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SOME ASPECTS OF THE CHEMISTRY OF PHOSPHINE–CYANIDE COMPLEXES OF TRANSITION METALS

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Studies of the cyanide complexes of transition metals are of considerable current interest, attention being paid to synthetic chemistry[1,2] and problems of catalysis[3] as well as to bonding characteristics of the cyanide group[4]

The bonding properties of the cyanide group in transition metal complexes appear to be a function of both σ-donor and π-acceptor abilities This situation places the cyanide group in a rather peculiar position as a mononegative ligand The relative importance of these two extreme types of bonding is difficult to evaluate and it is reasonable to think that it will depend on the total intramolecular environment and the oxidation state of the metal atom

In consideration of the great parallel interest in the chemistry of the phosphine complexes of transition metals, we have initiated comparative studies on the effect of CN^- ligand on the general properties of mixed cyanide–phosphine complexes[5–9] The present paper is an extension of our previous work, with the primary objective being to study the effect of the CN^- group on the stability as well as on the reactivity of such complexes

A RELATIVE STABILITIES OF 4- AND 5-COORDINATE COMPLEXES

The reaction of $Ni(CN)_2$ with tertiary phosphines PR_3 (R = alkyl, aryl), in addition to the planar complexes $Ni(CN)_2P_2$, generally yields the low-spin tris-phosphine complexes $Ni(CN)_2P_3$ (P = phosphorus atom of a tertiary phosphine) Equilibria of the type

$$Ni(CN)_2P_3 \rightleftarrows Ni(CN)_2P_2 + P$$

are present in solution[5,7] The stability of the 5-coordinate complexes depends on the nature of the organic substituent R and follows the order $PEt_2Ph > PEt_3 \sim PEtPh_2 > PPr^n{}_3 \sim PBu^n{}_3$ This order does not correlate well with the size of the phosphines and must be attributed to electronic effects of the R substituent. The complexes with PPh_3 and PCy_3 are extremely unstable (Cy = cyclohexyl)

The reactions of NiX_2 (X = halide, NCO, NCS) with tertiary phosphines generally yield 4-coordinate complexes $NiX_2(PR_3)_2$ (even in excess of the phosphine)[5] Only the phosphines PMe_3 (ref. 10), 2-phenylphosphindoline and 9-phosphofluorene[11] can give 5-coordinate low-spin NiX_2P_3 complexes

With the secondary phosphines HPR_2, complexes NiX_2P_3 can be obtained[12] not only when X = CN but even when X = Cl, Br, I Spectrophotometric evaluation of the stability of these complexes towards the dissociation into NiX_2P_2 and phosphine reveals the sequence $HPEt_2 > HPEtPh > HPPh_2 > HPPhCy$ With the phosphine $HPCy_2$, the complexes NiX_2P_3 have been observed only for X = CN

The coordinating properties in the corresponding cobalt(II) complexes are similar to those described for nickel(II), although cobalt appears to attain 5-coordination more readily Thus tertiary phosphines can yield the CoX_2P_3 complexes not only[8] when X = CN, but also[13] when X = NCS Again, the complexes with PCy_3 and PPh_3 are extremely unstable The phosphines 2-phenyl-phosphindoline, 9-phosphofluorene[11], PMe_2Ph and PMe_3 (ref 14) also yield CoX_2P_3 complexes for X = Br Secondary phosphines easily give the CoX_2P_3 complexes even when X = halogen It is again found that CN^- increases the stability of the 5-coordinate complexes Thus with the phosphine $HPCy_2$, the complexes can be obtained[12] for X = CN (or NCS) and not for X = Br

The data presented here show that the cyanide group may be of critical importance in determining the stability of MX_2P_3 complexes In fact, some of the complexes can be formed only for X = CN When they are also given by X = halogen, the corresponding cyanides always prove to be much more stable

The electronic factors which depend on the nature of the organic substituent R appear to be of minor importance and are evident only in the tertiary phosphine complexes

Much more important appear to be steric effects depending upon the size of the phosphines, as is clearly shown by the instability of the cyanide complexes with PCy_3, PCy_2Et and PPh_3 It is concluded that the size of the phosphines[15] is the factor which primarily determines the stability of the MX_2P_3 complexes. From this point of view the phosphines mentioned above can be divided into three classes of compound.

