Transition Met. Chem. 3, 165–169 (1978)

Table 5. Comparison of some kinetic and thermodynamic parameters for $[Fe(5\text{-}Brphen)_3]^{2+}$, $[Fe(5\text{-}Brphen)_3]^{3+}$ and 5-Brphen with those for other substituted 1,10-phenanthrolines and their iron(II) and iron(III) tris-complexes

Thermodynamic				Kinetic			
				Iron(II)			Iron(III)
Ligand	Ligand pK_a	Complex $\log \beta_3$	$[Fe(LL)_3]^{2+/3+}$ $\epsilon^{\ominus}$	$10^4 k_{aq}$ (308.2)[g] 0.54 M H_2SO_4	k_{OH^-}(298 K)[h] I = 0.243 M (NaOH/NaCl)	k_{CN^-}(308.2)[i] I = 0.5 M (KCN/KCl)	$10^4 k_{aq}$ (307.5 K)[j] 1.09 M H_2SO_4
5-NO_2phen	3.57[a]	17.8[a]	1.25[e]	23	0.094	0.51	200
5-Clphen	4.26[a]	19.7[a]	1.12[e]	12	0.052	0.10	22
5-Brphen	4.20[k]		1.12[e]	8.6	0.057	0.11	6.4
phen	4.96[a]	21.2[c]	1.06[e]	3.8	0.011	0.034	1.2
4,7-Me_2phen	5.94[b]	23.1[d]	0.87[f]	1.1	0.007	*ca.* 0.006	0.13

[a] Ref. 21; [b] ref. 22; [c] ref. 23; [d] ref. 24; [e] ref. 25; [f] ref. 26; [g] sec^{-1}, ref. 13; [h] mol $dm^{-3}s^{-1}$, ref. 16; [i] mol $dm^{-3}s^{-1}$, ref. 17; [j] s^{-1}, ref. 6; [k] ref. 27.

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TMC 77/138

Some Complexes of Rhodium and Iridium with 2-(Di-t-butylphosphinomethyl)-1-methoxy-4-methylbenzene*

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Summary

The new tertiary phosphine $t\text{-}Bu_2(2\text{-}MeO\text{-}5\text{-}MeC_6H_3CH_2)P$, L, was prepared by the base treatment of the phosphonium salt, LH^+I^-, which was in turn prepared from $t\text{-}Bu_2PH$, $2\text{-}MeO\text{-}5\text{-}MeC_6H_3CH_2Cl$ and sodium iodide. This phosphine, L, reacts with various chloro-rhodium and -iridium species without O-demethylation. This contrasts with the behaviour of $t\text{-}Bu_2PC_6H_4OMe\text{-}2$ which demethylates readily on similar treatment to give chelate complexes. The completely different behaviour between this new 2-methoxybenzylphosphine, L, and the 2-anisylphosphine, $t\text{-}Bu_2PC_6H_4OMe\text{-}2$, is explained in terms of steric effects.

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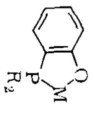
Table 1. ^{1}H n.m.r.[a] and i.r. data for the rhodium and iridium complexes

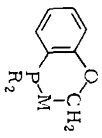
Complex	^{1}H n.m.r.	J(PH)[b]	OMe	Me	t-Bu	Hydride	δ	^2J(PH)	I.r. (cm^{-1})	ν(M−H)		ν(C≡O)	
	Methylene δ	δ	δ	δ	δ	J(PH)[c]			ν(M−Cl) Nujol	Nujol	Benzene	Nujol	Benzene
trans-$RhCl_2L_2$[d]									349, 342sh				
$RhHClL_2$	4.42		3.32s	2.32s	1.58t	12.7	−29.8dt[e]	12.9	349, 341sh	1939			
trans-$RhCl(CO)L_2$	4.11[f]		3.43s	2.31s	1.48t	12.7			293			1935 1960, 1965	1940, 1965
trans-$Rh_2Cl_2(CO)_2L_2$	2.69[f]		3.38s	1.69s	1.37	13.7[g]						1957, 1962	1957, 1960
IrH_2ClL_2	3.83t	6.8	3.78s	2.15s	1.29t	12.7	−32.6t	13.2	273	2300	2310		
$IrH_2Cl(CO)L_2$	3.67t	8.1	3.77s	2.22s	1.42t 1.30t	13.2 13.2	− 8.75dt[h] −20.85dt	18.0 13.0	254	2360 2135	2380 2130	1955	1970
$IrH_2Cl(MeNC)L_2$[i]	3.50t	7.5	3.74s	2.21s	1.34t	12.0	−11.3dt[j] −23.5dt	18.0 14.5					
trans-$IrCl(CO)L_2$[i]	3.92t	7.0	3.77s	2.17s	1.45t	12.6			303			1935	1933
LH^+I^-	3.63d	5.8[k]	3.93s	2.25s	1.54d	16.1[g]							
L	2.83d	3.7[k]	3.80s	2.25s	1.16d	10.8[g]							

