Adducts of Co-ordination Compounds. Part IX.[1] Halogenocarbon Solvates of Trihalogenotripyridinerhodium(III)

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Synthetic and spectroscopic studies are reported of several crystalline solvates of the type *mer*-$[Rh(L)_3X_2Y],S_n$, where L may be pyridine, perdeuteriopyridine, or γ-picoline, X and Y are Br and Cl, $S = CH_2Cl_2$, $CHCl_3$, or $CDCl_3$, and $1 \leqslant n \leqslant 3$. An Appendix lists known halogenocarbon solvates of metal complexes.

HALOGENOCARBON solvates of organic compounds are not particularly common,† but among inorganic compounds there are numerous examples, such as $[Ph_2PN]_3,3Cl_2CH\cdot CHCl_2$[2] and $[NR_4]X\cdot CY_4$ or C_2Y_4,[3] where R = Me, Et *etc.*, X = Cl, Br, or I, and Y = Cl, Br, or I. Specific interaction of co-ordination compounds in solution with dichloromethane, chloroform, or carbon tetrachloride is now commonly suggested. For example, the toxicity of carbon tetrachloride has been said[4] to arise (in part) from its interaction as a ligand with cytochrome P-450. Dissolved copper(II) complexes of β-diketonates have been shown[5] to interact with chloroform *via* its hydrogen and one chlorine atom.

Co-ordination compounds which occur as crystalline halogenocarbon solvates are not so unusual as comments in the literature suggest. Those (mostly involving chloroform) known to us are listed in the Appendix. They include[6] *abd*-$[M(py)_3Cl_3],2CHCl_3$ (M = Rh, the

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† *Cf.*, for example, the solvate of bikaverin [J. J. de Boer, D. Bright, G. Dallinga, and T. G. Hewitt, *J. Chem. Soc.* (*C*), 1971, 2788].

[1] Part VIII, R. D. Gillard and S. H. Laurie, *J. Inorg. Nuclear Chem.*, 1971, **33**, 947.

[2] R. H. Cragg, in 'Essays in Chemistry,' eds. J. N. Bradley, R. D. Gillard, and R. F. Hudson, Academic Press, London, 1970, vol. 1, p. 89.

[3] J. A. Creighton and K. M. Thomas, *J.C.S. Dalton*, 1972, 403.

[4] O. Reiner and H. Uehleke, *Z. physiol. Chem.*, 1971, **352**, 1048.

[5] S. Antosik, N. M. D. Brown, A. A. McConnell, and A. L. Porte, *J. Chem. Soc.* (*A*), 1969, 545 (and *cf.* E. Sinn, *Inorg. Nuclear Chem. Letters*, 1970, **6**, 811).

[6] (*a*) M. Delépine, *Ann. Chim.*, 1923, [9], **19**, 172, and also (*b*) 1935, [11], **4**, 279, *cf.* (*c*) 1,2,4-$[Mo(py)_3Cl_3],2CHCl_3$ and 1,2,4-$[Cr(py)_3Cl_3],2CHCl_3$ in E. König, *Naturwiss.*, 1963, **50**, 643.

subject of the present paper, or Ir: for M = Ir, a monosolvate was also described).

The relationship between solutions of the various pyridine complexes of rhodium(III) and the solid phases with which they are in equilibrium reflects the ' mixed ' character of these complexes (*i.e.*, the ambiguity between the polar oligohalogenorhodium moiety and the relatively non-polar pyridine ligands). In the dual hope that the nature of solvation of non-electrolytes in halogenocarbon solvents would be a slightly simpler problem than that bugbear of inorganic mechanisms, solvation of ions in polar media, and that there is a more than semantic distinction between ' halogenocarbon solvent of crystallisation ' and ' clathrated halogenocarbon,' we have studied these halogenopyridinerhodium(III) species in chloroform and in dichloromethane.

RESULTS

Formation and Composition.—Delépine[6] observed that *mer*-[$\mathrm{Rh(py)_3Cl_3}$] formed a chloroform solvate, and by drying the orange-red crystals at 120 °C showed that they could be formulated as $\mathrm{Rh(py)_3Cl_3,2CHCl_3}$. The same solvation was observed later[7] by Holtzclaw and Collman, although they say that their solvate (red crystals, which they assumed, probably correctly, to be the same solvate with $\mathrm{2CHCl_3}$ as was reported[6] by Delépine) on being kept in air lost solvent, leaving a mixture of the isomers of [$\mathrm{Rh(py)_3Cl_3}$], so perhaps it differed from our samples, which contain only the *abd*- or *mer*-isomer.

With a selection of compounds of the type *mer*-$\mathrm{RhL_3X_2Y}$ available[8] (L = substituted pyridine or pyridine; X, Y = Cl, Br), we studied their behaviour toward a small number of halogenocarbon solvents. The method followed naturally from the way we prepared the compounds; they were allowed simply to crystallise from solution in the given solvent. The results are in Table 1. Two methods were used to determine composition; either the crystals were weighed, desolvated, and re-weighed, or else they were weighed out and the absorbance of a solution measured at the wavelength of known ε, at the maximum of a band if possible, to reduce error. The latter method, used also in Part X,[9] has the advantage that it incurs less error when determining the composition of a single crystal, a measure which had to be taken when it was realised that more than one type of solvate can form.

TABLE 1

Compositions of chlorocarbon solvates

Compound	Appearance	Solvent (%)		Method
		Calc.	Found	
$\mathrm{Rh(py)_3Cl_3,2}S$ [a]	Orange rhombs	34·8	31·9	*c*
$\mathrm{Rh(py)_3Cl_3}D$ [a]	Clusters of orange prisms	21·2	21·6	*b*
$\mathrm{Rh(py)_3Cl_3,2}D$	Orange rhombs	35·0	34·9	*b*
$\mathrm{Rh(py)_3Cl_3,2CH_2Cl_2}$	Orange rhombs	27·6	27·3	*c*
$\mathrm{Rh(dpy)_3Cl_3,2}S$ [d]	Orange rhombs	34·0	34·6	*b*
$\mathrm{Rh(pic)_3Cl_3,1{\cdot}5}S$	Orange rhombs	26·8	26·9	*b*
$\mathrm{Rh(py)_3Cl_2Br,2}S$	Orange-red rhombs	32·2	32·9	*c*
$\mathrm{Rh(py)_3ClBr_2,3}S$	Deep red lozenges	40·0	38·8	*b*
$\mathrm{Rh(py)_3ClBr_2,}S$	Deep red prisms	18·2	18·4 [e]	*b, c*

[a] $S = \mathrm{CHCl_3}$, $D = \mathrm{CDCl_3}$. [b] By oven drying. [c] Spectrophotometrically. [d] Pentadeuteriopyridine complex. [e] Mean of 17·8% and 18·9%.

The first occasions on which attempts were made to grow crystals of $\mathrm{Rh(py)_3Cl_3,2CHCl_3}$ met with failure, as the product proved to be unsolvated orange-red crystals. However, the ambient temperature may have been a significant factor, affecting either solubility equilibria or simply rate of evaporation or nucleation. Refrigeration of the solution, but still allowing slow evaporation of solvent, was found to induce crystallisation of the solvate.

