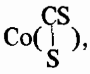
the CS_2 itself, coordinated in different ways to the cobalt atoms. The C atom, even when it is part of the heavy-atom framework as isolated atom, comes from the CS_2, as demonstrated by the IR spectroscopic analysis of the vibration of the carbide C atom of $Co_6C(CO)_{12}S_2$ [5].

The reaction mechanism is certainly very complex but it could be rationalised, at least at initial stages, according to the experimental evidence, in terms of formation of a monometallic intermediate $(CO)_3$-  $Co(\overset{CS}{\underset{S}{|}})$, which can react further with the excess of $Co_2(CO)_8$; giving rise in particular to more stable Co_3E structure. Among them, $SCo_3(CO)_9$ seems to play an important role in the formation paths of the reaction products, for it has been identified as the main product at the beginning of the reaction.

The different ways of coordination and fragmentation of CS_2, as shown by the structures of the reaction products, point out that this reaction is a good example of the activation of a not very reactive molecule, like CS_2, by cobalt carbonyls.

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Influence of the Solvent on the Reactivity of $Co^IX(PMe_3)_3$ with Ethylene: Synthesis, Molecular and Solid State Structure of $[Co(PMe_3)_3(C_2H_4)(CH_3CN)]BPh_4, CH_3CN$

BRIGITTE CAPELLE, MICHÈLE DARTIGUENAVE, YVES DARTIGUENAVE

Laboratoire de Chimie de Coordination du C.N.R.S. associé à l'Université P. Sabatier, 205 Route de Narbonne, Toulouse 31140, France

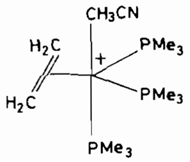
and ANDRÉ BEAUCHAMP

Department de Chimie, Université de Montreal, Montreal, Que., Canada

The importance and hardly explored role played by the solvents in the $Co^IX(PR_3)_3$ chemistry [1], the use of such complexes as catalysts due to their analogy with Wilkinson's catalyst $RhCl(PPh_3)_3$ are the *raison d'être* of investigating their chemistry.

Reaction of $CoBr(PMe_3)_3$ with ethylene has been followed in various solvents, such as acetone, ether, alcohol and a reversible color change of the solutions has been observed at very low temperature (–70 °C). However, no compound can be isolated.

When CH_3CN is used as solvent, the reversible color change is observed at 0 °C – the blue green solution turns yellow brown – indicating the formation of diamagnetic species (by NMR) but no solid can be obtained. Adding $NaBPh_4$ in methanol precipitates at –70 °C an orange diamagnetic Co(I) complex, which analyses as $[Co(PMe_3)_3(C_2H_4)(CH_3CN)]$-$BPh_4$, CH_3CN. The crystal structure confirms the presence of two molecules of acetonitrile, one in the coordination sphere of Co(I) and one in the lattice. The inner coordination sphere around the cobalt atom approximates a trigonal bipyramid with the ethylene group lying in the equatorial plane and the acetonitrile ligand occupying one axial position as shown in the figure:



Rhenium(III) and (V) Complexes with Schiff Bases

A. MARCHI, A. DUATTI, R. ROSSI, L. MAGON

Istituto Chimico dell'Università di Ferrara, Ferra, Italy

E. RONCARI and U. MAZZI

Laboratorio di Chimica e Tecnologia dei Radioelementi del C.N.R., Padua, Italy

Some rhenium(V) complexes with Schiff base (S.B.) of the type *cis* or *trans*-$ReOX_2$(S.B.)PPh_3 and ReOX$(S.B.)_2$ (X = Cl or Br and S.B. = N-methylsalicylideneiminate (Me-sal), N-phenylsalicylideneiminate (Ph-sal), half N,N′-ethylenebis(salicylideneiminate) (half sal_2en) or 8-hydroxyquinolinate-(Oxine)) have been already published [1, 2]. In this note we report the results of the reactions between $ReOX_2$(S.B.)PPh_3 and dimethylphenylphosphine (PMe_2Ph). By reaction of *cis* or *trans*-$ReOX_2$(S.B.)-PPh_3 with an excess (1:8) of PMe_2Ph in dry benzene

TABLE I.

