Inorganica Chimica Acta, 62 (1982) 75–86

Bridged Homobimetallic Complexes as Models of Dimetal Active Centres: the Role of Metal–Metal Bonding

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Introduction

The most likely reason for the present interest in polymetallic species is the hope that a number of them may offer new possibilities for activating organic and inorganic molecules by a co-operative involvement of their active sites [1]. In that case, a 'true' bimetallic catalytic process would result from the meeting of the substrate(s) with the two metallic centres during one or more steps of the reaction.

As far as we consider *a priori* the involvement of two metal centres in some hypothetical homogeneous catalytic process, *three* cases can be distinguished. In the first case, two catalytic cycles, each one involving one metal site, are independent, with the exception that the product of the first one is the substrate of the second one. In the second case, organometallic species, each one produced by one of the two different catalytic cycles, are supposed to meet leading to the final product, and in the third case the bimetallic site subsists during a significant part of the whole catalytic process. Only the last two cases conceptually require the existence of some pathway with *bimetallic activation*; some of these most easily conceivable encounters are tentatively depicted in Fig. 1.

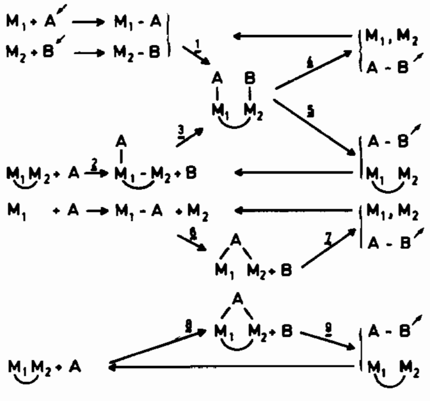

Fig. 1. Principle of some conceivable processes of bimetallic activation for the reaction A + B → A – B: events like 2, 3, 4, 5, 7, 8 and 9 could be modeled by adequate stoichiometric reactions of dinuclear complexes, while 1 and 6 are supposed to occur by reaction between two monometallic complexes.

Supporting the contemporary search for new catalytic processes, recent results of the coordination chemists are clear examples, at least as far as the *balance* of reactions is considered, of such an involvement of a dimetal centre. In the context descending from Fischer Tropsch and metathesis reactions, studies of the reactivity of μ-carbene and carbyne species were thus developed [2], as well as observations on the metal promoted alkyl migration [3] or on the formation of a bridging acetyl group from the reaction of a binuclear methyl complex with carbon monoxide [4]. Suggesting new pathways in the isomerisation [5], dimerisation or oligomerisation [6] and metathesis [7] of unsaturated hydrocarbons result also from considerations of dimetal intermediates. Of irreplaceable value, analyses of the transport and multi-electron redox reactions of molecular oxygen with binuclear copper systems are performed with the hope to clarify or to replicate the oxido-reductive function of copper protein [8]. More general (and so broad that it is impossible to sum them up here) searches for functional models of polymetallic sites of metal proteins [9] are largely developed. It is also established that ligands such as hydride, alkyl and carbonyl—all important substrates in catalytic reactions—can freely migrate between different metal centres [10, 11].

Nevertheless, despite these numerous studies already carried out in the field of polymetallic homogeneous catalysis, the achievement, and partly the *a priori* conception, of the potentialities of real bimetallic catalytic systems will remain an unsolved and interesting problem. That is why we thought that the search for other model compounds for bimetallic activation was essential.

A main leading idea aiming at determining the possibilities of bimetallic activation lies in investigating the fundamental reactions and the reactions of coordinated ligands on bimetallic complexes in the same way as has been performed on mononuclear complexes. Many types of binuclear and polynuclear compounds, including simple and multiple metal–metal bonded binuclear compounds [11], clusters [12], complexes derived from binucleating ligands [13] and macropolycyclic structures [14], are more or less suitable for this purpose.

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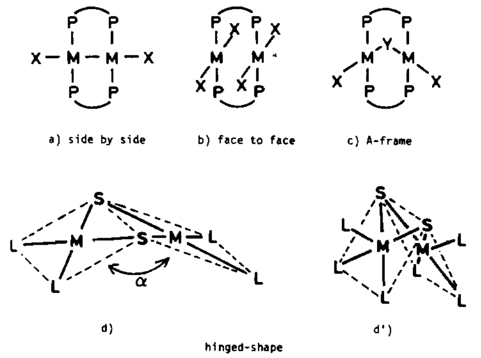
It was our opinion [1a, c] that one of the most simple experimental approaches of the bimetallic activation can proceed by:

(i) the synthesis of compounds with metallic reaction sites kept close to one another by means of bridging ligands, which might be defined as *assembling* ligands as far as they are assumed to be inert during the reactions which the complex undergoes;

(ii) the use of couples with different active centres in order to combine their activation effects on the substrate, with much more result than if only one was used.

