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STRUCTURES AND REACTIVITY OF SOME BRIDGED DINUCLEAR d^8 AND d^7 COMPLEXES*

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Comprehension of the fundamental differences between homogeneous and heterogeneous catalysis is one of the aims of the studies on "model" complexes in the field of coordination chemistry. Conceptually, one of the main distinguishing features between both modes of catalytic action would concern a potential simultaneous intervention of two or more atoms at the surface leading to some cooperative effect of these atoms on the substrate during one or several steps of the heterogeneous mechanism. This situation is, by nature, forbidden for the various homogeneous catalytic reactions which are known to proceed through mononuclear metallic intermediates and transition states. Moreover, most of the presently known cases of the so-called "bimetallic homogeneous catalysis" [1] seem to proceed either from successive interventions of each of the engaged metal complexes (Wacker process) or from the catalytic action of only one metal atom whose electronic state in its complex is judiciously modified by the second metal atom acting as a ligand (Pt/Sn catalyst).

It is our opinion that a really true "bimetallic catalysis" would result from a sort of "super template" effect involving the substrate and two metal atoms; such a closely defined concerted mechanism has been postulated in some cases (polymerisation on Ti/Al catalyst) or shown in others [2] but its general application is still questionable. Hence the development of studies, on the reactivity of two (or more) metallic centers will be a challenge for the coordination chemist in the second half of this decade.

Preparative researches in the field of bridged dinuclear d^8 and d^7 metal complexes

From the points raised so far it is clear that the dinuclear bridged complexes of d^8 and d^7 metals are of special interest because of their varying degrees of metal—metal interaction.

The present studies have been undertaken in the expectation that the reactivities would be different for complexes with different degrees of metal—metal

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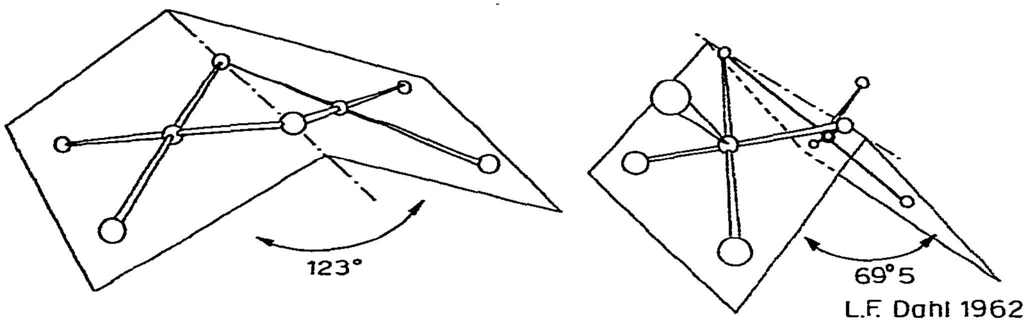


$Rh_2Cl_2(CO)_{4-n}L_n$ $Fe_2(SR)_2(CO)_{6-n}L_n$

In the iron series a "hinge-shaped" structure with a smaller angle α around the axis of the hinge is expected from the X-ray determination by Dahl [3] of the parent compound $Fe_2(SR)_2(CO)_6$. In the rhodium series the quasi invariability of α seems to be proved [4-12].

Fig. 1. Examples of "hinge-shaped" molecules.

interaction and especially for the μ complexes of the series: $Rh_2{}^IA_2(CO)_{4-n}L_n$ and $Fe_2{}^IA_2(CO)_{6-n}L_n$, as suggested by the geometry of the parent compounds (Fig. 1) and their respective metal—metal distances.

In order to reveal the reactivity of these types of complexes, initially we had to use the most basic ligand reactants. Our first aim was to investigate the reaction of the $Rh_2Cl_2(CO)_4$ complexes with phosphines with the purpose of "tailoring" adequate model complexes.

