233

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# Palladium(II) Chelate Complexes derived from 3-Hydroxyiminopentane-2,4-dione and Some Related Complexes

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Nitric oxide reacts with bis(pentane-2,4-dionato)palladium giving a mixture of 3-hydroxyiminopentane-2,4-dionato (pentane-2,4-dionato)palladium and bis-(3-hydroxyiminopentane-2,4-dionato)palladium. More convenient routes to both these compounds are discussed. An analogue of the latter compound derived from ethyl 2-hydroxy-imino-3-oxobutyrate is described. The chemistry and spectra of these complexes are discussed in relation to their structures.

DURING a study of the reactions of nitric oxide with a variety of transition-metal compounds a reaction was observed with bis(pentane-2,4-dionato)palladium (I). With a nitric oxide pressure of 30 lb/sq in at room temperature in benzene solution (I) was converted into a new compound (II) in low yield. The new compound was easily separated by chromatography and found to have the formula  $C_5H_7O_2PdC_5H_6NO_3$ . Its <sup>1</sup>H n.m.r. spectrum showed four methyl resonances; a closely spaced pair, close in chemical shift to that of (I), was assigned to the methyl groups of the unchanged chelate ring and a more widely spaced pair at lower field was assigned to the new ligand  $C_5H_6NO_3^-$ . The solitary central proton of the unchanged ligand was observed at a characteristic chemical shift.

With longer reaction times, two further new methyl \* Present address: Monsanto Company, Central Research Department, St. Louis, Missouri 63166, U.S.A. resonances were observed in the n.m.r. spectrum of the total reaction product. These appeared as a band very close to and slightly downfield from each of the methyl



# J. Chem. Soc. (A), 1971

resonances of the new ligand in complex (II) and they are attributed to another new product (III). Compounds (II) and (III) could not be separated by chromatography, but it seemed likely that (III) was  $Pd(C_5H_6NO_3)_2$ . These products then correspond to formal substitution of hydrogen in (I) by nitric oxide [reaction (1) and (2)]. Such substitution in (I) has been shown<sup>1</sup> for other substituents.

$$\begin{array}{rl} {\rm Pd}({\rm C}_{5}{\rm H}_{7}{\rm O}_{2})_{2}+2{\rm NO} \longrightarrow \\ {\rm C}_{5}{\rm H}_{7}{\rm O}_{2}{\rm Pd}{\rm C}_{5}{\rm H}_{6}({\rm NO}){\rm O}_{2}+1/2{\rm H}_{2}{\rm N}_{2}{\rm O}_{2} & (1) \\ {\rm C}_{5}{\rm H}_{7}{\rm O}_{2}{\rm Pd}{\rm C}_{5}{\rm H}_{6}({\rm NO}){\rm O}_{2}+2{\rm NO} \longrightarrow \\ {\rm Pd}[{\rm C}_{5}{\rm H}_{6}({\rm NO}){\rm O}_{2}]_{2}+1/2{\rm H}_{2}{\rm N}_{2}{\rm O}_{2} & (2) \end{array}$$

The free acid of the new ligand in these compounds should have the formula  $C_5H_7NO_3$ : such a compound is the so-called isonitroso-derivative of pentane-2,4-dione,<sup>2</sup> actually an oxime (IV) and obtained by the reaction of the  $\beta$ -diketone with nitrous acid (3). On reaction of this compound with tetrachloropalladite ion a red,

$$Ac_2CH_2 + HNO_2 \longrightarrow Ac_2CN \cdot OH + H_2O$$
 (3)  
(IV)

crystalline compound, Pd(C5H6NO3)2, was obtained and a comparison of its n.m.r. and i.r. spectra with those of the mixture of (I), (II), and (III) obtained above suggested that this was indeed (III). Compound (III) has been prepared, using essentially the same method, by other authors.3

In an attempt to obtain a high-yield reaction, (I) was treated with nitric oxide in the presence of a base, sodium carbonate. Surprisingly, since acid is formed in reactions (1) and (2), compound (I) could be recovered quantitatively. This suggested that reactions (1) and (2) were acid catalyzed. A possible mechanism for this catalysis involves intermediate formation of the free ligand (IV) as outlined in reactions (4), (5), and (6).

$$\begin{array}{c} \mathrm{Pd}(\mathrm{C_{5}H_{7}O_{2}})_{2} + \mathrm{H^{+}} \longrightarrow [\mathrm{Pd}(\mathrm{C_{5}H_{7}O_{2}})]^{+} + \mathrm{C_{5}H_{8}O_{2}} & (4) \\ \mathrm{C_{5}H_{8}O_{2}} + 2\mathrm{NO} \longrightarrow \mathrm{C_{5}H_{7}NO_{3}} + 1/2\mathrm{H_{2}N_{2}O_{2}} & (5) \\ \mathrm{[Pd}(\mathrm{C_{5}H_{7}O_{2}})]^{+} + \mathrm{C_{5}H_{7}NO_{3}} \longrightarrow (\mathrm{II}) + \mathrm{H^{+}} & (6) \end{array}$$

Compound (IV) is prepared in acidic medium, 10%sulphuric acid, and experiment showed that (III) could also be prepared in this solvent. Thus, (III) might be prepared directly from tetrachloropalladite ion, nitrite ion, and pentane-2,4-dione. This was demonstrated but preparation via (IV) gives a better yield of the product. The similarity of this direct preparation to the previously reported<sup>4</sup> reaction of tetranitropalladite ion with pentane-2,4-dione prompted a reinvestigation of the product of that reaction, which was formulated as  $C_{10}H_{15}NO_5Pd$ , very close to the empirical formula of (II). This product proved to be identical with (II) and is

<sup>1</sup> A. Kasahara, K. Uji-ie, and K. Tanaka, Bull. Chem. Soc. Japan, 1966, **39**, 2227.

hence reformulated as C<sub>10</sub>H<sub>13</sub>NO<sub>5</sub>Pd. This method<sup>4</sup> offers a much more attractive method of preparing (II). Thus, both (II) and (III) may be conveniently obtained by methods other than the initially investigated reaction of nitric oxide with (I).

The formation of transition-metal complexes of the oxime (IV) was reported some 40 years ago by Taylor and Ewbank.<sup>5</sup> These complexes have not been further investigated until recently.  $Co(C_5H_6NO_3)_3$ , originally prepared by Taylor and Ewbank, has been reinvestigated <sup>6,7</sup> and given the formulation (V). Compound (III) has been prepared<sup>3</sup> and two methyl resonances were observed in its n.m.r. spectrum, consistent with a structure similar to that of the cobalt complex. Both compounds and also (II) show bands in their i.r. spectra near 1660 and 1520 cm<sup>-1</sup> assigned to the free and coordinated acyl groups, respectively.

Analogues of Compound (III).---Attempts were made to obtain complexes containing unco-ordinated groups other than an acyl group. Examination of their i.r. spectra should provide evidence that the band near 1660  $\text{cm}^{-1}$  in the spectrum of (III) has been correctly



assigned. Of the compounds investigated, (VI), (VII), and (VIII), only (VI) gives an analogous compound. This product is thought to be (IX) rather than (IXa) on



the basis of comparative spectral data discussed below. Instead of an i.r. band near 1660 cm<sup>-1</sup> this compound exhibited two bands at 1700 and 1717 cm<sup>-1</sup>. It is of interest to compare these values with those typical of an  $\alpha\beta$ -unsaturated ketone (1665-1685 cm<sup>-1</sup>) and of an αβ-unsaturated ester  $(1717-1730 \text{ cm}^{-1}).^8$ 

 <sup>&</sup>lt;sup>2</sup> E. Wolff, Annalen, 1902, **325**, 139.
<sup>3</sup> U. B. Talwar and B. C. Haldar, Proceedings Xth I.C.C.C.

Japan, 1967, p. 395. <sup>4</sup> C. Djordjevic, J. Lewis, and R. S. Nyholm, Chem. and Ind., <sup>1</sup> C. Djordjevic, J. Lewis, and R. S. Nyholm, Chem. and Ind.,

<sup>&</sup>lt;sup>5</sup> T. W. J. Taylor and E. K. Ewbank, J. Chem. Soc., 1926,

<sup>2818.</sup> <sup>6</sup> C. Matsumoto and K. Shinra, Nippon Kagaku Zasshi, 1967, **88**, 340.