[a] At 90 MHz in $CDCl_3$ soln. at ca. 25°, unless stated otherwise, δ-values ±0.02, J-values ±0.5 Hz. s = singlet, d = doublet, t = triplet, dt = doublet of triplets.
[b] $^2J(PH) + {}^4J(PH)$; [c] $^3J(PH) + {}^5J(PH)$; [d] L = t-Bu_2(2-MeO-5-$MeC_6H_3CH_2$)P; [e] ^1J(RhH) = 32; [f] Broad signals; [g] ^3J(PH) = 5.4; [h] ^3J(HH) = 5.4;
[i] At 60 MHz in $CDCl_3$ at 34°; [j] ^3J(HH) = 4.8; [k] ^2J(PH).

Introduction

We have shown that tertiary 2-anisylphosphines generate some unusual chemistry when reacted with platinum metal salts. This is especially so when the other groups on phosphorus are bulky, *e.g.* t-Bu or Ph. Thus with phosphines such as 2-$MeOC_6H_4PR_2$(1, 2), 2,6-$(MeO)_2C_6H_3PR_2$ or 2,3-$(MeO)_2C_6H_3PR_2$(3) (R = t-Bu or Ph), O-metallation (with loss of the methyl group) commonly occurs to give a chelate ring of type (*1*) (M = metal),


(*1*)

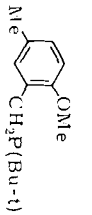

(*2*)

but in nonpolar solvents C-metallation can occur preferentially to give a six-membered chelate ring of type (*2*)(1). Using chelate rings of type (*1*) we have stabilized unusual valency states such as iridium(II)(2) and rhodium(II)(4), (the iridium(II) complexes take up dioxygen reversibly) and also stabilized five-coordinate iridium(III) hydrides which showed some unusual properties(2, 3). It therefore seemed of interest to study the behaviour of an analogous 2-methoxybenzylphosphine towards platinum metals. If a similar demethylation occurred then a six-membered chelate ring would form.

Results and Discussion

We chose to study the new tertiary phosphine 2-(di-t-butyl-phosphinomethyl)-1-methoxy-4-methylbenzene L (*3*) which we readily prepared by treating the known 2-chloromethyl-1-methoxy-4-methylbenzene with di-t-butylphosphine and sodium iodide and subsequent treatment of the resultant phosphonium iodide with base (see Experimental and Table 1 for characterizing data).

We have shown previously that di-t-butyl-2-methoxyphenylphosphine does not react readily with rhodium trichloride in propan-2-ol (or ethanol) at room temperature and when the mixture is heated demethylation occurs to give the P- and O-bonded chelate complex $\overline{Rh(t\text{-}Bu_2PC_6H_4O})_2$(4). In contrast, the new ligand, L (*3*), reacts readily with an ethanolic solution of rhodium trichloride to give an emerald green crystalline material which we formulate as the rhodium(II) species *trans*-$RhCl_2L_2$. The ^{1}H n.m.r. spectrum of this complex in deuteriochloroform is very broad, in agreement with its being paramagnetic and the microanalytical and molecular weight data (Table 2) are in agreement with the formulation. A band (at 349 cm^{-1}) with a shoulder (at 342 cm^{-1}) is assignable to ν(Rh-Cl): this band is very strong and at a value typical of a *trans*-Cl-Rh-Cl moiety. The electronic absorption spectrum of this green complex in benzene solution shows λ_{max} values at 587 and 321 nm with ε = 286 and 8090 l mol^{-1} cm^{-1}, respectively. When a propan-2-ol solution of rhodium trichloride was heated under reflux for 2 h with L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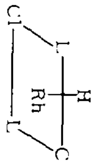
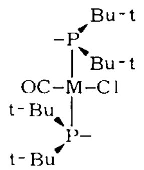