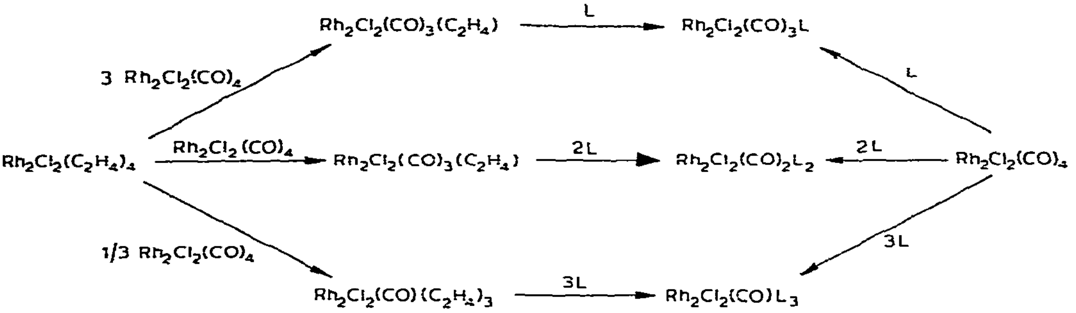
An infrared study has shown that the $[Rh(CO)_2Cl]_2$/phosphine(L) systems in solution are composed of two series of complexes, mononuclear complexes X_n of formula $RhCl(CO)_{3-n}L_n$ ($n = 1, 2, 3$) and dinuclear complexes Y_m of formula $Rh_2Cl_2(CO)_{4-m}L_m$ ($m = 0, 1, 2, 3, 4$) [5]. Some of the compounds Y_2 and Y_3 were sufficiently stable to allow elemental analyses to be made and in the case of Y_2 molecular weight measurements, but the structures of compounds X_1 and Y_1 were obtained by chemical observations and by mass spectrometric investigations. Consequently a reexamination of the chemical properties [6,7] of the Y_2 derivatives of triphenylphosphine, previously considered as X_1 complexes [6] is necessary in the light of their true dinuclear structures.

The composition of mixtures obtained by the reaction of phosphines and μ-dichlorotetracarbonyldirhodium, $[Rh(CO)_2Cl]_2$, is very dependent on factors such as the relative concentration of ligand L to metal, the pressure of CO, the nature of the solvent and the temperature. It is to be noted that Scholten and Van der Ploeg using a variation in the L/Rh ratio [8] suggest a specific catalytic role of the dinuclear species in polymerisation, which supports our general hypothesis on the reactivity of the μ-complexes.

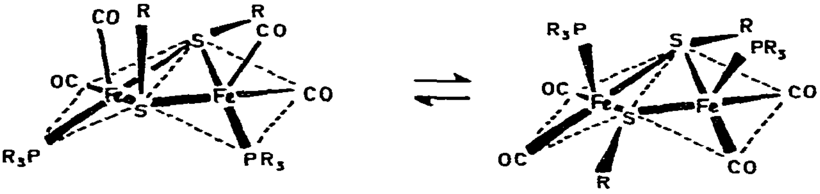
Although, the fact that the Y_2 complexes in solution always redistribute themselves partially into Y_1 and Y_3 must never be forgotten, a preparative method giving almost pure compounds was needed. This leads us to an indirect synthesis using as starting materials various ratios of both complexes $Rh_2(CO)_2(C_2H_4)_4$ and $Rh_2Cl_2(CO)_4$.

Scheme 1 gives an insight into the flexibility of such a process using the redistribution phenomenon. For example, by Scheme 1 complexes Y_2, for a range of basicity of L from L = n-$C_3H_7OPF_2$ to L = $P(C_2H_5)_3$, have been obtained with equal facility [9]. The method is also useful in the preparation of amine complexes [10].

SCHEME 1



Our synthetic work starting from the reaction of phosphines on the $[Fe(SR)(CO)_3]_2$ complexes also renders available a series of compounds $Fe_2(SR)_2(CO)_{6-n}L_n$ (n = 0, 1, 2, 3, 4). In this case various isomers with respect to the ligand L positions and the *syn—anti* disposition of the methyl group [11] were detected. For instance the observed equilibrium:



exemplified the connection between both types of isomerisation. Moreover, the generalisation of the preparative studies has been recently undertaken in our laboratory and concerns various iridium, cobalt, nickel and platinum dinuclear complexes.

Crystal and molecular structures of the dinuclear bridged d^8 complexes

The validity of our lines of research was strongly dependent on the analogy of structure between the Y_2 compounds and the Y_0 parent compounds (Fig. 1). It is interesting to note that, in the almost analogous μ phosphido complex $[IrP(C_6H_5)_2CO(PC_6H_5)]_2$, each iridium atom lies in a tetrahedral configuration and that even if the double square planar structure is preserved, in some rhodium compounds, the dihedral angles between the two planes is not necessarily fixed around 124° (for $[RhCl(C_8H_{12})]_2$ α = 180°).