<sup>&</sup>lt;sup>7</sup> I. Masuda, M. Tamaki, and K. Shinra, Bull. Chem. Soc. Japan, 1969, 42, 157. <sup>8</sup> L. J. Bellamy, 'The Infrared Spectra of Complex Mole-

cules,' Methuen, London, 1958, pp. 132, 178.

On reaction with tetrachloropalladite ion in water (VII) was hydrolyzed and the anionic complex [(IXa) or (Xb)] was obtained on addition of caesium fluoride. On reaction in ethanol an anionic complex (XI) was also formed. This was isolated as the sodium salt and was found to have the formulation  $Na_2[Cl_2Pd(C_5H_5N_2O_3)_2],H_2O$ . Presumably it contains the conjugate base of (VII) functioning as a monodentate ligand. On treatment with water it yielded the salt  $Na_2[Pd(C_3N_2O_3)_2],3H_2O$ , containing the same complex anion as (X). No identifiable complexes were obtained from (VIII).

Derivatives of Compounds (III) and (IX).—As compound (III) contains a free acyl group, it was expected to form characteristic ketone derivatives. On reaction with phenylhydrazine in methanol a compound was isolated whose formula corresponded to the condensation 235

the phenylhydrazone complex were isolated from the reactions of (III) with ethylamine, butylamine, benzyl-



amine, and acetone hydrazone, respectively. With ammonia a compound (XVII) of similar stoicheiometry

|         |                                   |                    | A      | nalyti                        | cal da       | ta for                      | com         | plexes                     | of gei       | ieral f                    | ormul | a (XXX         | IIX)*   |                         |
|---------|-----------------------------------|--------------------|--------|-------------------------------|--------------|-----------------------------|-------------|----------------------------|--------------|----------------------------|-------|----------------|---|-------------------------|
| Compd.  | x                                 | Y                  |        | C (                           | %)           | Н (                         | %)          | N ('                       | %)           | C ('                       | %)    | Pd (%)         | <i>M</i> ª †                                      | Method »                |
| (ÎII)   | 0                                 | Ac                 | F      | 33 <b>·</b> 1                 | 33.1         | 3.3                         | 3.3         | 7.6                        | 7.6          | 26.3                       |       | 29.0           | 363 (0·22), 363 (0·33),<br>383 (0·44), 396 (0·66) | VPO(CHCl <sub>3</sub> ) |
|         |                                   |                    | С      | $33 \cdot 1$                  |              | 3.3                         |             | 7.7                        |              | 26.5                       |       | 29.4           | 362.6   |                         |
| (IX)    | 0                                 | CO2Et              | F      | 34.1                          | 34.4         | 3.9                         | 3.9         | 6.6                        | 6.5          | 29.5                       | 29.7  | 25.3           | 444 (0·49), 421 (0·95),<br>471 (1·89)             | $VPO(C_6H_6)$           |
|         |                                   |                    | С      | $34 \cdot 1$                  |              | $3 \cdot 8$                 |             | 6.6                        |              | 30.3                       |       | 25.2           | 422.7   |                         |
| (XII)   | N·NHPh                            | Ac                 | F<br>C | 49∙3<br>48∙7                  | <b>48</b> ·9 | 4∙5<br>4∙5                  | <b>4</b> ·5 | $15 \cdot 2 \\ 15 \cdot 4$ | $15 \cdot 2$ | $11.9 \\ 11.8$             |       | 19∙3<br>19∙6   | 559 (1·31)<br>542·9                               | VPO(CHCl <sub>3</sub> ) |
| (XIII)  | NEt                               | Ac                 | F<br>C | $40.3 \\ 40.3$                | <b>40·3</b>  | $5.3 \\ 5.3$                | $5 \cdot 0$ | $13.5 \\ 13.4$             | 13.3         | $14.6 \\ 15.4$             |       |                | 412<br>416·8                                      | $CRY(C_6H_6)$           |
| (XIV)   | NBun                              | Ac                 | F<br>C | 46∙0<br>45∙7                  | <b>46</b> ·1 | 6∙6<br>6∙4                  | <b>6</b> ∙7 | $12.0 \\ 11.9$             | 12.0         |                            |       |                | 461<br>472·9                                      | $CRY(C_6H_6)$           |
| (XV)    | $\rm N{\boldsymbol{\cdot}}CH_2Ph$ | Ac                 | F<br>C | $53 \cdot 4 \\ 53 \cdot 3$    | 53.7         | $5.0 \\ 4.9$                | <b>5</b> ·0 | $10.4 \\ 10.4$             | 10.5         |                            |       | $19.3 \\ 19.7$ | 513<br>540·9                                      | $CRY(C_6H_6)$           |
| (XVI)   | $\text{N}{\cdot}\text{N=CMe}_2$   | Ac                 | F<br>C | $40.5 \\ 40.8$                | 40.5         | $4 \cdot 9 \\ 5 \cdot 1$    | $5 \cdot 0$ | $17.8 \\ 17.8$             | 17.8         | $13.5 \\ 13.6$             |       | $22.5 \\ 22.6$ | 487<br>470·8                                      | $CRY(C_{6}H_{6})$       |
| (XVII)  | NH                                | Ac                 | F<br>C | 33∙1<br>33∙3                  | <b>33</b> ·0 | 3∙8<br>3∙9                  | 3.8         | $15.3 \\ 15.5$             | 15.3         | $18.8 \\ 17.8$             |       |                | I.S.  |                         |
| (XVIII) | $\rm N{\cdot}NH_2$                | Ac                 | F<br>C | $31.0 \\ 30.7$                | 31-1         | 4∙4<br>4∙1                  | <b>4</b> ·3 | $21.0 \\ 21.5$             | 21.7         | $16.5 \\ 16.4$             |       | $26.8 \\ 27.2$ | I.S.  |                         |
| (XIX)   | $N \cdot CH_2$                    | Ac                 | F<br>C | $37.3 \\ 37.3$                | 37.5         | ${f 4\cdot 2} {f 4\cdot 2}$ | <b>4</b> ·2 | $14 \cdot 4 \\ 14 \cdot 5$ | 14.3         |                            |       |                | I.S.  |                         |
| (XX)    | N·NHPh                            | CO <sub>2</sub> Et | F      | <b>47</b> ·8                  | <b>47</b> ·5 | <b>4</b> ·5                 | <b>4</b> ·6 | 13.8                       | 13.9         | 15.7                       |       | 17.7           | 616 (0·76), 613 (1·15),<br>648 (1·8)              | $VPO(C_6H_6)$           |
|         |                                   |                    | С      | <b>47</b> ·8                  |              | 4.7                         |             | 13.9                       |              | 15.9                       |       | 17.6           | 602-9   |                         |
| (XXI)   | $N \cdot NH_2$                    | CO <sub>2</sub> Et | F<br>C | ${32 \cdot 1} \ {32 \cdot 0}$ | $32 \cdot 2$ | 4·5<br>4·5                  | <b>4</b> ∙3 | $18.5 \\ 18.6$             | 18.3         | $21 \cdot 6 \\ 21 \cdot 3$ |       |                | I.S.  |                         |

TABLE 1

\* F = Found, C = Calc. for.  $\dagger I.S. = Insufficiently soluble.$ 

<sup>a</sup> At concentration (weight/weight percentage) shown in parenthesis. <sup>b</sup> Abbreviations VPO = vapor pressure osmometry, CRY = cryoscopy. Solvent shown in parenthesis.

of one molecule of the complex with two of the reagent. It showed an i.r. band near 1660 cm<sup>-1</sup> but none near 1520 cm<sup>-1</sup> and so was assigned the structure (XII) rather than the alternate and hoped-for (XIIa). The coordination of a second pair of nitrogen atoms is not surprising as Pd-N bonds appear to be more stable than Pd-O bonds.<sup>9</sup> In contrast, when (I) was treated with phenylhydrazine under the same conditions, it was reduced to metal. The behaviour of complex (II) was intermediate between that of (I) and (III), much metal was produced, and (XII) was isolated in less than 50% yield.