(*4*)

Table 2. Yield, colour, m.p., analytical and molecular weight data for the rhodium and iridium complexes

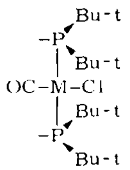
Complex	Yield (%)	Colour	M.p. (°)	Found Calcd.)% C	H	Hal	M.W.
trans-$RhCl_2L_2$ [a)]	79	green	201–107 [b)]	55.4(55.6)	7.95(7.95)	9.6(9.65)	710(734)
$RhHCl_2L_2$	72	green	183–189 [b)]	55.35(55.5)	8.05(8.1)	9.5(9.65)	
trans-$RhCl(CO)L_2$	75	yellow	218–221	56.8(56.8)	8.1(8.05)	5.25(4.9)	
$Rh_2Cl_2(CO)_2L_2$	63	yellow	214–216	47.85(48.4)	6.45(6.55)	7.95(8.15)	857(894)
IrH_2ClL_2	68	orange	190–194 [b)]	51.1(51.65)	7.5(7.5)	4.6(4.5)	817(790)
$IrH_2Cl(CO)L_2$	82	white	242–244 [b)]	50.95(51.35)	7.25(7.4)	4.3(4.35)	843(818)
$IrH_2Cl(MeNC)L_2$	93	white	190–192 [b)]	51.55(52.0)	7.7(7.65)		831(832)
trans-$IrCl(CO)L_2$	58	yellow	246–249 [b)]	51.45(51.5)	7.45(7.15)	4.4(4.35)	801(816)

[a)] L = $t\text{-}Bu_2(2\text{-}MeO\text{-}5\text{-}MeC_6H_3CH_2)P$; [b)] Dec.

(4 mole per Rh atom) the green crystalline five-coordinate rhodium(III) hydride, $RhHCl_2L_2$ (*4*), was obtained. This formulation follows from the microanalytical data (Table 2) the ^1H n.m.r. spectrum, which shows a high field doublet of triplet hydride resonance at −29.8 δ, ^2J (PH) = 12.9, ^1J (RhH) = 31.6 Hz and a t-butyl triplet resonance showing mutually *trans*-phosphorus nuclei; the ^{31}P n.m.r. spectrum which shows a 1 : 1 doublet at 55.2 δ, ^1J (RhP) = 95 Hz; and the i.r. spectrum, which shows a weak band due to ν(Rh-H) (at 1939 cm^{-1}), the remainder of the spectrum being virtually identical to that of *trans*-$RhCl_2L_2$ discussed above. We could find no evidence of complexes in which demethylation had occurred which contrasts with the behaviour of $t\text{-}Bu_2PC_6H_4OMe\text{-}2$ which, as mentioned above reacts with rhodium trichloride to give the bis-chelate complex $Rh(t\text{-}Bu_2PC_6H_4O\text{-}2)_2$⁽⁴⁾, possibly contaminated with a little $RhH(t\text{-}Bu_2PC_6H_4O\text{-}2)_2$. When carbon monoxide was bubbled through a benzene solution of this red five-coordinate rhodium(III) hydride, $RhHCl_2L_2$ (*4*), the solution became pale yellow almost immediately and the pale yellow rhodium(I) complex, *trans*-$RhCl(CO)L_2$ was isolated readily from the solution. The ^1H n.m.r. spectrum shows a 'virtually coupled' 1 : 2 : 1 triplet resonance at 1.48 δ J(PH) = 12.7 Hz but the ^{31}P n.m.r. spectrum at *ca.* 300 K shows a broad resonance at *ca.* 53 δ, indicative of relatively slow rotation around the rhodium-phosphorus bonds since at 233 K a doublet resonance at 60.6 δ ^1J(RhP) = 120 Hz and an *ABX*-pattern, δ_A = 39.75, δ_B = 62.2 p.p.m., $^2J_{AB}$ = 318, $^1J(RhP_A)$ = 120 Hz, $^1J(RhP_B)$ = 120 Hz with approximate intensity ratios of 1 : 1 indicates the presence of two rotamers (5), and either (*6*) or (*7*) (M = Rh). Strong interaction between the t-butyl groups and the chlorine or carbonyl ligands lead to high energy barriers to rotation⁽⁵⁾. One rotamer, (*6*) or (*7*), is for some reason present in only small (and undetected) amount.



