

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 $\text{Pd}(\text{OCOR})_2$; 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*- $[\text{Pd}(\text{OCOR})_2\text{L}_2]$ 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 $[\text{Pd}(\text{OCOMe})_2]_3$, and does not undergo cleavage reactions with donor ligands.

Studies on rhodium(II) carboxylates¹ 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 $m\mu$) shows a single broad charge-transfer band ($\epsilon \sim 1000$) at 394 $m\mu$, although a stronger band below 280 $m\mu$ is indicated. Solid-state reflectance spectra of the acetate (750—1000 $m\mu$) showed weak peaks at 730, 820, and 910 $m\mu$ whilst the propionate had peaks at 760, 823, and 920 $m\mu$; since these bands were not observed in solutions (0.1M) a value of $\epsilon < 1$ is indicated. The longest wavelength *d-d* band in PtCl_4^{2-} that is assigned to a singlet-triplet transition occurs² at 565 $m\mu$, 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 $m\mu$ 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 bisacetylacetonate-ethylenedi-imine and bis-salicylaldehyde-ethylenedi-imine to produce the completely substituted $\text{Pd}(\text{enbisacac})$ and $\text{Pd}(\text{enbissal})$. With various nitrogen donors, triphenylphosphine and triphenylarsine (a large excess required for complete reaction), yellow crystalline monomeric adducts of the type $[\text{Pd}(\text{OCOR})_2\text{L}_2]$ are obtained (Table I).

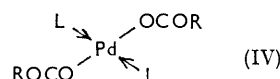
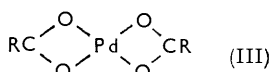
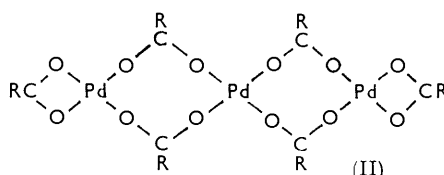
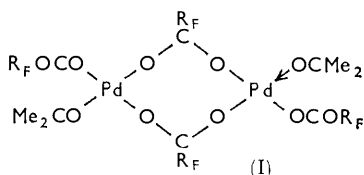
TABLE I
Infrared spectra of palladous carboxylates and adducts (cm^{-1})

Compound	ω_2	ω_1	Separation $\Delta(\omega_2 - \omega_1)$	Difference ω_2 (adduct) - ω_2 (carb)	Difference ω_1 (carb) - ω_1 (adduct)
$[\text{Pd}(\text{OCOPh})_2]_3$	1567	1404	163	—	—
$[\text{Pd}(\text{OCOPh})_2(\text{Ph}_3\text{P})_2]$	1623	1319	304	56	85
$[\text{Pd}(\text{OCOPh})_2(\text{Ph}_3\text{As})_2]$...	1626	1325	301	59	79
$[\text{Pd}(\text{OCOPh})_2(\text{py})_2]$	1603	1342 and/or 1323	≥ 261	36	≥ 62
$[\text{Pd}(\text{OCOCF}_3)_2]$	1572	1456	116	—	—
$[\text{Pd}(\text{OCOCF}_3)_2(\text{Ph}_3\text{P})_2]$...	1684	1393	291	112	63
$[\text{Pd}(\text{OCOCF}_3)_2(\text{OSMe}_2)_2]$...	1681	1408	273	109	48
$[\text{Pd}(\text{OCOC}_2\text{F}_5)_2]$	1567	1431	136	—	—
$[\text{Pd}(\text{OCOC}_2\text{F}_5)_2(\text{Ph}_3\text{As})_2]$...	1678	1372	306	111	59
$[\text{Pd}(\text{OCOEt})_2]_3$	1595	1425	170	—	—
$[\text{Pd}(\text{OCOEt})_2(\text{Ph}_3\text{P})_2]$	1618	1359 and/or 1311	≥ 259	23	≥ 66
$[\text{Pd}(\text{OCOMe})_2]_3$	1600	1427	173	—	—
$[\text{Pd}(\text{OCOMe})_2(\text{Ph}_3\text{P})_2]$	1634	1353, 1307 ^a and/or 1297	≥ 281	34	≥ 74
$[\text{Pd}(\text{OCOMe})_2(\text{Et}_3\text{N})_2]$	1626	≤ 1377 ^{a, b}	≥ 249	26	≥ 50
$[\text{Pd}(\text{OCOMe})_2(\text{Et}_2\text{NH})_2]$...	1582	≤ 1370 ^{a, b}	≥ 212	(-)(18)	≥ 57
$[\text{Pd}(\text{OCOMe})_2(\text{py})_2]$	≤ 1626 ^b	1377, 1361, 1314, ^a and/or 1297	≥ 239	≤ 23	≥ 50
$[\text{Pd}(\text{OCOMe})_2\text{bipy}]$	≤ 1626 ^b	1370 and/or 1328 ^a	≥ 256	≤ 26	≥ 57

