## 667. *Carboxylates of Palladium, Platinum, and Rhodium, and their Adducts*

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The interaction of palladium(II) nitrate with acetic and propionic acids produces the brown carboxylates $Pd(OCOR)_2$; the benzoate, trifluoroacetate, and pentafluoropropionate are obtained *via* exchange reactions. Although the fluoro-carboxylates are monomeric, the other compounds are trimers in solution at 37°.

The interaction of the carboxylates with various amines, triphenylphosphine and triphenylarsine gives complexes of the type *trans*-$[Pd(OCOR)_2L_2]$ with unidentate carboxylate groups.

Diacetatoplatinum(II) was obtained by the reduction of an acetic acid solution of hexahydroxyplatinate(IV) with formic acid. It is trimeric, not isomorphous with $[Pd(OCOMe)_2]_3$, and does not undergo cleavage reactions with donor ligands.

Studies on rhodium(II) carboxylates [1] have been confirmed and extended.



*Palladium Carboxylates.*—Diacetatopalladium(II) can be obtained as brown crystals from the interaction of slightly acid solutions of palladium(II) nitrate with glacial acetic acid, or by dissolving palladium sponge suspended in hot glacial acetic acid, by the addition of the minimum quantity of nitric acid. The propionate can be made directly in the same way, while the benzoate, trifluoroacetate, and pentafluoropropionate can be obtained from the acetate by exchange reactions.

An unusual feature of the acetate and propionate is that in benzene solution at 37°, osmometric determinations show that they are trimeric, whereas ebullioscopically in benzene (80°) they are monomeric. Attempts to study the trimer–monomer equilibrium by infrared, absorption, and high-resolution nuclear magnetic resonance spectral measurements over a temperature range were unsuccessful since the spectra of the two species appear to show no features that are characteristic (single peak only).

On the other hand, the benzoate is trimeric at 37° (osmometer) and remains trimeric when its molecular weight is measured ebullioscopically in both benzene (80°) and chlorobenzene (132°), while the two fluoro-carboxylates are both monomeric in ethyl acetate at 37°.

The absorption spectrum of the acetate in benzene or toluene solution (280—1000 mμ) shows a single broad charge-transfer band ($\varepsilon \sim 1000$) at 394 mμ, although a stronger band below 280 mμ is indicated. Solid-state reflectance spectra of the acetate (750—1000 mμ) showed weak peaks at 730, 820, and 910 mμ whilst the propionate had peaks at 760, 823, and 920 mμ; since these bands were not observed in solutions (0·1M) a value of $\varepsilon < 1$ is indicated. The longest wavelength *d–d* band in $PtCl_4^{2-}$ that is assigned to a singlet–triplet transition occurs [2] at 565 mμ, and substitution of ammonia for chloride shifts all the bands to shorter wavelengths. Since the carboxylate group produces a stronger ligand field than chloride, it seems unlikely that the weak bands here are due to *d–d* transitions in these $d^8$ spin-paired species; any *d–d* bands in the 300—700 mμ region are obscured by the broad charge-transfer band.

The carboxylates are stable indefinitely in air. They are soluble in a number of organic solvents, but decompose when warmed with alcohols, giving palladium metal; prolonged boiling in other solvents gives the same result.

The lability of palladium oxygen bonds is confirmed by the ease with which the carboxylate groups can be wholly or partially replaced by various mono-, bi-, and tetradentate ligands. Thus, the acetate and propionate react in the cold with acetylacetone

[1] Preliminary Note: *Chem. and Ind.*, 1964, 544.
[2] J. Chatt, G. A. Gamlen, and L. E. Orgel, *J.*, 1958, 486.

or with salicylaldehyde to give well-known compounds of the type $PdL_2$, and with bisacetylacetone-ethylenedi-imine and bis-salicylaldehyde-ethylenedi-imine to produce the completely substituted Pd(enbisacac) and Pd(enbissal). With various nitrogen donors, triphenylphosphine and triphenylarsine (a large excess required for complete reaction), yellow crystalline monomeric adducts of the type $[Pd(OCOR)_2L_2]$ are obtained (Table 1).

TABLE 1

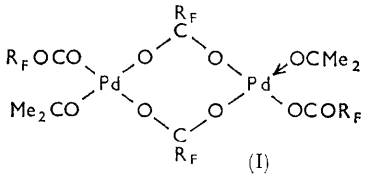
Infrared spectra of palladous carboxylates and adducts ($cm.^{-1}$)

| Compound | $\omega_2$ | $\omega_1$ | Separation $\Delta(\omega_2 - \omega_1)$ | Difference $\omega_2$ (adduct) − $\omega_2$ (carb) | Difference $\omega_1$ (carb) − $\omega_1$ (adduct) |
|---|---|---|---|---|---|
| $[Pd(OCOPh)_2]_3$ | 1567 | 1404 | 163 | — | — |
| $[Pd(OCOPh)_2(Ph_3P)_2]$ | 1623 | 1319 | 304 | 56 | 85 |
| $[Pd(OCOPh)_2(Ph_3As)_2]$ | 1626 | 1325 | 301 | 59 | 79 |
| $[Pd(OCOPh)_2(py)_2]$ | 1603 | 1342 and/or 1323 | ⩾261 | 36 | ⩾62 |
| $[Pd(OCOCF_3)_2]$ | 1572 | 1456 | 116 | — | — |
| $[Pd(OCOCF_3)_2(Ph_3P)_2]$ | 1684 | 1393 | 291 | 112 | 63 |
| $[Pd(OCOCF_3)_2(OSMe_2)_2]$ | 1681 | 1408 | 273 | 109 | 48 |
| $[Pd(OCOC_2F_5)_2]$ | 1567 | 1431 | 136 | — | — |
| $[Pd(OCOC_2F_5)_2(Ph_3As)_2]$ | 1678 | 1372 | 306 | 111 | 59 |
| $[Pd(OCOEt)_2]_3$ | 1595 | 1425 | 170 | — | — |
| $[Pd(OCOEt)_2(Ph_3P)_2]$ | 1618 | 1359 and/or 1311 | ⩾259 | 23 | ⩾66 |
| $[Pd(OCOMe)_2]_3$ | 1600 | 1427 | 173 | — | — |
| $[Pd(OCOMe)_2(Ph_3P)_2]$ | 1634 | 1353, 1307 [a] and/or 1297 | ⩾281 | 34 | ⩾74 |
| $[Pd(OCOMe)_2(Et_3N)_2]$ | 1626 | ⩽1377 [a, b] | ⩾249 | 26 | ⩾50 |
| $[Pd(OCOMe)_2(Et_2NH)_2]$ | 1582 | ⩽1370 [a, b] | ⩾212 | (−)(18 | ⩾57 |
| $[Pd(OCOMe)_2(py)_2]$ | ⩽1626 [b] | 1377, 1361, 1314, [a] and/or 1297 | ⩾239 | ⩽23 | ⩾50 |
| $[Pd(OCOMe)_2bipy]$ | ⩽1626 [b] | 1370 and/or 1328 [a] | ⩾256 | ⩽26 | ⩾57 |

