# Studies on Metal Carboxylates. Part IV.[1] Pyridine-2,6-dicarboxylate Complexes of Cobalt(II), Nickel(II), Rhodium(II), and Rhodium(III). Synthesis, Spectral and Magnetic Properties, and a Study of Rhodium 3*d* Binding Energies by *X*-Ray Photoelectron Spectroscopy

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The synthesis and characterization of the 1 : 1 and 1 : 2 complexes of cobalt(II) and nickel(II) with pyridine-2,6-dicarboxylic acid ($dpcH_2$) are reported. The 1 : 2 complexes are shown to have the structure $M(dpcH)_2,3H_2O$, containing monoanionic terdentate dpcH ligand molecules, with three molecules of ' lattice ' water, whereas the 1 : 1 complexes $M(dpc),3H_2O$ are six-co-ordinate and contain co-ordinated water. Anhydrous polymeric $[Co(dpc)]_n$ has been prepared and its chemical reactivity investigated. Rhodium(II) acetate reacts with $dpcH_2$ to afford a rhodium(II) complex $Rh(dpc),3H_2O$. The rhodium(III) complexes $Na[Rh(dpc)_2],2H_2O$ and $Ph_4As[Rh(dpc)_2],xH_2O$ have also been prepared. Characterization of the rhodium complexes has included a study of their *X*-ray photoelectron spectra and a measurement of the rhodium $3d_{3/2}$ and $3d_{5/2}$ binding energies.

THE structural characterization of the 1 : 2 silver(II) complex of pyridine-2,6-dicarboxylic acid (dipicolinic acid, $dpcH_2$) showed that it contained both neutral and dianionic terdentate ligand molecules and could accordingly be formulated as $Ag(dpc)(dpcH_2),xH_2O$ ($x = 1$ or 4).[2-4] This marked disparity in the ligand molecules resulted in a severely distorted octahedral stereochemistry about silver. To assess whether this behaviour was unique to silver, we have investigated the related complexes of cobalt(II) and nickel(II). Our studies on these systems, together with investigations of the rhodium complexes of this acid are now described.

The reaction of cobalt(II) and nickel(II) carbonates or hydroxides with aqueous solutions of pyridine-2,6-dicarboxylic acid affords the complexes $M(dpc),3H_2O$ and $M(dpcH)_2,3H_2O$. A single-crystal *X*-ray analysis on $Ni(dpcH)_2,3H_2O$, prepared by this route, has been carried out and a preliminary report published.[5] This provided unambiguous evidence for the formulation involving co-ordination from two equivalent terdentate monoanionic dpcH ligand molecules, rather than the alternative of $Ni(dpc)(dpcH_2),3H_2O$, similar to that found for the related and unique silver(II) complex.[3,4] *X*-Ray powder data for the cobalt(II) and nickel(II) complexes of the type $M(dpcH)_2,3H_2O$ show them to be isomorphous and a consideration of *d*-spacings and relative intensities suggests that they are isostructural. The 1 : 1 and 1 : 2 complexes exhibited the same general i.r. spectral features in the 4000—600 $cm^{-1}$ region.

The electronic spectral properties are, as expected, typical of a pseudo-octahedral environment [6] for these four complexes, and assignments in accord with this conclusion can readily be made (Table 1). The band frequencies resemble those previously found [7,8] for other pyridine carboxylates of cobalt(II) and nickel(II) containing the $MO_4N_2$ chromophore. The magnetic properties of $M(dpc),3H_2O$ and $M(dpcH)_2,3H_2O$, which are summarized in Table 2, are in accord with the proposed stereochemistries.[9]

Both $Co(dpc),3H_2O$ and $Co(dpcH)_2,3H_2O$ undergo partial dehydration at 100° *in vacuo* to afford $Co(dpc),2H_2O$ and $Co(dpcH)_2,H_2O$, respectively. The electronic absorption spectra of both complexes (Table 1) closely resemble those of the parent hydrates, indicating that no gross structural changes had occurred. Accordingly it seems likely that $Co(dpc),2H_2O$ possesses a similar structure to that of $Cu(dpc),2H_2O$,[10] in which the sixth ligand position, resulting from the loss of a water molecule, is occupied by an oxygen atom from a neighbouring dpc ligand molecule.