(*i*) Phosphines with critical size PCy_3, PCy_2Et, PPh_3 The tris-phosphine complexes are unstable even when X = CN

(*ii*) Phosphines with intermediate size PEt_3, PEt_2Ph, $PEtPh_2$, PEt_2Cy, $PMePh_2$, $PPr^n{}_3$, $PBu^n{}_3$, $HPCy_2$ In this case, steric effects can be compensated for by good bond energies, which can arise from the binding of CN groups Only the complexes $M(CN)_2P_3$ are stable

(*iii*) Phosphines with relatively small sizes PMe_3, PMe_2Ph, 2-phenylphosphindoline, 9-phosphofluorene and secondary phosphines with the exception of $HPCy_2$ The complexes MX_2P_3 can be stable even when X = halogen

The unique role played by the CN group in promoting stabilization of MX_2P_3 complexes is also apparent in the chemistry of the ditertiary phosphine complexes of nickel(II) and cobalt(II) The metal halides react with the diphosphines $Ph_2P(-CH_2-)_nPPh_2$ (diphosph, n = 2, 3, 4) giving either[16–18] 4-coordinate complexes MX_2(diphosph) or[19] ionic 5-coordinate complexes $[MX(diphosph)_2]X$ When X is the CN group, the stable 5-coordinate complexes shown in Fig 1 are obtained, in which the characteristic $M(CN)_2P_3$ grouping given by the tertiary phosphines is maintained[6,8,9]

The stabilization of 5-coordination by CN^- found for the nickel(II) and cobalt(II) complexes is also evident in the complexes of cobalt(I) and rhodium(I) Thus, the complex

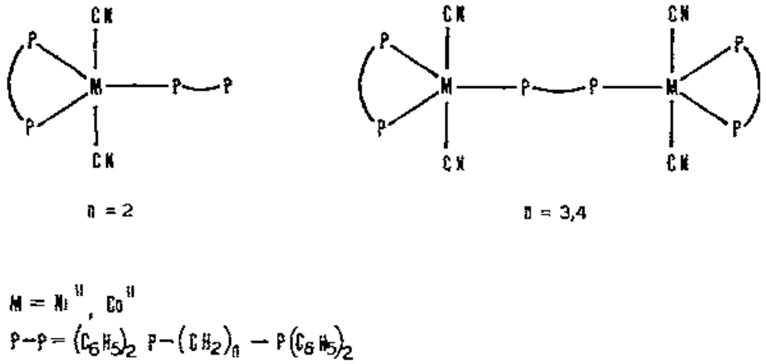


Fig 1 Schematic representation of the structure of 5-coordinate complexes $M(CN)_2(diphosph)_2$ and $[M(CN)_2(diphosph)_{1.5}]_2$

