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# NEW ISOCYANIDE COMPLEXES OF RUTHENIUM(II) CONTAINING TRIPHENYLPHOSPHINE, TRIPHENYLARSINE AND TRIPHENYLSTIBINE

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## SUMMARY

The new complexes $Ru(CNEt)_2(EPh_3)_2X_2$ (where E = P, As or Sb and X = Cl or Br) have been prepared, and are found to exist in two isomeric forms. In one form the CNEt groups are *trans*, and in the other *cis*. The conversion of the *trans* to the *cis* isomer can be carried out either in the solid state or in solution. The structures of these complexes are discussed in the light of their vibrational spectra.

## INTRODUCTION

Despite the current interest in isocyanide complexes of the platinum group of metals[1-3], there have been few reports of ruthenium compounds containing isocyanide ligands since the complexes $RuX_2(CNR)_4$ (X = Cl, Br, I or CN; R = alkyl or aryl group) were described[4-6]. The reaction between ethyl isocyanide and complexes such as $RuX_2(PPh_3)_3$ (X = Cl or Br) has now been investigated, and the new compounds $Ru(CNEt)_2(EPh_3)_2X_2$ (E = P, As or Sb; X = Cl or Br) have been isolated. A preliminary account of this work has already been published[7].

## RESULTS AND DISCUSSION

The complex $RuCl_2(PPh_3)_3$, first described by Stephenson and Wilkinson[8], has been used extensively as an entry-point into ruthenium chemistry (see, for example, refs. 9 and 10). When a solution of $RuCl_2(PPh_3)_3$ in warm acetone is treated with ethyl isocyanide under nitrogen, the solution rapidly becomes paler and on cooling deposits yellow crystals of the complex *trans*-$Ru(CNEt)_2(PPh_3)_2Cl_2$. This compound is soluble in dichloromethane and chloroform, from either of which it can be crystallised by the addition of ether. The corresponding bromo-complex is obtained from $RuBr_2(PPh_3)_3$[8] in a similar reaction. However, attempts to recrystallise *trans*-$Ru(CNEt)_2(PPh_3)_2Br_2$ from chloroform/ether appear to cause halogen exchange between the complex and solvent, resulting in a mixed chlorobromo complex. This problem can be avoided by using bromoform in place of chloroform.

Ruthenium(II) triphenylarsine complexes analogous to $RuX_2(PPh_3)_3$ are unknown and in order to prepare the compounds *trans*-$Ru(CNEt)_2(AsPh_3)_2X_2$