Indeed the X-ray analysis of a triclinic crystal of the complex $[RhCl(CO)\{P(C_6H_5)(CH_3)_2\}]_2$ [12] shows a true (but approximate) square planar configuration of the rhodium atoms (Fig. 2). An interesting feature is that this double square planar structure (Fig. 3) is bent, forming a dihedral angle of

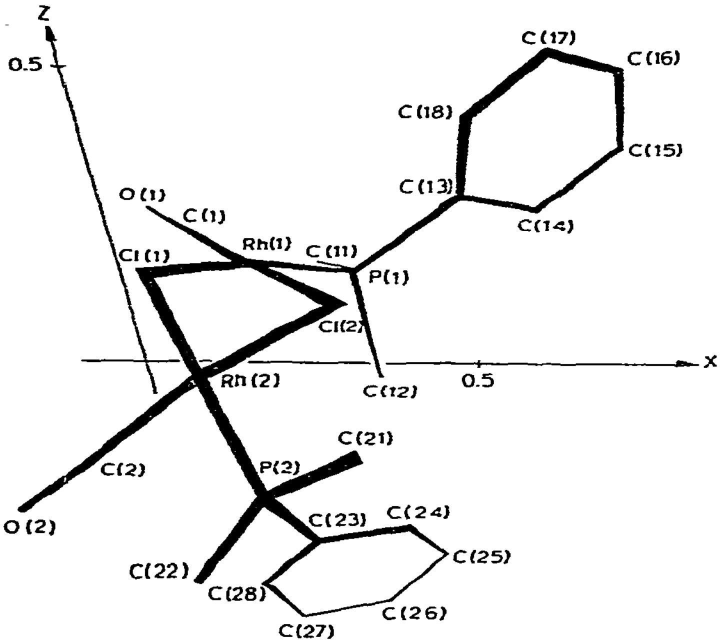


Fig. 2. Perspective view along the axis of the complex $[RhCl(CO)\{P(C_6H_5)(CH_3)_2\}]_2$ [12].

123.0° comparable with the 124° value determined by Dahl et al. [3] for $Rh_2Cl_2(CO)_4$ where the intramolecular metal interaction had been postulated. The bent structure is indeed an intrinsic characteristic of the Y_2 complexes.

The infrared spectra of selected crystals with the same morphology as those studied by X-ray analysis exhibit, from caesium bromide pellets, two stretching bands at 1986 and 1971 cm^{-1} (Fig. 4a). The presence of only two CO bands of almost equal intensity is in agreement with the *cis* structure revealed by the X-ray determination. All attempts to find some crystals of the *trans* isomer or to detect some mixture of both isomers in the solid state failed. Nevertheless curve analysis (Fig. 4b), of cyclohexane solutions of the crystals revealed a system of three