Although solvates could not be obtained with *mer*-$\mathrm{Rh(py)_3Br_3}$ involving $\mathrm{CHCl_3}$, $\mathrm{CH_2Cl_2}$, or $\mathrm{CH_2Br_2}$ this does not necessarily mean that they do not exist in the solid state, but probably that they are not stable. Formation of solvates could not be induced for $\mathrm{CH_2Br_2}$ or $\mathrm{CHBr_3}$ with *mer*-$\mathrm{Rh(py)_3Cl_3}$ while $\mathrm{CH_2Cl_2}$ formed a disolvate with $\mathrm{Rh(py)_3Cl_3}$ which was very unstable, the rapid loss of $\mathrm{CH_2Cl_2}$ making determination of its composition difficult. With $\mathrm{CHCl_3}$, $\mathrm{Rh(py)_3Cl_3}$ and $\mathrm{Rh(py)_3Cl_2Br}$ formed disolvates, which crystallised as brightly coloured, chunky rhombs with dimensions of 5 mm or more. The presumptions (*a*) that $\mathrm{Rh(py)_3ClBr_2}$ could be solvated only by one chloroform and (*b*) that each rhodium compound formed only *one* definite solvate crystal lattice were dispelled when a crop of chloroform-solvated $\mathrm{Rh(py)_3ClBr_2}$ crystals proved to be $\mathrm{Rh(py)_3ClBr_2,3}S$, the trisolvate.* This formed as a large single crystal, *ca.* 10 × 4 × 2 mm. Its stability towards loss of solvent to the atmosphere was comparable with that of $\mathrm{Rh(py)_3Cl_3,2CH_2Cl_2}$, the resulting desolvated product being orange-brown and looking micaceous.

Solvent Loss.—A sample of $\mathrm{Rh(py)_3Cl_2Br,2}S$ was oven-dried for 10 min to remove solvent, then placed in a desiccator over chloroform and left for several days. After that, the unsolvated compound had not changed in appearance. That it had absorbed some chloroform was shown when a second treatment in the oven caused a weight loss of *ca.* 18%, equivalent to previous uptake of *ca.* $0{\cdot}9\mathrm{CHCl_3}$. Hence, the desolvated crystals are permeable. Coupled with these observations, in general the relatively translucent, crystalline solvates on desolvation give products which are opaque, and so apparently of a lighter colour. Although the exterior morphology of the originally solvated crystals is retained, the products are very friable. The *X*-ray powder diffraction patterns are listed in Table 2, as *d*-spacing values, for three forms of *mer*-$\mathrm{Rh(py)_3Cl_3}$; these are (i) the unsolvated material, from the action of aqueous hydrochloric acid on *a*-chloro-*bd*-oxalatotripyridinerhodium(III), (ii) the dichloroform solvate, with a small amount of chloroform added to the diffracting sample, and (iii) the desolvated material, from drying the disolvate at 110 °C. Inclusion of chloroform clearly alters the crystal structure of the compound, since several strong lines associated with large interplanar spacings (4·8—7·3) in the parent compound are absent from the disolvate. When the chloroform is driven off, the crystal structure is changed again. Two factors suggest this. First, strong lines (7·35, 6·65, and 4·86) appear in the desolvated compound, having been absent from $\mathrm{Rh(py)_3Cl_3,2}S$. Secondly, the change in the lattice on desolvation is probably not merely a reversion to

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* $S = \mathrm{CHCl_3}$ of solvation, $D = \mathrm{CDCl_3}$ of solvation.

[7] H. F. Holtzclaw and J. P. Collman, *J. Amer. Chem. Soc.*, 1958, **80**, 2054.

[8] A. W. Addison, Ph.D. Thesis, University of Kent, 1970; A. W. Addison, R. D. Gillard, P. S. Sheridan, and L. R. H. Tipping, *J.C.S. Dalton*, submitted for publication.

[9] A. W. Addison and R. D. Gillard, following paper.

the original structure, since some lines which appear in the original crystals are changed in intensity in the desolvated material. For example, the line with $d = 5{\cdot}33$ is of medium intensity in the ' unsolvate ' (i) but very strong in the ' desolvate ' (iii). Other changes from (i) to (iii) are: 3·64, very strong, to medium; 2·88, strong, disappears; 5·06, strong, disappears. Hence, on loss of included solvent, a new form of Rh(py)$_3$Cl$_3$ is obtained, so that it, and presumably the other compounds with the possible exception of *mer*-Rh(py)$_3$Br$_3$, are at least dimorphic. Although no diffraction pattern was obtained for a monosolvate, the facts that they form stoicheiometrically and exhibit a crystal morphology different from that of the disolvated material, suggest that at least Rh(py)$_3$Cl$_3$ [and Rh(py)$_3$ClBr$_2$, by virtue of its trisolvate formation] will be trimorphic, if not (literally) polymorphic.

TABLE 2

X-Ray powder diffraction results for Rh(py)$_3$Cl$_3$ (*d*-spacings)

(i)	(ii)	(iii)
7·75s	7·8vs	7·75s
7·3s		7·35s
6·58s		6·65s
6·23w		
5·77vs	5·72m	5·78vs
		5·52m
5·33m	5·28s	5·30vs
5·06s		
4·84s		4·86s
	4·64m	
	4·57s	
4·48w	4·47m	4·50w
4·23w	4·26s	4·23w
4·17w	4·17s	4·18w
3·90s	3·90m	3·91s
	3·87m	
	3·80m	3·80w
3·64vs	3·65m	3·67m
3·55w	3·57m	3·56w
	3·49m	3·47w
3·37w	3·34w	
	3·28s	
3·04m	3·08m	3·03s
3·02m		
	2·93w	2·95m
2·88s		
	2·83w	
2·73w	2·76w	2·74m
2·66m	2·68w	2·66m
	2·60w	
2·55m	2·58w	
2·52m		
2·42m	2·41m	
2·39m		
2·38w		2·38m
2·36m		
2·34w		2·34m
2·28s	2·32m	2·28m
		2·17m
2·07m	2·08m	
2·00s		
1·72s		

(i) Unsolvated. (ii) Chloroform disolvate, Rh(py$_3$Cl$_3$,2*S*. (ii) Desolvated at 110 °C.

The apparent sequence of increasing stability, trisolvate < disolvate < monosolvate, is supported by a pair of differential thermal analyses, which gave endothermal maxima corresponding to loss of chloroform from Rh(py)$_3$-Cl$_2$Br,2*S* (*ca.* 55—60 °C) and Rh(py)$_3$ClBr$_2$,*S* (*ca.* 70—75 °C). Rh(py)$_3$Cl$_3$,2*S* had a well-defined endothermal peak but the position of its maximum varied somewhat (63—69 °C over four runs) while the monosolvate had a peak at *ca.* 105 °C. For comparison, the chloroform solvate[10] of Cu$_2$(salen)$_2$ (in which the hydrogen of the solvent makes a bond to a phenolic oxygen) was prepared as red-purple prisms, and these lost chloroform to give an endothermal peak at 48 °C.

Vibrational Spectra.—The presence of the halogenocarbon is evident from the strong i.r. absorption at *ca.* 750 cm^{-1} in the CHCl$_3$ and CH$_2$Cl$_2$ solvates. This band, attributed[11] to ν_5 in CHCl$_3$ and ν_9 in CH$_2$Cl$_2$, unfortunately cannot generally be accurately placed, as out-of-plane C–H bending bands of the ligands are also strong in this region. However, it can be distinguished in the following compounds: Rh(py)$_3$Cl$_3$,2CH$_2$Cl$_2$ (729 cm^{-1}), Rh(dpy)$_3$Cl$_3$,2*S* (748 cm^{-1}), and Rh(pic)$_3$Cl$_3$,1·5*S* (751 cm^{-1}), where dpy is pentadeuteriopyridine and pic is γ-picoline. These values are below those observed for liquid CH$_2$Cl$_2$ (737 cm^{-1})[11] and for *gaseous*[12] or liquid[11] CHCl$_3$ (760—770 cm^{-1}). The ν_3 (C–Cl) vibration of CHCl$_3$ occurs in all the solvates, only slightly shifted from the vapour value (672 cm^{-1}) to *ca.* 662—667 cm^{-1}.