^a Among bands in the ω_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 $[\text{Pd}(\text{OCOMe})_2\text{bipy}]$ 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 $[\text{Pd}(\text{OCOR}_\text{F})_2\text{Me}_2\text{CO}]_2$; these are dimeric in ethyl acetate at 37° and presumably have a structure of type I. Their infrared



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 ω_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 complex³ ($1714 \rightarrow 1640 \text{ cm}^{-1}$). A further strong band around 1540 cm^{-1} can be assigned to ω_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 $[\text{Pd}(\text{OCOR})_2(\text{Me}_2\text{CO})_2]$ 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 $[\text{Pd}(\text{OCOCF}_3)_2(\text{Me}_2\text{SO})_2]$ (the acetate complex could not be solidified). Dissolution of these oils in aqueous acidified tetraphenylarsonium chloride solution gave the salt of the anion $[\text{PdCl}_3(\text{Me}_2\text{SO})]^-$. The infrared spectra contained a strong band at 1148 cm^{-1} (former) and 1124 cm^{-1} (latter) assigned to the S:O stretching mode⁴ (*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 $[\text{PdCl}_2(\text{Me}_2\text{SO})_2]$ (prepared by Cotton *et al.*⁴). Precipitation of the anion is inhibited in alkaline solution, 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 $[\text{PdBr}_2(\text{Et}_2\text{NH})_2]$ 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 (ω_2) increased and the symmetric COO⁻ stretching frequency (ω_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 ω_1 and ω_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 ω_1 and ω_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 $[\text{Pd}(\text{OCOR})_2\text{L}_2]$ (in compounds where ligand bands do not interfere with the assignment of ω_2 and in spite of ambiguities in assigning ω_1 in several instances) ω_2 increases and ω_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.

(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 ω_1 region, whereas the fluoro-carboxylates have only one, is unknown; the rhodium carbonyl carboxylate adducts also contain several.

In the compound $\text{Pd}(\text{OCOME})_2(\text{Et}_2\text{NH})_2$, the decrease of 18 cm.^{-1} in ω_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 analysis⁸ indicates monodentate co-ordination, but a comparison with the free ion shows a *lowering* of ω_2 and a *decrease* in the separation⁹ between ω_1 and ω_2 . This is attributed to hydrogen bonding (with water molecules) tending to equate the C-O bond lengths⁸ (1.29 ± 0.02 and $1.31 \pm 0.02 \text{ \AA}$), thus compensating for the asymmetry produced through monodentate co-ordination.

Finally, although several investigators have shown that ω_2 is more sensitive than ω_1 to changes in the metal,^{5a} the decrease in ω_1 in this system, for the alkane- and arene-carboxylates, is larger than the increase in ω_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)		Dissolved state (CCl_4) — monodentate		Difference ω_2 (soln.) — ω_2 (solid)	Difference ω_1 (solid) — ω_1 (soln.)
	ω_2	ω_1	ω_2	ω_1		
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 ω_1 is less than the increase in ω_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 ω_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 $[\text{Pt}_3(\text{OCOCH}_3)_6(\text{Et}_2\text{NH})_4]$. The absorption spectrum of the acetate in benzene solution (deep red) shows two charge-transfer bands at $519 \text{ m}\mu$ ($\epsilon = 2000$) and $402 \text{ m}\mu$ ($\epsilon = 1940$). However, the solid-state reflectance spectrum ($350\text{--}1000 \text{ m}\mu$) is completely different, showing a weak band at $925 \text{ m}\mu$, a broad band $567 \text{ m}\mu$ and indications of another charge-transfer band at $350 \text{ m}\mu$ (cf. solid and solution spectra for palladous acetate, which are virtually identical).