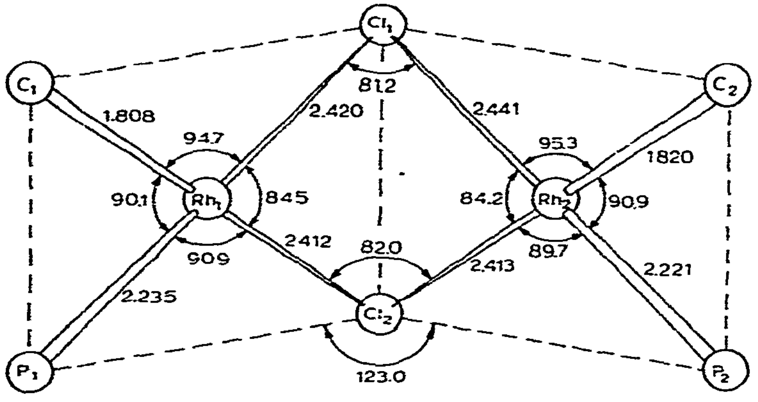
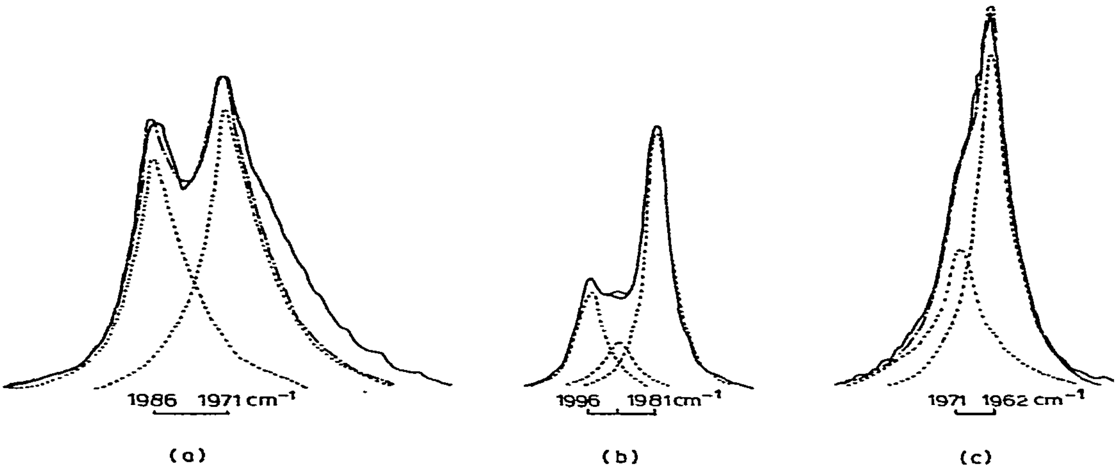


Fig. 3. Some structural parameters in the complex $[RhCl(CO)\{P(C_6H_5)(CH_3)_2\}]_2$ [12].



(a) (b) (c)

Fig. 4. Infrared spectra of Y_2 compounds [12], (a) spectrum in the solid state of the complex [RhCl(CO)-$\{P(C_6H_5)(CH_3)_2\}]_2$, (b) spectrum in cyclohexane solution of the same complex, (c) spectrum in the solid state of the complex $[RhCl(CO)P(NMe_3)_3]_2$.

CO bands. Assuming the transferability [13] of interaction force constants *k*(*cis*) and *k*(*trans*) from the parent carbonyl complex $Rh_2Cl_2(CO)_4$ [14], the splitting of 15 cm^{-1} between furthermost bands is characteristic of the *cis* structure. Assuming the same intensity ratio as for the solid state, we can evaluate the contribution of this isomer by the intensity of the band at 1981 cm^{-1}. Thus starting from *cis*-$[RhCl(CO)\{PMe_2Ph\}]_2$ in the solid state, a mixture (30/70) of the *cis* and *trans* compound occurs in cyclohexane solution. Therefore, both absorptions at 1990 and 1981 cm^{-1} are assigned to the *trans* isomer with respect to their relative intensities (the contribution of the *cis* isomer to the intensity of the band at 1981 being taken into account).

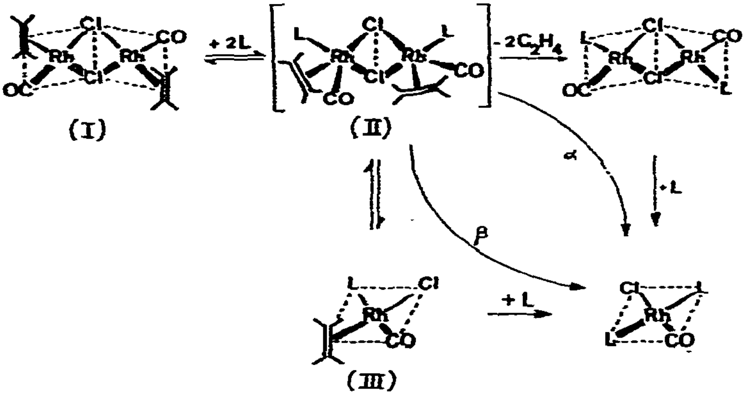
A similar spectroscopic investigation shows that the *cis* isomer of the complex $[RhCl(CO)PMe_3]_2$ is the only one recovered from solutions containing both isomers. Whereas it seems that the complex $[RhCl(CO)P(NMe_3)_3]_2$ adopts a *trans* geometry in the solid state (Fig. 4c), the *cis* isomer occurring by isomerisation in solution.

