TABLE I. Some Representative Complexes of the Ligand TPyEA.

	μ_{eff} μ_B	Coordination Geometry
$\{V(NCS)_2(TPyEA)\}$	3.81	octahedral
$[CrBr(TPyEA)]BPh_4 \cdot C_2H_5OH$	4.83	trig. bipy ⟷ square pyr.
$[MnBr(TPyEA)]BPh_4 \cdot 0.5CH_2Cl_2$	5.86	trigonal bipyramidal
$[FeCl(TPyEA)]BPh_4 \cdot 0.5CH_2Cl_2$	5.50	trigonal bipyramidal
$[Co(NCS)(TPyEA)]BPh_4$	4.43	trigonal bipyramidal
$[Co(TPyEA)](BPh_4)_2$	4.22	trigonal pyramidal
$[Co(TPyEA)]CoBr_4$	4.48	trig. pyr. + tetrahed.
[NiBr(TPyEA)]BPh4	3.26	trigonal bipyramidal
$[Cu(ClO_4)(TPyEA)]ClO_4$	1.88	trig. bipy. ⟷ square pyr.

The formulae of some representative complexes are reported in Table I. The assignment of the coordination geometry (Table I) is straightforward for the complexes of vanadium(II), manganese(II), iron(II), and nickel(II) on the basis of their physicochemical properties. The chromium(II) and copper(II) complexes, which are five-coordinate, presumably possess geometries intermediate between a trigonal bipyramid and a square pyramid.

Cobalt(II) complexes with different stoichiometries have been obtained depending on the starting materials and experimental procedures. The complexes with formulae $[Co(TPyEA)]Y_2$ ($Y = BPh_4, BF_4, ClO_4$) and $[Co(TPyEA)][MX_4]$ ($M = Co$, $X = Br, I$; $M = Zn$, $X = Br$) possess some unusual properties. As the ligand is potentially tetradentate, the coordination number of cobalt(II) cannot be more than four. However the electronic spectra of solid complexes as well as of the acetone and methanol solutions are typical of five-coordinate trigonal bipyramidal complexes of high-spin cobalt(II) [3] and are close to the spectrum of the five-coordinate $[Co(NCS)(TPyEA)]BPh_4$ derivative. A trigonal pyramidal geometry is tentatively assumed for the $[Co(TPyEA)]^{2+}$ cation in which the apical nitrogen atom averages the donor strength of two donors in an axially elongated trigonal bipyramidal geometry.

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Interaction of Dicobaltoctacarbonyl with Some Organic Solvents

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$Co_2(CO)_8$ is known to have different chemical behaviour when it is dissolved in common organic solvents, according to their properties.

Hydrocarbon solvents do not react with the solute: anyway, an equilibrium is established between at least three isomeric forms of $Co_2(CO)_8$, one with bridging COs (the only form present in solid state), the others with all COs terminal [1].

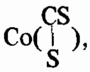
Solution in solvents which are hard Lewis bases, B, gives rise to a disproportionation reaction [2], whose general stoichiometry is:

$$3\,Co_2(CO)_8 + 12\,B \rightarrow 2[CoB_6^{++}][Co(CO)_4^-]_2 + 8CO$$

The kinetic behaviour is very complicated and suggests the presence of several competing mechanisms, involving CO dissociation, base coordination and electron transfer [3]. The reaction rates are sensitive more to the steric characteristic of the base than to its basicity or to its dielectrinc constant.

When $Co_2(CO)_8$ is dissolved in CS_2 at room temperature, it reacts slowly with the solvent to yield a great variety of C–, S– or C_xS_y– containing cobalt carbonyl derivatives [4].

The most part of them shows structures in which a particular stable pyramidal unit Co_3E ($E = C$ or S) is present. The pyramids are linked by metal–metal bond or by groups (or atoms) formed from CS_2 or by 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^I-$X(PMe_3)_3$ with Ethylene: Synthesis, Molecular and Solid State Structure of $[Co(PMe_3)_3(C_2H_4)(CH_3CN)]BPh_4, CH_3CN$

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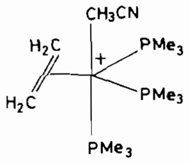
The importance and hardly explored role played by the solvents in the $Co^IX(PR_3)_3$ chemistry [1], the use of such complexes as catalysts due to their analogy with Wilkinson's catalyst $RhCl(PPh_3)_3$ are the *raison d'être* of investigating their chemistry.

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

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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