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TABLE 1

ANALYTICAL DATA

| Compound | Colour | Analyses found (calcd.) (%) | | | |
|---|---|---|---|---|---|
| | | C | H | N | X[a] |
| *trans*-Ru(CNEt)$_2$(PPh$_3$)$_2$Cl$_2$ | Yellow | 62.9 | 4.9 | 3.4 | 8.7 |
| | | (62.5) | (5.0) | (3.5) | ( 8.8) |
| *trans*-Ru(CNEt)$_2$(PPh$_3$)$_2$Br$_2$ | Orange | 55.8 | 5.3 | 3.2 | 17.8 |
| | | (56.3) | (4.5) | (3.1) | (17.8) |
| *trans*-Ru(CNEt)$_2$(AsPh$_3$)$_2$Cl$_2$ | Orange | 56.6 | 4.7 | 3.0 | 8.1 |
| | | (56.4) | (4.5) | (3.1) | ( 7.8) |
| *trans*-Ru(CNEt)$_2$(AsPh$_3$)$_2$Br$_2$ | Red-brown | 51.8 | 4.1 | 2.8 | 16.2 |
| | | (51.3) | (4.1) | (2.8) | (16.2) |
| *trans*-Ru(CNEt)$_2$(SbPh$_3$)$_2$Cl$_2$ | Orange-pink | 50.9 | 4.2 | 2.8 | 7.1 |
| | | (51.0) | (4.0) | (2.8) | ( 7.2) |
| *trans*-Ru(CNEt)$_2$(SbPh$_3$)$_2$Br$_2$ | Red | 47.4 | 4.0 | 2.7 | 14.8 |
| | | (46.8) | (3.7) | (2.6) | (14.8) |
| *cis*-Ru(CNEt)$_2$(PPh$_3$)$_2$Cl$_2$ | Colourless | 62.2 | 5.0 | 3.7 | 9.0 |
| | | (62.5) | (5.0) | (3.5) | ( 8.8) |
| *cis*-Ru(CNEt)$_2$(PPh$_3$)$_2$Br$_2$ | Very pale yellow | 55.8 | 5.3 | 3.2 | 17.9 |
| | | (56.3) | (4.5) | (3.1) | (17.8) |
| *cis*-Ru(CNEt)$_2$(AsPh$_3$)$_2$Cl$_2$ | Pale yellow | 56.0 | 4.8 | 3.1 | 8.2 |
| | | (56.4) | (4.5) | (3.1) | ( 7.8) |
| *cis*-Ru(CNEt)$_2$(AsPh$_3$)$_2$Br$_2$ | Pale yellow | 51.2 | 4.2 | 3.0 | 16.4 |
| | | (51.3) | (4.1) | (2.8) | (16.3) |
| *cis*-Ru(CNEt)$_2$(SbPh$_3$)$_2$Cl$_2$ | Yellow | 50.9 | 4.3 | 3.0 | 7.1 |
| | | (51.0) | (4.1) | (2.8) | ( 7.2) |
| *cis*-Ru(CNEt)$_2$(SbPh$_3$)$_2$Br$_2$ | Yellow | 47.3 | 4.0 | 2.8 | 14.5 |
| | | (46.8) | (3.7) | (2.6) | (14.8) |

[a] X=Cl or Br

TABLE 2

$\nu$(NC) FREQUENCIES (cm$^{-1}$) IN THE INFRARED

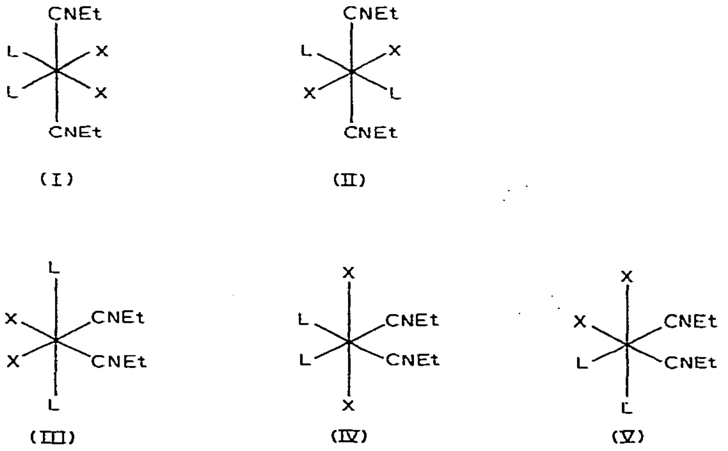
| Compound | Nujol Mull | Soln.[a] |
|---|---|---|
| *trans*-Ru(CNEt)$_2$(PPh$_3$)$_2$Cl$_2$ | 2146 s | 2151 s |
| *trans*-Ru(CNEt)$_2$(PPh$_3$)$_2$Br$_2$ | 2183 vw, 2135 s | 2141 s |
| *trans*-Ru(CNEt)$_2$(AsPh$_3$)$_2$Cl$_2$ | 2146 s | 2151 s |
| *trans*-Ru(CNEt)$_2$(AsPh$_3$)$_2$Br$_2$ | 2185 vw, 2140 s | 2148 s |
| *trans*-Ru(CNEt)$_2$(SbPh$_3$)$_2$Cl$_2$ | 2136 s | 2148 s |
| *trans*-Ru(CNEt)$_2$(SbPh$_3$)$_2$Br$_2$ | 2135 s | 2146 s |
| *cis*-Ru(CNEt)$_2$(PPh$_3$)$_2$Cl$_2$ | 2182 s, 2139 s, ~2110(sh)w | 2179 s, 2139 s |
| *cis*-Ru(CNEt)$_2$(PPh$_3$)$_2$Br$_2$ | 2186 s, 2137 s, ~2115(sh)w | 2178 s, 2138 s |
| *cis*-Ru(CNEt)$_2$(AsPh$_3$)$_2$Cl$_2$ | 2181 s, 2140 s, ~2110(sh)w | 2173 s, 2134 s |
| *cis*-Ru(CNEt)$_2$(AsPh$_3$)$_2$Br$_2$ | 2187 s, 2142 s, ~2115(sh)w | 2177 s, 2138 s |
| *cis*-Ru(CNEt)$_2$(SbPh$_3$)$_2$Cl$_2$ | 2165 s, 2127 s, ~2105(sh)w | 2167 s, 2130 s |
| *cis*-Ru(CNEt)$_2$(SbPh$_3$)$_2$Br$_2$ | 2168 s, 2121 s | 2168 s, 2131 s |