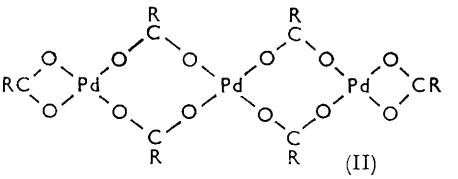
[a] Among bands in the $\omega_1$ region is the $CH_3$ rock (*ca.* 1350). [b] Band obscured by absorption due to $Et_3N$, $Et_2NH$, py, or bipy.

The compounds with nitrogen ligands are the most stable; the triphenylphosphine adducts dissociate and decompose readily in warm solvents making measurement of molecular weights impossible. A determination of the dipole moment of the diethylamine complex indicated a *trans*-configuration, and the other complexes are presumably also *trans* with the exception of the 2,2′-bipyridyl complex $[Pd(OCOMe)_2bipy]$ which, since it is monomeric, must have *cis*-carboxylate groups.

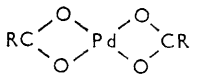
The fluoro-carboxylates dissolve in warm acetone and yield well-defined air-stable orange-red crystalline complexes of the composition $[Pd(OCOR_F)_2Me_2CO]_2$; these are dimeric in ethyl acetate at 37° and presumably have a structure of type I. Their infrared



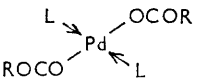

(I)




(II)




(III)




(IV)

spectra show strong bands at 1650 $cm.^{-1}$ ($CF_3$ complex) and 1653 $cm.^{-1}$ ($C_2F_5$ complex) with weaker shoulders at 1626 and 1629 $cm.^{-1}$, respectively, one of which can be assigned to the co-ordinated C:O (acetone), and the other to $\omega_2$ of the unidentate carboxylates. This is comparable with the shift of the carbonyl band to lower frequencies (compared to free acetone) in, say, the boron trifluoride–acetone complex [3] (1714 ⟶ 1640 $cm.^{-1}$). A further strong band around 1540 $cm.^{-1}$ can be assigned to $\omega_2$ of the bridged carboxylates.

For the propionate and acetate, molecular weights indicating dissociation of the trimers

[3] P. Chalandon and B. P. Susz, *Helv. Chim. Acta*, 1958, **41**, 697.

and corresponding to $[Pd(OCOR)_2(Me_2CO)_2]$ were obtained in boiling acetone, but crystalline adducts could not be isolated. Interaction of the acetate and trifluoroacetate with dimethyl sulphoxide yielded brown oils. Washing with diethyl ether produced the yellow-brown powder $[Pd(OCOCF_3)_2(Me_2SO)_2]$ (the acetate complex could not be solidified). Dissolution of these oils in aqueous acidified tetraphenylarsonium chloride solution gave the salt of the anion $[PdCl_3(Me_2SO)]^-$. The infrared spectra contained a strong band at 1148 cm.$^{-1}$ (former) and 1124 cm.$^{-1}$ (latter) assigned to the S:O stretching mode [4] (*i.e.*, S-bonded). Palladous chloride shaken with aqueous dimethyl sulphoxide followed by acidified tetraphenylarsonium chloride produced the anion, further shaking of the original solution giving orange crystals of $[PdCl_2(Me_2SO)_2]$ (prepared by Cotton *et al.*[4]). Precipitation of the anion is inhibited in alkaline soution, suggesting that the hydroxy-compound is an intermediate. No precipitation occurred with tetraethyl(or methyl)-ammonium salts but with n-butyltriphenylphosphonium bromide it did, showing that the physical size of the cation is an important factor.

The carboxylate adducts containing nitrogen also dissolved in water, whereas the phosphorus (and arsenic) adducts were completely insoluble. Furthermore, addition of halogen ions to these aqueous solutions produced immediate precipitation of the corresponding halogeno-complex. Thus, the compound $[PdBr_2(Et_2NH)_2]$ was prepared from the acetate complex and potassium or tetramethylammonium bromide. The compound is a non-electrolyte in nitromethane, and precipitation is again inhibited in alkaline solution.