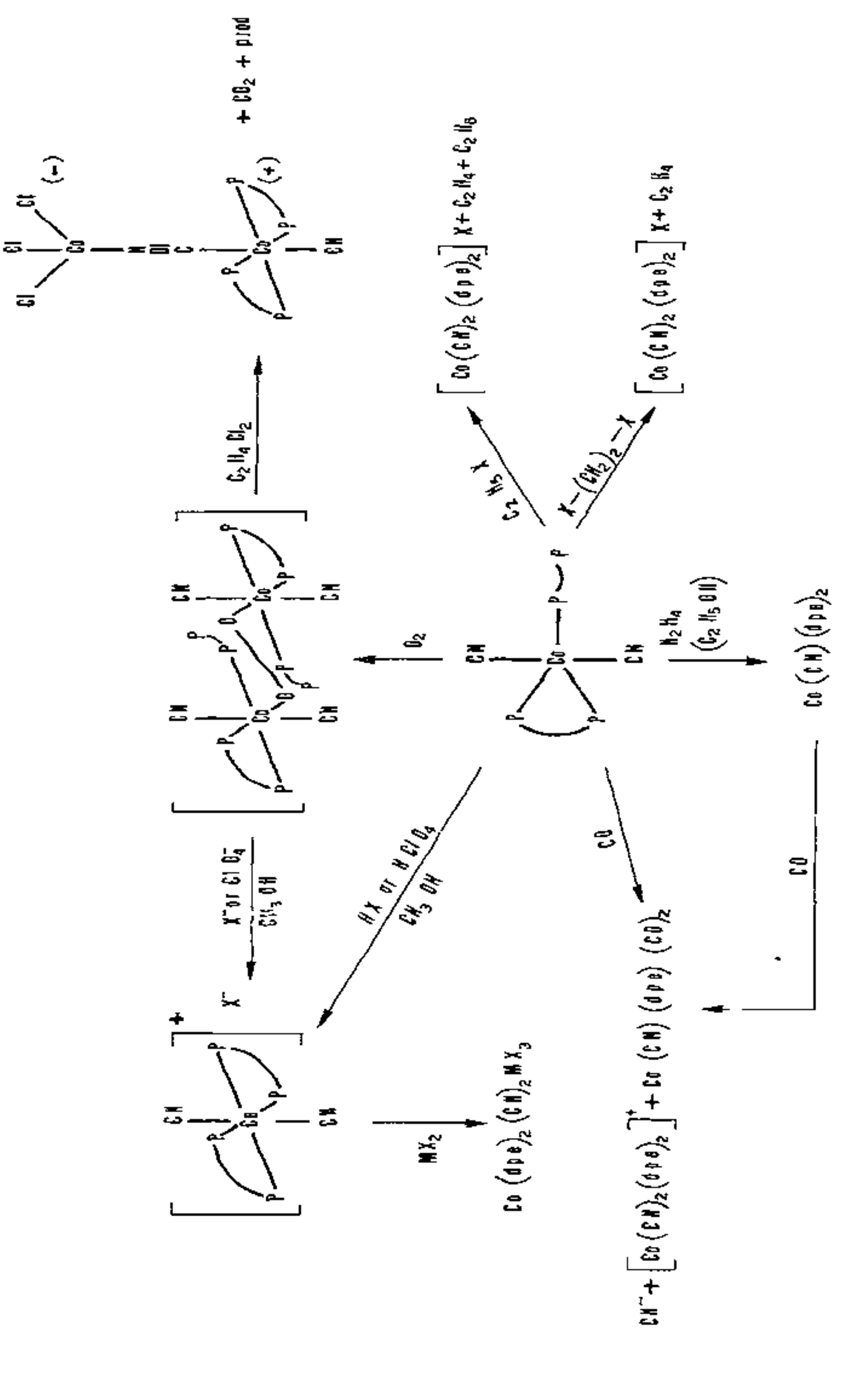
$Co(CN)(dpe)_2$ (dpe = $Ph_2P(-CH_2-)_2PPh_2$) is a stable 5-coordinate compound[14] in the solid and in solution. By contrast the bromide, $CoBr(dpe)_2$, is extensively dissociated in polar solvents, where it gives[20] the 4-coordinate ion $[Co(dpe)_2]^+$. As expected, the corresponding 5-coordinate complexes of rhodium(I) are less stable. Thus with X = Cl, only ionic 4-coordinate complexes, $[Rh(dpe)_2]^+$, have been reported[21]. Again, one finds that the cyanide $Rh(CN)(dpe)_2$ is a stable 5-coordinate compound[22], although in polar solvents it slowly undergoes solvolysis to $[Rh(dpe)_2]^+$ and CN^-. In a non-polar solvent such as benzene, the compound slowly transforms into an insoluble 4-coordinate polynuclear complex which analyzes as $Rh(CN)(dpe)_{1.5}$, and is possibly the binuclear (dpe)Rh(CN)dpeRh(CN)(dpe), with one dpe molecule acting as a bridge between two rhodium atoms.