[a] Dichloromethane for the *cis* complexes and chloroform for all the *trans* complexes except *trans*-Ru(CNEt)$_2$(PPh$_3$)$_2$Br$_2$ for which bromoform was used. The *cis* complexes all exhibit weak absorptions at ca. 2210 and 2110 cm$^{-1}$ in solution.

(X=Cl or Br) it is necessary to react EtNC with the ruthenium(III) complexes $RuX_3(AsPh_3)_2(MeOH)$(X=Cl or Br)[8]; in this case the isocyanide is acting as both ligand and reducing agent, a technique frequently used in the preparation of isocyanide complexes[11]. The triphenylstibine complexes *trans*-$Ru(CNEt)_2(SbPh_3)_2X_2$ (X=Cl or Br) are formed when EtNC reacts with $RuCl_2(SbPh_3)_3$[8] or $RuBr_2(SbPh_3)_4$ in chloroform solution. $RuBr_2(SbPh_3)_4$, which does not appear to have been reported previously, is readily obtained from $RuCl_3 \cdot 3H_2O$ and $SbPh_3$ in the presence of a large excess of lithium bromide. Its formulation as a tetrakis(triphenylstibine) complex is supported by analytical data (see Experimental section).

A *trans* configuration is assigned to the EtNC groups in these complexes (for which analytical data are given in Table 1) on the basis of their IR spectra in the ν(NC) region (see Table 2). Only one strong absorption is observed, both in the solid state and in solution, and the similarity between the mull and solution frequencies suggests that the solid state structure persists in solution. The two configurations possible [(I) and (II)] for these *trans* complexes are illustrated in Fig. 1, which also lists the number of IR- and Raman-active vibrations of a given type expected on the basis of simple point-group theory. Both structures have been found in other, similar ruthenium(II) compounds containing nitrile[9] or carbon monoxide[10] ligands instead of isocyanides.

In principle, configurations (I) and (II) are readily distinguishable by, for exam-



| Configuration | Symmetry | ν(NC) | | δ(RuCN) | | ν(Ru–X) | | ν(Ru–L) | |
|---|---|---|---|---|---|---|---|---|---|
| | | IR | R | IR | R | IR | R | IR | R |
| (I) | $C_{2v}$ | 1 | 1 | 3 | 4 | 2 | 2 | 2 | 2 |
| (II) | $D_{2h}$ | 1 | 1 | 2 | 2 | 1 | 1 | 1 | 1 |
| (III) | $C_{2v}$ | 2 | 2 | 3 | 4 | 2 | 2 | 1 | 1 |
| (IV) | $C_{2v}$ | 2 | 2 | 3 | 4 | 1 | 1 | 2 | 2 |
| (V) | $C_1$ | 2 | 2 | 4 | 4 | 2 | 2 | 2 | 2 |

Fig. 1. The possible configurations for *trans*- and *cis*-$Ru(CNEt)_2L_2X_2$, where L=$PPh_3$, $AsPh_3$, or $SnPh_3$, and X=Cl or Br. The number of IR- and Raman-active vibrations of a given type are also listed for each configuration.