The infrared spectrum contains strong bands at 1562 (ω_2), 1429 (ω_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 10⁻³molar 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 solution¹¹) suggesting the equilibrium



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 ω_2 and ω_1 : rhodium formate hydrate 1587 (ω_2), 1430 (ω_1), $\Delta\omega$ 157 cm.⁻¹; rhodium propionate hydrate 1570 (ω_2), 1420 (ω_1), 150 cm.⁻¹; rhodium acetate hydrate 1580 (ω_2), 1430 (ω_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 platinum 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 PdNO₂·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 PdI₂(s) and a red solution of PdI₄²⁻, but is insoluble in aqueous solutions of sodium chloride, nitrite, and acetate. It is soluble with decomposition in aqueous hydrochloric acid to give PdCl₄²⁻. 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 (%)						Required (%)						
	C	H	N	O	M	M (solvent)	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) 225	
						253 * 357 * 767	acetone benzene					759 (trimer) 253	
Pd(EtCO ₂) ₂	28.6	4.0	—	25.1	—	249 * 386 * 1023	acetone benzene	28.5	4.4	—	25.3	—	1047 (trimer)
Pd(PhCO ₂) ₂	47.8	3.2	—	18.4	—	1010 * 1010 *	benzene chloro- benzene	48.0	2.9	—	18.3	—	333
Pd(CF ₃ CO ₂) ₂	14.8	—	—	—	31.5	332 ethyl acetate	14.4	—	—	—	32.1	333	
Pd(C ₂ F ₅ CO ₂) ₂	16.9	—	—	—	25.2	434	16.6	—	—	—	24.7	433	
Pd(MeCO ₂) ₂ Py ₂	43.4	4.3	7.4	16.7	—	509 benzene	43.8	4.2	7.3	16.7	—	383	
Pd(PhCO ₂) ₂ Py ₂	56.3	4.3	5.6	12.8	—	418 chloro- form	56.8	3.9	5.5	12.6	—	507	
Pd(MeCO ₂) ₂ quin 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 ₃ CO ₂) ₂ (AsPh ₃) ₂ ...	50.8	3.3	—	—	10.7	954	50.8	3.2	—	—	11.3	945	
Pd(C ₂ F ₅ CO ₂) ₂ (AsPh ₃) ₂	48.6	3.0	—	—	10.4	1070	48.2	2.9	—	—	10.2	1045	
[Pd(CF ₃ CO ₂) ₂ Me ₂ CO ₂]	21.7	1.9	—	—	—	781 ethyl acetate	21.5	1.5	—	—	—	782 (dimer)	
[Pd(C ₂ F ₅ CO ₂) ₂ Me ₂ CO ₂]	22.9	2.1	—	—	—	912	22.0	1.2	—	—	—	982 (dimer)	
Pd(CF ₃ CO ₂) ₂ [Me ₂ SO] 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

<i>Palladous acetate</i>				<i>Platinous acetate</i>				
<i>d</i> (spac- ing)	<i>Q</i> = 1/ <i>d</i> ²	Intens- ity)	<i>d</i> (spac- ing)	<i>Q</i> = 1/ <i>d</i> ²	Intens- ity)	<i>d</i> (spac- ing)	<i>Q</i> = 1/ <i>d</i> ²	Intens- ity)
8.067	0.015367	s	3.261	0.0940	s	8.857	0.012748	s
7.099	0.019843	vs	3.237	0.0954	s	7.800	0.016437	vs
6.521	0.023516	s	2.974	0.1131	w	7.160	0.019506	s
5.864	0.029081	s	2.889	0.1198	w	6.570	0.023167	vw
5.546	0.032512	m	2.826	0.1252	vw	5.917	0.028563	vw
4.962	0.040615	m	2.756	0.1317	m	5.469	0.033434	m
4.794	0.043511	w	2.651	0.1462	m	4.952	0.040779	m
4.503	0.049317	w	2.574	0.1509	m	4.557	0.048155	m
4.131	0.058599	w	2.462	0.1650	m	4.151	0.058036	s
3.715	0.0725	m	2.389	0.1752	m	3.898	0.0658	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 diacetato-palladium (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 re washed 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, 1124s (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 re washed 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.

Diacetato platinum.—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.

3640 Carboxylates of Palladium, Platinum, and Rhodium, and Adducts

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-CH₃ (Kuhn Roth), 17.5%; *M* (osmometer) at 37° acetone and chloroform, 950 ± 2; (ebullioscopically) in benzene, 937; chlorobenzene, 888. C₄H₈O₄Pt requires O, 20.4; Pt, 62.3; C-CH₃, 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.

Diacetatoypyridinerhodium(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 C₉H₁₁NO₄Rh: 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. C₁₁H₁₅NO₄Rh 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 C₇H₇NO₄Rh: 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. C₂₂H₂₁O₄PRh 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. C₂₄H₂₅O₄PRh 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. C₂₆H₁₇O₄PRh 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. C₁₁H₂₁NO₄Rh 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. C₁₅H₁₇NO₄Rh 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. C₉H₅F₆NO₄Rh 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.