Complexes (XIII), (XIV), (XV), and (XVI) similar to

was obtained as brown needles. It was not identical with the previously prepared orange compound of the same empirical formula,<sup>4</sup>  $C_{10}H_{14}N_4O_4Pd$ . The two compounds had very similar, but not identical i.r. spectra, both showing several bands in the region 1600—1700 cm<sup>-1</sup>. Their X-ray powder patterns, however, indicated isomorphism and they are also isomorphous with the previously prepared <sup>4</sup> nickel compound,  $C_{10}H_{14}N_4NiO_4$ . These data may be consistent with (XVII) having the formulation shown and the isomer the originally proposed structure (XVIIa). These two differ only in the

<sup>9</sup> For example, B. B. Smith and D. T. Sawyer, Chem. Comm., 1968, 1454.

positioning of two hydrogen atoms. The nickel compound is probably the same as that prepared in early work.<sup>5</sup> Hydrazine reduced (III) to metal, but the hydrazone-type derivative, (XVIII), was obtained by



methanolysis of (XVI). With ethylenediamine, (III) gave a low yield of the complex (XIX), which had been previously prepared by reaction of the bisacetylacetone-

 $(III) + H_2 N \cdot CH_2 \cdot CH_2 NH_2$ 



ethylenedi-imine complex with nitric oxide,<sup>7</sup> a reaction similar to that of (I) with nitric oxide.

In some cases (IX) showed condensation reactions similar to those of (III). Thus, with phenylhydrazine it gave (XX) and with acetone hydrazone a compound (XXI), analogous to (XVIII), was isolated. However with ethylamine a strikingly different reaction was



observed, the alkylamido-bridged compound (XXII) being isolated as the product. It is possible that the condensation reactions of (III) and (IX) may proceed through intermediates similar to (XXII); such a scheme is shown in reactions (7), (8), and (9). The isolation of

(XXII) suggests that such a mechanism is plausible and that these condensations do not necessarily take place on the metal atom.



Phosphine and Arsine Adducts of Compounds (III) and (IX).—Compound (III) formed 2:1 adducts with



phosphines and arsines and, similarly, (IX) formed a phosphine adduct:

(

In the solid state their i.r. spectra were found to be more complex than those of (III) and (IX), additional bands being observed in the region 1600-1720 cm<sup>-1</sup>. This was taken as evidence of a monodentate mode of coordination for the originally chelated ligand. Presumably the ligands co-ordinate via nitrogen. No similar adduct of (XII) was obtained, possibly because of the greater strength of the palladium-nitrogen bond which must be broken. These adducts dissociated considerably in chloroform or benzene.

Platinum(II) Compounds.—Because of the characteristic <sup>195</sup>Pt-H coupling usually observed in their n.m.r. spectra, preparation of some platinum analogues of the above palladium compounds has been attempted. Observation of such coupling should confirm the structures assigned to the palladium compounds. Reaction of potassium chloroplatinite with (IV) in boiling water, followed by extraction with methylene chloride yields tiny orange crystals, which mat together giving a brownish appearance to the bulk material. This material (XXIXa) has an analysis consistent with the molecular formula  $Pt(C_5H_6NO_3)_2$ . If the aqueous solution is extracted with benzene instead of methylene chloride, green crystals (XXIXb) with the same empirical formula are obtained. Filtration of the aqueous solution also affords (XXIXb). Recrystallization of either (XXIXa) or (XXIXb) from hot benzene produces a compound, (XXIXc), as discrete brown needles which has an analysis consistent with the molecular formula  $Pt(C_5H_6NO_3)_2$ ,  $1/2C_6H_6$ . These three forms all show identical n.m.r. spectra in the methyl region, in which no

two types of ligands can be judged by reaction of the mixed complex (II) which on similar treatment gave a 5:1 mixture of (XXXI) and (XXXII).

Isomerism of Compound (III).—On mixing, aqueous solutions of potassium tetrachloropalladite and 3-hydroxyiminopentane-2,4-dione (IV) a heavy dark green precipitate (IIIa) formed. On addition of methylene chloride to the aqueous suspension, this precipitate dissolved in the organic phase giving a red solution. Compound (III) was obtained as a red solid on evaporation of this solution. The green compound (IIIa) was found to be isomeric with (III). On contact with

|          |        |                            |              |              | Analyt      | ical da                  | ta for      | phosp          | hine/a | rsine con      | mplexes *                                   |                         |
|----------|--------|----------------------------|--------------|--------------|-------------|--------------------------|-------------|----------------|--------|----------------|---|-------------------------|
| Compd.   |        | С (                        | %)           | $\mathbf{H}$ | (%)         | N (                      | %)          | 0              | (%)    | Pd (%)         | M ª   | Method <sup>a</sup>     |
| (XXV)    | F<br>C | $62 \cdot 3 \\ 62 \cdot 3$ | <b>62</b> ·0 | 4∙9<br>4∙8   | 4.7         | $3 \cdot 1 \\ 3 \cdot 2$ | 3.1         | 9·4<br>10·8    | 11.3   | $11.6 \\ 12.0$ | 673 (0·98), 793 (1·90), 781 (2·85)<br>887·2 | $VPO(C_6H_6)$           |
| (XXVI)   | F<br>C | $64 \cdot 1 \\ 64 \cdot 2$ | <b>64</b> ·3 | $5.4 \\ 5.2$ | 5.5         | $2.5 \\ 2.4$             | 2.6         | 8∙6<br>9∙2     |        |                | 804 (0·32—0·99, average)<br>1159·5          | VPO(CHCl <sub>3</sub> ) |
| (XXVII)  | F<br>C | $56.5 \\ 56.7$             | 56.2         | 4∙3<br>4∙3   | <b>4</b> ·2 | $2.6 \\ 2.9$             | 2.6         | 9·9<br>9·8     |        |                | 369 (0.62), 380 (0.77), 389 (1.03)<br>975.1 | $VPO(C_6H_6)$           |
| (XXVIII) | F<br>C | 60·9<br>60·9               | 60.7         | 5∙3<br>4∙9   | 5.3         | 2∙9<br>3∙0               | <b>2</b> ·8 | $13.0 \\ 13.5$ |        |                | 831 (0·94), 887 (1·90), 935 (2·90)<br>947·3 | $VPO(C_6H_6)$           |
| (XXXII)  | F<br>C | $52.5 \\ 52.7$             | 52.4         | 3·8<br>4·0   | 3.7         | $1.5 \\ 1.5$             | 1.5         | _              |        |                |   |                         |

TABLE 2

<sup>a</sup> See footnotes in Table 1.

coupling to the <sup>195</sup>Pt nucleus to neither methyl resonance can be positively detected. Forms (XXIXa) and (XXIXb) decompose slowly in the solid state as evidenced by the n.m.r. spectra of samples stored for 1 month. In these spectra the higher field methyl resonance had decreased in intensity and a new peak at slightly lower field had appeared. All three forms decomposed during 15 h in methylene chloride solution, and no crystalline material could be recovered from such solutions.

Reaction of form (XXIXa) with ethylamine yielded a stable, red, crystalline material, (XXX), identified as the platinum analogue of (XIII). The couplings to the



<sup>195</sup>Pt nucleus observed in its n.m.r. spectrum are consistent with the structure shown. The powder pattern of this compound is not identical with that of (XIII) but there are several coincident strong lines in both patterns suggesting that there might be a common isomorphous phase.

Acidolysis of Compound (III).—Bis- $\beta$ -diketonatopalladium complexes are susceptible to cleavage by acids; for example,<sup>10</sup> (I) on treatment with tetrafluoroboric acid followed by addition of triphenylarsine gives the cationic complex (XXXI). A similar reaction with (III) gave (XXXII). The relative susceptibilities of the organic solvents or their vapours it isomerized to the red form. The same conversion occurred slowly on heating or exposure to sunlight. The i.r. spectra of (III) and (IIIa) were found to be remarkably similar,



differing only in band intensities. The presence of bands near 1660 and 1520 cm<sup>-1</sup> in the spectra of both isomers was taken to indicate that both contain free and co-ordinated acyl groups. The formation of the green isomer (IIIa) has been observed by Talwar and Haldar.<sup>3</sup>

The green isomer (IIIa) has been found to be isomorphous with the green isomer of  $Pt(C_5H_6NO_3)_2$ , (XXIXb), and the red isomer (III) is isomorphous with (XXIXc). The other form of the platinum compound (XXIXa) has a powder pattern different from that of the other two forms but which is similar to that of the green

<sup>10</sup> B. F. G. Johnson, J. Lewis, and D. A. White, J. Amer. Chem. Soc., 1969, **91**, 5186.

isomer (XXIXb); it may be a multiphase material containing one phase isomorphous with (XXIXb).

