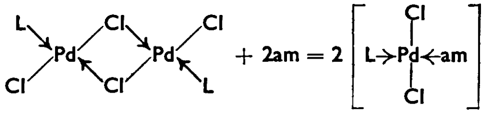
477. *The Reaction of Monoamines with Chloro-bridged Complexes of Palladium*(II).

By J. Chatt and L. M. Venanzi.

Most chloro-bridged complexes of the type $L_2Pd_2Cl_4$ (I) react with monoamines, am, as follows: $[L_2Pd_2Cl_4] + 2am \rightleftharpoons 2[L,amPdCl_2]$ (II), but the product (II) can be isolated only when the donor atom in the ligand L is phosphorus and arsenic. When the donor atom is sulphur, selenium, or tellurium, the mixed product disproportionates measurably slowly in solution at room temperature: $2[L,amPdCl_2] \longrightarrow [L_2PdCl_2] + [am_2PdCl_2]$. When L is an olefin, immediate decomposition of the product occurs even at −70°. When the halogen is iodine the equilibrium lies so far to the side of the bridged complex that the mixed product can be isolated, if at all, only in the presence of a large excess of the amine.

The reaction of amines with the halogen-bridged complexes of palladium, $[L_2Pd_2Cl_4]$ (I), containing tertiary phosphines and arsines as ligands L has been studied by Mann and his co-workers.[1] They showed that the following reaction occurs almost instantaneously in organic solvents at room temperature:



(I) (II)

We needed compounds such as (II) with a large variety of ligands L to further our study of inductive and mesomeric effects in complex compounds,[2] so we attempted to obtain them by this reaction from the bridged compounds previously described.[3] However, the only mixed complexes which we could isolate were those containing phosphorus and arsenic as donor atoms in the ligands L, and new compounds of this type are listed in the Table.

Complex	M. p.	Colour
PEt_3,piperidine$PdCl_2$	73·5—75°	Orange-yellow
PPr^n_3,piperidine$PdCl_2$	116—118	Orange-yellow
PBu^n_2Ph,piperidine$PdCl_2$	64—64·5	Orange-yellow
PPh_3,piperidine$PdCl_2$	160—172 (decomp.)	Yellow-orange
$P(MeO)_3$,piperidine$PdCl_2$	90—91	Orange-yellow
$P(PhO)_3$,piperidine$PdCl_2$	131—132	Orange-yellow
$AsEt_3$,piperidine$PdCl_2$	68—70	Yellow-orange
PPr^n_3,*p*-toluidine$PdCl_2$	91·5—92·5	Yellow-orange
PBu^n_2Ph,*p*-toluidine$PdCl_2$	111·5—113	Yellow-orange
PPh_3,*p*-toluidine$PdCl_2$,MeOH	218 (decomp.)	Dark orange
PPh_3,*p*-toluidine$PdCl_2$,EtOH	218—220 (decomp.)	Dark orange
PPh_3,*p*-toluidine$PdCl_2$,PrOH	200—220 (decomp.)	Orange
$P(MeO)_3$,*p*-toluidine$PdCl_2$	131—131·5	Yellow-orange
$P(PhO)_3$,*p*-toluidine$PdCl_2$	115·5—116·5	Yellow-orange
PPr^n_3,*p*-toluidinePdI_2	107	Red

Finck[4] obtained two mixed phosphite–*p*-toluidine complexes, $[P(MeO)_3$,*p*-toluidine-$PdCl_2]$ and $[P(EtO)_3$,*p*-toluidine$PdCl_2]$, by reaction of an excess of *p*-toluidine with $[\{P(MeO)_3\}_2PdCl_2]$ and $[\{P(EtO)_3\}_2PdCl_2]$ respectively. He describes them as white solids. The compounds of that type which we have obtained are orange-yellow and certainly have a *trans*-configuration. If Finck's compounds have the formula claimed, it seems that they might have *cis*-configurations, and the mixed phosphite–*p*-toluidine

---

[1] Mann, *Ann. Reports*, 1938, **35**, 148; Chatt and Mann, *J.*, 1939, 1622.