As shown in Figure 1 there are three strong bands between 200 and 400 cm^{-1} in the Raman spectrum of Rh(py)$_3$Cl$_3$, at 268, 299, and 336 cm^{-1}, associated with the A_1 type rhodium–pyridine and rhodium–chlorine (latter two) stretches respectively; the deuteriopyridine complex is similar. In Rh(py)$_3$Cl$_3$,2*S*, four strong bands are seen (Figure 1). They are described in Table 3 as are those for the partially deuteriated compounds Rh(py)$_3$Cl$_3$,*D* and Rh(dpy)$_3$Cl$_3$,2*S*. Some changes are apparent; first, the A_1 vibration associated with the chloride *trans* to the pyridine ligand moves up in energy by 6—7 cm^{-1}. Secondly, a strong band arises at *ca.* 365 cm^{-1}, due to ν_3 of the chloroform, only slightly shifted. In addition, the ν_6 (C–Cl$_3$ bending) mode of the chloroform is not immediately apparent, although it is reported[11] to give a very strong

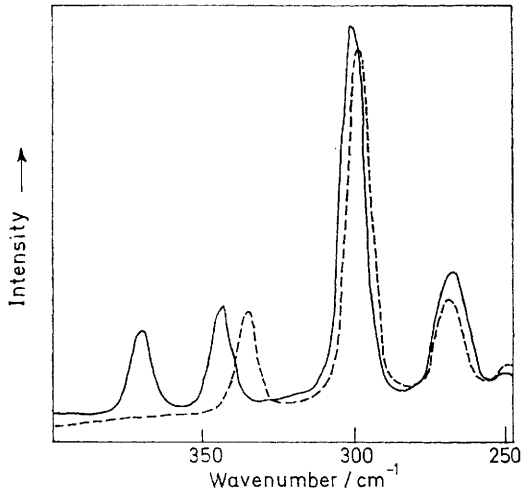

FIGURE 1 Raman spectra of *abd*-[Rh(py)$_3$Cl$_3$] (——) and its disolvate with chloroform (- - - -) in the region 250—400 cm^{-1}

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[10] E. N. Baker, D. Hall, and T. N. Waters, *J. Chem. Soc.* (*A*), 1970, 406.

[11] G. Herzberg, ' Molecular Spectra and Molecular Structure,' vol. II, van Nostrand, New York, 1945, pp. 316—317.

[12] A. Ruoff and H. Bürger, *Spectrochim. Acta*, 1970, **26**, A, 989.

band at 262 cm^{-1} in $CHCl_3$ vapour. It may be obscured by the band at 268 cm^{-1} in $Rh(py)_3Cl_3$ and 261 cm^{-1} in $Rh(dpy)_3Cl_3$.

TABLE 3

Raman spectra of chloroform solvates/cm^{-1} [a]

Compound	Wavenumber	Substrate	Solvent
$Rh(py)_3Cl_3,2CHCl_3$	268s	268s	261vs [b]
	301vs	299vs	
	342s	336s	
	369s		363s [b]
		1019s	
	1021s	1026s	
$Rh(py)_3Cl_3,CDCl_3$	218s		
	268s	268s	262s
	300vs	299vs	
	342s	336s	
	363s		366s [c]
		1019s	
	1020s	1026s	
$Rh(dpy)_3,2CHCl_3$	262s	261m	261vs
	299vs	298vs	
	335s	328s	
	365s		363s
		987s	
	985s	979s	

[a] The size and transparency of the solvate crystals allow one to obtain good Raman spectra, although the laser beam tends to cause local heating which desolvates the crystal and makes it opaque. [b] Vapour-phase energy, liquid-phase intensity. [c] Liquid phase.

Another effect appears at higher frequency (see Figure 2). In the unsolvated crystalline RhL_3Cl_3 compounds there are two strong bands, not seen at low resolution, associated with the symmetric ring breathing mode of the pyridine. They occur at 1026 and 1019 cm^{-1} in $Rh(py)_3Cl_3$ and $Rh(py)_3Cl_2Br$, with an intensity ratio of *ca.* 2·5 : 1, and again separated by *ca.* 8 cm^{-1} in $Rh(dpy)_3Cl_3$. By contrast, in the solvates, it appears that the more intense band at higher energy moves down and merges with the lesser band.

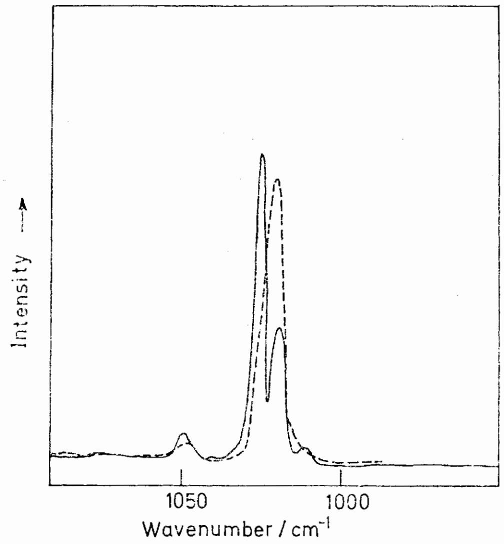

FIGURE 2 Raman spectra of *abd*-[$Rh(py_3)Cl_3$] (——) and its disolvate (– – – –) showing the region of the ν_1 mode of pyridine

The i.r. spectra show a minor change in the environment of the pyridine rings in passing from unsolvated to solvated compound. In the compounds $Rh(py)_3X_3$ a group of three strong sharp bands occurs due to the ν_{25} C–H bending mode of pyridine, *e.g.*, at 757, 764, and 783 cm^{-1} in $Rh(py)_3Cl_3$. The highest-energy band is affected by solvation since it is absent from the spectra of $Rh(py)_3Cl_3,D$ and $Rh(dpy)_3Cl_3,2S$ (otherwise 557 cm^{-1}), weak in $Rh(py)_3ClBr_2,S$, but strong again in $Rh(py)_3Cl_2Br,2S$, $Rh(py)_3Cl_3,2D$, and $Rh(py)_3Cl_3,2S$.

The $A_1\nu_1$ (C–H) vibration of $CHCl_3$ occurs [11] at 3019 cm^{-1} in the vapour-phase Raman spectrum and the weak 3034 cm^{-1} band in the vapour's i.r. spectrum is attributed [12] to it; $CDCl_3$ has ν_1 at 2265 cm^{-1} in the i.r. (weak band). In the solvates, medium to strong i.r. absorption occurs between 2900 and 3000 cm^{-1} (Table 4). We were unable to observe this ν_1 band in $Rh(pic)_3Cl_3,1{\cdot}5S$ or $Rh(py)_3ClBr_2,3S$.