*Infrared Spectra.*—Previous work [5a] has shown that, since the acetate ion possesses low symmetry ($C_{2v}$), no marked differences in spectra are to be expected for the various types of co-ordinated structure possible. However, the effect on the frequency of changing the metal is different for each structural type. Nakamoto *et al.*[5b] have shown that for a series of α-amino-acid complexes, bonded through only one oxygen, the antisymmetric $COO^-$ stretching frequency ($\omega_2$) *increased* and the symmetric $COO^-$ stretching frequency ($\omega_1$) *decreased* as the M–O bond became stronger. Similar trends were also found in edta complexes,[5c] the conclusion being that the shift in frequency is due to a breakdown in the equivalence of the C–O bonds so that the spectrum of the complex resembles more closely that of the acid. For symmetrical co-ordination of the carboxylate ion, Nakamoto *et al.*[5a] showed that both $\omega_1$ and $\omega_2$ shifted in the same direction when the metal was changed. For the present compounds, it seems reasonable to assume that the palladium atom has its normal square planar co-ordination, the trimers having both bridging and chelate groups, and the monomers only chelate groups (II, III). Separation values of $\omega_1$ and $\omega_2$ comparable to that of the free ion support these symmetrically co-ordinated structures, *e.g.*, for sodium acetate [5a] 164 cm.$^{-1}$.

However, infrared spectra (Table 1) show that, with one exception (the diethylamine acetate complex), in their adducts of the type $[Pd(OCOR)_2L_2]$ (in compounds where ligand bands do not interfere with the assignment of $\omega_2$ and in spite of ambiguities in assigning $\omega_1$ in several instances) $\omega_2$ *increases* and $\omega_1$ *decreases* compared with the original carboxylates. Similar variations of the $COO^-$ stretching frequency bands have been observed with organotin carboxylates when the compounds are melted or dissolved in non-polar solvents (conversion from co-ordination polymers containing bridged groups into monomolecular species resembling organic esters being the explanation offered),[6a,b] and in the cleavage of bridged carboxylate systems such as rhodium carbonyl acetate and phthalate with pyridine and triphenylphosphine.[7] Hence, unidentate carboxylate co-ordination as in (IV) rather than chelation is indicated. Why the acetate and propionate adducts contain

[4] F. A. Cotton and R. Francis, *J. Amer. Chem. Soc.*, 1960, **82**, 2986.
[5] For references and discussion see Y. Nakamoto, "Infrared Spectra of Inorganic and Co-ordination Compounds," (*a*) p. 197 *et seq.*, (*b*) p. 202 *et seq.*, (*c*) p. 205 *et seq.*, Wiley, New York and London, 1963.
[6] (*a*) M. J. Janssen, J. G. A. Luijten, and G. J. M. van der Kerk, *Rec. Trav. chim.*, 1963, **82**, 90; (*b*) R. A. Cummins and P. Dunn, *Aust. J. Chem.*, 1964, **17**, 185.
[7] D. N. Lawson and G. Wilkinson, *J.*, 1965, 1900.

several bands in the $\omega_1$ region, whereas the fluoro-carboxylates have only one, is unknown; the rhodium carbonyl carboxylate adducts also contain several.

In the compound $Pd(OCOMe)_2(Et_2NH)_2$, the decrease of 18 cm.$^{-1}$ in $\omega_2$ can be attributed to intramolecular hydrogen bonding between the NH hydrogen and the unco-ordinated oxygen of the carboxylate group. A similar effect is observed in nickel acetate tetrahydrate, where an *X*-ray structural analysis [8] indicates monodentate co-ordination, but a comparison with the free ion shows a *lowering* of $\omega_2$ and a *decrease* in the separation [9] between $\omega_1$ and $\omega_2$. This is attributed to hydrogen bonding (with water molecules) tending to equate the C–O bond lengths [8] (1·29 ± 0·02 and 1·31 ± 0·02 Å), thus compensating for the asymmetry produced through monodentate co-ordination.

Finally, although several investigators have shown that $\omega_2$ is more sensitive than $\omega_1$ to changes in the metal,[5a] the decrease in $\omega_1$ in this system, for the alkane- and arene-carboxylates, is larger than the increase in $\omega_2$ and can only be attributed to the change in the mode of carboxylate bonding. Further evidence of this effect comes from the work on organotin carboxylates (Table 2) and the cleavage of rhodium carbonyl carboxylates; the explanation is at present unknown.

TABLE 2 [6a]

| Compound | Solid state (bridging) $\omega_2$ | Solid state (bridging) $\omega_1$ | Dissolved state ($CCl_4$) — monodentate $\omega_2$ | Dissolved state ($CCl_4$) — monodentate $\omega_1$ | Difference $\omega_2$ (soln.) — $\omega_2$ (solid) | Difference $\omega_1$ (solid) — $\omega_1$ (soln.) |
|---|---|---|---|---|---|---|
| Triethyltin acetate ..... | 1572 | 1412 | 1655 | 1302 | 83 | 110 |
| Tributyltin acetate ..... | 1572 | 1410 | 1647 | 1300 | 75 | 110 |
| Trihexyltin acetate ..... | 1570 | 1408 | 1650 | 1304 | 80 | 104 |
| Trimethyltin laurate ..... | 1567 | 1410 | 1642 | 1302 | 75 | 108 |

In the fluoro-carboxylates, the decrease in $\omega_1$ is less than the increase in $\omega_2$, but here the strong positive inductive effect of the fluoro-group will accentuate the initial asymmetry of the carboxylate group just as variation of metal–oxygen bond strength does, thus accounting for a large increase in $\omega_2$.

*Diacetatoplatinum*(II).—Diacetatoplatinum(II) was obtained by careful reduction with formic acid of solutions of hexahydroxyplatinate(IV) in acetic acid. From chloroform, purple crystals were obtained, which are trimeric in acetone, or chloroform at 37° (osmometer), and trimeric ebullioscopically in benzene (80°) and chlorobenzene (132°). However, *X*-ray powder photographs of platinum and palladium acetates show that the compounds are not isomorphous, and therefore it is probable, but not necessarily so, that the compounds also have different molecular structures.