(5)



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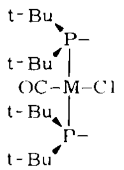
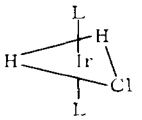


(7)

When the phosphine, L, (2.2 mole equivalents per Rh atom) is added to a yellow solution of the binuclear chlorocarbonyl $Rh_2Cl_2(CO)_4$ and the mixture is heated under reflux for 1 h the *trans*-$RhCl(CO)L_2$ complex, described above, is not formed in significant quantities. Somewhat surprisingly, only one phosphine per rhodium atom is taken up and the binuclear $Rh_2Cl_2(CO)_2L_2$ complex, with bridging chlorines, is formed. Presumably steric hindrance greatly reduces the rate of incorporation of a second mole of phosphine per rhodium atom. The microanalytical and molecular weight data (Table 2) shows the complex to be binuclear and in the ^1H n.m.r. spectrum the t-butyl hydrogens resonate as a doublet at 1.37 δ, ^3J(PH) = 13.7 Hz. The ^{31}P n.m.r. spectrum shows a doublet resonance at 80.0 δ with ^1J(RhP) = 174 Hz.

When a suspension of iridium trichloride in propan-2-ol was heated with the ligand (4 mole equivalents per iridium atom) and the resultant green slurry heated under reflux, a dark orange solution formed over 2 days. From this solution a five-coordinate iridium(III) dihydride $IrClH_2L_2$ was isolated as orange crystals. The formulation follows from the microanalytical data (Table 2) and the i.r. and n.m.r. data (Table 1). The i.r. spectrum shows a band at 273 cm^{-1} due to ν(Ir-Cl) and a band at 2300 cm^{-1} due to ν(Ir-H). The ^1H n.m.r. hydride resonance occurs at −32.6 δ, ^2J(PH) = 13 Hz and the virtually coupled 1 : 2 : 1 triplet pattern of the t-butyl hydrogens (Table 1) indicates mutually *trans*-phosphines. In fact the ligand L behaves very similarly to $t\text{-}Bu_2PPh$ towards iridium chloride and the complex $IrH_2Cl(t\text{-}Bu_2PPh)_2$ has very similar i.r. and n.m.r. parameters⁽⁶⁾. We thus formulate $IrClH_2L_2$ as the trigonal bipyramidal structure (*8*).



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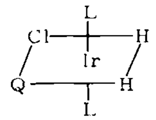
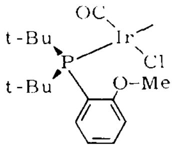


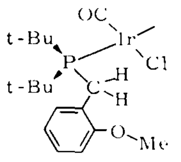
(9)

The somewhat less bulky phosphines $t\text{-}Bu_2PR$ (R = Me, Et, n-Pr) with iridium trichloride in propan-2-ol preferentially give 5-coordinate monohydrides $IrHCl_2(t\text{-}Bu_2PR)_2$⁽⁷⁾ and presumably the formation of dihydrides from $t\text{-}Bu_2PPh$ or L is a consequence of the greater steric bulk and therefore a greater relief of steric strain on replacing a second chlorine by hydrogen. As expected, IrH_2ClL_2 reacts rapidly with carbon monoxide to give the white complex (*9*, Q = CO) in a very similar manner to $IrH_2Cl(t\text{-}Bu_2PPh)_2$. For this complex, the very low value of 254 cm^{-1} for ν(Ir-Cl) is indicative of Cl *trans* to H and the two values of ν(Ir-H) 2360 and 2135 cm^{-1} and the value of ν(CO) at 1955 cm^{-1} are in agreement with this structure. The hydride resonances in the ^1H n.m.r. spectra occur at −8.75 (*trans*-CO) and −20.85 δ (*trans*-Cl) both doublets of triplets. Both the benzylic hydrogens and the t-butyl hydrogens resonate as 'virtually coupled' doublets of 1 : 2 : 1 triplets indicating mutually *trans* and strongly coupled phosphorus nuclei with no plane of symmetry through the phosphorus-iridium bonds. An analogous complex $IrH_2Cl(MeNC)L_2$ was prepared from methyl isocyanide and IrH_2ClL_2 and given an analogous configuration (*9*, Q = MeNC).