Nucleophilic attack on bimetallic complexes

By the above preparative method it is reasonable to assume that from a purely electronic consideration, any complex Y_2 with L having a basicity in the range from L = n-$C_3H_7OPF_2$ to L = $P(C_2H_5)_3$ may be prepared. The steric properties of L, however, play an important role in the reaction. For example with the bulky phosphine $P(C_6H_{11})_3$ using the ratio L/Rh = 1, the mononuclear complex $RhCl(CO)[P(C_6H_{11})_3]_2$ (type X_2) is preferentially formed with a transformation ratio of starting material ca. 50% and only a small quantity of Y_2. This observation may be discussed and rationalised on the ground of Scheme 2.

For ligands of low steric requirements rapid formation of II with subsequent loss of ethylene to form Y_2 seems a reasonable mechanism. Bulky groups are expected to retard, to some extent, the formation of II and hence the re-

SCHEME 2.



sulting large concentration of free ligand in solution would react with Y_2 and/or III to form X_2 (path α and/or β). Thus it is possible to attribute the observed distribution of products (X_2 and Y_2) either to the disappearance of ligand by path α (as L/Rh = 1) or to a kinetic competition between α and β. Furthermore, it is plausible that, with bulky ligands L, an attack on the sterically hindered Y_2 would be prevented and path β favored.

With 2-methylpyridine the reaction was slow and further addition of ligand (L/Rh = 2) gave the X_2 complex $RhCl(CO)(2\text{-}NC_6H_7)_2$*. In this case, path α can be excluded and the postulated intermediate III is clearly involved in the substitution reaction.

The use of the very sterically hindered 2,6-dimethylpyridine ligands gave exclusively the complex $RhCl(CO)(C_2H_4)(2,6\text{-}NC_7H_9)$** even in the presence of excess ligand (the same amine ligand). This can be considered as the isolation of the intermediate III in a case where further attack is hindered by the steric effect.

Finally, the addition at room temperature of the stoichiometric quantity of the diethylamine (L/Rh = 1) to $[RhCl(CO)C_2H_4]_2$ in toluene solution gives quantitatively, after recrystallisation at −20°C, a yellow product. Elemental analysis, relative intensities of ethylene and amine proton NMR signals are consistent with the formula $RhCl(CO)(C_2H_4)(NHEt_2)$ leading apparently to the same conclusion as in the previous case. Preliminary X-ray analysis [18] confirms a mononuclear square planar structure with the ethylene ligand *trans* to the chlorine. But surprisingly, osmometric measurements in benzene solution under argon, gave a double molecular weight and suggests a dinuclear complex $[RhCl(CO)(C_2H_4)(NHEt_2)]_2$ (hereafter referred as $W_2(NHEt_2)$). This product, $W_2(NHEt_2)$, in solution slowly loses ethylene under reduced pressure to give a dark brown product, $[RhCl(CO)(NHEt_2)]_2$ of low solubility, considered to be a Y_2 complex of the amine ligand. The same behaviour is observed with n-propylamine, 3,5-dimethylpyridine and pyridine.

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* First example, for amine ligand, of a mononuclear disubstituted rhodium(I) complex *trans*-$RhCl(CO)L_2$ ($\nu(CO)$ = 1963 cm^{-1}) [10].

** Two isomers were detected in solution and their structures as represented in Scheme 3, were determined by NMR and Nuclear Overhauser Enhancement (NOE) [10].

So in the case of L = diethylamine, the members of the equilibrated first step of the path β seem to have been observed. Indeed the structure of the W_2 compound should be intimately related to the geometry of the transition state implied in the substitution and bridge splitting reactions of the $[RhCl(CO)(C_2H_4)]_2$ complex.