TABLE 3

LOW FREQUENCY INFRARED AND RAMAN DATA ($cm^{-1}$)[a]

| Compound | Configuration | δ(RuCN) IR | ν(Ru–X)[b] |  | Other Absorptions below 400 $cm^{-1}$ |  |
|---|---|---|---|---|---|---|
|  |  |  | IR | Raman | IR | Raman |
| *trans*-Ru(CNEt)$_2$(PPh$_3$)$_2$Cl$_2$ | (II) | [c] | 316 vs | 275(10) | 301 vs, 280 m | ~283(sh), 262(7.5), ~228(sh), 199(2.5), 187(1.5), 160(5), ~116(sh) |
| *trans*-Ru(CNEt)$_2$(PPh$_3$)$_2$Br$_2$ | (II) | [c] | 268 m<br>or 253 m | 210(3.5) | 295 vs, 280 w, 228 m | 262(sh), 260(3), 170 (10), 147(8.5), ~116(sh) |
| *trans*-Ru(CNEt)$_2$(AsPh$_3$)$_2$Cl$_2$ | (II) | 541 m, 528 m | 314 s | 275(5.5) | 337 vs, 330 m, 326 s, 283 m, 222 w | 258(3), 248(5.5), 218(4), 192(10) |
| *trans*-Ru(CNEt)$_2$(AsPh$_3$)$_2$Br$_2$[d] | (II) | 543 m, 535(sh) | ?266 w | [f] | 334 vs, 327 vs, 286 m, 266 w, 239 w | ~190, ~170 |
| *trans*-Ru(CNEt)$_2$(SbPh$_3$)$_2$Cl$_2$ | (II) | 544 m, 529 m | 311 s | 286(5.5) | 291 vs, 278 vs, 268 vs | 276(5.5), 266(4), 226(10), 218(sh), 189(8), 164 (2), ~115(sh) |
| *trans*-Ru(CNEt)$_2$(SbPh$_3$)$_2$Br$_2$[e] | (II) | 539(br) m | ~270(br) vs | [f] | 290 vs, 274 vs | 277(2), 267(2.5), 228(9), 191(6.5) 171(10), 112(6.5) |
| *cis*-Ru(CNEt)$_2$(PPh$_3$)$_2$Cl$_2$ | (III) | [c] | 283 vs<br>260 s<br>or 257(sh) | 286(6)<br>257(10) | 266 vs, 236 w, 228 m, 196 m | 231(5), 198(3), ~188(sh), 158(9) |
| *cis*-Ru(CNEt)$_2$(PPh$_3$)$_2$Br$_2$ | (III) | [c] | [f]<br>188 vs | 193(8.5)<br>~188 (sh) | 330 w, 312 w, 256 vs, 168 w, 154 w, 143 w, 118 m | 285(3), 261(10), ~188(sh), 156(10) |
| *c*[illegible]-Ru(CNEt)$_2$(AsPh$_3$)$_2$Cl$_2$ | (III) | 556 mw, 524 mw | 284 m | 289(2) | 332 vs, 326 s, 265 m | 334(1), 325(1), 266(4), 241(10), 213(3), 186(0·5), 178(0.5), 138(8) |
| *cis*-Ru(CNEt)$_2$(AsPh$_3$)$_2$Br$_2$ | (III) | 553 mw, 518 mw | 190 ms | 191(10) | 331(br) vs, 325 m, 261 w, 242 m, 214 m | 264(4), 247(7), 217(2.5) |
| *cis*-Ru(CNEt)$_2$(SbPh$_3$)$_2$Cl$_2$ | (III) | 553 m, 519 m, 499 w | ?284 vs | ?284(4) | 336 w, 328 m, 268 vs, 190 m | 269(3.5), 224(10), 189(10), 168(4), 118(9) |
| *cis*-Ru(CNEt)$_2$(SbPh$_3$)$_2$Br$_2$ | (III) | 549 mw, 517 m | [f] | [f] | 334 w, 282 vs, 267 vs, 184 m | 285(3), 267(4), 227(10), ~200(sh), 188(7.5), 172(vw), 119(8.5) |