Complexes of Other Metals.—As reported by Taylor and Ewbank <sup>5</sup> and confirmed by Matsumoto and Shinra,<sup>6</sup>  $Co(C_5H_6NO_3)_3$ , (V), is obtained on reaction of cobalt(II) acetate with (IV). In a similar reaction with rhodium(III) chloride,  $Ph_4As[Rh(C_5H_6NO_3)_2Cl_2]$ , (XXXIII), was isowith (III), similar reactions attempted with (I) and its higher homologue, bis-(2,2,6,6-tetramethylheptane 3,5dionato)palladium (XXXIV), gave unexpected products. White crystalline solids were isolated and were found to be 4:1 adducts of the amine and the metal complex. Compound (I) gave  $(EtNH_2)_4Pd(C_5H_7O_2)_2$ , (XXXV): (XXXIV) gave similar adducts [(XXXVI) and

| TABLE | 3 |
|-------|---|
|-------|---|

| Compd.    |        | C                          | (%)          | н                          | (%)         | N              | (%)  | 0                          | (%)  | Pd (%)         | M ª   |
|-----------|--------|----------------------------|--------------|----------------------------|-------------|----------------|------|----------------------------|------|----------------|---|
| (XXXV)    | F<br>C | 44·3<br>44·6               | <b>44</b> ·3 | 8·8<br>8·8                 | 8.6         | $11.5 \\ 11.6$ | 11.9 | $13 \cdot 1 \\ 13 \cdot 2$ | 13.4 | (,,,,          | 336 (0·28), 378 (0·39), 389 (0·59), 399 (0·77)<br>485·0     |
| (XXXVI)   | F<br>C | $55 \cdot 2 \\ 55 \cdot 1$ | $55 \cdot 4$ | $10 \cdot 1 \\ 10 \cdot 2$ | 10.1        | 8·7<br>8·6     | 8.6  | 9·9<br>9·8                 | 10.0 |                | <b>476</b> (0·30), 503 (0·36), 389 (0·60), 380 (0·83) 653·3 |
| (XXXVII)  | F<br>C | 59∙8<br>59∙6               | <b>60</b> •0 | $11.0 \\ 10.8$             | 11.2        | 7·4<br>7·3     | 7.4  | 8∙6<br>8∙4                 |      | $13.8 \\ 13.9$ | I.S.  |
| (XXXVIII) | F<br>C | $52 \cdot 6 \\ 52 \cdot 6$ | 52.5         | $9 \cdot 2 \\ 9 \cdot 2$   | <b>9</b> ∙1 | 9·7<br>9·5     | 9.6  | $10.5 \\ 10.8$             |      | $17.9 \\ 17.9$ | I.S.  |
| -         |        |                            |              |                            |             |                |      |                            |      |                |   |

Determined by vapour pressure osmometry in chloroform, concentration (weight/weight percentage) shown in parenthesis.

lated. A similar dibromide was also obtained but *cis*- or *trans*-structures could not be assigned because of the complexity of their i.r. spectra in the metal-halogen stretching region.

No complexes were isolated from the reactions of (IV) with  $(C_5H_5)_2$ TiCl<sub>2</sub>, Mn(CO)<sub>5</sub>Br, hydrated ferric chloride, hydrated nickel acetate, or Ph<sub>2</sub>PAuCl.

Reaction of bis- $\beta$ -diketonatopalladium Complexes with Primary Amines.—Whereas primary amines condensed

TABLE 4

I.r. spectra of the complexes, measured as Nujol mulls, between caesium iodide plates: carbonyl stretching frequencies (cm<sup>-1</sup>)

| C 1  | T 1              | <b>T</b> (  | <b>C</b> 1 1               |
|--|------------------|-------------|----------------------------|
| Compa.                                       | Free acyi        | Free ester  | Co-ord, acyl               |
| (II)   | 1654             |             | Obscured                   |
| (III)  | 1662             |             | 1520                       |
| (IIIa)                                       | 1675sh, 1660     |             | 1520                       |
| `(V) ´                                       | 1674             |             | 1525                       |
| $(\mathbf{IX})$                              |                  | 1717, 1700  | 1532                       |
| (XII)  | 1676             | •           |                            |
| (XIII)                                       | 1680             |             |                            |
| `(XIV)                                       | 1686             |             |                            |
| $(\mathbf{X}\mathbf{V})$                     | 1657             |             |                            |
| (XVI)  | 1665, 1655, 1632 |             |                            |
| (XVII)                                       | 1676, 1667, 1643 |             |                            |
| C.H.N.O.Pd                                   | 1673, 1638       |             |                            |
| C.H.N.O.Ni                                   | 1684 1670 1643   |             |                            |
|  | 1630sh           |             |                            |
| (XVIII)                                      | 1652             |             |                            |
|  | 1675 1666        |             |                            |
| $(\mathbf{X}\mathbf{X})$                     | 1010, 1000       | 1718        |                            |
| $(\mathbf{X}\mathbf{X}\mathbf{I})$           |                  | 1714 1700sh |                            |
|  |                  | 1795        |                            |
| (XXV)  | 1718 1660eb 1650 | 1720        | 1594(22)                   |
| XXVI   | 1705 1668 1603   |             | 1024()                     |
| (XXVII)                                      | 1687 1668        |             |                            |
| (XXVIII)                                     | 1685             | 1720 1797   | 1599(22)                   |
| (XXIII)                                      | 1600             | 1159, 1121  | 1022(??)                   |
| (XXX)  | 1675             |             | 1490(!)                    |
| (XXXII)                                      | 1075             |             | 1594                       |
| (XXXIII)                                     | 1660             |             | 1510                       |
| $(\mathbf{X}\mathbf{X}\mathbf{X}\mathbf{V})$ | 1000             |             | 1019<br>1890ab 1804        |
| (XXV)  |                  |             | 1620511, 1004              |
| (AAVI)                                       |                  |             | 1020, 109050,              |
| (XXXVII)                                     |                  |             | 1810 1507                  |
| (2222 (211)                                  |                  |             | 1588 1570                  |
| (XXXVIII)                                    |                  |             | 1699 1500                  |
| (2222 (211)                                  |                  |             | 1040, 1090,<br>1505-b 1500 |
|  |                  |             | 100050, 1000               |

(XXXVII)] with ethylamine and butylamine and also  $(H_2NCH_2CH_2NH_2)_2Pd(C_{11}H_{19}O_2)_2$ , (XXXVIII), from reaction with ethylenediamine. Compounds (XXXV) and (XXXV) dissociated considerably in solution. In the solid state their carbonyl stretching frequencies were observed to be within the range 1500—1620 cm<sup>-1</sup>, characteristic of the chelated ligand. Their n.m.r. spectra showed single bands for the  $\beta$  diketonate methyl protons. The structure of these compounds is not known.

Spectroscopic Data.—The carbonyl stretching frequencies of some of the complexes are recorded in Table 4. Of particular interest is the presence or absence of a co-ordinated acyl group revealed by the presence or absence of a band near  $1520 \text{ cm}^{-1}$ .

Table 5 shows the n.m.r. spectra of compounds of the general formula (XXXIX). In the spectra of the compounds (III), (XII)---(XV) derived from 3 hydroxy-



iminopentanedione, two methyl resonances are observed. In all these spectra slightly different band widths for these methyl resonances were indicated by one peak being more intense than the other. In the spectrum of the platinum compound (XXX) a similar difference is also apparent, and in this case it is the peak which does not show coupling to platinum that is the most intense, even after allowing that the existence of coupling to platinum in the other resonance would reduce its peak height by two-thirds. By analogy with this spectrum the most intense peak in the spectra of the palladium compounds has been assigned to the free acyl group (Y). This assignment produces a reasonable and consistent picture. Except for (XII) which contains an aromatic ring which may exert a shielding effect, the resonances of the free acyl methyl groups all lie within the narrow co-ordinated acyl group, confirming that it has this structure and not the alternative (IXa). The i.r. data on this compound (Table 4) are also consistent with this conclusion.