Attempts to prepare similar monomeric adducts with nitrogen and phosphorus donors produced compounds of uncertain compositions and very high molecular weights, *e.g.*, with diethylamine a deep green solution was produced, with an analysis close to the formula $[Pt_3(OCOCH_3)_6(Et_2NH)_4]$. The absorption spectrum of the acetate in benzene solution (deep red) shows two charge-transfer bands at 519 mμ ($\varepsilon = 2000$) and 402 mμ ($\varepsilon = 1940$). However, the solid-state reflectance spectrum (350—1000 mμ) is completely different, showing a weak band at 925 mμ, a broad band 567 mμ and indications of another charge-transfer band at 350 mμ (cf. solid and solution spectra for palladous acetate, which are virtually identical).

The infrared spectrum contains strong bands at 1562 ($\omega_2$), 1429 ($\omega_1$), and 689 cm.$^{-1}$ ($COO^-$ deformation band). Thus, the retention of a trimeric structure at 132°, non-isomorphism of powder photographs, and inability to cleave the acetate are clear evidence for a difference in structure between these platinum metal carboxylates. Metal–metal interaction is a possible explanation of the intense coloration and stability of diacetatoplatinum.

*Rhodium Carboxylates.*—The original Russian findings on rhodium(II) acetate hydrate

[8] J. N. van Niekerk and F. R. L. Schoening, *Acta Cryst.*, 1953, **6**, 609.
[9] K. Nakamoto, J. Fujita, S. Tanaka, and M. Kobayashi, *J. Amer. Chem. Soc.*, 1957, **79**, 4904.

have been confirmed as in recently published work.[10] The formate, propionate, and trifluoroacetate have also been prepared by the action of the appropriate acid upon rhodium hydrous oxide. All these carboxylates readily react with donor-type ligands such as triphenylphosphine, piperidine, etc., which replace the two water molecules of the dimer. These adducts were prepared in alcoholic solutions and recrystallised from a variety of solvents as pure crystalline species, for which complete analytical figures were obtained. The " extremely insoluble " pyridine complex prepared by Johnson *et al.*[10] from anhydrous rhodium acetate was prepared *via* the hydrate and could be recrystallised from chloroform and petroleum.

A $10^{-3}$molar aqueous solution of rhodium propionate hydrate has a molecular conductivity of 265 mhos and is acidic (cf. copper acetate hydrate which also ionises in aqueous solution [11]) suggesting the equilibrium

$$[Rh_2(OCOEt)_4(H_2O)_2] \rightleftharpoons [Rh_2(OCOEt)_4(OH)_2]^{2-} + 2H^+$$

Proton magnetic resonance spectra showed the compounds to be diamagnetic; this indicates that despite the formal bivalency of the rhodium, the $d^7$ configuration is absent.

Infrared spectra showed strong bands corresponding to $\omega_2$ and $\omega_1$: rhodium formate hydrate 1587 ($\omega_2$), 1430 ($\omega_1$), $\Delta\omega$ 157 cm.$^{-1}$; rhodium propionate hydrate 1570 ($\omega_2$), 1420 ($\omega_1$), 150 cm.$^{-1}$; rhodium acetate hydrate 1580 ($\omega_2$), 1430($\omega_1$), $\Delta\omega$ 150 cm.$^{-1}$.

## Experimental

Micro-analyses and molecular weight determinations (Mechrolab osmometer at 37°, and ebullioscopic) were made by the Microanalytical Laboratory, Imperial College. Infrared spectra were measured on a Grubb–Parsons spectromaster grating instrument in Nujol and hexachlorobutadiene mulls. Visible spectra were obtained with a Perkin-Elmer model 350 spectrophotometer and, in reflectance, with a Unicam S.P. 700 spectrophotometer. *X*-Ray powder photographs of palladium and platinium acetates in Lindemann glass tubes were taken with a Philips camera type PW 104 (11·46 cm. diam. with nickel-filtered copper radiation; *ca.* 3 hr. exposure).

Analyses of palladium compounds are given in Table 3.

*Diacetatopalladium*(II).—Palladium sponge (10 g.) was boiled gently under reflux with a solution of glacial acetic acid (250 ml.) and concentrated nitric acid (6 ml.) until evolution of brown fumes ceased. A small residue of palladium should remain undissolved; if not, a little more sponge should be added and boiling continued until no trace of brown fumes is observed. This procedure is necessary to avoid contamination of the product with $PdNO_2 \cdot OAc$. The boiling brown solution is filtered and allowed to cool whereupon most of the complex separates as orange-brown crystals [m. p., 205° (decomp.)] which are washed with acetic acid and water and air-dried; the pale reddish-brown acetic acid mother-liquor may be used for further preparations. The yield is virtually quantitative. Large crystals of the compound can be prepared by dissolving it in warm benzene, mixing the solution with half its volume of glacial acetic acid, and allowing the benzene to evaporate slowly at room temperature.

The diacetato-complex has also been prepared by the addition of glacial acetic acid to a warm aqueous solution of palladous sulphate. The product contains small amounts of impurities (or mixed complex) and always leaves an insoluble pink or brown residue when dissolved in benzene.

The compound is soluble in chloroform, methylene dichloride, acetone, acetonitrile, and diethyl ether, but is insoluble in water and petroleum and decomposes when warmed with alcohols, in which it is also insoluble. It dissolves in aqueous potassium iodide to give $PdI_2$(s) and a red solution of $PdI_4^{2-}$, but is insoluble in aqueous solutions of sodium chloride, nitrite, and acetate. It is soluble with decomposition in aqueous hydrochloric acid to give $PdCl_4^{2-}$. *X*-Ray data are given in Table 4.

*Dipropionatopalladium*(II).—This complex was obtained in virtually quantitative yield in a similar way, by using propionic acid and palladium sponge; it had m. p. 161—165°. The orange-brown compound has properties very similar to those of the diacetate complex, but is somewhat more soluble in cold organic solvents.

