doublet of doublets. In the ^{31}P n.m.r. spectrum the signals assigned to (III) were replaced by an AB pattern having ^{195}Pt satellites. These new signals we assigned to a complex of type (IV; L = $\mathrm{PEt_3}$, $\mathrm{PBu_3}$, or $\mathrm{PPr_2Bu^t}$, M = Pt). We followed the conversion of (III; L = $\mathrm{PPr_2Bu^t}$, L′ = $\mathrm{PBu_3}$, M = Pt) into (IV; L = $\mathrm{PBu_3}$, M = Pt) at 40 ± 2 °C by recording the ^{31}P n.m.r. spectrum of the mixture as a function of time over 15 h. The conversion followed first-order kinetics with $t_{\frac{1}{2}}$ = 330 ± 20 min.



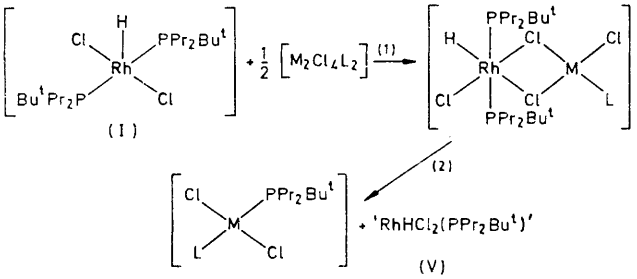
(IV)

Using $[\mathrm{Pd_2Cl_4(PBu_3)_2}]$ in place of $[\mathrm{Pt_2Cl_4L'_2}]$ (L = $\mathrm{PEt_3}$, $\mathrm{PBu_3}$, or $\mathrm{PPr_2Bu^t}$) we observed an analogous sequence of reactions. However, with the palladium complexes the reactions were about an order of magnitude faster; the formation of (III; L = $\mathrm{PPr_2Bu^t}$, L′ = $\mathrm{PBu_3}$, M = Pd) was essentially complete within 5 min of mixing $[\mathrm{RhHCl_2(PPr_2Bu^t)_2}]$ and $[\mathrm{Pd_2Cl_4(PBu_3)_2}]$ in $C_6D_5CD_3$. The conversion of (III) into (IV; M = Pd, L = $\mathrm{PBu_3}$) at 40 °C had a half-life of 19 ± 2 min.

The reaction sequence is summarized in the Scheme and the n.m.r. data are presented in Tables 1 and 2. Table 3 contains some n.m.r. data for the dimeric platinum and palladium complexes.

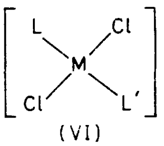
We have been unable, as yet, to characterize the rhodium species (V) formed in step (2) of the above sequence. Our initial observations suggest a fluxional system, since in the ^{1}H n.m.r. spectrum of the final mixture, recorded at

−100 °C, we found a broad signal at *ca.* δ −19 p.p.m., which disappeared on increasing the temperature. Similarly, in the ^{31}P n.m.r. spectrum, recorded at −90 °C, we observed broad signals which disappeared above *ca.* −50 °C.



SCHEME L = PEt_3, PBu_3, or PPr_2Bu^t and M = Pt; L = PBu_3 and M = Pd

With $[RhHCl_2(PPrBu^t_2)_2]$, *Configuration* (I).—With $[RhHCl_2(PPrBu^t_2)_2]$ in place of $[RhHCl_2(PPr_2Bu^t)_2]$ the sequence of reactions shown in the Scheme occurred much more rapidly. Indeed, we were unable to detect the presence of the mixed-metal hydrido-species, (III), at ambient temperature. Conversion into complexes of type (VI) was essentially complete within *ca.* 3 min of mixing solutions of $[RhHCl_2(PPrBu^t_2)_2]$ and $[M_2Cl_4L_2]$ (L = PEt_3, PBu_3, or PPr_2Bu^t, and M = Pt; L = PBu_3 and M = Pd) at ambient temperature. In the ^1H n.m.r. spectra of the mixtures we observed the expected doublet of doublets for the t-butyl resonance, and in the ^{31}P n.m.r. spectra the expected AB patterns. N.m.r. data are listed in Table 2. We isolated three of these mixed tertiary-phosphine complexes as stable yellow compounds; analytical, melting-point, and far-infrared data are presented in Table 4.



(VI)

TABLE 3

Phosphorus-31 (36.43 MHz) and ^1H (90 MHz) n.m.r. data, recorded in $C_6D_5CD_3$ at 30 °C, of complexes of the type $[L'ClM(\mu\text{-}Cl)_2MClL']$

		^{31}P				
L′	M	δ [a]	^1J(Pt–P) [b]	^3J(Pt–P) [b]	^4J(P–P) [b]	J(Pt–Pt) [c]
PEt_3	Pt	9.3	3 849	23.6	3.0	193
PPr_2Bu^t	Pt [d]	20.7	3 972	21.3	2.6	125
PBu_3	Pd [e]	37.3				

[a] In p.p.m. Relative to 85% H_3PO_4 (see Experimental section) with the sign convention that increasing frequency is positive. [b] ±1.0 Hz. [c] ±2.0 Hz. [d] Hydrogen-1 n.m.r. data for PPr_2Bu^t; δ(Bu^t) 1.03 p.p.m., $|^3J(P\text{–}H) + {}^5J(P\text{–}H)|$ 14.9 Hz. [e] Previously measured in $CDCl_3$.[7]