[2] Chatt, Duncanson, and Venanzi, *J.*, 1955, 4461.

[3] Chatt and Venanzi, *J.*, 1957, 2351.

[4] Finck, *Compt. rend.*, 1896, **123**, 603.

complexes could thus provide another example of non-labile geometrical isomerism, which is very rare in the palladous series of complexes.

Mixed complexes of the type *trans*-[L,am$PdCl_2$], containing donor atoms from Group VI, are formed by the reaction of amines with the appropriate bridged complex $[(R_2M)_2Pd_2Cl_4]$ (M = S, Se, or Te), but they disproportionate spontaneously into $(R_2M)_2PdCl_2$ and am_2PdCl_2 at room temperature, and could not be isolated :

$$[(\mathrm{Et_2Te})_2\mathrm{Pd_2Cl_4}] + 2\mathrm{Piperidine} \longrightarrow 2[\mathrm{Et_2Te,piperidinePdCl_2}]$$

$$2[\mathrm{Et_2Te,piperidinePdCl_2}] \longrightarrow [(\mathrm{Et_2Te})_2\mathrm{PdCl_2}] + [(\mathrm{piperidine})_2\mathrm{PdCl_2}]$$

This disproportionation was evident from the infrared spectrum of a solution of the freshly mixed components. For example, a freshly prepared solution of $[(Et_2Te)_2Pd_2Cl_4]$ and piperidine (1 : 2) in carbon tetrachloride has an absorption band at 3249 cm.$^{-1}$ attributable to the N–H stretching vibration of the complex, [Et_2Te,piperidine$PdCl_2$], but this band gradually decreases in intensity while a second band appears at 3237 cm.$^{-1}$ corresponding to the N–H stretching vibration of the complex [(piperidine)$_2PdCl_2$].

The reaction of *p*-toluidine with the bridged olefin complex [(*cyclo*hexene)$_2Pd_2Cl_4$] in methylene chloride at −70° led to the immediate decomposition of the complex.[3]

Attempts to obtain mixed amine complexes, [am,am'$PdCl_2$], were unsuccessful.

The reaction of the *p*-toluidine with the bridged iodo-complex $(PPr^n{}_3)_2Pd_2I_4$ indicated that the components are in labile equilibrium in solution :

$$(\mathrm{PPr^n}_3)_2\mathrm{Pd_2I_4} + 2\mathrm{C_7H_7NH_2} \rightleftharpoons 2[\mathrm{PPr^n}_3,\mathrm{C_7H_7NH_2PdI_2}].$$

The mixed product was obtained only by using an excess of amine in the reaction, and by recrystallising the product from a solution of the amine in the appropriate organic solvent (light petroleum, b. p. 60—80°).

The complex [PPh_3,$C_7H_7NH_2PdCl_2$] is peculiar in crystallising from alcohols with one molecule of the alcohol tenaciously held in the crystal.

We checked the configuration of the mixed complexes by measuring their $\Delta\varepsilon/f$ in benzene solution ($\Delta\varepsilon$ = the increment in dielectric constant due to the solute, f = mol. fraction of solute), and all had *trans*-configurations, as expected.[5]

Generally it appears that the mixed complexes [L,am$PdCl_2$] have a somewhat similar pattern of relative stabilities to that of their platinous analogues. However, they are less stable and more soluble in organic solvents, and so fewer types can be isolated at ordinary temperatures.

EXPERIMENTAL

Microanalyses are by Messrs. W. Brown and A. G. Olney of these laboratories.