We have reported previously that when $t\text{-}Bu_2PC_6H_4OMe\text{-}2$ is added to a solution prepared by passing carbon monoxide through a boiling 2-methoxyethanol solution of sodium chloroiridate demethylation occurs and the yellow iridium(I) complex $\overline{Ir(CO)(t\text{-}Bu_2PC_6H_4O)}$ $(t\text{-}Bu_2PC_6H_4OH\text{-}2)$ is formed which, in air, gives the blood-red iridium(II) complex $\overline{Ir(t\text{-}Bu_2PC_6H_4O)}_2$ and, subsequently, other complexes(8). It was clearly therefore of interest to study the action of our new 2-methoxybenzylphosphine, L, on a similarly carbonylated solution of sodium chloroiridate. However, in this case demethylation did not occur and the pale yellow complex *trans*-$IrCl(CO)L_2$ was isolated readily. This formulation follows from the microanalytical, i.r. and ^1H n.m.r. data (Tables). The proton decoupled ^{31}P n.m.r. spectrum at *ca.* 300 K shows a broad ill-defined resonance at *ca.* 45 δ whilst at 233 K an *AB*-pattern; δ_A = 50.0, δ_B = 21.6 p.p.m. J(AB) = 307 Hz, and a singlet resonance at 49.0 δ are observed in the approximate intensity ratios of 1 : 1. We suggest that as with the analogous rhodium complex the two conformers present are (*5*) and either (*6*) or (*7*) (M = Ir). Thus in no instance did we observe demethylation of the ligand $t\text{-}Bu_2(2\text{-}MeO\text{-}5\text{-}MeC_6H_3CH_2)P$, L, by rhodium or iridium although, as reported, demethylation was the commonly observed reaction with $t\text{-}Bu_2PC_6H_4OMe\text{-}2$. We offer the following explanation for this difference in behaviour. Whereas in the case of $t\text{-}Bu_2PC_6H_4OMe\text{-}2$ complexed to an OC-Ir-Cl moiety, restricted rotation around the Ir-P and aryl-P bonds due to the bulky t-butyl groups will lead to a preferred conformation in which the ether oxygen is held in close proximity to the metal-chlorine bond, as shown in (*10*) this will not be the case with the ligand (L). The extra methylene group between the arene ring and the phosphorus donor atom allows the 2-methoxyphenyl group to point away from the metal, as shown in (*11*). With $t\text{-}Bu_2PC_6H_4OMe\text{-}2$ therefore O-metallation with loss of methyl chloride relieves the steric strain and occurs readily but with the ligand (L) complex formation can and does occur without demethylation.



(*10*)



(*11*)

Experimental

The apparatus and general techniques used in this work were the same as in other recent publications from this laboratory(2).

$[t\text{-}Bu_2(2\text{-}MeO\text{-}5\text{-}MeC_6H_3CH_2)PH]^+I^-$

A solution of $t\text{-}Bu_2PH$ (6.75 g, 46 mmol) in Me_2CO (10 cm^3) was added to a mixture of NaI (7.0 g, 51 mmol) and $2\text{-}MeO\text{-}5\text{-}MeC_6H_3CH_2Cl$ (7.9 g, 46 mmol) in Me_2CO (30 cm^3) at room temperature. The product precipitated as white microcrystals, m.p. 206–208° (dec); precipitation was complete after 2 h. Yield 19.7 g, 45 mmol, 98% (Found: C, 49.75; H, 7.25. $C_{17}H_{30}IOP$ calcd.: C, 50.0; H, 7.4%).

$t\text{-}Bu_2(2\text{-}MeO\text{-}5\text{-}MeC_6H_3CH_2)P$ (L)

A mixture of the above phosphonium salt (9.54 g, 23.4 mmol) in MeOH (20 cm^3) and KOH (2.62 g, 46.8 mmol) in degassed H_2O (15 cm^3) was shaken for 5 min. The product was extracted with Et_2O under N_2 and isolated by distillation as a colourless liquid, b.p. 100–103°/0.003 mmHg. Yield 5.58 g, 19.8 mmol, 85%.

trans-$RhCl_2L_2$

The ligand (0.72 g, 2.55 mmol) was added to a solution of hydrated rhodium trichloride (0.166 g, 0.64 mmol) in EtOH (20 cm^3) and the resultant mixture was shaken for 20 h. This gave the required product (0.37 g, 0.50 mmol, 79%) as green prisms.