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| TABLE | 5 |
|-------|---|
|-------|---|

| N.m.r. spectra | of cor | npounds of | general | formula | (XXXIX) | j. |
|----------------|--------|------------|---------|---------|---------|----|
|----------------|--------|------------|---------|---------|---------|----|

|                          |                      |                    | Chemical shifts (p.p.                                 | $m$ . downneid from $me_451$ ) • |             |
|--------------------------|----------------------|--------------------|---|----------------------------------|-------------|
| Compd.                   | х                    | Y                  | X   | Y                                | Me          |
| $(\tilde{\mathbf{III}})$ | 0                    | Ac                 |   | 2.34 (s, 6)                      | 2.65 (s, 6) |
| ÌΙΧ                      | 0                    | CO <sub>s</sub> Et |   | 1.33 (t, 6), 4.32 (q, 4)         | 2.64 (s, 6) |
| (XII)                    | N·NHPh               | Ac                 | 6.7 - 7.5 (m, 10), $9.6$ (s, 2) <sup>a</sup>          | 2.50 (s, 6)                      | 2.32 (s, 6) |
| (XIII)                   | NEt                  | Ac                 | 1.30 (t, 6), $3.85$ (q, 4)                            | 2.35 (s, 6)                      | 2.28 (s, 6) |
| (XIV)                    | NBu <sup>n</sup>     | Ac                 | 1.15 (t, 6), $1.47$ (m, 8), $3.82$ (m, 4)             | 2.36 (s, 6)                      | 2.30 (s, 6) |
| (XV)                     | N·CH <sub>2</sub> Ph | Ac                 | 5.88 (s, 4), $7.32$ (s, 10)                           | 2.32 (s, 6)                      | 2.26 (s, 6) |
| (XX)                     | N∙NHPh               | $CO_2Et$           | $6 \cdot 6 - 7 \cdot 5$ (m, 10), $9 \cdot 7$ (s, 2) a | 1·33 (t, 6), 4·34 (q, 4)         | 2.26 (s, 6) |
| (XXI)                    | $N \cdot NH_2$       | CO <sub>2</sub> Et | 6.22 (s, 4) <sup>a</sup>                              | 1.44 (t, 6), 4.35 (q, 4)         | 2·12 (s, 6) |

<sup>a</sup> Multiplicity, relative area shown in parenthesis. Abbreviations s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Spectra obtained in CDCl<sub>3</sub> solution, with internal tetramethylsilane reference. <sup>b</sup> Broad signal, which disappears on addition of  $D_2O$ .

| TABLE | 6 |
|-------|---|
|-------|---|

N.m.r. spectra, various complexes

|                    | Chemical shifts (p.p.m. downfield from $Me_4Si$ )      |                                |  |                     |  |  |  |  |  |  |
|--------------------|--|--------------------------------|--|---------------------|--|--|--|--|--|--|
| Compd.             | Free acyl/ester<br>methyl                              | Coord.<br>acyl/imine<br>methyl | Other  | Assignment          |  |  |  |  |  |  |
| (II)<br>(V)        | 2·35 (s, 3)<br>2·40 (s, 9)                             | 2.45 (s, 3)<br>2.55 (s, 9)     | 2.08 (s, 3), 2.12 (s, 3), 5.47 (s, 1)                                    | $C_5H_7O_2$ Protons |  |  |  |  |  |  |
| (XVI) a            | 2.36   | 2.36                           | 1.75 + 1.82 (6), $2.21 + 2.23$ (6)                                       | N-Methyl groups     |  |  |  |  |  |  |
| (XXII)<br>(XXIX) d | 1.27 (t, 3), <sup>b</sup> $4.24$ (q, 2)<br>2.38 (s, 6) | 2·56 (s, 3)<br>2·76 (s, 6)     | 1.27 (t, 3), <sup>b</sup> ca. 3.8 (broad, 2), $1.82$ (s, 1) <sup>c</sup> | Bridging NHEt group |  |  |  |  |  |  |
| (XXX)              | 2.34 (s, 6)<br>I (Pt-H) = 5 Hz                         | 2·38 (s, 6)                    | 1.18 (t, 6), $4.01$ (q, 4)<br>I (Pt-H) = 33 Hz (-CH <sub>2</sub> -)      | N-Ethyl group       |  |  |  |  |  |  |
| (XXXIII)           | Ž·35 (s, 6)  | 2.58 (s, 6)                    | 7.5-8.0 (m, 20)  | Phenylprotons       |  |  |  |  |  |  |

<sup>a</sup> Spectrum was considerably different in  $C_6H_6$  and  $CCl_4$ . <sup>b</sup> These signals overlap. <sup>c</sup> Signal disappears on addition of  $D_2O$ . <sup>d</sup> All three forms (a), (b), and (c) gave the same spectrum in the methyl region. See footnote (a) in Table 5.

### TABLE 7

N.m.r. spectra of phosphine and arsine complexes

| Chemical | shifts  | $(\mathbf{p},\mathbf{p},\mathbf{m})$ | downfield   | from | Me.Si)  |
|----------|---------|--------------------------------------|-------------|------|---------|
| onomicai | 5111103 | 1 P. P. III.                         | downitutoid | monn | TITOTOT |

| Compd.   | chemical philos (p.p.m. download from 11040)                                 |  |  |  |
|----------|--|--|--|--|
|          | Methyl   | Ethyl  | Phosphine/Arsine   |  |
| (XXV)    | 1.16 (s, 3), 1.38 (s, 3)<br>1.42 (s, 3), 1.65 (s, 3)                         |  | $7 \cdot 1 - 8 \cdot 0 \ (m, \ 30)$  |  |
| (XXVI)   | 2·18 (s),ª 2·25 (s) ª<br>2·28 (s),ª 2·35 (s) ª                               |  | $2 \cdot 2 - 3 \cdot 9$ (m), <sup><i>a</i></sup> $2 \cdot 1 - 8 \cdot 0$ (m, 40) |  |
| (XXXVII) | 1.32 (s), 1.42 (s)<br>1.70 (s), 1.75 (s)<br>2.00 (s), $^{b}$ 2.27 (s) $^{b}$ |  | 7·2—7·7 (m, 30)  |  |
| (XXVIII) | 1·38 (s, 3), 1·53 (s, 3)   | ca. $4.5~(2 	imes q, 4)$<br>ca. $0.9~(2 	imes t, 6)$ | 7·2—7·8 (m, 30)  |  |

<sup>a</sup> These signals overlap, total integrated intensity 20 protons. <sup>b</sup> These signals due to free compound (III), total intensity of all methyl groups, 12H. See footnote (a) in Table 5.

range  $2\cdot32$ — $2\cdot34$  p.p.m. downfield from tetramethylsilane. The change in chemical shift of the other methyl group from  $2\cdot65$  p.p.m. in (III) to *ca*.  $2\cdot3$  p.p.m. in the imine-type derivatives (XII)—(XV) is expected, since a similar upfield change in chemical shift is observed between the methyl groups of (I) at  $2\cdot07$  p.p.m. and those of (XXXX) at  $1\cdot37$  and  $1\cdot57$  p.p.m.

A comparison of the spectra of these compounds derived from (IV) with those of (IX) and (XX), which are obtained from the hydroxyimino-keto-ester (VI), indicates that the methyl resonance in (IX) is due to a The methyl resonances in the spectra of the cobalt (V) and rhodium (XXXIII) complexes derived from the hydroxyimino- $\beta$ -diketone (IV) have also been assigned on the basis that the most intense peak is due to the free acyl group. These assignments (Table 6) compare favourably with that in the palladium compound, (III); in all three spectra the free acyl peak is observed at highest field. Only in (II) has the spectrum of the C<sub>5</sub>H<sub>6</sub>NO<sub>3</sub><sup>-</sup> ligand shown two methyl resonances of almost equal bandwidth. In this case the highest field resonance has been assigned to the free acyl group (Table 6).

In  $Pt(C_5H_6NO_3)_2$ , (XXIX), the most intense peak has also been assigned to the free acyl group though the absence of detectable coupling to <sup>195</sup>Pt nucleus precludes positive assertion that this compound has the expected structure. In the spectrum of (XVI) the free and coordinated acyl resonances appear to be coincident. Each



of the other two inequivalent methyl resonances appears as two bands of unequal intensity, which may indicate the presence of two isomeric forms, perhaps (XVIa) and (XVIb). Spectra of this compound obtained in carbon tetrachloride or [<sup>2</sup>H<sub>6</sub>]benzene were considerably different from each other and from that in [2H]chloroform. Whereas the methyl groups of the two ethyl groups present in (XXII) are coincident in their spectra, the methylene resonances are considerably shifted, that at higher field (ca. 3.8 p.p.m.) being assigned to the bridging ethylamido-group and that at 4.24 p.p.m. to the ester group. The latter compares favourably with the shifts of the similar protons in (IX) and (XX). The N-H resonance was also observed at rather high field. As pointed out above, the coupling to the <sup>195</sup>Pt nucleus observed in the spectra of (XXX) is consistent with the proposed structure.