[10] S. A. Johnson, H. R. Hunt, and H. M. Neumann, *Inorg. Chem.*, 1963, **2**, 960, and references therein.

[11] Y. Doucet and R. Cogniac, *Compt. rend.*, 1955, **240**, 968.

TABLE 3

Analytical results for palladium carboxylato-compounds

| Compound | Found (%) C | H | N | O | M | *M* (solvent) | Required (%) C | H | N | O | M | *M* |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $Pd(MeCO_2)_2$ ..... | 21·4 | 3·1 | — | 28·5 | — | 714 benzene | 21·4 | 2·7 | — | 28·5 | — | 675 (trimer) |
| | | | | | | 253 * ,, | | | | | | 225 |
| | | | | | | 357 * acetone | | | | | | |
| $Pd(EtCO_2)_2$..... | 28·6 | 4·0 | — | 25·1 | — | 767 benzene | 28·5 | 4·4 | — | 25·3 | — | 759 (trimer) |
| | | | | | | 249 * ,, | | | | | | 253 |
| | | | | | | 386 * acetone | | | | | | |
| $Pd(PhCO_2)_2$ ..... | 47·8 | 3·2 | — | 18·4 | — | 1023 benzene | 48·0 | 2·9 | — | 18·3 | — | 1047 (trimer) |
| | | | | | | 1010 * ,, | | | | | | |
| | | | | | | 1010 * chloro-benzene | | | | | | |
| $Pd(CF_3CO_2)_2$ ..... | 14·8 | — | — | — | 31·5 | 332 ethyl acetate | 14·4 | — | — | — | 32·1 | 333 |
| $Pd(C_2F_5CO_2)_2$ ..... | 16·9 | — | — | — | 25·2 | 434 ,, | 16·6 | — | — | — | 24·7 | 433 |
| $Pd(MeCO_2)_2py_2$ ..... | 43·4 | 4·3 | 7·4 | 16·7 | — | 509 benzene | 43·8 | 4·2 | 7·3 | 16·7 | — | 383 |
| $Pd(PhCO_2)_2py_2$ ..... | 56·3 | 4·3 | 5·6 | 12·8 | — | 418 chloro-form | 56·8 | 3·9 | 5·5 | 12·6 | — | 507 |
| $Pd(MeCO_2)_2quin_2$ † ... | 54·5 | 4·7 | 5·8 | 13·3 | — | 492 ,, | 54·8 | 4·2 | 5·8 | 13·3 | — | 483 |
| $Pd(MeCO_2)_2(NHEt_2)_2$... | 39·0 | 7·7 | 7·6 | 17·4 | — | 379 benzene | 38·9 | 7·6 | 7·5 | 17·3 | — | 371 |
| $Pd(MeCO_2)_2(NEt_3)_2$ ... | | | 6·6 | 14·5 | 24·7 | | | | 6·6 | 15·0 | 25·1 | |
| $Pd(MeCO_2)_2$bipy ..... | | | 7·3 | 17·3 | | 348 chloro-form | — | — | 7·4 | 17·0 | — | 377 |
| $Pd(PhCO_2)_2(AsPh_3)_2$ ... | 61·9 | 4·0 | — | 6·8 | — | 977 benzene | 62·4 | 4·2 | — | 6·7 | — | 961 |
| $Pd(PhCO_2)_2(PPh_3)_2$ ... | 68·3 | 4·9 | — | 7·4 | — | — | 68·7 | 4·5 | — | 7·3 | — | — |
| $Pd(MeCO_2)_2(PPh_3)_2$ ... | 64·4 | 5·0 | — | 8·8 | — | — | 64·1 | 4·8 | — | 8·5 | — | — |
| $Pd(EtCO_2)_2(PPh_3)_2$ ... | 65·2 | 5·2 | — | 8·3 | — | — | 64·9 | 5·2 | — | 8·2 | — | — |
| $Pd(CF_3CO_2)_2(AsPh_3)_2$... | 50·8 | 3·3 | — | — | 10·7 | 954 ,, | 50·8 | 3·2 | — | — | 11·3 | 945 |
| $Pd(C_2F_5CO_2)_2(AsPh_3)_2$ | 48·6 | 3·0 | — | — | 10·4 | 1070 ,, | 48·2 | 2·9 | — | — | 10·2 | 1045 |
| $[Pd(CF_3CO_2)_2Me_2CO]_2$ | 21·7 | 1·9 | — | — | — | 781 ethyl acetate | 21·5 | 1·5 | — | — | — | 782 (dimer) |
| $[Pd(C_2F_5CO_2)_2Me_2CO]_2$ | 22·9 | 2·1 | — | — | — | 912 | 22·0 | 1·2 | — | — | — | 982 (dimer) |
| $Pd(CF_3CO_2)_2[Me_2SO]_2$ ‡ | 20·0 | 2·8 | | | | — | 19·6 | 2·5 | | | | — |

* Ebullioscopic. † quin = isoquinoline. ‡ S: Found, 12·9; Required, 13·1.