The bridged complexes $[L_2Pd_2Cl_4]$ were prepared as previously described.[3] The low yields of the mixed complexes [L,am$PdCl_2$] reported below are to be attributed to the small scale on which the compounds were prepared and to their high solubilities in organic solvents. The reactions of formation appear to be almost quantitative.

trans-*Triethylphosphinepiperidinedichloropalladium*.—The bridged complex $[(PEt_3)_2Pd_2Cl_4]$ (1 g.) in methylene chloride (50 c.c.) was treated with piperidine (0·3 c.c.), and the orange-yellow solution taken to dryness at 15 mm. The residual *product* recrystallised from light petroleum (b. p. 60—80°) (yield 43%) (Found : C, 34·9; H, 6·8; N, 3·9. $C_{11}H_{26}NCl_2PPd$ requires C, 34·7; H, 6·9; N, 3·7%). $\Delta\varepsilon/f = 4{\cdot}3$.

Similarly prepared and purified were : trans-*tri*-n-*propylphosphinepiperidinedichloropalladium* (yield 92%) (Found : C, 39·7; H, 7·7; N, 3·75. $C_{14}H_{32}NCl_2PPd$ requires C, 39·75; H, 7·6; N, 3·3%), trans-*triethylarsinepiperidinedichloropalladium* (58%) (Found : C, 31·3; H, 6·3; N, 3·3. $C_{11}H_{26}NCl_2AsPd$ requires C, 31·1; H, 6·2; N, 3·3%), trans-*tri*-n-*propylphosphine*-p-*toluidinedichloropalladium* (37%) (Found : C, 43·3; H, 6·8. $C_{16}H_{30}NCl_2PPd$ requires C,

---

[5] Cf. Chatt and Wilkins, *J.*, 1953, 70.

43·2; H, 6·8%), and trans-*di*-n-*butylphenylphosphine*-p-*toluidinedichloropalladium* (recrystallised from methanol; yield 20%) (Found: C, 49·7; H, 6·3; N, 2·95. $C_{21}H_{32}NCl_2PPd$ requires C, 49·8; H, 6·4; N, 2·8%).

trans-*Di*-n-*butylphenylphosphinepiperidinedichloropalladium*.—The complex $[(PBu^n_2Ph)_2Pd_2Cl_4]$ (3 g.) was suspended in methanol (25 c.c.), and freshly distilled piperidine (0·7 c.c.) was added. The resultant orange solution on evaporation at 15 mm. left an orange oil. This was induced to crystallise by seeding with the corresponding crystalline *p*-toluidine complex, and the product was purified by making a saturated solution in methanol at room temperature and collecting the *product* which crystallised at $-5°$ (yield 75%) (Found: C, 47·0; H, 7·2; N, 2·75. $C_{19}H_{34}NCl_2PPd$ requires C, 47·1; H, 7·2; N, 2·9%). This compound tends to form oils which are difficult to crystallise.

trans-*Triphenylphosphinepiperidinedichloropalladium* was prepared by shaking a suspension of the stoicheiometric amount of $[(PPh_3)_2Pd_2Cl_4]$ with piperidine in methylene chloride until complete dissolution had occurred. It recrystallised from light petroleum (b. p. 80—100°) (yield 36%) (Found: C, 52·5; H, 5·1; N, 2·95%; *M*, ebullioscopic in 0·8% benzene solution, 543. $C_{23}H_{26}NCl_2PPd$ requires C, 52·6; H, 5·0; N, 2·7%; *M*, 525). It is a non-electrolyte in nitrobenzene solution.

trans-(*Trimethyl Phosphite*)*piperidinedichloropalladium*.—The amine was added to a solution of the bridged compound in methylene chloride at $-70°$, and the *product* which separated spontaneously was recrystallised from light petroleum (b. p. 60—80°) (yield 25%) (Found: C, 25·1; H, 5·2; N, 3·7. $C_8H_{20}O_3NCl_2PPd$ requires C, 24·8; H, 5·2; N, 3·6%).