The ease with which water was lost from $Co(dpcH_2),3H_2O$ led us to attempt the preparation of the anhydrous 1 : 2 complex by the reaction of cobalt(II) acetylacetonate with pyridine-2,6-dicarboxylic acid in ethanol. In all instances only the polymeric purple 1 : 1 complex $[Co(dpc)]_n$ formed. While its electronic absorption spectrum resembled those of other pseudo-octahedral cobalt(II) species (Table 1) and its room temperature magnetic moment (*ca.* 4·6 B.M.) was ' normal ' for high-spin cobalt(II), we have no definitive information on its structure; presumably, polymerization must involve some type of carboxylate bridge. This complex only dissolves in solvents with which it reacts, as typified by its reactions with water and pyridine to afford $Co(dpc),3H_2O$ and $Co(dpc),3py$, respectively (see Experimental section).

The rhodium(III) complex $Na[Rh(dpc)_2],2H_2O$ was

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[1] Part III, D. L. Hoof, D. G. Tisley, and R. A. Walton, *J.C.S. Dalton*, 1973, 200.

[2] G. W. A. Fowles, R. W. Matthews, and R. A. Walton, *J. Chem. Soc.* (*A*), 1968, 1108.

[3] M. B. G. Drew, G. W. A. Fowles, R. W. Matthews, and R. A. Walton, *J. Amer. Chem. Soc.*, 1969, **91**, 7769.

[4] M. G. B. Drew, R. W. Matthews, and R. A. Walton, *J. Chem. Soc.* (*A*), 1971, 2959.

[5] Part I, H. Gaw, W. R. Robinson, and R. A. Walton, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 695.

[6] C. J. Ballhausen, ' Introduction to Ligand-Field Theory,' McGraw-Hill, 1962, pp. 256, 261.

[7] R. W. Matthews and R. A. Walton, *Inorg. Chem.*, 1971, **10**, 1433.

[8] Part II, A. Anagnostopoulos, R. W. Matthews, and R. A. Walton, *Canad. J. Chem.*, 1972, **50**, 1307.

[9] B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, 1964, **6**, 37 and references therein.

[10] M. Biagini Cingi, A. Chiesi Villa, C. Guastini, and M. Nardelli, *Gazzetta*, 1971, **101**, 825.

characterized by i.r. spectroscopy, which revealed characteristic ν(O–H) and ν(COO) bands at *ca.* 3450m,br and 1670—1600s,br, respectively, and by an electronic absorption spectral study. A prominent band at 380 nm ($\varepsilon_{max.}$ *ca.* 700) was observed for an aqueous solution of this complex, consistent with a rhodium(III) species in which this band arises from a ligand-field ($^1A_{1g} \longrightarrow {}^1T_{1g}$) and/or an electron transfer $Rh(t_{2g}) \longrightarrow dpc(\pi^*)$ transition. Furthermore, the above formulation rather than the alternative of $Rh(dpc)(dpcH),3H_2O$, which would also be consistent with the carbon and nitrogen microanalyses, is supported by the following evidence. (1) An aqueous solution of this complex reacts with tetraphenylarsonium chloride to produce the related salt $Ph_4As[Rh(dpc)_2],3H_2O$. (2) Its *X*-ray photoelectron spectrum exhibited a sodium 1*s* binding energy at 1070·2 eV confirming the presence of this element. For an *undiluted* sample of this complex, the presence of two C 1*s* binding energies at 286·5 and 283·8 eV, exhibiting an intensity ratio of 2 : 5 (the peak at highest binding energy being associated with the carboxylate carbon atoms), confirmed[1] that decarboxylation had not occurred and that the dpc ligand molecules were intact.