B REACTIVITY OF $Co(CN)_2P_3$ COMPLEXES

Despite extensive interest[3,23] in the reactions of $Co(CN)_5{}^{3-}$ the study of mixed phosphine–cyanide cobalt(II) complexes has received attention only very recently[9].

The reactions of the $Co(CN)_2(PR_3)_3$ complexes lead to cobalt compounds of difficult characterization. More convenient systems have proved to be the complexes with ditertiary phosphines, particularly the compound $Co(CN)_2(dpe)_2$. The reactions studied with this compound are in part summarized in Fig. 2, and can be compared with those of $Co(CN)_5{}^{3-}$.

The reactions with the organic halides R–X and X–R–X appear[9,24] to follow patterns substantially similar to those of $Co(CN)_5{}^{3-}$. Thus $Co(CN)_2(dpe)_2$ at 40° reacts with C_2H_5I and, more slowly, with C_2H_5Br. During the reaction one first observes the formation of $CH_2{=}CH_2$, followed by $CH_3{-}CH_3$. No reaction has been observed with boiling C_2H_5Cl. The order of reactivity RI > RBr > RCl and the preliminary formation of $CH_2{=}CH_2$ suggest a halogen abstraction mechanism from the organic halide by the metal complex, similar to that previously found for $Co(CN)_5{}^{3-}$. The yellow cobalt complex cation $[Co(CN)_2(dpe)_2]^+$ can be isolated from the reaction solution (Fig. 2)



P—P = dpe = 1,2-bis(diphenylphosphino)ethane

X = Cl, Br, I

M = Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Zn^{II}

Fig 2 Some reactions of the complex $Co(CN)_2(dpe)_2$

The complex is diamagnetic, and its infrared spectrum shows only one absorption at 2112 cm^{-1}, attributable to the ν_{CN} stretching. Thus it is an octahedral complex of cobalt(III) with two CN^- groups in *trans* positions, with two chelating diphosphines.

Reaction with $ClCH_2CH_2Cl$, $BrCH_2CH_2Br$ and with a benzene solution of ICH_2CH_2I gives the same cobalt(III) complex and $CH_2{=}CH_2$. The reactivity order is again $I > Br > Cl$. Similar results have been found in the reaction of $Co(CN)_5{}^{3-}$ with organic dihalides, and have been interpreted in terms of a free radical mechanism involving halogen abstraction in the first reaction step[24].

The general features of the reactions with oxygen in CH_3OH or C_2H_5OH are also similar[25] to those shown by $Co(CN)_5{}^{3-}$. Manometric measurements of the oxygen absorbed by solutions of $Co(CN)_2(dpe)_2$ show that two moles of the complex absorb one mole of oxygen. After reaction, the solution contains aldehyde, and by treatment with $NaClO_4$ gives the perchlorate of the cation $[Co(CN)_2(dpe)_2]^+$. These results strongly suggest that the bridged oxygen adduct $(CN)_2(dpe)_2Co{-}O{-}O{-}Co(dpe)_2(CN)_2$ is initially formed (Fig. 2), which by further reaction with the solvent yields the aldehyde and the cobalt(III) complex. When the reaction with oxygen is carried out in $ClCH_2CH_2Cl$, the step involving the absorption of one mole of oxygen per two moles of complex is followed by further slower uptake of oxygen and simultaneous evolution of carbon dioxide. In this case, the reaction of the cobalt–oxygen adduct with the solvent is very complex and involves, inter alia, complete demolition of $Co(CN)_2(dpe)_2$ molecules to give $CoCl_3{}^-$ moieties which are stabilized[26] by binding to a CN^- group in the "zwitterion" $Co(CN)(dpe)_2CN{-}CoCl_3$.