It is clearly understood that these two aims gave rise to independent research lines; when combined, they may also lead to a third possibility. The latter implies the 'design' of assembling ligands suited for metallic sites possessing different characters (soft and hard for example) though proximity is required for them [15]. This association of two different sites is of special interest with respect to the challenge of carbon monoxide hydrocondensation [16].

Binuclear complexes using bis(diphenylphosphino)methane (dpm) or bis(diphenylarsino)methane (dam) [17], 2-(diphenylphosphino)pyridine [18], to hold two metal atoms in close proximity have received considerable attention in recent years. The first ligand has been found to bridge metal atoms with various coordination numbers in a number of different geometries [19]. Complexes formed from tetracoordinated planar ions (Fig. 2a, b, c) have received particular attention (19g, 19e, 20].



a) side by side b) face to face c) A-frame

d) d')
hinged-shape

Fig. 2. Bimetallic compounds formed from tetracoordinated planar ions or pentacoordinated ions (d').

We have been concerned with more simple assembling ligands, namely alkyl and aryl thiolato ligands which lead to a hinged shape for the two kinds of studied bridged binuclear complexes (d) and (d') (Fig. 2). *Assuming reactions with no breaking of bridging ligands*, such an open shape is an original feature which can *a priori* allow a better approach of the reactants inside the intermetallic area.

1 - Oxidative Addition on Dimetal Centres of d^7–d^7 and d^8–d^8 Bimetallic Complexes

1.1 - Reactivity of Some Thiolatobridged Bimetallic Complexes

Our very first studies have been concerned with d^7–d^7 di-iron complexes $Fe_2(\mu\text{-}SR)_2(CO)_{6-n}L_n$ [21] with one metal–metal simple bond. The geometry of such complexes is exemplified by the trimethylphosphine derivative $Fe_2(\mu\text{-}SMe)_2(CO)_4(PMe_3)_2$, in which the existence of a simple metal–metal bond is consistent with a short Fe–Fe distance of 2.518 Å [22]. The protonation of such metal–metal compounds, easily monitored by IR and NMR [23], leads to an increase of the Fe–Fe distance [24] to a value of 2.595 Å in a way which is well documented and was discussed by Ibers [25], Churchill [26] and Bau [26bis].

As the general features of the complexes are weakly modified by protonation, with the exception of the increase of the Fe–Fe distance and the opening of the book-shaped complex, we have regarded the reaction as an insertion of the proton in the metal–metal bond considered as the more nucleophilic site of the molecule. Such an insertion is also observed directly with SO_2 and $HgCl_2$ molecules [27], or indirectly as a result of multistep reactions leading to $[Fe(\mu\text{-}SMe)(CO)_2]_2A$ ($A = SO_4$, $(HgCl_2)_n$) or $[Fe(\mu\text{-}SMe)(CO)_2L_2X]^+$ cationic species ($X = F$, Cl, I). With SO_2 insertion, the metal–metal distance reaches a value of 3.117 Å: clearly consistent with an almost complete loss of the metal–metal direct interaction [28].

The concept of oxidative addition on metal–metal bonded centres is easily extended, concerning the studied binuclear iron complexes, to the cases of organic substances. This is shown from the results of Davidson and Sharp on $[Fe(\mu\text{-}SCF_3)(CO)_3]_2C_4F_6$ in which an important increase of the metal–metal distance to the value of 3.266 Å was observed. Recent observations on the reactions of the (a) type side by side dipalladium complex with acetylenes and olefines [29] parallel the same trend. In fact, we are prepared to accept that *oxidative addition reaction occurring on a dimetal centre leads to metal–metal bond breaking* with the formation of diamagnetic species, and a satisfactory rationalization is easily reached by electron counting. The scheme I, equation a, sums up this first type of behaviour in a symbolic way.

1.2 - Oxidative Addition Reactions on Series of Rhodium(I) and Iridium(I) Dinuclear Complexes

The d^8–d^8 binuclear complexes of type (d) (Fig. 2) do not admit true metal–metal bonding [30], but their assembling pattern and their usual folded configurations do ensure a close proximity of the metallic sites [31e, 32c–d]. Since 1972, suitable modes of preparation of different series of $[M(\mu X)(CO)L]_2$ have been found, allowing the introduction of more basic ligands L instead of CO in order to increase the nucleophilicity of the metal atoms [31] or of the thiolato ligand instead of halogeno bridging ligands [32, 35]. Spectroscopic investigations have also been performed [33].