TABLE 1

Electronic absorption spectra of complexes of pyridine-2,6-dicarboxylic acid

| | | Absorption maxima ($\times 10^{-3}$ cm$^{-1}$) and assignments | | |
|---|---|---|---|---|
| Cobalt(II) complexes | | $^4T_{1g} \longrightarrow {}^4T_{2g}(\nu_1)$ | | $^4T_{1g} \longrightarrow {}^4T_{1g}(P)(\nu_3)$ |
| $Co(dpcH)_2,3H_2O$ | D.R.[a] | 7·5; 9·9 | | 17·0; 18·6; 19·7; 21·0 |
| | N.M.[a] | 7·5; 10·0 | | 16·9; 18·7; 19·8; 21·3 |
| $Co(dpcH)_2,H_2O$ | N.M. | 6·8; 9·5 | | 17·0; 18·7; 19·6; 21·3 |
| $Co(dpc),3H_2O$ | D.R. | 7·5; 10·2 | | 16·9; 19·4; 2·08sh |
| | N.M. | 7·5; 10·6sh | | 17·5; 18·8; 21·3 |
| $Co(dpc),2H_2O$ | N.M. | 6·8; *ca.* 10·1sh | | 17·5; 18·7; 21·3 |
| $[Co(dpc)]_n$ | D.R. | *ca.* 8·1 [b] | | 18·0; 18·75 |
| | N.M. | 7·6; 9·5sh | | 18·0; 19·0 |
| Co(dpc),3py | D.R. | 7·6; 9·35 | | 18·2; 19·1; 21·75sh,br |
| | N.M. | *ca.* 7·0br; 9·6 | | 16·4sh; 18·2sh; 19·3sh; 20·0sh |
| $Co(dpc)(phen),H_2O$ | D.R. | 7·5; 10·5 | | 19·3; 20·0 |
| Nickel(II) complexes | | $^3A_{2g} \longrightarrow {}^3T_{2g}(\nu_1)$ | $^3A_{2g} \longrightarrow {}^3T_{1g}(F)(\nu_2)$ | $^3A_{2g} \longrightarrow {}^3T_{1g}(P)(\nu_3)$ |
| $Ni(dpcH)_2,3H_2O$ | D.R. | 9·5; *ca.* 11·0sh | 15·9 | *ca.* 30·6sh |
| | N.M. | 9·5; 10·7sh | 15·7 | 29·4 |
| $Ni(dpc),3H_2O$ | D.R. | 9·6 | 15·4 | 27·4sh; 30·4sh |

[a] D.R. = diffuse-reflectance; N.M. = Nujol mull. [b] Distinct asymmetry on the high energy side of this band.

A green complex of stoicheiometry $Rh(dpc),3H_2O$ is formed upon reacting an aqueous solution of rhodium(II) acetate with pyridine-2,6-dicarboxylic acid. *X*-Ray powder measurements on this complex and on $Co(dpc),3H_2O$ showed that these two species were not isomorphous. Confirmation that this was indeed an authentic complex of rhodium(II) was provided by an investigation of its *X*-ray p.e. spectrum. Rhodium $3d_{3/2}$ and $3d_{5/2}$ binding energies for a sample of this complex diluted with graphite (to eliminate surface charging effects), were located at 312·6 and 307·8 eV, respectively, in the range characteristic of other rhodium(II) complexes such as rhodium(II) acetate (*i.e.*, $3d_{3/2}$ 312·2—313·4 and $3d_{5/2}$ 307·8—308·5 eV).[11] In contrast, $Ph_4As[Rh(dpc)_2],3H_2O$, under comparable experimental conditions, had its related binding energies at 314·3 and 309·4 eV, typical of rhodium(III) species (*i.e.*, $3d_{3/2}$ 313·4—315·1 and $3d_{5/2}$ 309·0—310·6 eV).[11] Peak maxima were located with the following precision: Rh $3d_{3/2}$ ±0·2 and Rh $3d_{5/2}$ ±0·1 eV.

Carbon 1*s* binding energies for an *undiluted* sample of $Rh(dpc),3H_2O$ were at 286·4 and 283·9 eV, with an approximate intensity ratio of 2 : 5, confirming as for $Na[Rh(dpc)_2],2H_2O$, that decarboxylation of the ligand had not occurred.

$Rh(dpc),3H_2O$ was essentially diamagnetic ($\mu_{eff}$ = 0·15 B.M. at 299 K) indicating that the complex was not magnetically dilute. Further, its electronic absorption spectrum (Nujol mull and diffuse-reflectance) in the visible region exhibited a band at *ca.* 610 nm, similar in position to the lowest energy band of rhodium(II) acetate.[12] Accordingly, we propose that a likely structure would be one in which the $Rh_2(OOC-)_4$ unit is preserved through bridging dpc units in which the nitrogen donor atom is not co-ordinated. One of the three water molecules associated with each [Rh(dpc)] unit could be co-ordinated to the rhodium atom [*cf.* $Rh_2(OAc)_4,2H_2O$] and the remaining two present as 'lattice' water. By analogy with the conversion of