Complex	M.p.	colour	μ(eff.)	νRe=O	νC=N	νC–O	νRe–X
$ReCl_2$(Me-sal)$(PMe_2Ph)_2$	183	red	2.1		1589	1297	308
$ReBr_2$(Me-sal)$(PMe_2Ph)_2$	204	red	2.0		1590	1289	
$ReCl_2$(Ph-sal)$(PMe_2Ph)_2$	207	red	2.1		1590	1288	310
$ReBr_2$(Ph-sal)$(PMe_2Ph)_2$	190	red	2.0		1588	1286	
$Re_2Cl_4(sal_2en)(PMe_2Ph)_4$	199	red	2.0		1605	1300	308
cis-$ReOCl_2$(Me-sal)PMe_2Ph	182	light green	diam.	965	1610	1285	320, 292
trans-$ReOCl_2$(Me-sal)PMe_2Ph	179	dark green	diam.	975	1609	1290	308
cis-$ReOCl_2$(Ph-sal)PMe_2Ph	229	bright green	diam.	976	1600	1290	318, 273
cis-$ReOCl_2$(oxine)PMe_2Ph	274	dark green	diam.	962		1316	329, 290
trans-$ReOCl_2$(oxine)PMe_2Ph	258	dark green	diam.	974		1319	300
$Re_2O_2Cl_4(sal_2en)(PMe_2Ph)_2$	241	emerald green	diam.	960	1600	1285	321

the *trans*-ReX_2(S.B.)$(PMe_2Ph)_2$ complexes were obtained (save when S.B. = Oxine), with a reduction of rhenium from (V) to (III). The reaction goes through the formation of *cis* or *trans*-$ReOX_2$(S.B.)PMe_2Ph, according to the starting isomer, where the substitution of PPh_3 with PMe_2Ph is observed.

$$\mathrm{ReOX_2(S.B.)PPh_3} \xrightarrow[\mathrm{(PhH)}]{\mathrm{PMe_2Ph}}$$

$$\mathrm{ReOX_2(S.B.)PMe_2Ph} \xrightarrow[\mathrm{(PhH)}]{\mathrm{PMe_2Ph}} \mathrm{ReX_2(S.B.)(PMe_2Ph)_2}$$

The intermediate complexes were isolated only when the *cis* and *trans*-$ReOCl_2$(Me-sal)PPh_3, *cis*-ReOCl/(Ph-sal)/PPh_3, *trans*-$Re_2O_2Cl_4/(sal_2en)/(PPh_3)$ and *cis* and *trans*-$ReOX_2$(oxine)PPh_3 starting complexes were used. The *cis* isomers, with the exception of the complexes with Oxine ligand, were collected only when the reaction was carried out at room temperature. We can notice that the substitution of PPh_3 keeps the conformation unchanged. When 8-hydroxyquinolinate complexes are used only the substitution occurs and the reduction of rhenium involves the leaving of this ligand and the formation of the known $ReX_3(PMe_2Ph)_3$ complexes.

The reduction occurs with all the other complexes, even though the reaction time is very different according to the compound symmetry and, with subordinate importance, to the used Schiff base. *Cis* derivatives in general react very easily in respect to *trans* analogues as well as Ph-sal complexes in respect to the sal_2en or Me-sal analogues. It is important to notice that both *cis* and *trans* rhenium(V) complexes give rise to reduced complexes with the same *trans* configuration.

The characterization of all the complexes was performed by elemental analysis, magnetic susceptibility measurements in solid and in solution, i.r. spectra. In Table I some general properties and important i.r. frequencies are reported.

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Solvent Dependent Stereochemistry of Cyanide Anation of Some Chromium(III) Complexes

PIETRO RICCIERI and EDOARDO ZINATO

Dipartimento di Chimica, Università di Perugia, 06100 Perugia, Italy

The usual synthetic route to acidoamminechromium(III) ions is replacement of H_2O ligands by anionic groups [1]. So far, cyanoammine complexes have not been reported; a possible reason is that cyanide cannot be bound to chromium by such a procedure, as deprotonation of coordinated water by this strongly basic anion prevents substitution in both aqueous and nonaqueous media. An alternative reaction was therefore sought to obtain the previously unknown *trans*- and *cis*-$Cr(NH_3)_4(CN)_2^+$ species, particularly in order to investigate their