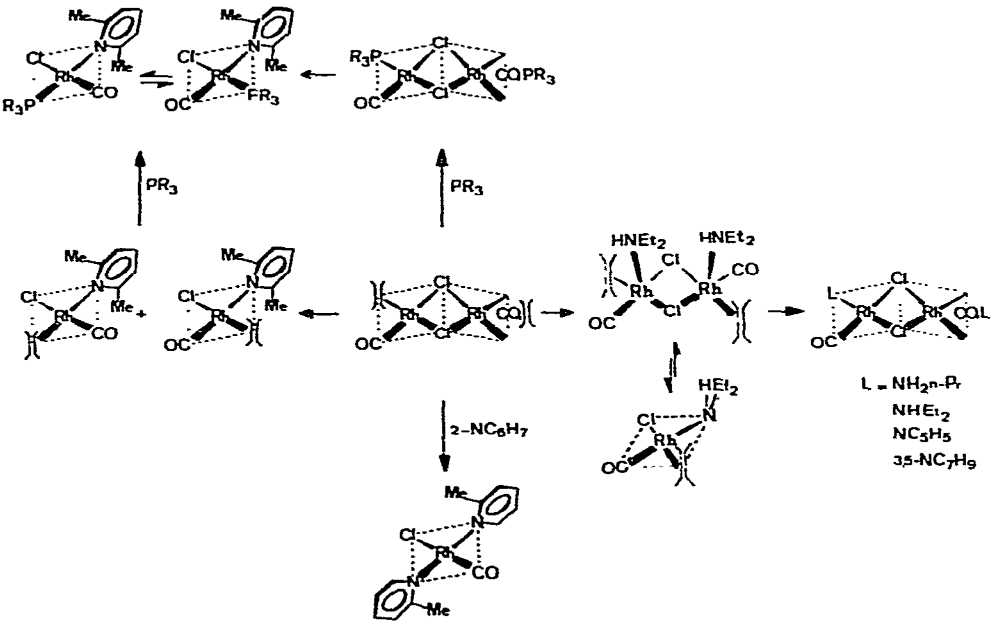
Due to the importance of such a basic conception as a dinuclear transition state, we further investigated the system $[RhSR(CO)_2]_2$/phosphine [15] in which the bridge splitting reaction was expected to be hindered.

New dinuclear pentacoordinated rhodium(I) complexes $[RhSR(CO)_2L]_2$ were therefore prepared*. Through slow decarbonylation these complexes lead to $[RhSR(CO)PA_3]_2$, complexes.

As a conclusion, the factors of the competition between substitution and bridge splitting reactions (observed during the nucleophilic attacks on the complex $[RhCl(CO)(C_2H_4)]_2$) are consistent with a doubly pentacoordinated intermediate in the corresponding pathways (Scheme 2). This hypothesis is open to challenge from a kinetic study.

The present detection or isolation of new types cf doubly pentacoordinated complexes, followed by the X-ray determination of their structures, will probably allow us to reach an idea of the geometry of the transition states involved in the reaction.

SCHEME 3.



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* At present NMR, IR, Raman data and infrared intensity measurements seem to be consistent with the structure shown in Fig. 5 [15].

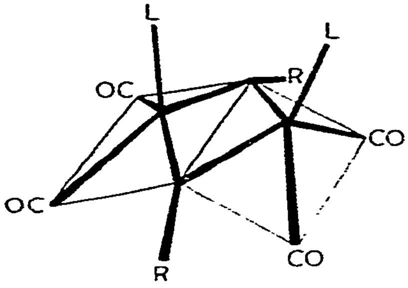


Fig. 5. Proposed structure of the complex $[Rh(St\text{-}Bu)(CO)_2(PMe_3)]_2$ [15].

Some aspects of the oxidative addition reactions on dinuclear d^8 and d^7 complexes

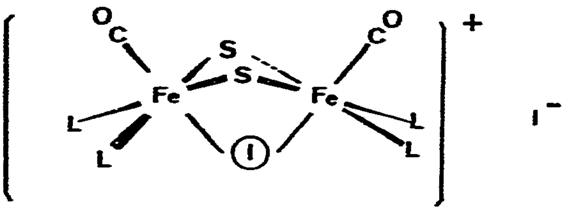
Comparative studies in this field have been undertaken by investigating the reaction of methyl iodide with the $Fe_2{}^I(SMe)_2\ CO_{6-n}L_n$ series of complexes. The cases $n = 2$ or 3 give complicated mixtures, containing for instance for $L = PMe_3$, the complexes $Fe^{II}(CO)_2(PMe_3)_2I_2$, $Fe^{II}(CO)_3(PMe_3)I_2$, $Fe^{II}(CO)_2(PMe_3)_2(CH_3)I$, and therefore the determination of the general pattern of the reaction is a considerable task.