TABLE 4

ν_1 of $CHCl_3$ or $CDCl_3$ of solvation/cm^{-1}

Compound		Shift from vapour ($\Delta\nu$)
$Rh(py)_3ClBr_2,S$	2978m	56
$Rh(py)_3Cl_2Br,2S$	2992s	32
$Rh(py)_3Cl_3,2S$	2992m	32
	2993m [a]	
$Rh(dpy)_3Cl_3,2S$	2998m	26
	2995m [a]	
$Rh(py)_3Cl_3,D$	2227m	38
	2228s [a]	
$Rh(py)_3Cl_3,2D$	2236s	29
	2236s [a]	

[a] Raman spectrum.

DISCUSSION

The measured difference (*ca.* 20 °C) between the temperatures of maximum rate of chloroform loss for the compounds $Rh(py)_3Cl_3,2S$ (66 °C) and $Cu_2(salen)_4,2S$ (48 °C) is well outside experimental error. Baker, Hall, and Waters suggested [10] that in the copper complex the $Cu_2(salen)_4$ dimers are hydrogen-bonded to the $CHCl_3$ *via* a ligand oxygen and the chloroform hydrogen atom. Hence our qualitative thermochemical evidence suggests that a hydrogen bond from the $CHCl_2$ is probable for the rhodium–pyridine complexes.

In analysing our results on the vibrational spectra of the solvates, we compare the values of the vibrational frequencies of the $CHCl_3$ molecule in the solvates with those of gaseous $CHCl_3$, since the latter should represent $CHCl_3$ in its state of least interaction with other molecules.

The low-frequency Raman-effect bands of the solvates are uninformative. The failure to observe ν_6 (C–Cl_3 bending) of $CHCl_3$ in the solvates may arise from one or more of several causes, worth considering, since ν_6 is known [11] to be very intense in $CHCl_3$ vapour (at 262 cm^{-1}). It may be perturbed in some way in the solvates, lowering its intensity in the Raman spectra. However, lowering of symmetry (*e.g.*, vapour ⟶ liquid) is not known to make ν_6 much weaker: it is very strong in both phases of $CHCl_3$, and in liquid $CDCl_3$. Interaction of one (or two) of the chlorine atoms of the chloroform with another molecule would reduce the symmetry to C_s, but have no effect on the allowedness of the ν_6 mode, although it seems probable that the consequent change of the ellipsoid of polarisability would lead to intensity changes.

The bands of Figure 2 may either (i) correspond to the ν_1 transitions of the different pyridine rings in the molecule, *i.e.*, one (position *f*) *trans* to chloride and two mutually *trans* (positions *c* and *e*) respectively or (ii) result from in-phase and out-of-phase ν_1 modes. The splitting in the solid state is reminiscent of the ^1H n.m.r. spectra of the compounds in solution, which show the heterocyclic ligands to be inequivalent in the ratio 2 : 1, but it is not determinable from the available facts whether the Raman inequivalence in crystalline *mer*-$[Rh(py)_3Cl_3]$ arises from the same cause or not. That is, it is possible that the Raman peak observed in the solvates (although single) corresponds to the same degree of ring equivalence as in indicated by solution n.m.r.

The decrease in energy (Table 4) of the CH vibration of $CHCl_3$ upon solvate formation is compatible with the formation of a weak hydrogen bond with the substrate complex. Unfortunately $Cu(salen)_2$ has aromatic C–H stretching absorption in this region, which obscures the solvent ν_1 band, so the value for a ν_1(C–H) shift in a known hydrogen-bonded solvate was not obtained. The effect of hydrogen-bonding on the ν_1CH frequency of $CHCl_3$ is otherwise well known; Allerhand and Schleyer examined [13] this phenomenon, and concluded that the effect of merely changing the dielectric properties of the medium was much smaller than the shifts engendered by the presence of proton acceptors, such as pyridine ($\Delta\nu = 46$ cm^{-1}). Therefore the simple change in bulk environment in passing from solution phase to solvate lattice is not responsible for the ν_1(C–H) frequency shift. They suggested that the $\Delta\nu$ value was not necessarily qualitatively related to the enthalpy of association of $CHCl_3$ with various proton acceptors, but agreed with Becker's suggestion [14] that a reduction of ν_1 was indicative *per se* of the formation of a hydrogen bond by the proton of $CHCl_3$, and that the enthalpy change for the process (1) could be significantly negative

$$CHCl_3 + \text{acceptor} \rightleftharpoons Cl_3C\text{–}H \ldots \text{acceptor} \quad (1)$$

even when Δ was very small. The $\Delta\nu$ values found in our solvates (Table 4) are significantly large. They probably correspond to the formation of hydrogen-bonded states, rather than just being concomitant with the changes in the lower-frequency vibrations, as the latter involve mainly the C–Cl bonds only; certainly on the Allerhand–Schleyer–Becker bases, the values of $\Delta\nu$ in Table 4 imply hydrogen-bonding. Mason and Towl [15] have recently described the structure of the related but non-stoicheiometric chloroform solvate * $[Rh(py)_2Cl_2(otb)],0{\cdot}61CHCl_3$ in terms of a weak hydrogen bond from the chloroform to a co-ordinated chloride *cis* to a pyridine, which thus prevents the solvent from becoming totally disordered throughout the lattice. Recalling the shift which we find in the A_1,ν(Rh–Cl) frequency, and the coalescence of the pyridine ν_1 bands in the Raman spectrum, we think it likely that the H-bond is indeed associated with the C_2 axis of the $[Rh(py)_3X_3]$ molecule, although it is not possible to determine which of the *trans*-ligands (py or Cl) on the axis is more affected. The $\Delta\nu$ values are greater for monosolvates than for disolvates, which may mean that the proton acceptor sites are more available in the former. The changes in i.r. intensity of the $CHCl_3$ ν_1 band from that of the vapour reflect the perturbation expected along the C_3 axis of $CHCl_3$ on H-bond formation.

Reaction (2) is, from our *X*-ray results, irreversible,

$$Rh(py)_3X_3,2CHCl_3 \xrightarrow{\Delta} Rh(py)_3X_3 + 2CHCl_3 \quad (2)$$

i.e., desolvation does not merely remove the solvent molecules, but alters the lattice so that their re-entry is not favoured. Loss of *absorbed* chloroform {*i.e.* occupying sites differing from those of the solvating chloroform in $[Rh(py)_3Cl_2Br],2S$ before desolvation} from desolvated $Rh(py)_3Cl_2Br$ was more rapid than from any of the solvates, implying that it corresponded merely to evaporation of the $CHCl_3$ from the large internal surface area.

These results are similar to those of Steinbach and Burns, who found [16] that the chloroform disolvates of the acetylacetonates of iron(III), chromium(III), and aluminium(III) on desolvation lead to formation of pseudomorphs of the original crystals of $[M(acac)_3]$. These, they claimed, could be held in equilibrium with the solvated material, their evidence being that linear plots of vapour pressure against reciprocal temperature were obtained. This difference from the present work may be related to the possibility that there exists a polymorph of $Rh(py)_3Cl_3$ which is the immediate product of desolvation and which participates in a reversible equilibrium, but which can also change to the form which will not accept solvent again.

APPENDIX

Solvates of Simple Halogenocarbon Solvents.—Since these halogenocarbon solvates (mostly involving chloroform) occur far more commonly than comments in the literature suggest, and since we know of no collection of reports of such solvates, we provide such a list. There seem to be several classes of complex which readily form halogenocarbon solvates, so we group reports according to the ligands present in the metal complex. This procedure is rather subjective. The running number of the compound(s) in the list is the number of the relevant reference.