TABLE 4

*X*-Ray values for palladium and platinum acetates

| *Palladous acetate* | | | | | | *Platinous acetate* | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| *d* (spacing) | $Q = 1\ d^2$ | Intensity | *d* (spacing) | $Q = 1/d^2$ | Intensity | *d* (spacing) | $Q = 1/d^2$ | Intensity | *d* (spacing) | $Q = 1/d^2$ | Intensity |
| 8·067 | 0·015367 | s | 3·261 | 0·0940 | s | 8·857 | 0·012748 | s | 3·285 | 0·0927 | w |
| 7·099 | 0·019843 | vs | 3·237 | 0·0954 | s | 7·800 | 0·016437 | vs | 3·188 | 0·0984 | vw |
| 6·521 | 0·023516 | s | 2·974 | 0·1131 | w | 7·160 | 0·019506 | s | 3·084 | 0·1051 | s |
| 5·864 | 0·029081 | s | 2·889 | 0·1198 | w | 6·570 | 0·023167 | vw | 2·798 | 0·1277 | m |
| 5·546 | 0·032512 | m | 2·826 | 0·1252 | vw | 5·917 | 0·028563 | vw | 2·684 | 0·1388 | s |
| 4·962 | 0·040615 | m | 2·756 | 0·1317 | m | 5·469 | 0·033434 | m | 2·539 | 0·1551 | m |
| 4·794 | 0·043511 | w | 2·651 | 0·1462 | m | 4·952 | 0·040779 | m | 2·424 | 0·1702 | m |
| 4·503 | 0·049317 | w | 2·574 | 0·1509 | m | 4·557 | 0·048155 | m | 2·357 | 0·1800 | m |
| 4·131 | 0·058599 | w | 2·462 | 0·1650 | m | 4·151 | 0·058036 | s | 2·253 | 0·1970 | m |
| 3·715 | 0·0725 | m | 2·389 | 0·1752 | m | 3·898 | 0·0658 | m | 2·171 | 0·2122 | m |
| 3·598 | 0·0772 | s | 2·316 | 0·1864 | s | 3·566 | 0·0786 | w | | | |
| 3·370 | 0·0881 | s | 2·206 | 0·2055 | vw | 3·430 | 0·0850 | w | | | |

*Dibenzoatopalladium*(II).—A benzene solution of palladium diacetate and benzoic acid (mole ratio 1 : 3) was evaporated on a steam-bath and the residue washed with acetone or diethyl ether to remove benzoic acid. Recrystallisation from benzene gave the *complex* as a yellowish brown solid, m. p. 220° (decomp.). It is soluble in chloroform and toluene, but decomposes on warming with alcohols.

*Di(trifluoroacetato)palladium*(II).—A trifluoroacetic acid (*ca.* 15 ml.) solution of diacetatopalladium (0·3 g.) was evaporated on a steam-bath and the evaporation repeated with a further

quantity (*ca.* 7 ml.) of acid. The residual *complex* was dried *in vacuo* (40°) to a brown powder, m. p. 210° (decomp.). It is soluble in ether and acetone, but insoluble in benzene, chloroform, and trifluoroacetic acid.

*Di(pentafluoropropionato)palladium*(II).—Like the di(trifluoroacetato)palladium(II) the complex is a brown powder, m. p. 195° (decomp.). Its solubility properties resemble those of the di(tri-fluoroacetato)-complex.

*Diacetatobispyridinepalladium*(II).—Diacetatopalladium(II) was dissolved in pyridine and the solution warmed (80°); chilling in ice gave pale yellow crystals of the *complex*, m. p. 185° (decomp.), which were recrystallised from cold benzene. The compound is soluble in water as well as in organic solvents.

*Diacetato-2,2′-bipyridylpalladium*(II).—Diacetatopalladium(II) (0·56 g.) in benzene (50 ml.) was added slowly to 2,2′-bipyridyl (0·4 g.) in benzene (10 ml.) with stirring. The mustard-coloured precipitate was washed with petroleum and recrystallised from benzene–dichloromethane to give the pale yellow *complex*, m. p. 195° (decomp.); it is soluble in water and ethanol, but insoluble in acetone and benzene.

*Dibenzoatobispyridinepalladium*(II).—Dibenzoatopalladium(II) (0·3 g.) in benzene was shaken with an excess (*ca.* 6 ml.) of pyridine and the white precipitate of the *complex*, m. p. 185°, were washed with diethyl ether and dried *in vacuo* at room temperature.

*Diacetatobisisoquinolinepalladium*(II).—A solution of isoquinoline (3 ml.) in diethyl ether (5 ml.) was added to diacetatopalladium(II) (0·3 g.) in benzene (5 ml.); the pale yellow *complex*, m. p. 205° (decomp.), was dried *in vacuo*. It is insoluble in water and benzene, but dissolves in warm nitromethane.

*Diacetobis(diethylamine)palladium*(II).—A solution of diacetatopalladium(II) (0·5 g.) in diethylamine (*ca.* 10 ml.) was filtered and evaporated to give pale yellow crystals of the *complex*, which were recrystallised from petroleum (b. p. 40—60°); it had m. p. 125°, soluble in water, ethanol, ether, petroleum, and benzene. By using the refraction method, the dipole moment was calculated from the dielectric constant (ε) measured with a heterodyne-beat capacitance meter; it was found to be zero within the limits of error.

*Diacetatobis(triethylamino)palladium*(II).—Diacetatopalladium(II) (0·2 g.) in triethylamine (*ca.* 10 ml.) was warmed, filtered, and chilled to 0° for 1 hr. The lemon yellow crystals of the compound, m. p. 75° (decomp.), were dried *in vacuo* and analysed immediately. It is soluble in organic solvents, but the solutions decompose rather quickly, especially on warming, making a molecular weight determination impossible.

*Diacetatobis(triphenylphosphine)palladium*(II).—Diacetatopalladium(II) (0·04 g.) in benzene was treated with an excess of triphenylphosphine (*ca.* 0·07 g.) in benzene. Addition of petroleum (60—80°) to the resulting pale yellow solution gave on shaking slowly lemon-yellow crystals of the *complex*, m. p. 135—136°, which were washed with petroleum and dried *in vacuo* (40°). It is sparingly soluble in cold solvents; when warmed with benzene, the initial yellow solution rapidly became red and then brown, depositing metallic palladium; attempts to isolate the red species failed.

*Dipropionatobis(triphenylphosphine)palladium*(II).—This was prepared in the same way as the corresponding diacetate-complex, it is a pale yellow *complex*, m. p. 147—148°, which decomposes rapidly in solution in warm solvents such as benzene and ethyl acetate.