But relevant to our aim is the case $n = 4$; from the mixtures obtained in the reaction with ICH_3 a dinuclear complex of formula $[Fe^{II}(SMe)(CO)(PMe_3)_2I]_2$ was isolated. From its IR and NMR data, a structure was postulated (Fig. 6) similar to that of the complexes $[Fe(CO)_2LEI_{0.5}]_2{}^+I^-$ prepared by halogenation by Professor W. Hieber [16] some years ago.

The reactivity of the dinuclear d^8 complexes with methyl halides is exemplified by the reactions of Y_2 complexes.

When an equimolar amount of ICH_3 is added to a solution of $[RhCl(CO)\text{-}PMe_3]_2$ in benzene the oxidative addition leads to the compounds $[RhCl(CO)\text{-}PMe_3CH_3I]_2$ ($\nu(CO) = 2068\ cm^{-1}$, $\tau\ CH_3 = 9.07$ ppm) and $[RhCl(COCH_3)(PMe_3)\text{-}I]_2$ ($\nu(CO) = 1685\ cm^{-1}$).

The last compound and its homologous derivatives are thought to be solvated species with probable formula $[RhCl(COCH_3)(PR_3)I(S)]_2$ (S = molecule of solvent). All attempts to isolate the acetyl form were unsuccessful. Let us



$\tau(PMe_3)$ 8.49 ppm

$\tau(SMe)$ 7.75 ppm $\nu(CO)$ 1942, 1932

Fig. 6. Proposed structure for the complex $[Fe^{II}SMeCO(PMe_3)I]_2I$ [11] (methyl groups have been omitted).

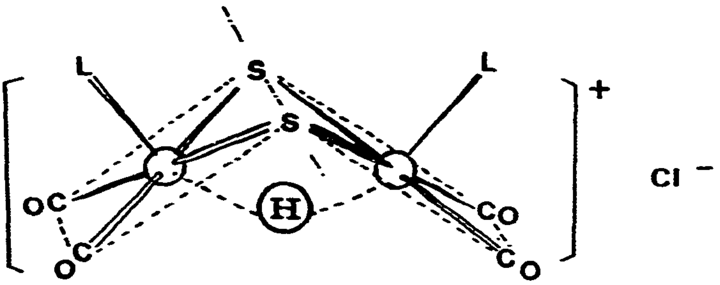


Fig. 7. Proposed structure for a protonated dinuclear complex [11] (methyl groups have been omitted).

consider as an example the complex $[RhCl(CO)(PMe_2Ph)(CH_3)Br]_2$ ($\nu(CO) = 2070\ cm^{-1}$ in CrBr pellets). Dissolving it in CH_2Cl_2 gives two CO stretching bands ($\nu(CO) = 2077$ and $1690\ cm^{-1}$) demonstrating the equilibrium between methyl and solvated acetyl compounds. Such an equilibrium is completely displaced when a ligand L ($L = CO$ or $P(OCH_3)_3$) is introduced into the solution. When $L = CO$, the species obtained are identical to the product of the oxidative addition of CH_3COCl to $[RhCl(CO)L]_2$ [17].

$$[RhCl(CO)(PR_3)I(CH_3)]_2 \overset{+2S}{\rightleftharpoons} [RhCl(COCH_3)(PR_3)I(S)]_2 \xrightarrow{+2L,\,-2S} [RhCl(COCH_3)(PR_3)I(L)]_2$$

We have previously described another example of oxidative addition of Y_2 complexes, namely the reaction of HCl which gives the rhodium(III) complexes $[RhCl_3(CO)L]_2$ [5]. With the iron(I) semi-homologous complex $[Fe(SMe)(CO)_2L]_2$, an intermediate state is obtained as a mono-protonated species ($\nu(CO) = 2045, 2026, 1990\ cm^{-1}$; τ H = 25.53 ppm (t); $J(PH) = 3.4$ Hz) with a symmetrical structure and the proton probably located in the metal—metal bond area (Fig. 7) [11].

As a conclusion we hope that these examples of reactivity, however preliminary they may be, will help to stimulate interest in "hinge-shaped" dinuclear complexes.

Acknowledgements

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