(A) *Halogeno-complexes* (*cf.* ref. 3).—(17), $[Me_2NH_2]$-

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* otb = *o*-Di-*o*-tolyphosphinobenzyl anion.

[13] A. Allerhand and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1963, **85**, 1715.

[14] E. D. Becker, *Spectrochim. Acta*, 1959, **15**, 743.

[15] R. Mason and A. D. C. Towl, *J. Chem. Soc.* (*A*), 1970, 1601.

[16] J. F. Steinbach and J. H. Burns, *J. Amer. Chem. Soc.*, 1958, **80**, 1839.

[17] W. Haegi, *Bull. Soc. chim. France*, 1955, **22**, 490.

[TiCl$_6$]Cl,CHCl$_3$; (18), GeCl$_4$(MeI)$_n$ ($n = 1$ and 2); (19), [(Ac)(Me$_2$O)][SbCl$_6$],$\frac{1}{2}$CH$_2$Cl$_2$; (20), AsBr$_3$ adducts of (RH)$^+$(X)$^-$,nCHCl$_3$ type; *ca.* 186 compounds, with As : R from 1 : 3 to 2 : 1, *e.g.*, [*N*-butyl-pyridinium]Br, AsBr$_3$,CHCl$_3$.

(B) β-*Diketonates and Similar Compounds.*—(21), M(acac)$_3$,-nS; (a), M = Fe, $n = 2$, S = CHCl$_3$; (b), M = Fe, Cr, Al; $n = 2$, S = CHCl$_3$; (c), M = Al, In, Fe, Sc; $n = 2$, S = CHCl$_3$, CH$_2$Br$_2$; M = Al, In, Fe, Cr; $n = 1$, S = CHBr$_3$; (22), [{ClTi(acac)}$_2$O],CHCl$_3$; (23), (i) Tris-(3-bromo-2-thioacetylacetonato)cobalt(III),CHCl$_3$; (ii), Tris-(2-bromo-1-phenyl-1-thio-1,3-butanedionato)cobalt(III),-CHCl$_3$; (24), Zn(tropolonate)$_4$,1·5CHCl$_3$; (25), [ClSn-(tropolonate)$_3$],CHCl$_3$; (26), [Co(paeonolate)$_3$],CHCl$_3$.

(C) *Oxine, Phenols, Oximes, and Related Ligands.*—(27), γ-Benzildioximinate–nickel (1 : 1 complex),CHCl$_3$; (28), bis-α-benzoinoximinatonickel(II),CCl$_4$; (29), Zr(π-C$_5$H$_5$)(oxinate)$_3$,CHCl$_3$; (30), [OMo(oxinate)$_2$O],2CH$_2$Cl$_2$, [OMo(oxinate)$_2$O],3CHCl$_3$, [OMo(oxinate)$_2$O],3C$_2$H$_4$Cl$_2$; (31), [UO$_2$(oxinate)$_2$(oxine)],CHCl$_3$, where the solvent is hydrogen bonded through its hydrogen to a phenolic oxygen of a bidentate oxinate ligand; (32), [Al(2-Me-8-OH-quinolinato)$_2$(OH)],CHCl$_3$; (33), tris-[*O*-(*N*-methylpropionamidoyl)-phenolato]cobalt,CH$_2$Cl$_2$; (34), [(6-Hydroxy-*m*-tolyl)-2-nitro-*p*-cresolato]Hg,CHCl$_3$; (35), bis[μ-{1-(*N*-benzulformimidoyl)-2-naphtholato}]dihalogenodicopper(II,II),2CHCl$_3$ (Cl or Br).

(D) *Schiff Bases.*—[acac = acetylacetonato; sal = salicylaldehydo-; en = ethylenedi-imino; stien = 1,2-diphenylethylenedi-imino, *etc.* Thus 5-Cl-sal$_2$en is the quadridentate Schiff base made by condensing 5-chlorosalicylaldehyde (2 mol) with 1,2-diaminoethane (1 mol)]. (36), acac$_2$-en-Pd$^{\rm II}$,2CHCl$_3$; (37), sal$_2$stienM$^{\rm II}$,CHCl$_3$ (M = Ni or Cu), sal$_2$enVO,CHCl$_3$; (38), [(Fesal$_2$en)$_2$O],CH$_2$Cl$_2$; (39), (i), [Fe$_2$(sal$_2$en)$_2$Cl$_2$],CHCl$_3$; (ii), [ClFe(sal$_2$en)]$_2$,4CHCl$_3$; (iii), [BrFe(sal$_2$en)]$_2$,4CHCl$_3$; (40), (i) [Co(sal$_2$en)],CHCl$_3$; (ii), [Co(sal$_2$en)],2CHCl$_3$; (41), [Co(sal$_2$en)],2CH$_2$Br$_2$, [Co-(sal$_2$-2,3-di-methylen)],2CHCl$_3$, [Co(sal$_2$-2,3-di-methylen)],-2CH$_2$Br$_2$, [Co(sal$_2$-2,3-di-methylen)],2CHBr$_3$, [Co(5-Cl-sal)$_2$-en],2CHBr$_3$, (42), [Cu$_2$(sal$_2$en)$_2$],2CHCl$_3$; (43), (i), [Cu{(5-Cl-sal)$_2$en}],2CHCl$_3$; (ii), [Cu{(5-Br-sal)$_2$en}],0·5CHCl$_3$; (iii), [Cu{(5-I-sal)$_2$en}],CHCl$_3$; (44), [(*N*-cyclohexyl-3-methoxy-salicylideniminato)$_2$Cu],2CHCl$_3$, [*N*-cyclohexyl-3-methoxy-salicylideniminato)$_2$Cu],2CHBr$_3$; (45), di-μ-*NN′*-*m*-phenyltetrakissalicylidiniminatodicopper(II,II),2CHCl$_3$.

(E) N-*Heterocyclic Ligands.*—(46), So-called ' β '-dichlorobisquinolineplatinum(II),2CHCl$_3$; (47), tetrachloro(pyridinium propylide)(pyridine)platinum(IV),S (S = CHCl$_3$ or CCl$_4$); (48), Ni(py)$_4$X$_2$,CHCl$_3$ (X = BF$_4^-$, ClO$_4^-$); (49), [M(py)$_3$X$_3$]S_n (M = Rh, Ir, Cr, or Mo; S = various); (50), Ni(benzimidazole)$_4$Br$_2$,3CHCl$_3$; (51), (i), ML$_2$Cl$_4$,CHCl$_3$ (M = Sn or Ti; L = benzimidazole); (ii), SnL$_2$Cl$_4$,CHCl$_3$ (L = ethylbenzimidazole or ethylimidazole); (iii), SnI$_2$Cl$_4$,-CHCl$_3$, TiL$_2$Cl$_4$,CHCl$_3$, TiLCl$_4$,CHCl$_3$ (L = imidazole); (52), [Ni(2,9-dimethyl-1,10-phenanthroline)Cl$_2$],2CHCl$_3$; (53), [Ru(bipy)$_2$Cl$_2$],CHCl$_3$; (54), [V(bipy)Br$_2$],CHCl$_3$; (55), [(4,4′-diMe-2,2′-bipyridyl)$_2$Fe(CN)$_2$],CHCl$_3$; (56), [Cu(3-nitrosalicylaldehydato)(bipy)],CHCl$_3$ (the analogous compounds of Ni and Co do not solvate with chloroform);

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[18] H. C. Brown, L. P. Eddy, and R. Wong, *J. Amer. Chem. Soc.*, 1953, **75**, 6275.