The spectra of the two phosphine adducts of (III) (Table 7) show four methyl resonances, which is consistent with the presence of monodentate C5H6NO3ligands. The spectrum of the arsine adduct (XXXVII) shows four weak signals attributable to the methyl resonances of the adduct, but the main feature is two strong methyl resonances due to free compound (III), suggesting an equilibrium between that compound and an adduct. The spectra of mixtures of (III) and the arsine confirm this conclusion. A 1:1 mixture showed >95% free (III) and a 1:16 (complex : arsine) mixture <10%, intermediate percentages being observed at intermediate ratios. It is noteworthy that the arsine adduct is considerably more dissociated in solution than the two phosphine ones and gives rise to approximately three osmotic particles, as expected for complete dissociation. The spectrum of (XXVIII) is similar to that of (XXXV), showing two methyl resonances and two ethyl resonances consistent with monodentate ligands also being present in this compound.

Little light is shed on the structure of the adducts of bis- $\beta$ -diketonatopalladium complexes with primary amines by their n.m.r. spectra (Table 8). Single resonances for the  $\beta$  diketonate methyl groups suggest no asymmetry of this ligand. The N-H protons are

observed in the spectrum of (XXXV) but not in those of the other two compounds which were sufficiently soluble for n.m.r. spectra to be obtained.

## TABLE 8

### N.m.r. spectra, amine complexes

| Chemical shifts (p.p.m. downfield from $Me_4Si$ ) |  |                           |  |
|---|--|---------------------------|--|
| Compd.  | Amine  | $\beta$ -Diketonate       |  |
| (XXXV)  | 1.15 (t, 12), ca. 2.67 (br, 8), <sup>a</sup>         | 1.72 (s, 12), 5.07 (s, 2) |  |
| (********   | ca. 5.62 (br, 8) $^{b}$                              |                           |  |
| (XXXVI)   | ca. $1.12$ (t), ca. $2.67$ (br, 8)                   | 1.00 (s), 5.42 (s, 2)     |  |
| (XXXVII)  | $0.8 - 1.9 \text{ (m)},^{a} ca. 2.5 \text{ (br, 8)}$ | 1.00  (s), d 5.42  (s, 2) |  |
| (I) e   |  | 2.07 (s, 12), 5.65 (s, 2) |  |
| (XXXIV) •   | 1  | 1·13 (s, 36), 5·45 (s, 2) |  |
| Resol   | ves into 7 line signal on ad                         | dition D.O. b Disan-      |  |

\* Resolves into 7 line signal on addition  $D_2O_{\cdot}$  \* Disappears on addition  $D_2O_{\cdot}$  \* These signals overlap, total integral *ca.* 48 protons. \* These signals overlap, total integral *ca.* 64 protons. • Included for comparison. See footnote (a) in Table 5.

The n.m.r. spectra of the free acids of the ligands used in this work, **3**-hydroxyiminopentane-2,**4**-dione (IV) and ethyl(2-hydroxyimino-3-oxobutyrate) (VI) are shown

### TABLE 9

| N.m      | .r. spectra o  | f the free acids of the         | he ligands                    |
|----------|----------------|---------------------------------|-------------------------------|
|          | Chemical       | shifts (p.p.m. downfi           | ield from Me <sub>4</sub> Si) |
| Compd.   | Methyl         | Ethyl                           | Hydroxyl ª                    |
| (IV)     | 2·43 (s, 6)    |                                 | 10.62 (s, 1)                  |
| (VI)     | 2·45 (s, 6)    | 1·36 (t, 3), 4·42 (q,           | 2) 10.76 (s, 1)               |
| Signa    | ls disappear o | n addition of D <sub>2</sub> O. | See footnote (a) in           |
| Table 5. |                | -                               | • ·                           |

in Table 9. The presence of a resonance at low field exchangeable with  $D_2O$  confirms the oxime structure of these compounds.

The structure of some of the complexes described above has been confirmed by mass spectroscopy. Some of the parent ions observed are detailed in Table 10.

TABLE 10

Selected complexes, parent ions observed in mass spectra

|        |                           |                  | -  |
|--------|---------------------------|------------------|--|
| Compd. | <i>m</i> / <i>e</i> Found | m/e Calc.        | Assignment                               |
| (II)   | $332 \cdot 9830$          | $332 \cdot 9823$ | $C_{10}H_{13}NO_{5}^{106}Pd^{+}$         |
| (III)  | 361.9737                  | 361.9724         | $C_{10}H_{12}N_2O_6^{106}Pd^+$           |
| (XII)  | $542 \cdot 9092$          | $542 \cdot 0888$ | $C_{22}H_{24}N_6O_4^{106}Pd^+$           |
|        | 541.0904                  | 541.0907         | $C_{29}H_{24}N_{6}O_{4}^{105}Pd^{+}$     |
|        | 540.0890                  | 540.0892         | $C_{22}H_{24}N_6O_4^{104}Pd^+$           |
| (XX)   | $602 \cdot 1121$          | $602 \cdot 1099$ | $C_{24}H_{28}N_6O_6^{106}Pd^+$           |
|        | $601 \cdot 1112$          | $601 \cdot 1118$ | $C_{24}H_{28}N_6O_6^{105}Pd^+$           |
|        | $600 \cdot 1120$          | $600 \cdot 1103$ | $C_{24}^{24}H_{28}^{20}N_6O_6^{104}Pd^+$ |
| (XVI)  | 470.0875                  | 470.0888         | $C_{16}H_{24}N_6O_4^{106}Pd^+$           |
| (XXIX) | 450.0325                  | 450.0328         | $C_{10}H_{12}N_2O_6^{194}Pt^+$           |
| (V)    | 443.0402                  | 443.0374         | $C_{15}H_{18}N_{3}O_{9}Co^{+}$           |

### EXPERIMENTAL

The Reaction of Bis(pentane-2,4-dionato)palladium withNitric Oxide.—The reaction was carried out in a closed system of volume 405 ml. A glass pressure bottle was charged with the complex (3.04 g, 10.0 mmol) and a magnetic stirring bar. The bottle was then connected to a pressure manifold with connections to air, vacuum, and nitric oxide. The system was evacuated and benzene (100 ml) was admitted through a serum cap. It was then

pressured to 30 lb/sq. in with nitric oxide, freed of acidic oxides by passage through Ascarite. The mixture was stirred for 20 h during which the pressure fell to 11 lb/sq. in. The system was pumped free of nitric oxide and opened to air. The brown solution was filtered and the filtrate was poured into a column of silica gel. Elution of the column with benzene gave a rapidly moving yellow band, followed by a slow moving orange band. Collection of the yellow eluate and evaporation yielded the starting material. The orange eluate was collected in 500-ml portions and evaporated to dryness. The first two were observed by n.m.r. spectroscopy to contain some starting material. Six subsequent portions were evaporated and the residues were combined and recrystallized from benzene-hexane (3:2) pentane-2,4-dionato-(3-hydroxyiminopentane-2,4give to dionato)palladium (II) (528 mg, 16%) [Found: C, 36.0, 35.7; H, 3.7, 3.9; N, 4.5, 4.4; Pd, 34.8%; M (v.p.o. of 0.66% w/w solution in chloroform), 341.  $C_{10}H_{13}NO_5Pd$ requires C, 36.0; H, 3.9; N, 4.2; Pd, 31.9%, M, 333.6].

Bis-(3-hydroxyiminopentane-2,4-dionato)palladium (III). —Solutions of potassium tetrachloropalladite (6.52 g, 20.0 mmol) in water (500 ml) and 3-hydroxyiminopentane-2,4-dione  $^2$  (5.16 g, 40.0 mmol) in water (500 ml) were mixed in a 2-l separating funnel. A deep-green precipitate formed instantaneously. Methylene chloride (250 ml) was added and the mixture was shaken. The green precipitate rapidly dissolved to give a red organic phase. The methylene chloride solution was separated and dried (CaCl<sub>2</sub>). Filtration and evaporation of the filtrate yielded a red solid, which was recrystallized from benzene-hexane (3: 2) to give the product as red crystals (5.45 g, 75%); analytical data are shown in Table 1.

During a similar reaction a small amount of the initially formed green precipitate was filtered off, washed with water, and dried *in vacuo*. It was found to be an isomer of (III) (Found: C, 33·1, 32·9; H, 3·4, 3·4; N, 7·6, 7·5; O, 26·7; Pd, 28·7. Calc. for  $C_{10}H_{12}N_2O_6Pd$ : C, 33·1; H, 3·3; N, 7·7; O, 26·5; Pd, 29·4%).