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[a] IR data for nujol mulls; Raman for solids. v very, s strong, m medium, w weak, sh shoulder, br broad. Relative intensities of the Raman lines are given in parentheses. [b] X=Cl or Br. [c] Obscured by PPh$_3$ bands. [d] Strongly absorbs the Raman exciting line. [e] Decomposes slowly in Raman beam. [f] No definite assignment can be made.

ple, the number of δ(RuCN) and ν(Ru–X) vibrations found in the IR and Raman spectra of the complexes. In Table 3 are given some assignments for these modes. Absorptions in the region 550–500 cm$^{-1}$ have been assigned to δ(RuCN) by analogy with cobalt[12] and other ruthenium[13] isocyanide complexes. It can be seen that the all *trans* configuration (II) is indicated by the number of δ(RuCN) absorptions when these are not obscured by bands arising from the other ligands present. Where assignments of ν(Ru–X) can be made, there appear to be no IR and Raman coincidences. This also supports the centrosymmetric structure (II). Considerable difficulty was experienced in interpreting the low frequency vibrational spectra, and some of the ν(Ru–X) assignments are tentative. In the complexes *trans*-$Ru(CNEt)_2(AsPh_3)_2X_2$ (X = Cl or Br), the strong IR absorptions at 337 and 334 cm$^{-1}$, respectively, probably arise from ν(Ru–As) vibrations. Metal–arsenic vibrations have been located in this region for arsine complexes of osmium, iridium and platinum[14]. Although the evidence is by no means conclusive, it appears that these *trans* complexes have the structure (II) on the basis of their vibrational spectra.

When the *trans* complexes are heated dry at ca. 240° in air, they isomerise to *cis* complexes (*i.e.* ones in which the EtNC groups are *cis*). In the case of the triphenylstibine complexes, isomerisation is accompanied by a considerable amount of decomposition. A more suitable method of effecting isomerisation is to reflux the *trans* isomer in a high-boiling solvent such as 2-methoxyethanol (although for *trans*-$Ru(CNEt)_2(PPh_3)_2Cl_2$, isomerisation occurs in refluxing methanol). The *cis* isomers can be recrystallised from dichloromethane/ether to give colourless to yellow airstable crystals. Chloroform should be avoided as a recrystallisation solvent for the *cis* chloro-complexes, since it appears that they form adducts with it. Thus the IR spectra of the chloroform/ether recrystallised complexes show one or two strong absorptions in the region 760–730 cm$^{-1}$ [where ν(C–Cl) vibrations occur] which are absent from the spectra of dichloromethane/ether recrystallised samples. In the triphenylarsine and triphenylstibine complexes this chloroform is removed by pumping on the adducts; for the triphenylphosphine complex, though, both IR spectra and analytical data indicate that the chloroform remains even after prolonged pumping. It is, however, readily lost when the adduct is recrystallised from dichloromethane/ether.

The *cis* arrangement of the EtNC ligands in these isomers is evident from their IR spectra (Table 2) which show two strong absorptions assignable to ν(NC), that at higher frequency being due to the symmetric ν(NC) vibration. The positions of these bands show little sensitivity to a change in either the halogen or the Group VB ligand, especially in solution. Referring to Fig. 1 and Table 3, it can be seen that the number of δ(RuCN) absorptions observed in the IR is usually two, and that this does not enable the three configurations (III)–(V) to be distinguished. However, the ν(Ru–X) bands are much more informative. Firstly, they occur at much lower frequencies than in the *trans* complexes, which indicates that structure (IV), in which the halogen atoms are *trans*, is most unlikely. Furthermore, the existence of IR and Raman coincidences among these absorptions again militates against structure (IV). Chlorine *trans* to phosphine or arsine ligands usually gives rise to ν(Ru–Cl) absorptions below 300 cm$^{-1}$; however, for triphenylphosphine and triphenylarsine, it has been pointed out that these vibrations can (and do) occur well above 300 cm$^{-1}$ [15]. For this reason structure (III) is preferred to structure (V) since the latter contains one halogen *trans* to $EPh_3$ (E = P, As or Sb).