The binuclear complexes $[Co(CN)_2(diphosph)_{1.5}]_2$ (diphosph = $Ph_2P(-CH_2-)_nPPh_2$, where $n = 3, 4$)[8] do not react with oxygen in alcohols or $C_2H_4Cl_2$. This result is easily understood considering the structure of the compounds depicted in Fig. 1. Steric reasons prevent the intermolecular formation of the oxygen bridge between cobalt atoms of two binuclear complexes, nor can one oxygen molecule "insert" intramolecularly between the two cobalt atoms bound by a bridging diphosphine.

The lack of reactivity connected with the structure of such complexes is confirmed for other reagents which can give "insertion" reactions. Thus we find that the complex $Co(CN)_2(dpe)_2$ reacts readily at room temperature with SO_2 in benzene or with $SnCl_2$ in ethanol, whereas the binuclear complexes mentioned above do not show any reactivity towards the same reagents under the same experimental conditions. Although the reaction products given by $Co(CN)_2(dpe)_2$ have not been fully characterized, there is little doubt[27] that the first reaction step with SO_2 and $SnCl_2$ involves the formation of

$$\begin{array}{c} X \\ | \\ Co{-}Y{-}Co \\ | \\ X \end{array}$$

binuclear compounds similar to those already observed in the reaction of $Co(CN)_5{}^{3-}$.

The behaviour of the 5-coordinate complex $Co(CN)_2(dpe)_2$ in the reactions discussed so far is very similar to that of the $Co(CN)_5{}^{3-}$ ion. This shows that substitution of three CN^- groups by three phosphorus atoms in the absence of important steric effects does not perceptibly alter the chemical behaviour of the cobalt atom In particular, the "free radical" character of the d^7 "low spin" configuration of cobalt(II) is preserved, as shown by the reactions with oxygen or with organic halides

However, there is an important difference between $Co(CN)_5{}^{3-}$ and the $Co(CN)_2P_3$ complexes, and the evidence for this comes from the reactivity towards the H_2 molecule In contrast to the easy reaction[3] of $Co(CN)_5{}^{3-}$ with H_2 leading to $CoH(CN)_5{}^{3-}$ we find that the mixed cyano–tertiary or –ditertiary phosphine complexes do not appreciably react with H_2 even under a pressure of 100 atm, in several solvents The lack of reactivity with H_2 is a little surprising considering that other substituted cobalt(II) cyanides, for example the mixed amine–cyanide complexes, give hydrides by reaction[28,29] with H_2. The lack of reactivity may arise from the low stability of $CoH(CN)_2P_3$ complexes, however, one cannot rule out that it is due to kinetic inertness In fact, a "concerted" mechanism similar to that of the reaction[30] of $Co(CN)_5{}^{3-}$ with H_2 may represent a difficult pathway in the case of the phosphine–cyanide complexes where more severe steric restrictions are operative

Another interesting aspect in the chemistry of the phosphine–cyanide complexes of cobalt(II) is that they do not appear to catalyze the hydrogenation of activated olefins, in contrast to $Co(CN)_5{}^{3-}$ (ref 3) and the amine–cyanide complexes[28,29] Thus we find that the complexes with PEt_2Ph, $PEtPh_2$ and diphosphines, in ethanol, benzene or $C_2H_4Cl_2$ do not catalyze the hydrogenation of styrene and cinnamic acid under ambient conditions