[19] F. Klages, E. Mühlbauer, and G. Lukasdzyk, *Chem. Ber.*, 1961, **94**, 1464.

[20] P. Popov, *Zhur. obshchei Khim.*, 1949, **19**, 47.

[21] (*a*) G. Urbain and A. Debierne, *Compt. rend.*, 1899, **129**, 302; (*b*) ref. 16, and *cf.* J. P. Fackler, *Inorg. Chem.*, 1965, **4**, 130; 1966, **5**, 242; (*c*) F. R. Clarke, J. F. Steinbach, and W. F. Wagner, *J. Inorg. Nuclear Chem.*, 1964, **26**, 1311.

[22] K. W. Watenpaugh and C. N. Caughlan, *Inorg. Chem.*, 1967, **6**, 963.

[23] Compounds (i) and (ii): A. Yokoyama, S. Kawanishi, M. Chikuma, and H. Tanaka, *Chem. Pharm. Bull* (*Tokyo*), 1967, **15**, 540: Compound (ii) also in A. Yokoyama, S. Kawanishi, and H. Tanaka, *ibid.*, 1970, **18**, 356.

[24] E. L. Muetterties and C. M. Wright, *J. Amer. Chem. Soc.*, 1965, **87**, 4706.

[25] J. J. Park, D. M. Collins, and J. L. Hoard, *J. Amer. Chem. Soc.*, 1970, **92**, 363.

[26] (*a*) P. Pfeiffer, S. Golther, and O. Angern, *Chem. Ber.*, 1927, **60**, *B*, 305; (*b*) R. D. Gillard and L. R. F. Vilas Boas (unpublished work) find that this is probably the 1,2,3-isomer.

[27] F. W. Atack, *J. Chem. Soc.*, 1913, 1317.

[28] J. S. Jennings, E. Sharratt, and W. Wardlaw, *J. Chem. Soc.*, 1935, 818.

[29] E. M. Brainina, E. I. Mortikova, L. A. Petrashkevich, and R. K. Fredlii, *Doklady Akad. Nauk, S.S.S.R.*, 1966, **169**, 335.

[30] C. B. Riolo and F. Guerrieri, *Ann. Chim.* (*Rome*), 1967, **57**, 873.

[31] D. Hall, A. D. Rae, and T. N. Waters, *Acta Cryst.*, 1967, **22**, 258.

[32] P. R. Scherer and Q. Fernando, *Chem. Comm.*, 1967, 1107.

[33] O. Chakravorty and B. Behera, *Inorg. Chem.*, 1967, **6**, 1812.

[34] Z. Tamura, Y. Iitaka, and Y. Kido, *Chem. Pharm. Bull.* (*Tokyo*), 1969, **17**, 1767.

[35] R. B. Coles, C. M. Harris, and E. Sinn, *Austral. J. Chem.*, 1970, **23**, 243.

[36] G. T. Morgan and J. D. Main-Smith, *J. Chem. Soc.*, 1926, 912.

[37] P. Pfeiffer, T. Hesse, H. Pfitzner, W. Scholl, and H. Thielert, *J. prakt. Chem.*, 1937, **149**, 217.

[38] (*a*) L. O. Atovmayan, O. A. Dyachenko, and S. B. Soboleva, *Zhur. strukt. Khim.*, 1970, **11**, 557; (*b*) J. Lewis, F. E. Mabbs, and A. Richards, *J. Chem. Soc.* (*A*), 1967, 1014.

[39] G. M. Bancroft, A. G. Maddock, and R. Prandl, *J. Chem. Soc.* (*A*), 1968, 293.

[40] Compound (i) in (*a*) W. P. Schafer and R. E. Marsh, *Acta Cryst.*, 1969, **25**, *B*, 1675, and in (*b*) S. Katagiri and J. Endo, *Nippon Kagaku Zasshi*, 1963, **84**, 1 (*Chem. Abs.*, 1964, **60**, 2422h) where it is described as paramagnetic: compound (ii) in (*b*), described as diamagnetic.

[41] J. Endo, *J. Chem. Soc. Japan*, 1949, **70**, 77; 1955, **65**, 34.

[42] E. N. Baker, D. Hall, A. J. McKinnon, and T. N. Waters, *Chem. Comm.*, 1967, 134; *cf.* ref. 10.

[43] Compound (i) in (*a*) T. Tanaka, *J. Amer. Chem. Soc.*, 1958, **80**, 4108; compounds (ii) and (iii) in (*b*) T. Tanaka, *Bull. Chem. Soc. Japan*, 1960, **33**, 259.

[44] A. Takeuchi and S. Yamada, *Bull. Chem. Soc. Japan*, 1970, **43**, 3629.

[45] C. A. Bear and T. N. Waters, *J. Chem. Soc.* (*A*), 1970, 2494.

[46] E. G. Cox, H. Saenger, and W. Wardlaw, *J. Chem. Soc.*, 1932, 2216.

[47] (*a*) N. A. Bailey, R. D. Gillard, M. Keeton, R. Mason, and D. R. Russell, *Chem. Comm.*, 1966, 396; (*b*) M. Keeton, R. Mason, and D. R. Russell, *J. Organometallic Chem.*, 1971, **33**, 259.

[48] M. R. Rosenthal and R. S. Drago, *Inorg. Chem.*, 1966, **5**, 492.

[49] Ref. 6*c* and the present paper.

[50] D. M. L. Goodgame, M. Goodgame, and M. J. Weeks, *J. Chem. Soc.* (*A*), 1967, 1125.

[51] A. D. Garnovskii, O. A. Osipov, V. T. Panyushkin, and A. F. Pozharskii, *Zhur. obshchei Khim.*, 1966, **36**, 1063.

[52] H. S. Preston and C. H. L. Kennard, *Chem. Comm.*, 1968, 219; *cf.* reformulation as di-μ-chloro-*sym*-*trans*-dichlorobis-(2,9-dimethyl-1,10-phenanthroline)dinickel(II,II) in H. S. Preston and C. H. L. Kennard, *J. Chem. Soc.* (*A*), 1969, 2682.

[53] C. F. Liu, N. C. Liu, and J. C. Bailar, jun., *Inorg. Chem.*, 1964, **3**, 1197.

[54] G. W. A. Fowles and P. T. Greene, *J. Chem. Soc.* (*A*), 1967, 1869.

[55] G. M. Bryant, J. E. Ferguson, and H. K. J. Powell, *Austral. J. Chem.*, 1971, **24**, 257.

[56] Y. Muto, *Bull. Chem. Soc. Japan*, 1960, **33**, 604.

(57), bis[2-(2-pyridylamino)-4-(2-pyridyl)-thiazolato]Fe,$1{\cdot}33CHCl_3$.

(F) *Sulphur Ligands.*—(58), (i), Dichloro(*SS′*-di-*p*-tolyl-1,2-ethanedithiol)palladium(II),$CHCl_3$, and *cf.* (ii) *trans*-$[Pt(Bu^i{}_2S_2Cl_2],n\text{-}CHCl_3$; (59), ' $Ir(Et_2S)_3Cl_3,CHCl_3$ '; (60), [μ-2-(dimethylamino)ethanethiolato-tris-2-(dimethylamino) ethanethiolatodinickel(II,II)] tetrahydrochloride,$2CHCl_3$; (61), $[Fe_2(NO)_2(S_6C_6Ph_6)],CHCl_3$; (62), $Co_4(\pi\text{-}C_5H_5)_4S_6,\frac{1}{2}CHCl_3$.