Isomerisations such as those described here have been reported for the nitrile complexes $Ru(NCR)_2(PPh_3)_2Cl_2$ ($R=CH_3$ or $CH_2=CH$) and configurations (II) and (III) were assigned to the *trans* and *cis* isomers, respectively, on the basis of IR evidence[9]. Similar isomerisations are known to occur in a variety of octahedral ruthenium(II) carbonyl complexes, the structures of the different isomers having been investigated by both NMR and IR techniques[8,10,16].

## EXPERIMENTAL

Microanalyses (Table 1) were carried out by Alfred Bernhardt, W. Germany. Infrared spectra were recorded on Perkin–Elmer 457 and RIIC FS-520 spectrometers, and Raman spectra on a Cary 81 instrument fitted with a Coherent Radiation krypton ion laser.

### *Preparation of starting materials*

Ethyl isocyanide was obtained from *N*-ethylformamide by the method of Casanova *et al.*[17]. The complexes $RuX_2(PPh_3)_3$ (X = Cl or Br), $RuX_3(AsPh_3)_2(MeOH)$ (X = Cl or Br) and $RuCl_2(SbPh_3)_3$ were prepared according to Stephenson and Wilkinson[8]. The preparation of $RuBr_2(SbPh_3)_4$ is described below.

### *Dibromotetrakis(triphenylstibine)ruthenium(II)*

$RuCl_3 \cdot 3H_2O$ (0.20 g, 0.77 mmole) and lithium bromide (2.00 g, 23 mmoles) were shaken in methanol (50 ml) for 5 min. Triphenylstibine (1.7 g, 4.8 mmoles) was added and the shaking continued for a further 5 min. The solution was filtered and allowed to stand at room temperature overnight. The dull purple solid which precipitated was filtered off and washed with methanol. Yield 705 mg (55%), (Found: C, 47.4; H, 4.0; Br, 14.8; N, 2.7%. $C_{72}H_{60}Br_2RuSb_4$ calcd.: C, 46.8; H, 3.7; Br, 14.8; N, 2.6%.)

### *trans-Bis(ethyl isocyanide) complexes*

*trans-Bis(ethyl isocyanide)bis(triphenylphosphine)dichlororuthenium(II).* $RuCl_2(PPh_3)_3$(200 mg, 0.21 mmole) was dissolved in ca. 60 ml of warm acetone under nitrogen. Ethyl isocyanide (35 mg, ~0.05 ml; 0.63 mmole) was added and the solution soon became paler, dirty yellow crystals being precipitated. The mixture was cooled and the product filtered off and washed with ethanol and ether. Yield 140 mg (83%). It was recrystallised from $CHCl_3/Et_2O$ to give pale yellow needles.

*trans-Bis(ethyl isocyanide)bis(triphenylphosphine)dibromoruthenium(II).* $RuBr_2(PPh_3)_3$ (500 mg, 0.48 mmole) in 60 ml of hot acetone under nitrogen was treated with EtNC (85 mg, ~0.11 ml; 1.54 mmoles). The orange solution which soon formed was cooled to room temperature and 200 ml of ether was added, causing the precipitation of the product as orange crystals. Yield 340 mg (80%). It was recrystallised from $CHBr_3/Et_2O$. For the difficulties encountered in the purification of this compound, see text.

*trans-Bis(ethyl isocyanide)bis(triphenylarsine)dichlororuthenium(II).* $RuCl_3(AsPh_3)_2(MeOH)$ (500 mg, 0.59 mmole) and EtNC (142 mg, 0.19 ml, 2.6 mmoles) were refluxed together under nitrogen in 10 ml methanol for 1 h. The mixture was cooled and the brownish-orange crystals of product filtered off. Yield 150 mg (29%). They were recrystallised from $CHCl_3/Et_2O$.