*Dibenzoatobis(triphenylphosphine)palladium*(II).—This was prepared in the same way as the corresponding diacetate-complex, giving very pale yellow crystals m. p. 192—193°. It dissolves in warm benzene to give a yellow solution; low osmometric molecular weights (~500, req. 800) indicate some dissociation.

*Dibenzoatobis(triphenylarsine)palladium*(II).—This was prepared in the same way as the triphenylphosphine complex, but with an excess of triphenylarsine, to give bright yellow crystals, m. p. 198—199°.

*Di(trifluoroacetato)bis(triphenylarsine)palladium*(II).—The ditrifluoroacetate-complex (0·03 g.), suspended in benzene (*ca.* 7 ml.), and a large excess of triphenylarsine (0·15 g.) were shaken together until the solid had almost disappeared. The pale yellow solution was filtered, and petroleum (b. p. 100—120°) was added slowly to give bright yellow crystals of the *complex*, m. p. 192—193°, which were washed with petroleum (b. p. 30—40°) and dried *in vacuo*. The compound is insoluble in water, but soluble in benzene, acetone, and chloroform, etc.

*Di(pentafluoropropionato)bis(triphenylarsine)palladium*(II).—Prepared in the same way as the corresponding trifluoroaceto-complex. It formed bright yellow crystals, m. p. 204—205°.

*Di(trifluoroacetato)(acetone)palladium*(II).—The bis(trifluoroacetato)-complex was dissolved in warm acetone to give a reddish-yellow solution, which when cooled gave the orange-red crystalline *complex*, m. p. 183° (decomp.). It is soluble in warm ethyl acetate (decomposing rapidly), but insoluble in acetone, benzene, chloroform, and ether. The bispentafluoropropionato-complex gave a similar *complex*, m. p. 180° (decomp.).

*Ditrifluoroacetatobis(dimethyl sulphoxide)palladium*(II).—Dimethyl sulphoxide was added dropwise to a suspension of ditrifluoroacetopalladium(II) in benzene. The resulting yellow solution was filtered, the benzene removed (<45° *in vacuo*), and the residual oil washed several times with excess of diethyl ether to give a yellow-brown powder, m. p. 100° (decomp.).

*Tetraphenylarsonium Trichloro(dimethyl sulphoxide)palladate*(II).—Diacetatopalladium(II) in benzene was shaken for several hours with excess of dimethyl sulphoxide. After removal of the benzene, the residual oil (or that from the corresponding trifluoroacetate reaction) was dissolved in water and filtered into a concentrated acidified (hydrochloric acid) solution of tetraphenylarsonium chloride. The lemon-yellow crystalline *salt*, m. p. 190° (decomp.) was washed with water, dried in a desiccator, and finally rewashed with ether (Found: C, 46·0; H, 4·0; Cl, 16·1; O, 2·5; S, 4·6. $C_{26}H_{26}AsCl_3OPdS$ requires C, 46·3; H, 3·8; Cl, 15·8; O, 2·4; S, 4·7%). The salt is a 1 : 1 electrolyte in nitromethane.

Infrared spectrum: 1471w, 1433s, 1389w, 1333vw, 1309vw, 1176vw, 1124*s* (S:O, S-bonded), 1078m, 1020m, 995m, 965w, 930(w,broad), 746s, 741s, 694m, and 685s cm.$^{-1}$.

An identical material was obtained by shaking palladium(II) chloride with a 1 : 1 mixture of dimethyl sulphoxide and water for several minutes, filtering the mixture, and then adding a concentrated aqueous solution of acidified tetraphenylarsonium chloride. When the original solution was shaken for *ca.* 30 min., orange crystals [4] of $[PdCl_2(OSMe_2)_2]$ were obtained; they were washed with water and ether and dried; they had m. p. 190° (decomp.) [Found: Cl, 21·3. Calc. for $C_4H_{12}Cl_2O_2PdS_2$: Cl, 21·2%]. The infrared spectrum is identical with that previously reported.[12]

*Dibromobis(diethylamine)palladium*(II).—Diacetatobis(diethylamine)palladium(II) was added to a warm concentrated aqueous solution of potassium bromide. The immediate yellowish-green precipitate was filtered off, washed several times with water, dried in a desiccator, and then rewashed with ether; it had m. p. 180° (decomp.) [Found: C, 23·9; H, 5·25; Br, 38·5; N, 6·7. Calc. for $C_8H_{22}Br_2N_2Pd$: C, 23·2; H, 5·3; Br, 38·7; N, 6·8%]. The compound is a non-electrolyte in warm nitromethane.

*Diacetatoplatinum*.—Sodium hexahydroxyplatinate, $Na_2Pt(OH)_6$ (10 g.), was slowly added with shaking to concentrated nitric acid (25 ml.) and the mixture heated until the solid had dissolved. Most of the acid was removed by heating the flask over a free flame until a brown syrup containing crystals of sodium nitrate remains. Glacial acetic acid (30 ml.) was added and the mixture boiled until the nitrate crystals had become white; the solution was cooled and filtered and the sodium nitrate crystals washed with acetic acid. The filtrate and washings were transferred to another flask and boiled by swirling over a free flame until only a thick orange-brown syrup remained; this treatment expelled most of the nitric acid. A further 30 ml. of acetic acid was added and a 20 : 80 mixture of 90% formic acid and glacial acetic acid was added slowly with swirling to the boiling solution until no further brown fumes were evolved. At this stage, the solution became dark brown and further addition of the formic acid solution caused it suddenly to become bright green. The formic acid mixture was now added a few drops at a time with vigorous boiling, whereupon the colour gradually turned to bright ultramarine blue and, with the addition of further formic acid, to deep purple. Crystals of the *complex* were suddenly precipitated at this point, but were always contaminated with a little platinum black. The solution was cooled and the precipitate washed with cold acetic acid. It should be noted that at every stage in this reduction with formic acid, the solution must be kept boiled and well stirred for some time after every small addition of reducing agent; addition of an excess causes rapid deposition of platinum black. After the brown fumes from the nitric acid ceased to form, about 4—5 ml. of the formic acid solution were required to give the maximum yield.