TABLE 4

Analytical, melting-point, and far-infrared data of some complexes of type *trans*-$[MCl_2L(PPrBu^t_2)]$

			Analysis (%) [b]			Far-infrared [c] data (cm^{-1})
L	M	M.p. [a] (θ_c/°C)	C	H	Cl	ν(M–Cl)
PEt_3	Pt	98—99	36.5 (35.7)	7.1 (7.0)	12.9 (12.4)	335s, 321m
PPr_2Bu^t	Pt	182—183	39.7 (40.1)	7.7 (7.6)	11.3 (11.3)	330s, 334 (sh)
PBu_3	Pd	232—236 [d]	46.9 (48.7)	9.2 (9.2)	12.8 (12.5)	349s

[a] Uncorrected. [b] Calculated values are given in parentheses. [c] Measured as CsI disc. [d] With decomposition.

DISCUSSION

The importance of the steric requirements of the tertiary-phosphine ligands on the nature and speed of reactions found in organometallic chemistry has received considerable attention over the last few years.[9-14] We suggest that both the nature of the reaction reported here, *i.e.* transfer of a tertiary-phosphine ligand from rhodium to either platinum or palladium, and the difference in rate of reaction observed on going from $[RhHCl_2(PPr_2Bu^t)_2]$ to $[RhHCl_2(PPrBu^t_2)_2]$ may be rationalized in terms of steric considerations. Complexes containing two t-butyl-substituted phosphines co-ordinated to the same metal atom are sterically very crowded and have been found to undergo a variety of reactions, *e.g.* internal metallation,[9,10] which result in relief of steric strain. Clearly, in the reaction reported here considerable relief of steric strain would result in transfer of one of the t-butyl-substituted phosphines from the rhodium centre to the less crowded platinum or palladium centre. Further, this relief will be more marked for the $PPrBu^t_2$ than for the PPr_2Bu^t complex, as can be seen from the considerable differences in reaction rate. The increase in reaction rate observed on going from a platinum to a palladium chloro-bridged dimer may be rationalized in terms of a decrease in bridge strength in going from platinum to palladium. A similar trend has previously been observed in exchange reactions between $[PtPdCl_4(PBu_3)_2]$ and either $[PtCl_4(PBu_3)_2]$ or $[Pd_2Cl_4(PBu_3)_2]$.[7]

The system reported here offers a facile synthetic route to platinum(II) and palladium(II) complexes containing two different mutually *trans* tertiary-phosphine ligands. Since the dimeric platinum and palladium species of type (II) are easily synthesized [15] with

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a wide range of tertiary-phosphine ligands and since rhodium(III) species of type (I) are known[8] with L = PBu^tR_2 and $PBu^t{}_2R$ (R = Me, Et, or Pr), a wide spectrum of complexes of type (VI; M = Pd or Pt, L and L′ = tertiary phosphine) are readily available.

EXPERIMENTAL

Complexes of type $[M_2Cl_4L_2]$ (M = Pd or Pt, L = PEt_3, PBu_3, or PPr_2Bu^t) and $[RhHCl_2L_2]$ (L = PPr_2Bu^t or $PPrBu^t{}_2$) were prepared using previously published procedures.[8,15] Hydrogen-1 n.m.r. spectra of solutions in $[^2H_8]$toluene (*ca.* 0.05 mol dm^{-3}) were recorded at 90 MHz and ^{31}P n.m.r. spectra at 36.43 MHz using a Bruker WH 90 spectrometer in the pulse Fourier-transform mode. Phosphorus-31 chemical shifts were measured with respect to *ca.* 25% trimethyl phosphite in $[^2H_8]$toluene, and are quoted in the Tables with respect to 85% phosphoric acid assuming that the ^{31}P chemical shift of $P(OMe)_3$ is +140 p.p.m. relative to 85% H_3PO_4,[16] with the sign convention that increasing frequency is positive.[17] In the ^{31}P n.m.r. spectra all proton couplings were removed using a random-noise decoupler. Infrared spectra (caesium iodide; 200—4 000 cm^{-1}) were recorded on a Perkin-Elmer 225 apparatus. Melting points were measured with a Mettler FPI/FP21 apparatus and are uncorrected.

trans-*Dichloro(propyldi-t-butylphosphine)(triethylphosphine)platinum*(II).— Di-μ-chloro-bis[chloro(triethylphosphine)platinum(II)] (0.2 g, 0.26 mmol) in dichloromethane (5 cm^3) was added to dichlorohydridobis(propyldi-t-butylphosphine)rhodium(III), configuration (I) (0.287 g, 0.521 mmol), in dichloromethane (5 cm^3) and propan-2-ol (20 cm^3). The resulting mixture was stirred (5 min at 20 °C). Removal of the solvent gave a brown solid, which on recrystallization from methanol–dichloromethane yielded the *product* (0.145 g, 0.253 mmol) as yellow prisms.

trans-*Dichloro(dipropyl-t-butylphosphine)(propyldi-t-butylphosphine)platinum*(II) and trans-*dichloro(propyldi-t-butylphosphine)(tributylphosphine)palladium*(II) were similarly prepared.

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