(G) *Phosphine and Similar Ligands.—Unidentate phosphines.*—(63), $Ph_3AsBr_2,CHCl_3$; (64), $Ph_3Sb(X)OOSb(X)Ph_3,CHCl_3$ ($X = Cl$ or Br); (65), *trans*-$[Ir(SbPh_3)_3Br_3]CHCl_3$; (66), (i), [(*p*-tolyl isocyanide)$_5$Fe(PPh_3)](ClO_4)$_2$,$CHCl_3$; (ii), [(*p*-tolyl isocyanide)$_5$Fe($SbPh_3$)](ClO_4)$_2$,$\frac{1}{2}CH_2Cl_2$; and *cf.* (iii) [Rh(*p*-methoxyphenylisocyanide)$_4$](ClO_4),$CHCl_3$; (67), (2-Phenylisophosphoindole)$PdCl_2,CHCl_3$; (68), $[OMoBr_3(Ph_3PO)_2],2CHCl_3$; (69), $(NO)Ir(PPh_3)_3,CH_2Cl_2$, $IrCl_3(py)(PPh_3)_2,CH_2Cl_2$; (70), $[Mn(CO)_3(PPh_3)_2],\frac{1}{2}CHCl_3$; (71), $[(PPh_3)_2Co(CO)_3][Co(CO)_4],CHCl_3$, $[(PPh_3)_2Co(CO)_3][CuI_2],CHCl_3$; (72), $[Ir(C_3Ph_3)Cl(CO)(PMe_3)_2]BF_4,CH_2Cl_2$; (73), $BzRh(CO)_2Cl_2(PPh_3),\frac{1}{2}CH_2Cl_2$, $BzRh(py)Cl_2(PPh_3),\frac{1}{2}CH_2Cl_2$, $BzRhCl_2(PPh_3),\frac{1}{2}CH_2Cl_2$, ($\alpha$-Chloro-*m*-tolyl)$Ir(CO)Cl_2(PPh_3)_2,\frac{1}{2}CH_2Cl_2$; (74), $[RIr(\pi\text{-}C_5H_5)(CO)(PPh_3)]Y,\frac{1}{2}CH_2Cl_2$, for R = Et or *n*-hexyl and $Y = I^-$ for R = Me, Y = Cl, Br, or I; (75), $[C_4ClRh(SbPh_3)_2(CF_3)_4]CH_2Cl_2$; (76), (i), $[(\pi\text{-}C_5H_5)Mo(CO)(PPh_3)_2(NCO)],\frac{1}{2}CH_2Cl_2$ and *cf.* (ii), $[Ir(CO)(PPh_3)_2(NCO)(NO_3)_2],CH_2Cl_2$; (77), $[(R_3P)_2N]_2[M_2(CO)_{10}]CH_2Cl_2$ (R = Et or Ph: M = Cr or Mo); (78), ' $H{\cdot}(PPh_3)MBr_3(CO)_3(PPh_3)$',$CH_2Cl_2$ (M = Mo or W); (79), $H_2Ru(PPh_3)_3(CO),CH_2Cl_2$; (80), $IrI(CO)(O_2)(PPh_3)_2,CH_2Cl_2$; (81), $[Pt(O_2)(PPh_3)_2],2CHCl_3$; (82), $[RhCl(O_2)(PPh_3)_2]_2,2CH_2Cl_2$; (83), $[Pt(CO_3)(PPh_3)_2]S$ ($S = CHCl_3$ or CH_2Cl_2); (84), *p*-fluorophenylazo-bistriphenylphosphine($RhCl_2$),$\frac{1}{2}CHCl_3$; (85), ' $H{\cdot}PPh_3{\cdot}[Re^{II}Br_5(PPh_3)]$ ',CH_2Cl_2; (86), $[RhCl(PPh_3)_2H_2]_2,CH_2Cl_2$: for this compound, which, after drying *in vacuo* for several days analysed well as the solvate, it was suggested that the CH_2Cl_2 was co-ordinated, bridging two rhodium atoms $[RhCl(PPh_3)_2H_2],CHCl_3$(?); (87), $[RhCl(AsPh_3)_2H_2]_2,CH_2Cl_2$: the solvent was not removed by pumping for several days at 25 °C. Mague and Wilkinson suggest that CH_2Cl_2 is co-ordinated *via* its chlorine atoms to two rhodium ions. This suggestion was extended to: $[RhCl_2(AsPh_3)_2H]_2,CH_2Cl_2$, $[RhCl(AsPh_3)_2(O_2)],n\text{-}CH_2Cl_2$; (88), $[RhCl_2(PPh_3)_2H]_2,CH_2Cl_2$.

Bidentate Phosphines.—(89), $[Os(diphos)_2Cl_2],n\text{-}CHCl_3$, (i), *trans*-isomer: $n = \frac{1}{3}$, lost by efflorescence, (ii), *cis*-isomer: $n = 1$, not completely removed by heating (80 °C, 10 h, *in vacuo*); (90), [Br_2Ni diphenyl-(*o*-diphenylarsinophenyl)phosphine]$ClO_4,\frac{1}{2}CH_2Cl_2$; (91), *cis*-$[Re(diphos)_2(CO)_2]I,CH_2Cl_2$; (92), $[Mn(diphos)(CO)_2]Br,2CHCl_3$; (93), $[MI_2(diphos)(CO)_3],CH_2Cl_2$ (M = Mo or W); (94), $[WBr_2(L)(CO)_3],CH_2Cl_2$ ($L = Ph_2As{\cdot}CH_2{\cdot}AsPh_2$); (95), $[MoCl_2(P)(CO)_2],CH_2Cl_2$ ($P = Ph_2P{\cdot}CH_2{\cdot}PPh_2$); (96), bis[*PP*-diethyl-*P′P′*-diphenyl-*PP*-*o*-phenylenebis(phosphine)gold (2-oxobornanesulphonate),$CHCl_3$; (97), dibromo[dimethyl-*o*-([*p*-nitrobenzyl]thio)phenylarsine]palladium(II)$\frac{1}{3}CHCl_3$, [dimethyl-*o*-(propylthio)phenylarsine]$PdI_2,\frac{1}{2}CH_2Cl_2$; (98), $[HgLX]ClO_4,CH_2Cl_2$: L = tris-[*o*-(diphenylphosphino)phenyl]phosphine, X = Cl, Br, or I; $[HgL(NCS)_2],CH_2Cl_2$.

---

[57] A. A. Goodwin and R. N. Sylva, *Austral. J. Chem.*, 1968, **21**, 1081.

[58] (i) G. M. Bennett, A. N. Mosses, and F. S. Statham, *J. Chem. Soc.*, 1930, 1668; (ii) P. Pfeiffer, in K. Freudenberg, 'Stereochemie,' Deuticke, Leipzic, **1933**, p. 1243.

[59] (i) This red compound was formulated as 1,2,4-$[Ir(Et_2S)_3Cl_3],CHCl_3$ by P. C. Ray and N. N. Ghosh, *J. Indian Chem. Soc.*, 1936, **13**, 138, though later workers (ii) G. B. Kauffman, J. H-S. Tsai, R. C. Fay, and C. K. Jorgensen, *Inorg. Chem.* 1963, **2**, 1233, gave the isomeric ionic formulation to the same complex crystallised from chloroform, while not mentioning the solvation.