*trans-Bis(ethyl isocyanide)bis(triphenylarsine)dibromoruthenium(II).* $RuBr_3(AsPh_3)_2(MeOH)$ (500 mg, 0.51 mmole) and EtNC (170 mg, 0.22 ml, 3.1 mmoles) in 10 ml methanol were refluxed together under nitrogen for one hour. After cooling, the grey-pink microcrystals of product were filtered off. These were purified by dissolving in chloroform (to give a deep purple solution), filtering, and adding ether to the filtrate to crystallise the compound. This process was repeated until the purple colour disappeared. Yield of red-brown crystals 135 mg (27%).

*trans-Bis(ethyl isocyanide)bis(triphenylstibine)dichlororuthenium(II).* $RuCl_2(SbPh_3)_3$ (250 mg, 0.20 mmole) was dissolved in chloroform (15 ml) under nitrogen and the solution treated with EtNC (34 mg, 0.05 ml, 0.62 mmole). After half an hour reflux, the solution was cooled and filtered. Addition of ether to the orange-pink filtrate gave orange-pink crystals of product. Yield 100 mg (55%). It was recrystallised from $CHCl_3/Et_2O$.

*trans-Bis(ethyl isocyanide)bis(triphenylstibine)dibromoruthenium(II).* $RuBr_2(SbPh_3)_4$ (290 mg, 0.17 mmole) and EtNC (30 mg, 0.04 ml, 0.54 mmole) were refluxed under nitrogen in chloroform (15 ml) for 40 min. The deep purple solution became red during this time. It was then cooled and filtered, and ether added to the filtrate to give red crystals of the product. Yield 110 mg (59%). Recrystallisation was from $CHCl_3/Et_2O$.

### *cis-Bis(ethyl isocyanide)complexes*

These are best prepared by refluxing the corresponding *trans* complex in 2-methoxyethanol (10 ml for every 100 mg of complex) for three quarters of an hour under nitrogen, and if necessary adding ether to the cooled solution to crystallise the product. Yields of the *cis* isomers are in the range 55–90%, and they should be recrystallised from dichloromethane/ether, since the chloro-complexes form adducts with chloroform (see text).

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## REFERENCES

1 A. Araneo, F. Bonati and G. Minghetti, *J. Organometal. Chem.*, 25 (1970) C25.
2 B. Crociani, T. Boschi and M. Nicolini, *Inorg. Chim. Acta*, 4 (1970) 577.
3 E. M. Badley, J. Chatt and R. L. Richards, *J. Chem. Soc. A*, (1971) 21.
4 L. Malatesta, G. Padoa and A. Sonz, *Gazz. Chim. Ital.*, 85 (1955) 1111.
5 L. Malatesta and G. Padoa, *Rend. Ist. Lombardo Sci. Pt. I*, 91 (1957) 227.
6 W. Hieber and H. Heusinger, *J. Inorg. Nucl. Chem.*, 4 (1957) 179.
7 B. E. Prater, *J. Organometal. Chem.*, 27 (1971) C17.
8 T. A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 28 (1966) 945.
9 J. D. Gilbert and G. Wilkinson, *J. Chem. Soc. A*, (1969) 1749.
10 B. R. James and L. D. Markham, *Inorg. Nucl. Chem. Lett.*, 7 (1971) 373.
11 L. Malatesta and F. Bonati, *Isocyanide Complexes of Metals*, Wiley, New York, 1969, p. 24.

12 P. M. Boorman, P. J. Craig and T. W. Swaddle, *Can. J. Chem.*, 48 (1970) 838.
13 B. E. Prater, *J. Organometal. Chem.*, 33 (1971) 215.
14 J. Chatt, G. J. Leigh and D. M. P. Mingos, *J. Chem. Soc. A*, (1969) 1674.
15 T. A. Stephenson, *J. Chem. Soc. A*, (1970) 889.
16 B. F. G. Johnson, R. D. Johnston, J. Lewis and I. G. Williams, *J. Chem. Soc. A*, (1971) 689.
17 J. Casanova, Jr., R. E. Schuster and N. D. Werner, *J. Chem. Soc.*, (1963) 4280.