The reactions of the diphosphine complexes with dilute solutions of perchloric acid or hydrogen chloride in ethanol have also been studied Under strictly controlled anaerobic conditions, we find that the complex $Co(CN)_2(dpe)_2$ reacts with H^+ giving the cobalt(III) complex ion $[Co(CN)_2(dpe)_2]^+$ By contrast, complexes with the other two diphosphines (Fig. 2) do not react with $HClO_4$ under the same conditions We believe that this different behaviour is due to the availability in the $Co(CN)_2(dpe)_2$ molecule of one un-coordinated phosphorus atom Thus, loss of one electron from the cobalt(II) atom may readily lead to a 6-coordinate cobalt(III) complex by further coordination of the free phosphorus end of the diphosphine The driving force for the oxidation reaction is provided by the simultaneous formation of a cobalt–phosphorus bond With regard to the mechanism of oxidation it is possible that the nitrogen atom of a coordinated CN group is preferred as a reaction site of the protonated species, and that an inner-sphere CN-bridged electron transfer occurs from the cobalt(II) atom to the proton The destiny of the reduced proton has not yet been ascertained. In fact, only trace amounts of H_2 are evolved during the reaction

Finally, we shall comment briefly on the reactions of the $Co(CN)_2P_3$ complexes with carbon monoxide. Complexes with tertiary phosphines react in solution with carbon monoxide giving first the substitution products $Co(CN)_2P_2(CO)$ The latter compounds give by disproportionation the cobalt(I) derivatives $Co(CN)P_2(CO)_2$ and un-characterized cobalt(III) complexes[31] The complex $Co(CN)_2(dpe)_2$, however, in alcohols, benzene or CH_2Cl_2 also reacts with carbon monoxide to give a stable cobalt(III) complex[12] The stoichiometry of the reaction is depicted by

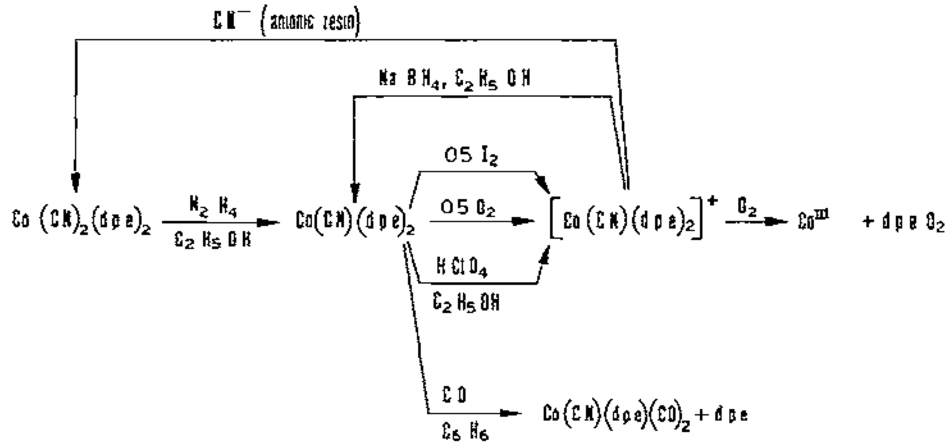
$$2\,Co(CN)_2(dpe)_2 + 2\,CO \rightarrow Co(CN)(dpe)(CO)_2 + [Co(CN)_2(dpe)_2]^+ + dpe + CN^-$$

and is similar to that found[23] in the disproportionation of $Co(CN)_5{}^{3-}$ to $Co(CN)_3(CO)_2{}^{2-}$ and $Co(CN)_6{}^{3-}$

C REACTIONS OF COBALT(I) AND RHODIUM(I) COMPLEXES

Most of the work has been carried out with the complex $Co(CN)(dpe)_2$ (ref 14) The compound can be obtained by reduction of $Co(CN)_2(dpe)_2$ with hydrazine in boiling ethanol. It undergoes characteristic oxidation reactions to the complex ion $[Co(CN)(dpe)_2]^+$ This ion can revert to $Co(CN)(dpe)_2$ by reduction with $NaBH_4$ or go back to $Co(CN)_2(dpe)_2$ by controlled addition of cyanide ions