[60] P. C. Jain and H. L. Nigam, *Inorg. Chim. Acta*, 1967, **1**, 265.

[61] (i) J. Locke, J. A. McCleverty, E. J. Wharton, and C. J. Winscom, *Chem. Comm.*, 1967, 1289: (ii) T. Birchall and N. N. Greenwood, *J. Chem. Soc.* (*A*), 1969, 286.

[62] V. A. Uchtman and L. F. Dahl, *J. Amer. Chem. Soc.*, 1969, **91**, 37.

[63] D. E. Worrall, *J. Amer. Chem. Soc.*, 1930, **52**, 664.

[64] J. Dahlmann and A. Rieche, *Chem. Ber.*, 1967, **100**, 1544.

[65] A. Araneo, S. Martinengo, P. Pasquale, and F. Zingales, *Gazzetta*, 1965, **95**, 1435.

[66] (i) and (ii) F. Bonati, A. Minghetti, and R. Leoni, *J. Organometallic Chem.*, 1970, **25**, 223; (iii) L. Malatesta and L. Vallarino, *J. Chem. Soc.*, 1956, 1867.

[67] J. W. Collier, F. G. Mann, and D. G. Watson, *J. Chem. Soc.*, 1964, 180.

[68] J. Lewis and R. Whyman, *J. Chem. Soc.*, 1965, 6027.

[69] W. R. Roper and C. A. Reed, *J. Chem. Soc.* (*A*), 1970, 3054.

[70] H. Nakayama, *Bull. Chem. Soc. Japan*, 1970, **43**, 2057.

[71] A. Sacco and M. Freni, *J. Inorg. Nuclear Chem.*, 1958, **8**, 566; *Ann. Chim.* (*Rome*), 1958, **48**, 218).

[72] R. M. Tuggle and D. Weaver, *J. Amer. Chem. Soc.*, 1970, **92**, 5523.

[73] C. O'Connor, *J. Inorg. Nuclear Chem.*, 1970, **32**, 2299.

[74] W. A. Graham and A. J. Oliver, *Inorg. Chem.*, 1970, **9**, 2653.

[75] J. T. Mague, *J. Amer. Chem. Soc.*, 1969, **91**, 3983; *Inorg. Chem.*, 1970, **9**, 1610.

[76] (i) A. T. McPhail, T. Andrew, G. R. Knox, C. G. Robertson, and G. A. Sim, *J. Chem. Soc.* (*A*), 1968, 2012; (ii) D. N. Cash and R. O. Harris, *Canad. J. Chem.*, 1971, **49**, 867.

[77] L. B. Handy, J. K. Ruff, and L. F. Dahl, *J. Amer. Chem. Soc.*, 1970, **92**, 7312.

[78] J. Lewis and R. Whyman, *J. Chem. Soc.* (*A*), 1967, 77.

[79] S. Robinson and J. J. Levinson, *J. Chem. Soc.* (*A*), 1970, 2947.

[80] J. A. McGinnety, R. J. Doedens, and J. A. Ibers, (*a*) Science, 1967, **155**, 709; (*b*) *Inorg. Chem.*, 1967, **6**, 2243.

[81] C. D. Cook, P-T. Cheng, and S. C. Nyburg, *J. Amer. Chem. Soc.*, 1969, **91**, 2123.

[82] M. J. Bennett and P. B. Donaldson, *J. Amer. Chem. Soc.*, 1971, **93**, 3307.

[83] C. J. Nyman, C. E. Wymore, and G. Wilkinson, *Chem. Comm.*, 1967, 407: the solvate with CH_2Cl_2 is also described in C. J. Nyman, C. E. Wymore, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1968, 561.

[84] M. C. Baird and G. Wilkinson, *J. Chem. Soc.* (*A*), 1967, 865.

[85] M. Freni, V. Valenti, and R. Pomponi, *Gazzetta*, 1964, **94**, 521.

[86] J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc.*, 1966, 1711.

[87] J. T. Mague and G. Wilkinson, *J. Chem. Soc.*, 1966, 1736.

[88] M. C. Baird, J. T. Mague, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1967, 1347.

[89] J. Chatt and R. G. Hayter, *J. Chem. Soc.*, 1961, 896.

[90] T. D. Dubois and D. W. Meek, *Inorg. Chem.*, 1967, **6**, 1395.

[91] M. Freni, V. Valenti, and D. Giusto, *J. Inorg. Nuclear Chem.*, 1965, **27**, 2635.

[92] A. G. Osborne and M. H. B. Stiddard, *J. Chem. Soc.*, 1965, 700.

[93] J. Lewis and R. Whyman, *J. Chem. Soc.*, 1965, 5486.

[94] M. W. Anker, R. Colton, and I. B. Tomkins, *Austral. J. Chem.*, 1968, **21**, 159.

[95] M. W. Anker, R. Colton, and I. B. Tomkins, *Austral. J. Chem.*, 1968, **21**, 1143.

[96] M. Davies and F. G. Mann, *J. Chem. Soc.*, 1964, 3791.

[97] L. Lindoy, S. E. Livingstone, and T. N. Lockyer, *Inorg. Chem.*, 1967, **6**, 652.

[98] G. Dyer, D. G. Goodall, R. H. B. Mais, H. M. Powell, and L. M. Venanzi, *J. Chem. Soc.* (*A*), 1966, 1110.

The four analogous compounds with the arsenic analogue were also reported.

(H) *Miscellaneous*.—(99), $[\mathrm{EtPh_2CrI}],\mathrm{CHCl_3}$; (100), $[\mathrm{Cr(C_6H_6)_2}][\mathrm{AlCl_4}],\frac{1}{4}\mathrm{C_6H_6},\frac{1}{4}\mathrm{CH_2Cl_2}$; (101), $\mathrm{PhCH(OCMe)CH(HgCl)CO_2H,CHCl_3}$; (102), $[\mathrm{ClRu(PhCO_2)_4RuCl}],2\mathrm{CHCl_3}$; (103), $[\mathrm{Fe(CN)_2(CH_3NC)_4},4\mathrm{CHCl_3}$; (104), $\mathrm{(Ph_3P)_2Rh(Me)ClI,MeI}$.

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[99] L. N. Vertyulina, G. D. Domrachev, I. A. Korshunov, and G. A. Razuvaev, *Zhur. obshchei Khim.*, 1963, **33**, 285.

[100] F. Hein and K. Karrte, *Z. anorg. Chem.*, 1960, **307**, 52.

[101] W. R. R. Park and G. F. Wright, *J. Org. Chem.*, 1954, **19**, 1325.

[102] M. J. Bennett, W. K. Bratton, F. A. Cotton, and W. R. Robinson, *Inorg. Chem.*, 1968, **7**, 1540.

[103] J. B. Wifford, N. O. Smith, and H. M. Powell, *J. Chem. Soc.* (*A*), 1968, 1544.

[104] D. N. Lawson, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc.*, 1966, 1733. The methyl iodide is thought to be co-ordinated to rhodium through iodine: apart from the compounds in ref. 18, there are very few solvates of iodocarbons yet known. Those described by E. C. J. Hartley of silver cyanide (*J. Chem. Soc.*, 1916, 1296) and copper cyanide (*J. Chem. Soc.*, 1928, 780) are thought, in ref. 104, to be nitrile complexes.