The Reaction of Tetranitropalladite Ion with Pentane-2,4dione.—A mixture of potassium tetranitropalladite (740 mg, 2.0 mmol), pentane-2,4-dione (1.0 ml), and water (20 ml) was stirred for 7 h. The precipitate was collected and after drying *in vacuo* overnight afforded an orange-red solid, identified as pentane-2,4-dionato-(3-hydroxyiminopentane-2,4-dionato)palladium (II) (546 mg, 82%) (Found: C, 35.7; H, 3.9; N, 4.2.  $C_{10}H_{13}NO_5Pd$  requires C, 36.0; H, 3.9; N, 4.2%).

This reaction was also performed with the addition of (a) sodium carbonate (212 mg, 2.0 mmole) and (b) 1 drop of conc. hydrochloric acid. The results are shown below.

| Reactions  | Vield | Product composition |      |       |
|------------|-------|---------------------|------|-------|
| conditions | (mg)  | (I)                 | (II) | (III) |
| Basic (a)  | 464   | 80%                 | 20%  |       |
| Neutral    | 546   | ,,,                 | 100  |       |
| Acidic (b) | 463   |                     | 95   | 5%    |

Bis(ethyl-2-hydroxyimino-3-oxobutyrato)palladium (IX).— A mixture of potassium tetrachloropalladite (3.26 g, 10.0 mmol) and ethyl 2-hydroxyimino-3-oxobutyrate <sup>11</sup> in water (700 ml) was stirred for 30 min. It was then filtered and the red residue was dried *in vacuo* and then recrystallized from heptane-toluene (9:1) to give the *product* as red needles (3.18 g, 75%). Analytical data are shown in Table 1.

Reactions of Ethyl Hydroxyiminocyanoacetate (VII).-

(a) In water. Solutions of the ester <sup>12</sup> (284 mg, 2.0 mmol) in water (40 ml) and potassium tetrachloropalladite (326 mg, 1.0 mmol) were mixed. No change was observed until potassium carbonate (276 mg, 20 mmol) was added, whereupon the solution turned light yellow. Addition of caesium fluoride (750 mg) precipitated a yellow solid, which was filtered off and dried *in vacuo* to give compound (X) (263 mg, 42%) (Found: C, 11.5, 11.6; H, 0.4, 0.4; N, 8.7, 8.8; O,17.1, 18.8.  $C_6H_2Cs_2N_4O_7Pd$  requires: C, 11.7; H, 0.3; N, 9.1; O, 18.2%).

(b) In ethanol. The ester (568 mg,  $4\cdot 0$  mmol) in ethanol (20 ml) was added to a solution of disodium hexachlorodipalladate in ethanol (20 ml;  $[Pd^{II}] = 0\cdot I_M$ ) and sodium carbonate (400 mg) was added to the combined solutions. The mixture was stirred for 30 min after filtration to give a red filtrate which was kept at  $-78^{\circ}$  overnight. Large orange needles formed and the mixture was filtered at  $-78^{\circ}$ . The crystals were allowed to warm to room temperature which caused them to crumble to a yellow powder; this was dried *in vacuo* yielding *compound* (XI) (330 mg, 32%) (Found: C,  $22\cdot 9$ ,  $22\cdot 8$ ; H,  $2\cdot 2$ ,  $2\cdot 2$ ; Cl,  $16\cdot 0$ ; N,  $10\cdot 4$ ,  $10\cdot 2$ ; O,  $22\cdot 3$ ,  $18\cdot 1$ ; Pd,  $20\cdot 3$ . C<sub>10</sub>H<sub>12</sub>Cl<sub>2</sub>N<sub>4</sub>Na<sub>2</sub>O<sub>7</sub>Pd requires C,  $22\cdot 9$ ; H,  $2\cdot 3$ ; Cl,  $13\cdot 5$ ; N,  $10\cdot 7$ ; O,  $21\cdot 4$ ; Pd,  $20\cdot 3\%$ ).

On dissolution in the minimum volume of water, (XI) formed a yellow solution which when set aside for a few minutes deposited yellow crystals of  $Na_2[Pd(C_3N_2O_3)_2]$ ,  $3H_2O$ ; this contains the same anion as complex (X) (Found: C, 16.5, 16.7; H, 1.1, 1.1; N, 12.5, 12.5; O, 32.7; Pd, 24.3.  $C_6H_6N_4Na_2O_9Pd$  requires C, 16.7; H, 1.4; N, 13.0; O, 33.4; Pd, 24.7%).

Bis-(3-hydroxyimino-4-phenylhydrazidopentane-2-onato)palladium (XII).---(a) From compound (II). 3-Hydroxyiminopentane-2,4-dionato(pentane-2,4-dionato)palladium (II) ( $3\cdot33$  g, 10\cdot0 mmol) and phenylhydrazine ( $2\cdot16$  g, 20·0 mmol) were dissolved in methanol (60 ml). The mixture was boiled until its volume was reduced to 30 ml. It was then cooled in an ice-bath and filtered to give a black solid, which was dried *in vacuo*. This was extracted with acetone and the orange-red extract was evaporated to dryness. The deep-red residue was recrystallized from benzenehexane to give the *product* as red-brown needles (1.62 g, 30% based on ratio of palladium in product to palladium in starting material: maximum yield would be 50%). Analytical data are shown in Table 1.

(b) From compound (III). Bis-(3-hydroxyiminopentane-2,4-dionato)palladium (III) (724 mg, 2.0 mmol) and phenyl-hydrazine (475 mg, 4.4 mmol) were stirred in methanol (5 ml) for 90 min. Filtration of the mixture afforded a deep-red solid, which was recrystallized from hexanebenzene (2:3) (40 ml) to give the *product* as red-brown needles (624 mg, 57%) (Found: C, 48.7, 49.1; H, 4.6, 4.5; N, 15.2, 15.7.  $C_{22}H_{24}N_6O_4Pd$  requires C, 48.7; H, 4.5; N, 15.4%).

Similarly prepared from compound (III) were the compounds (XIII) as yellow needles (78%); (XIV) as yellow needles (83%); (XV) as orange-yellow crystals (82%); (XVI) as red needles (33%); (XVII) as brown needles (83%); and (XIX) as yellow plates (34%); and from (IX) the compounds (XX) as yellow needles (61%); and (XXI) as red crystals (60%). Analytical data are shown in Table 1.

<sup>11</sup> H. Adkins and E. W. Reeve, J. Amer. Chem. Soc., 1938, **60**, 1328.

<sup>12</sup> M. Conrad and A. Schulze, Chem. Ber., 1909, 42, 735.

# J. Chem. Soc. (A), 1971

Di- $\mu$ -ethylamido-bis(ethyl 2-hydroxyimino-3-oxobutyrato)palladium (XXII).—Complex (IX) (422 mg, 1.0 mmol) was suspended in methanol (3 ml) and ethylamine (0.3 ml) was added to it. The mixture was shaken to give a clear, yellow solution which when set aside for 3 h deposited yellow crystals. These were filtered off and dried *in vacuo* to give the *product* as yellow plates (128 mg, 41%) (Found: C, 30.9, 31.2; H, 4.3, 4.6; N, 8.9, 9.0. C<sub>16</sub>H<sub>28</sub>N<sub>4</sub>O<sub>8</sub>Pd requires C, 31.1; H, 4.6; N, 9.1%).

Compounds  $C_{10}H_{14}N_4O_4M_4$  (M = Ni, Pd).—These compounds were prepared by literature methods<sup>4</sup> and recrystallized from large volumes of acetone: Found: C, 38·3, 38·2; H, 4·5, 4·6; N, 18·3, 18·3; O, 17·7. Calc. for  $C_{10}H_{14}N_4O_4Ni$ : C, 38·4; H, 4·5; N, 17·9; O, 18·1. Found: C, 32·7, 32·7; H, 4·0, 3·9; N, 15·1, 15·1; O, 17·8. Calc. for  $C_{10}H_{14}N_4O_4Pd$ : C, 33·3; H, 3·9; N, 15·5; O, 17·8%.

Methanolysis of Compound (XVI).—A mixture of the azine-type complex (XVI) (942 mg, 2.0 mmol), methanol (10 ml), and concentrated sulphuric acid (2 drops) was stirred overnight. Filtration afforded the hydrazone derivative bis-(4-hydrazido-3-hydroxyiminopentane-2-onato)palladium as a red powder (444 mg, 57%). Analytical data are shown in Table 1. The filtrate when set aside overnight yielded more of the complex as red needles.