By testing the reactivity of chloro bridged rhodium compounds [34] with methyl chlorine or bromine, only the products of simple oxidative additions occurring on both metal atoms were detected, *i.e.*:

$$[RhCl(PA_3)CO]_2 + MeX \longrightarrow [RhCl(PA_3)(CO)Me(X)]_2$$

(X = Cl, Br; equilibrated reaction when A = OMe)

The rhodium(III) compounds can be further transformed into acetyl derivatives stabilized by solvent coordination (by reacting in benzene), then by coordination with CO extra ligands:

$$[RhCl(PA_3)(CO)Me(I)]_2 \xrightarrow{S} [RhCl(PA_3)S(C(O)Me)(I)]_2 + CO \xrightarrow{-S} [RhCl(PA_3)(CO)(C(O)Me)(I)]_2$$

In every case, the oxidative additions with methyl halides give identical states of hexacoordination around both Rh(III) metal centres. In addition, clear structural arguments of some bridge-breaking occurring in the reaction solution were obtained by crystallographic investigation of the adduct of the methyl bromine with the chloro bridged rhodium(I) compound: indeed, in this hexacoordinated rhodium(III) dinuclear compound, bromine and chlorine statistically occupy both terminal and bridging positions (Fig. 3a).

Facing these last results, thiolato bridged compounds were prepared *with the aim of reaching a more inert dimetallic core.* Metathetic reactions [32] are very convenient for such a purpose in the case of rhodium compounds as well as in the case of iridium compounds:

$$[RhCl(C_8H_{12})]_2 \xrightarrow{LiSR} [Rh(SR)(C_8H_{12})]_2 \xrightarrow{CO} [Rh(SR)(CO)_2]_2$$

$$[IrCl(C_8H_{12})]_2 \xrightarrow{LiSR} [Ir(SR)(C_8H_{12})]_2 \xrightarrow{CO} [Ir(SR)(CO)_2]_2$$

($R = C_6H_5, Bu^t, C_6F_4H$ [35])

The same process is also valuable to prepare polymer-anchored dinuclear rhodium(I) catalysts attached by the bridging group [36]. Further substitutions of CO ligands by phosphine or phosphite ligands allow the adjustment of the nucleophilicity of the metal centres (*vide infra*).

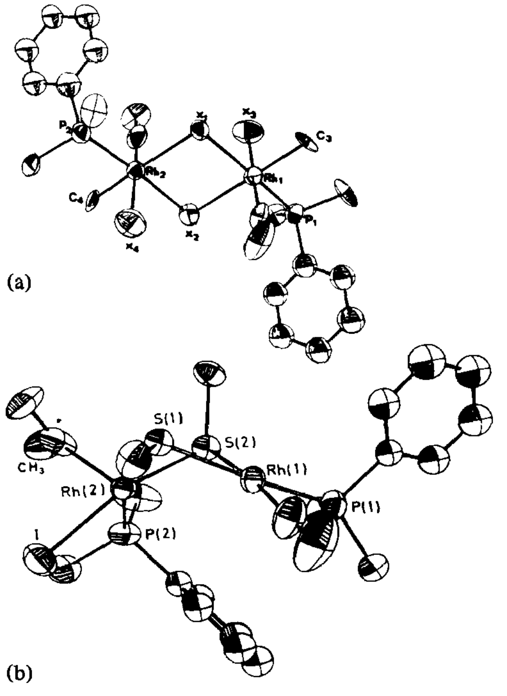


Fig. 3. Isolated products of the reactions of methyl halides on dinuclear rhodium(I) complexes: a 2:1 adduct in the case of halogen bridged (X) compounds and a 1:1 adduct in the case of thiolato bridged compounds, respectively.

Characterized by the value of the dihedral angle α, "the opening of the hinge, or of the book" and by the metal–metal distance, the core Rh_2S_2 ($\alpha = 113.0°$; Rh–Rh = 3.0611°) appears [32d] to be more compact than Rh_2Cl_2 in $[RhCl(CO)(PMe_2Ph)]_2$ [31e].