TABLE 2

Summary of magnetic properties of several cobalt(II) and nickel(II) complexes of pyridine-2,6-dicarboxylic acid [a]

| Complex | $\mu_{eff}$/B.M. | *T*/K | θ/K |
|---|---|---|---|
| $Co(dpcH)_2,3H_2O$ | 5·25 | 298 | |
| $Co(dpc),3H_2O$ | 4·73 | 298 | |
| $[Co(dpc]_n$ | 4·54 | 298 | |
| | 4·63 [b] | 297 | |
| $Ni(dpcH)_2,3H_2O$ [c] | 3·45 | 299 | +12 |
| $Ni(dpc),3H_2O$ [c] | 3·30 | 299 | +14 |

[a] All measurements recorded by the Gouy technique unless otherwise stated. [b] Faraday technique. [c] Temperature range magnetic susceptibility studies were carried out at ten temperatures between 299 and 89 K. Both sets of data obeyed the Curie–Weiss Law. Full details of the magnetic data are available on request to R. A. W.

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[11] A. D. Hamer, D. G. Tisley, and R. A. Walton, *J.C.S. Dalton*, 1973, 116.

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

$Rh_2(OAc)_4$, or its hydrate, to the pyridine adduct $Rh_2(OAc)_4,2py$,[12] $Rh(dpc),3H_2O$ reacts with pyridine and α-picoline to afford the adducts $Rh(dpc),L,H_2O$. That these complexes are still derivatives of rhodium(II) is suggested by the value for the rhodium 3*d* binding energies of the pyridine adduct, 312·4 and 308·2 eV, which are very similar to those of $Rh(dpc),3H_2O$.

## EXPERIMENTAL

Most reagents were readily available from commercial sources, and unless otherwise stated were used without further purification. Rhodium(II) acetate, $Rh_2(OAc)_4$, was prepared by the method of Legzdins *et al.*[13]

(a) *Preparation of the Cobalt*(II) *and Nickel*(II) *Complexes.*—The crystalline 1 : 1 and 1 : 2 complexes $M(dpc),3H_2O$ and $M(dpcH)_2,3H_2O$ were readily prepared by dissolving the metal carbonate or the freshly prepared hydroxide in a hot aqueous solution of pyridine-2,6-dicarboxylic acid while ensuring that the metal to ligand ratio was 1 : 1 or 1 : 2.

In an attempt to isolate the anhydrous complex $Co(dpcH)_2$, the acetylacetone complex $[Co(acac)_2]_4$ (0·77 g), first dried *in vacuo* at 100° for 2·5 h, was reacted with two mole equivalents of pure dry pyridine-2,6-dicarboxylic acid (1·0 g) in de-oxygenated absolute ethanol (95 ml) containing 5 ml triethylorthoformate as a drying agent. The reaction mixture was refluxed under nitrogen for 4 h, whereupon the anhydrous bright purple 1 : 1 complex $[Co(dpc)]_n$ precipitated in quantitative yield. Work-up of the mother-liquor yielded unreacted acid only.

*Reactions of* $[Co(dpc)]_n$ *with Donor Molecules.*—(i) When refluxed with dry pyridine or γ-picoline the complex dissolved to give clear red solutions which, when evaporated to dryness, afforded salmon coloured products with compositions close to $Co(dpc),3py$ and $Co(dpc),3\gamma$-pic, respectively. These very rapidly lost amine at room temperature, which prevented us from obtaining good analytical data on these systems (Table 3). When these complexes were exposed to the atmosphere, the loss of amine was enhanced, and the purple trihydrate $Co(dpc),3H_2O$ formed ($C_7H_9NO_7Co$ requires C, 30·25; H, 3·2; N, 5·0. Found: C, 30·3; H, 3·4; N, 5·1%). $Co(dpc),3py$ reverted to $[Co(dpc)]_n$ when it was heated *in vacuo* at 100 °C for 3 days or refluxed in acetone.

When the pyridine adduct (0·1 g) was refluxed with an acetone solution of 1,10-phenanthroline monohydrate (0·041 g in 30 ml) for 3 days, the air-stable complex $Co(dpc),phen,H_2O$ was produced.

(ii) It dissolved slowly in boiling water to give a purple solution from which crystals of $Co(dpc),3H_2O$ were isolated upon evaporation (identified by i.r. spectroscopy).

(iii) No reaction was observed between $[Co(dpc)]_n$ and acetonitrile, dimethylformamide, or α-picoline.