Similarly prepared were: trans-(*triphenyl phosphite*)*piperidinedichloropalladium* (33%) (Found: C, 48·1; H, 4·5; N, 2·5. $C_{23}H_{26}O_3NCl_2PPd$ requires C, 48·2; H, 4·6; N, 2·4%); trans-(*trimethyl phosphite*)-p-*toluidinedichloropalladium* (recrystallised from methanol; yield 59%) (Found: C, 29·5; H, 4·4; N, 3·6%; *M*, ebullioscopic in 1·2% benzene solution, 434. $C_{10}H_{18}O_3NCl_2PPd$ requires C, 29·4; H, 4·4; N, 3·4%; *M*, 489), $\Delta\varepsilon/f = 7{\cdot}6$; and trans-(*triphenyl phosphite*)-p-*toluidinedichloropalladium* (purified, with great loss, by repeated recrystallisation from *cyclo*hexane and then ether–light petroleum) (Found: C, 50·5; H, 4·1%; *M*, ebullioscopic in 0·8% benzene solution, 515. $C_{25}H_{24}O_3NCl_2PPd$ requires C, 50·5; H, 4·1%; *M*, 595), $\Delta\varepsilon/f = 7{\cdot}9$. The above phosphite complexes are non-electrolytes in nitrobenzene solution.

trans-*Triphenylphosphine*-p-*toluidinedichloropalladium*.—The complex $[(PPh_3)_2Pd_2Cl_4]$ (2 g.) in methylene chloride (50 c.c.) suspension was shaken with *p*-toluidine (0·45 g.) for several hours. The solution was filtered from a small amount of unchanged material and taken to dryness at 15 mm., leaving an orange crystalline residue (2 g.). This product could be satisfactorily recrystallised, as *solvates*, only from methanol (Found: C, 53·6; H, 4·9; N, 2·75. $C_{25}H_{24}NCl_2PPd,CH_4O$ requires C, 53·9; H, 4·9; N, 2·4%), ethanol (Found: C, 54·7; H, 5·3; N, 2·4. $C_{25}H_{24}NCl_2PPd,C_2H_6O$ requires C, 54·7; H, 5·1; N, 2·4%), or propanol (Found: C, 55·2; H, 5·35; N, 2·7. $C_{25}H_{24}NCl_2PPd,C_3H_8O$ requires C, 55·4; H, 5·3; N, 2·3%). Drying the above compounds in a high vacuum caused only partial loss of the alcohol and, when heat was applied, decomposition set in. The products with alcohol of crystallisation are non-electrolytes in nitrobenzene solution.

trans-*Tri*-n-*propylphosphine*-p-*toluidinedi-iodopalladium*.—*p*-Toluidine (0·5 g.) was added to a solution of the complex $[(PPr^n_3)_2Pd_2I_4]$ (2·3 g.) in acetone. No change in colour was observed. The solution was taken to dryness at 15 mm., and on attempted recrystallisation the residue from light petroleum (b. p. 80—100°) re-formed a large amount of the original binuclear complex. *p*-Toluidine was then added in sufficient quantity to redissolve the binuclear complex in the boiling solvent, and then, on cooling, a crop of red plate-like crystals was obtained. Recrystallisation from light petroleum in presence of an excess of *p*-toluidine was repeated. The *product* was then washed with light petroleum (b. p. 40—60°) and dried in a vacuum-desiccator. The yield was poor (Found: C, 30·8; H, 4·7; N, 2·4. $C_{16}H_{30}NI_2PPd$ requires C, 30·6; H, 4·8; N, 2·2%).

The authors thank Dr. L. A. Duncanson for the infrared spectroscopic data and Mr. P. F. Todd and Mr. M. L. Searle for experimental assistance.

AKERS RESEARCH LABORATORIES, IMPERIAL CHEMICAL INDUSTRIES LIMITED,
THE FRYTHE, WELWYN, HERTS.
[*Received, January 3rd*, 1957.]