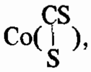
the CS_2 itself, coordinated in different ways to the cobalt atoms. The C atom, even when it is part of the heavy-atom framework as isolated atom, comes from the CS_2, as demonstrated by the IR spectroscopic analysis of the vibration of the carbide C atom of $Co_6C(CO)_{12}S_2$ [5].

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.

References

1 G. Bor, U. K. Dietler and K. Noak, *J. Chem. Soc. Chem. Comm.*, 914 (1976), and references therein.
2 W. Hieber, J. Sedlmeier and W. Abeck, *Chem. Ber.*, *86*, 700 (1953).
3 E. Mentasti, E. Pelizzetti, R. Rossetti and P. L. Stanghellini, *Inorg. Chim. Acta*, *22*, 19 (1977), and *25*, 7 (1977).
4 G. Bor, G. Gervasio, R. Rossetti and P. L. Stanghellini, *J. Chem. Soc. Chem. Comm.*, 841 (1978), and references therein.
5 G. Bor and P. L. Stanghellini, *J. Chem. Soc. Chem. Comm.*, 886 (1979).

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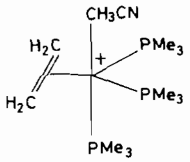
The importance and hardly explored role played by the solvents in the $Co^IX(PR_3)_3$ chemistry [1], the use of such complexes as catalysts due to their analogy with Wilkinson's catalyst $RhCl(PPh_3)_3$ are the *raison d'être* of investigating their chemistry.

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$_2$en) 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