The reactions studied with the complex $Co(CN)(dpe)_2$ are depicted in Fig 3



dpe = 1,2–bis(diphenylphosphino)ethane

Fig 3 Some reactions of the complex $Co(CN)(dpe)_2$

The compound reacts rapidly with oxygen at 25°C in $C_2H_4Cl_2$ or C_2H_5OH solution The reaction requires 1 5 moles of oxygen per mole of the complex After reaction, the solution contains cobalt(III) cyanide complexes and the diphosphine dioxide $dpeO_2$

When the reaction is carried out at 0°C in $C_2H_4Cl_2$, two distinct oxygen absorption steps can be observed Manometric measurements show that about 0 5 moles of oxygen per mole complex are taken up during the first reaction step This step can be better investigated by carrying out the reaction in ethanol in the presence of excess sodium perchlorate, only 0 5 moles of oxygen are taken up in this case with the precipitate $[Co(CN)(dpe)_2]^+$ forming in practically quantitative yield during the reaction Acetaldehyde is another reaction product. A solution of the compound $[Co(CN)(dpe)_2]ClO_4$ in $C_2H_4Cl_2$ can further react with oxygen (1.1 molar ratio) giving cobalt(III) cyanide complexes and diphosphine oxide

The overall patterns of the reaction with oxygen may be depicted as follows A reactive cobalt–oxygen adduct is formed in the first reaction step during which 0.5 moles of oxygen per mole complex are consumed The oxygen adduct reacts readily with the solvent giving the complex ion $[Co(CN)(dpe)_2]^+$, which can further react with one mole of oxygen to give finally cobalt(III) complexes and phosphine oxide With regard to the nature of the cobalt–oxygen adduct, the stoichiometry O_2 ·2 Co found for the first reaction step may indicate, although it does not prove, the formation of a bridged Co–O–O–Co binuclear complex This type of binding, unusual for 4-coordinate d^8 complexes, is conceivable for d^8 5-coordinate compounds

The compound $Co(CN)(dpe)_2$ is also readily oxidized to $[Co(CN)(dpe)_2]^+$ by reaction with stoichiometric iodine in ethanol or benzene The compound $Co(CN)I(dpe)_2$, which can be obtained from the solution, is probably 6-coordinate in the solid and extensively dissociated into $[Co(CN)(dpe)_2]^+$ and I^- in $C_2H_4Cl_2$ solution

Finally, easy oxidation of $Co(CN)(dpe)_2$ to $[Co(CN)(dpe)_2]^+$ was also observed by reaction with 0 1 *M* $HClO_4$ in ethanol The reaction leads to $[Co(CN)(dpe)_2]^+$ both with stoichiometric amounts or with a large excess of perchloric acid Evolution of hydrogen was not observed during the course of the reaction Considering that the 5-coordinate $CoH(dpe)_2$ reacts[21] with $HClO_4$ in ethanol to give $[CoH_2(dpe)_2]^+$ and that the complexes $[CoHCl(dpe)_2]^+$ (ref 20) and $[Co(CN)_2(dpe)_2]^+$ are stable, it was expected that $[CoH(CN)(dpe)_2]^+$ could be a product of the reaction However, the data presented here suggest that $[CoH(CN)(dpe)_2]^+$ is an unstable compound which, if formed, readily decomposes in ethanol to give $[Co(CN)(dpe)_2]^+$ and other products

Coming to the reactions with H_2, we find that $Co(CN)(dpe)_2$ in ethyl ether solution does not react with H_2 at 70 atm By contrast, it is known[20] that the ionic 4-coordinate $[Co(dpe)_2]^+$ readily adds hydrogen to give $[CoH_2(dpe)_2]^+$ It thus appears that the oxidative addition process, typical of d^8 4-coordinate complexes, is suppressed in the case of $Co(CN)(dpe)_2$, which is a stable 5-coordinate compound In principle, oxidative addition in the latter case could occur if accompanied by substitution It seems evident that in the present case oxidation to cobalt(III) and substitution of phosphine or cyanide groups by hydrogen atoms is energetically unfavourable