(b) *Preparation of the Rhodium*(III) *and Rhodium*(II) *Complexes.*—$Na[Rh(dpc)_2],2H_2O$.—Hydrated rhodium(III) chloride (0·13 g) was dissolved in water (15 ml) containing $Na_2dpc$ (0·21 g) and, the solution refluxed for 5 h and then taken to dryness. The residue was extracted with methanol (3 × 10 ml), the volume of the extract reduced to half by evaporation and then set aside. After three weeks a mixture of large orange-brown crystals and a yellow powder had separated. The crystals were separated by hand and recrystallized slowly from aqueous methanol. This complex is extremely soluble in water thereby making its isolation from aqueous solutions rather difficult.

$Ph_4As[Rh(dpc)_2],3H_2O$.—A hot aqueous solution containing rhodium(III) chloride (0·16 g) and $Na_2dpc$ (0·30 g) was prepared as described above. A solution of tetraphenylarsonium chloride (0·3 g) in hot water (20 ml) was added and the reaction mixture allowed to cool to room temperature. The yellow precipitate of $Ph_4As[Rh(dpc)_2],3H_2O$ was filtered off and the remaining filtrate set aside. Over a period of several days more of the above yellow complex separated together with a very low yield of unidentified orange crystals.

$Rh(dpc),3H_2O$.—Rhodium(II) acetate (0·22 g) was dissolved in hot water (15 ml) and an aqueous solution of pyridine-2,6-dicarboxylic acid (0·17 g in 20 ml) added. The resulting dark green solution was refluxed for a period of from 48 to 70 h, and the light green solid (0·16 g) which precipitated during this time, was filtered off, washed with water (*ca.* 20 ml) and dried *in vacuo* over NaOH. This complex was insoluble in acetic acid, acetone, tetrahydrofuran, methyl cyanide, dichloromethane, carbon tetrachloride, water, and sulphuric acid and slightly soluble in dimethylformamide.

*Reactions of* $Rh(dpc),3H_2O$ *with Pyridine and α-Picoline.*—Pyridine (5 ml) was added to a sample of $Rh(dpc),3H_2O$ (0·07 g) under nitrogen, and the reaction mixture stirred at room temperature. There was an immediate colour change of the solid from green to brown. After 20 h the brown insoluble product (0·08 g) was filtered off, washed with diethyl ether, and dried *in vacuo.* Analytical data for this complex (Table 3) approximated to the composition $Rh(dpc),py,H_2O$, but the carbon analysis was invariably high (by 2—3%). Unfortunately, this product was insoluble in all solvents tried and so could not be purified by recrystallization. However, the related α-picoline product was prepared by a similar procedure and its composition $Rh(dpc),\alpha$-pic,$H_2O$ (Table 3) supports that proposed for the pyridine complex.

*Oxidation of* $Rh(dpc),3H_2O$.—A sample of this complex (0·07 g) was suspended in water (30 ml) and pyridine-2,6-dicarboxylic acid (0·036 g) and potassium peroxodisulphate (0·06 g) added. When this mixture was refluxed a yellow solution formed. This was filtered to remove a trace of black solid, and an excess of tetraphenylarsonium chloride (0·2 g) added to the clear filtrate. There was an immediate precipitation of a yellow solid which was filtered off and washed with water, ethanol, and ether. The i.r. spectrum of this product was very similar to that of $Ph_4As[Rh(dpc)_2],3H_2O$, but its carbon and hydrogen microanalyses indicated it was the dihydrate ($C_{38}H_{30}AsN_2O_{10}Rh$ requires C, 53·5; H, 3·6. Found: C, 53·6; H, 4·0%).

*Disproportionation of* $Rh(dpc),3H_2O$.—When $Rh(dpc),3H_2O$ was extracted with boiling water in a Soxhlet apparatus, a mirror of rhodium metal and a yellow solution were produced in the reservoir. The electronic absorption spectrum of the solution indicated that it contained rhodium(III) since a band at 380 nm is characteristic of the $[Rh(dpc)_2]^-$ anion. Although after 100 h a significant proportion of $Rh(dpc),3H_2O$ remained unchanged, it appeared that slow extraction into water is accompanied by disproportionation to $Rh^0$ and $Rh^{III}$.