The crude purple crystals were extracted with chloroform and the filtered solution mixed with half its volume of glacial acetic acid and set aside to evaporate at room temperature, the resulting large crystals of the acetate were collected, washed with water, and dried in air.

The yield varied considerably; in some experiments most of the platinum was recovered as

[12] F. A. Cotton, R. Francis, and W. D. Horrocks, jun., *J. Phys. Chem.*, 1960, **64**, 1534.

the acetate but in others the purple solutions gave no crystals. The compound gave almost black *crystals*, m. p. 245° (decomp.) [Found: O, 19·3; Pt, 64·0; C–$CH_3$ (Kuhn Roth), 17·5%; *M* (osmometer) at 37° acetone and chloroform, 950 ± 2; (ebullioscopically) in benzene, 937; chlorobenzene, 888. $C_4H_6O_4Pt$ requires O, 20·4; Pt, 62·3; C–$CH_3$, 17·3%; *M*, 940 (trimer)].

The compound is soluble in chloroform, benzene, and toluene, giving purple solutions.

*Rhodium Carboxylates.*—The rhodium carboxylates were prepared by refluxing rhodium hydrous oxide in an excess of formic, acetic, or propionic acid and ethanol. The yellow solution gradually turned amber and then green. The solution was cooled, and the dark green powder that was precipitated was filtered off. The products were recrystallised from methanol or water and were stable up to 240°.

The trifluoroacetatorhodium(II) complex was prepared by the action of trifluoroacetic acid on the hydrous oxide followed by extraction of the reaction mixture with dichloromethane. The blue-green product was recrystallised from benzene.

*Diacetatopyridinerhodium*(II). Pyridine was added dropwise to a cold, methanolic solution of the trifluoroacetato-complex (mole ratio 2 : 1), and the product was obtained as dark red crystals, which after recrystallisation from chloroform and petroleum had m. p. 225° (decomp.) (Found: C, 36·4; H, 3·7; N, 4·8; O, 21·6. Calc. for $C_9H_{11}NO_4Rh$: C, 36·0; H, 3·7; N, 4·7; O, 21·3%).

*Dipropionatopyridinerhodium*(II) *and diformatopyridinerhodium*(II). These were similarly prepared, the propionate complex being recrystallised from cyclohexane and petroleum and the formate complex from dichloromethane. The *propionato-complex* (Found: C, 40·8; H, 4·6; N, 4·8; O, 19·7. $C_{11}H_{15}NO_4Rh$ requires C, 40·3; H, 4·6; N, 4·8; O, 19·7%); the formate complex (Found: C, 31·6; H, 3·5; N, 5·4. Calc. for $C_7H_7NO_4Rh$: C, 31·0; H, 2·6; N, 5·2%) m. p. 145° (decomp.). This compound was first prepared by Chernyaev *et al.*[13] who assigned it the composition [$PyHRh^{I}(HOCO)_2$].

*Diacetato(triphenylphosphine)rhodium*(II). This complex was prepared by the addition of triphenylphosphine in diethyl ether to a cold methanolic solution of the diacetato-complex. The orange powder that was immediately precipitated, was recrystallised from chloroform (Found: C, 54·8; H, 4·6. $C_{22}H_{21}O_4PRh$ requires C, 54·6; H, 4·6%).

*Dipropionato(triphenylphosphine)rhodium*(II). This complex was similarly prepared from the dipropionato-complex and was recrystallised from cyclohexane [Found: C, 56·4; H, 4·9; O, 12·3%; *M* (ebullioscopic in benzene), 992. $C_{24}H_{25}O_4PRh$ requires C, 56·4; H, 4·9; O, 12·5%; *M*, 1023 (dimer)].

*Diformato(triphenylphosphine)rhodium*(II). This complex was similarly prepared from the diformato-complex; it was recrystallised from chloroform and petroleum giving orange crystals, m. p. 165° (decomp.) (Found: C, 52·8; H, 4·6. $C_{20}H_{17}O_4PRh$ requires C, 52·6; H, 3·8%).

*Dipropionatopiperidinerhodium*(II). This was prepared by the dropwise addition of piperidine to a cold, methanolic solution of dipropionatorhodium(II). It was recrystallised from petroleum, forming dark red crystals, m. p. 115° (Found: C, 40·0; H, 6·1; N, 4·3. $C_{11}H_{21}NO_4Rh$ requires C, 39·5; H, 6·3; N, 4·2%).

*Dipropionatoisoquinolinerhodium*(II). Isoquinoline in diethyl ether was added to a cold, methanolic solution of dipropionatorhodium(II). Dark red crystals formed immediately and were recrystallised from cold benzene and petroleum (Found: C, 48·3; H, 4·9; N, 3·6; O, 16·9. $C_{15}H_{17}NO_4Rh$ requires C, 47·6; H, 4·5; N, 3·7; O, 16·9%).

*Di(trifluoroacetato)pyridinerhodium*(II). Pyridine was added dropwise to a cold ethanolic solution of di(trifluoroacetato)rhodium(II). Red crystals formed, and were recrystallised from dichloromethane (Found: C, 26·5; H, 2·1. $C_9H_5F_6NO_4Rh$ requires C, 26·4; H, 1·2%).

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[13] I. I. Chernyaev, E. V. Shenderatskaya, and L. A. Karyakina, *Russian J. Inorg. Chem.*, 1960, **5**, 559.