$RhHCl_2L_2$

The ligand (1.23 g, 4.37 mmol) was added to a solution of hydrated rhodium trichloride (0.285 g, 1.09 mmol) in H_2O (1 cm^3) and propan-2-ol (10 cm^3) and the resultant red slurry heated under reflux for 2 h. The solution was then cooled to room temperature, giving the required product as green prisms (0.57 g, 0.78 mmol, 72%).

trans-$RhCl(CO)L_2$

Carbon monoxide was bubbled through a solution of $RhHCl_2L_2$ (0.36 g, 0.49 mmol) in C_6H_6 (30 cm^3). The solution, which rapidly became pale yellow, was then evaporated under reduced pressure to give the required product (0.27 g, 0.37 mmol, 75%) as yellow prisms from C_6H_6 : MeOH.

$Rh_2Cl_2(CO)_2L_2$

Carbon monoxide was bubbled through a solution of hydrated rhodium trichloride (0.44 g, 1.68 mmol) in EtOH (10 cm^3) at 60° for 3 h. The resultant pale yellow solution containing rhodium chlorocarbonyl was treated with the phosphine, L (1.03 g, 3.68 mmol) and the resultant mixture heated under reflux for 1 h, and then cooled to give the binuclear species (0.47 g, 0.52 mmol, 63%) as yellow prisms.

IrH_2ClL_2

The ligand, L, (1.07 g, 3.8 mmol) was added to a suspension of hydrated iridium trichloride (0.34 g, 0.94 mmol) in

Transition Met. Chem. 3, 169–171 (1978)

propan-2-ol (10 cm^3). The resultant green slurry was heated under reflux for 50 h to give a dark orange solution from which the required product (0.51 g, 0.64 mmol, 68%) separated as orange prisms on cooling.

$IrH_2Cl(CO)L_2$

Carbon monoxide was bubbled through a solution of IrH_2ClL_2 (0.22 g, 0.28 mmol) in C_6H_6 (10 cm^3) until it turned pale yellow (*ca.* 1 min). The required product was isolated by evaporation and recrystallization from C_6H_6 : MeOH. It formed white prisms (0.185 g, 0.23 mmol, 82%).

$IrH_2Cl(MeNC)L_2$

Methyl isocyanide (0.09 g, 2.2 mmol) was added to a solution of IrH_2ClL_2 (0.176 g, 0.22 mmol) in C_6H_6 (10 cm^3). The resultant colourless solution was evaporated under reduced pressure and the residue recrystallized from C_6H_6: MeOH to give the required product (0.17 g, 0.21 mmol, 93%) as white prisms.

trans-$IrCl(CO)L_2$

Carbon monoxide was bubbled through a refluxing solution of sodium chloroiridate (0.70 g, 1.36 mmol) in 2-methoxyethanol (15 cm^3) for 3 h. The resultant pale yellow solution was cooled and the ligand, L, (0.84 g, 3.0 mmol) added. The resultant solution was then heated under reflux for 1 h and cooled to *ca.* $-15°$ giving the required product (0.65 g, 0.79 mmol, 58%) as yellow plates.

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TMC 78/5

Zinc(II), Cadmium(II) and Mercury(II) Halide Pyrrolidine-2-selone Complexes*

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Summary

Reaction of zinc(II), cadmium(II) and mercury(II) halides with pyrrolidine-2-selone yields complexes of general formula ML_2X_2 (X = Cl, Br or I) which are monomeric, tetrahedral and Se-bonded to the metals. The comparison of their i.r. spectra with the spectrum of the free ligand confirms that the band at 1005 cm^{-1} in pyrrolidine-2-selone arises predominantly from the C=Se stretching vibration. The metal-halogen absorptions above 200 cm^{-1} are identified.

Introduction

Recently(1), we reported zinc(II), cadmium(II) and mercury(II) halide complexes containing pyrrolidine-2-thione

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