*Physical Measurements.*—These were carried out as

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[13] P. Legzdins, R. W. Mitchell, G. L. Rempel, J. D. Ruddick, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1970, 3322.

described in Part III of this series.[1] A Hewlett–Packard 5950A ESCA spectrometer was used for the measurement of the core-electron binding energies [14] of the rhodium complexes. The aluminium $K_{\alpha 1,2}$ line (1486·6 eV) was used as the $X$-ray excitation source and the powdered samples were dispersed on a gold-plated copper surface. Spectra were also recorded on the compounds diluted with graphite. This latter procedure satisfactorily eliminated surface charging effects and afforded a method of referencing the rhodium 3*d* and nitrogen 1*s* binding energies to the C 1*s* line of graphite (284·0 eV). Further experimental details are described elsewhere.[11]

Magnetic studies were carried out using a Newport Instruments variable temperature Gouy balance. Mercury tetrathiocyanatocobaltate(II) was used as calibrant and diamagnetic corrections were estimated from Pascal's constants. The magnetic moment of polymeric [Co(dpc)]$_n$ was kindly checked for us by Dr. D. P. Murtha on a Faraday balance at Wayne State University.

TABLE 3

Analytical data for cobalt(II), nickel(II), rhodium(II), and rhodium(III) complexes of pyridine-2,6-dicarboxylic acid [a]

| Complex | Colour | % C | % H | % N |
|---|---|---|---|---|
| Co(dpc),$3H_2O$ | Purple | 30·2 (30·25) | 3·4 (3·2) | 5·15 (5·0) |
| Co(dpc),$2H_2O$ | Purple | 32·7 (32·3) | 2·8 (2·7) | 5·4 (5·4) |
| Co(dpcH)$_2$,$3H_2O$ | Purple | 37·65 (37·7) | 3·0 (3·15) | 6·2 (6·3) |
| Co(dpcH)$_2$,$H_2O$ | Purple | 41·1 (41·1) | 2·8 (2·4) | 6·7 (6·85) |
| Ni(dpc),$3H_2O$ [b] | Green | 30·9 (30·25) | 2·95 (3·3) | 5·1 (5·0) |
| Ni(dpcH)$_2$,$3H_2O$ [c] | Green | 37·7 (37·8) | 3·3 (3·2) | 6·4 (6·3) |
| [Co(dpc)]$_n$ | Bright purple | 37·5 (37·5) | 1·5 (1·3) | 6·2 (6·25) |
| Co(dpc),3pyridine [d] | Salmon-pink | 55·4 (57·3) | 4·6 (3·9) | 11·2 (12·15) |
| Co(dpc),3γ-picoline [d] | Salmon-pink | 57·3 (59·65) | 4·8 (4·8) | |
| Co(dpc),phen,$H_2O$ | Pink | 53·9 (54·0) | 3·3 (3·1) | 10·0 (10·0) |
| Rh(dpc),$3H_2O$ | Green | 26·3 (26·1) | 3·3 (2·8) | 4·2 (4·35) |
| Rh(dpc),py,$H_2O$ | Brown | 40·6 (39·5) | 3·0 (2·8) | 7·35 (7·7) |
| Rh(dpc),α-pic,$H_2O$ | Brown | 41·25 (41·1) | 3·3 (3·2) | 7·1 (7·4) |
| Na[Rh(dpc)$_2$],$2H_2O$ | Yellow | 34·2 (34·1) | 2·6 (2·1) | 5·7 (5·7) |
| $Ph_4As$[Rh(dpc)$_2$],$3H_2O$ | Yellow | 52·4 (52·4) | 3·3 (3·7) | 2·8 (3·2) |

[a] Theoretical figures are given in parentheses. [b] Nickel analysis: 21·5 (21·1%). [c] Nickel analysis: 13·1 (13·2%). [d] Rapid loss of pyridine and γ-picoline during analytical handling procedures accounts for the low carbon and nitrogen analyses.

*Microanalyses*.—C, H, and N analyses were determined by Dr. C. S. Yeh in the Purdue University Microanalytical Laboratory. Nickel was determined by the gravimetric dimethylglyoxime method. Analytical data for the complexes are given in Table 3.

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[14] K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S. E. Karlsson, I. Lindgren, and B. Lindberg, 'ESCA: Atomic Molecular Solid State Structure Studied by Means of Electronic Spectroscopy,' Almquist and Wiksells, Uppsala, 1967.