'Recrystallization' of the red powder (195 mg, 0.5 mmol) from o-dichlorobenzene gave an isomeric compound, as orange needles (176 mg, 90%) (Found: C, 30.9, 30.8; H, 4.2, 4.1; N, 21.2, 21.0; O, 16.4. C<sub>10</sub>H<sub>16</sub>N<sub>6</sub>O<sub>4</sub>Pd requires C, 30.7; H, 4.1; N, 21.5; O, 16.4%).

Neither isomer was sufficiently soluble for molecularweight measurement.

### Bis-(3-hydroxyiminopentane-2,4-dionato)platinum

(XXIX).—A mixture of potassium chloroplatinite (4·15 g, 10·0 mmol), 3-hydroxyiminopentane-2,4-dione (2·58 g, 20·0 mmol), and water (500 ml) was boiled and stirred for 15 min. The mixture was cooled to room temperature and extracted with methylene chloride (500 ml). The brown extract was dried for 10 min. (CaCl<sub>2</sub>), filtered, and evaporated to low volume (ca. 50 ml) as rapidly as possible without heat. The yield of product was reduced to zero if the extract was heated on a steam-bath or stored at room temperature overnight. The solution after evaporation to low bulk was filtered to give the *product* as a brown mat of tiny crystals, which when suspended in the solution appeared orange (XXIXa) (910 mg, 22%) (Found: C, 26·2, 26·3; H, 2·8, 2·7; N, 6·0, 6·0. C<sub>10</sub>H<sub>12</sub>N<sub>2</sub>O<sub>6</sub>Pt requires C, 26·6; H, 2·7; N, 6·2%.

A similar reaction was carried out with double the quantities of the starting materials stated above. The aqueous solution was cooled and extracted with benzene  $(3 \times 250 \text{ ml})$ ; the red extract was dried (CaSO<sub>4</sub>) and evaporated to low bulk. Filtration afforded a green solid (XXIXb) (430 mg, 5%) (Found: C, 26.6, 26.4; H, 2.6, 2.6; N, 6.0, 5.9; O, 20.4. C<sub>10</sub>H<sub>12</sub>N<sub>2</sub>O<sub>6</sub>Pt requires C, 26.6; H, 2.7; N, 6.2; O, 21.5%).

Better yields of the isomer (XXIXb) were obtained by simple filtration of the cooled aqueous solution, rather than extraction of the solution with benzene. In this way (XXIXb) was obtained in moderately good yield (42%based on K<sub>2</sub>PtCl<sub>4</sub>).

Recrystallization of either (XXIXa) or (XXIXb) from hot benzene afforded a hemi-benzene solvate,  $Pt(C_5H_6NO_3)_2, 1/2C_6H_6$ , (XXIXc), as discrete brown needles (Found: C, 31·1; H, 3·0; N, 5·7; O, 19·9.  $C_{13}H_{15}N_2O_6Pt$  requires C, 31·8; H, 3·0; N, 5·7; O, 19·6%).

Bis-(4-ethylimino-3-hydroxyiminopentane-2-onato)platinum (XXX).— Bis-(3-hydroxyiminopentane-2,4-dionato)-platinum (XXIXa) (902 mg, 2.0 mmol) was suspended in methanol (3 ml) and excess of ethylamine was added. The mixture was stirred for 90 min. and then filtered. The dark red residue was recrystallized from hexane to give the product as red plates (202 mg, 20%) [Found: C, 34.2, 34.3; H, 4.5, 4.6; N, 11.2, 11.1%; M (cryoscopic in benzene), 519.  $C_{14}H_{22}N_4O_4Pt$  requires C, 33.3; H, 4.4; N, 11.1%; M, 505.5].

Bis(triphenylphosphine)bis-(3-hydroxyiminopentane-2,4dionato)palladium (XXV).—A mixture of bis-(3-hydroxyiminopentane-2,4-dionato)palladium (362 mg, 1.0 mmol) and triphenylphosphine (552 mg, 2.1 mmol) was stirred in ether (20 ml) for 30 min. Filtration afforded the *product* as a tan powder. Analytical data are shown in Table 2.

The compounds (XXVI), (XXVII), and (XXVIII) were similarly prepared.

3-Hydroxyiminopentane-2,4-dionatobis(triphenylarsine)palladium Tetrafluoroborate.-Bis-(3-hydroxyiminopentane-2.4-dionato)palladium (III) (724 mg, 2.0 mmol) was dissolved in acetone (100 ml) containing fluoroboric acid (0.8 ml; 48% aqueous solution). The solution was diluted to 500 ml with ether and triphenylarsine (1.224 g, 4.0 mmol) was added to the clear, orange solution. Additional ether was added and when the volume of the solution was ca. 800 ml, an orange precipitate was formed. The mixture was allowed to stand for 15 min. and was then made up to 1 l with ether. The orange residue was filtered off, washed with ether, dried, and dissolved in acetone (75 ml); the solution was filtered. Addition of ether to the filtrate caused precipitation of the product which was filtered off (552 mg, 29%) (Found: C, 52.5, 52.4; H, 3.8, 3.7; N, 1.5, 1.5.  $C_{41}H_{36}AsBF_4NO_3Pd$  requires C, 52.7; H, 4.0; N. 1.5%).

Tris-(3-hydroxyiminopentane-2,4-dionato)cobalt (V).— Cobalt(II) acetate tetrahydrate (2·49 g, 10·0 mmol) dissolved in water (100 ml) was added to a solution of 3-hydroxyiminopentane-2,4-dione (3·87 g, 30·0 mmol) in water (500 ml) and the mixture was set aside; tan crystals were deposited and these were filtered off and dried *in vacuo* to give the product (0·66 g, 15%) (Found: C, 40·6; H, 4·0; N, 9·4%); a sample recrystallized from hexane afforded bronze plates (Found: C, 40·9, 40·6; H, 4·1; N, 9·5, 9·4; O, 32·5, 32·4. Calc. for  $C_{15}H_{18}CoN_3O_9$ : C, 40·6; H, 4·1; N, 9·5; O, 32·5%).

Tetraphenylarsonium Dichlorobis-(3-hydroxyiminopentane-2,4-dionato)rhodium (XXXIII).—A mixture of rhodium trichloride trihydrate (2.65 g, 10.0 mmol), 3-hydroxyiminopentan-2,4-dione (3.87 g, 30.0 mmol), and water (250 ml) was boiled for 30 min during which time it became yellow. The solution was cooled and tetraphenylarsonium chloride (4.18 g, 10.0 mmole) in water (75 ml) was added to it to give a yellow solid; this was filtered off and dried *in vacuo*. It was then recrystallized by dissolution in acetone (400 ml) and addition of ether (1 l) to the filtered solution; the product formed orange needles (4.33 g, 53%) (Found: C, 49.7; H, 4.0; N, 3.1.  $C_{34}H_{32}AsCl_2N_2O_6Rh$  requires C, 50.2; H, 4.0; N, 3.4%).

A similar reaction, in which lithium bromide (5.0 g) was added along with the rhodium trichloride, gave the corresponding *dibromo-complex* (6.68 g, 74%) (Found: C, 45.6, 45.6; H, 3.6, 3.9; N, 3.0, 3.0.  $C_{34}H_{32}AsBr_2N_2O_6Rh$  requires C, 45.3; H, 3.6; N, 3.1%).

Tetrakisethylaminebis-(2,2,6,6-tetramethylheptane-3,5-

243

dionato)palladium (XXXVI).—A mixture of bis-(2,2,6,6-tetramethylheptane-3,5-dionato)palladium (472 mg, 1.0 mmol), ethylamine (2 ml), and acetone (4 ml) was stirred for 10 min. Filtration afforded the *product* as a white solid (626 mg, 96%). Analytical data are shown in Table 3.

Similarly prepared were (XXXV), (XXXVII), and (XXXVIII).

Bis-(4-phenyliminopentane-2-onato)palladium (XXX).— Pentane-2,4-dione monoanil (2·12 g, 20·0 mmol) was added to a methanolic solution of disodium hexachlorodipalladate  $\{50 \text{ ml}, [Pd^{II}] = 0.10M\}$ . The mixture was stirred for 30 min and the orange solid was filtered off and dried *in vacuo*. The dry solid was recrystallized from toluene to give the product as orange crystals (1.76 g, 78%) (Found: C, 58.4, 58.2; H, 5.4, 5.5; N, 5.6, 6.0; O, 7.6, 7.5. Calc. for  $C_{22}H_{24}N_2O_2Pd$ : C, 58.1; H, 5.3; N, 6.2; O, 7.0%).

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