Finally, the reaction with carbon monoxide shows that one diphosphine is readily replaced by two carbon monoxide molecules to give the previously mentioned compound $Co(CN)(dpe)(CO)_2$ The rhodium(I) complex $Rh(CN)(dpe)_2$ yields by reaction with CO at 100 atm the 4-coordinate complex[22] Rh(CN)(dpe)CO This result differs from that given by the cobalt(I) complex, and is not unexpected considering the lower stability of the 5-coordinate complexes of rhodium as compared with those of cobalt

An interesting series of reactions with carbon monoxide and oxygen has been studied with the compound $Rh(CN)(PPh_3)_3$ (ref 22), which reacts with CO in benzene to give the substitution product $Rh(CN)(PPh_3)_2CO$ This reaction is similar to that given[32] by $RhCl(PPh_3)_3$. When the reaction of $Rh(CN)(PPh_3)_3$ with CO is carried out in the presence of excess phosphine in light petroleum, the 5-coordinate $Rh(CN)(PPh_3)_3CO$ slowly separates from the solution The compound is fairly stable in the solid state, but is, however, extensively dissociated in solution where it gives the 4-coordinate $Rh(CN)(PPh_3)_2CO$ By contrast, we find in accordance with other reports[32] that the tris-phosphine carbonyl complexes are not given by $RhCl(PPh_3)_3$ even in the presence of large amounts of the phosphine The instability of $RhCl(PPh_3)_3CO$ can be contrasted with the stability[33] of $RhH(PPh_3)_3CO$ and $Rh(CN)(PPh_3)_3CO$ These observations show that the 5-coordinate tris-phosphine carbonyl complexes of rhodium(I) are stable only when the anionic ligand gives good covalent bonds This conclusion is in agreement with the previous discussion on the 5-coordinate MX_2P_3 complexes of cobalt(II) and nickel(II)

The complex $Rh(CN)(PPh_3)_2CO$ in CH_2Cl_2 solution reacts with oxygen at 50 atm giving the adduct $Rh(CN)(PPh_3)_2(CO)(O_2)$ It is known that the corresponding chloride $RhCl(PPh_3)_2CO$ does not interact with oxygen and that attempts to prepare solid samples of $RhI(PPh_3)_2(CO)(O_2)$ have failed, although an interaction between $RhI(PPh_3)_2CO$ and O_2 may occur in solution[34] In keeping with the conclusions of Ibers and coworkers[34], the increasing capacity for uptake in the series Cl, I, CN should be interpreted in terms of increased electron density on the rhodium atom However, considering the electronegativity values of Cl, Br, I and CN this explanation does not appear to be satisfactory[35]. The capacity for oxygen uptake of the cyanide complexes of rhodium(I) is confirmed by the fact that $Rh(CN)(PPh_3)_3$ either in the solid or in petroleum ether solution readily yields the oxygen adduct $Rh(CN)(PPh_3)_2(O_2)$

In conclusion, these results confirm those on the complexes of cobalt(II) and nickel(II) The primary effect of the cyanide group is to stabilize 5-coordination as compared with 4-coordination Moreover, the cyanide group affects the reactivity of the complexes by a combination of two factors The first factor depends directly on the stabilization of the 5-coordinate substrates, the second comes from the effect of the CN^- group on the electronic properties of the central metal atom

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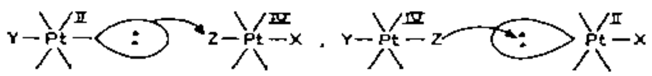
End of Bressanone Conference

Erratum

The following equation was printed incorrectly in *Coordination Chemistry Reviews*, Vol 7, No 3, p 248, and also in Vol 7, No 4, p. 420.



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