Used again as a test of reactivity, methyl iodide and bromide undergo oxidative addition to a *single metal centre* of the dinuclear $[Rh_2(\mu\text{-}SBu^t)_2(CO)_2(PMe_2Ph)_2]$ when stoichiometric quantities are added [37]. From a *cis*-migration of the methyl group, acetyl complexes are obtained. Infrared and NMR data, together with X-ray analysis, lead us to assign a dinuclear geometry to these complexes with rhodium atoms respectively in the formal oxidation states I and III (Fig. 3b). The molecule of the complex is bent along the S–S axis, Rh(I) being in a square-planar environment whereas Rh(III) exhibits a square pyramidal geometry. A salient feature of the structure is the rather long Rh–Rh distance (3.110 Å) which excludes any significant metal–metal interaction.

This lack of dative metal–metal bond in an apparently favorable situation of formation is in contrast with previously reported results [38] and our other cited observations. Attempts to perform further oxidative addition reactions to both metal centres have been achieved by treating the complex $[Rh(\mu\text{-}SBu^t)(CO)(PMe_2Ph)]_2$ in powder with CH_3Br in vapor. Infrared and NMR data recorded at −10 °C (in order to avoid the reverse reaction) are consistent with the existence of a dinuclear product having an acetyl group on one Rh(III) centre and a methyl group on the other Rh(III) centre.

In addition, it is noticeable that the very reactive acetyl chloride [37] leads to a chloro bridged complex, as the product of a multistep reaction, including the elimination of bridging ligands:

$$[Rh(\mu\text{-}SBu^t)(CO)(PMe)_2(Ph)]_2 + 4CH_3COCl \longrightarrow [Rh(\mu Cl)(Cl)(CO)_2(COCH_3)(PMe_2Ph)]_2 + 2CH_3COSBu^t$$

I.3 - Symmetrical and Non Symmetrical Oxidative Additions on Dinuclear Companions of Vaska's Compounds

It is probably superfluous to recall the importance of Vaska's complexes and the rôle of their reactivity patterns in the historical development of the concept of oxidative addition on mononuclear complexes. Therefore it seemed of interest to us to use the novel series of iridium(I) dinuclear complexes $[Ir(\mu SBu^t)(CO)(PA_3)]_2$ (A = Me, Ph, NMe_2, OMe, OBu^t) in an attempt to extend this concept to dimetal centres. Such needed complexes were prepared as the final products of the reaction of phosphines or phosphites on the tetracarbonyl $[Ir(\mu\text{-}SR)(CO)_2]_2$ compounds (but this reaction is probably not so simple as our first observations [39] suggested and, in particular, trimetallic and CO-bridged dimetallic intermediates have been observed [40]).

As shown by their CO-frequencies, the required dinuclear complexes lie in the same area of metal basicity as the mononuclear $Ir^I(CO)XL_2$ compounds (Table I). We have also inferred from these data, as expected from (d) type structures (see Fig. 2d), the existence in solution of *cis* and *trans* isomers of position of the CO groups with respect to the Ir_2S_2 core. The crystal structure of the *cis*$[Ir(\mu\text{-}SBu^t)CO(P(OMe)_3)]_2$ has been solved (Fig. 4a).

The $[Ir(\mu\text{-}SBu^t)(CO)(PA_3)]_2$ (with A = Me, Ph, NMe_2, OMe) complexes react irreversibly with molecular hydrogen to yield quantitatively thiolato-bridged dihydrodiiridium complexes $[Ir(H)(\mu\text{-}SBu^t)(CO)(PA_3)]_2$ [32c, 41]. The hydrogenation is accompanied by a shift of *ca.* 20–30 cm^{-1} of the ν(CO) bands toward higher frequencies in the IR spectra. The occurrence of three ν(CO) bands, as well as the NMR data, are consistent with the presence in solution of two isomeric forms of the dihydride species. The ^1H NMR spectra are temperature dependent, indicating a dynamic equilibrium between the two isomers, but in the slow exchange region they show two high field triplets (of unequal intensities) attributable to isomers in which the hydrides are equivalent. In addition, in the case of the phosphite derivative, 'deceptively simple' triplets due to the phosphite protons indicate a strong coupling between equivalent ^{31}P, for both isomers, whereas this coupling appears to be very small in the starting compound.

TABLE I. Infrared Spectra for Complexes $[Ir(\mu\text{-}SBu^t)CO(PR_3)]_2$.

R	$\nu(CO)^a$ cm^{-1}
Me	1955(vs), 1941(vs)
Ph	1965(vs), 1951(vs), 1935(s)
NMe_2	1959(vs), 1943(vs)
OMe	1985(vs), 1975(vs), 1964(vs)

[a] Hexadecane solution.

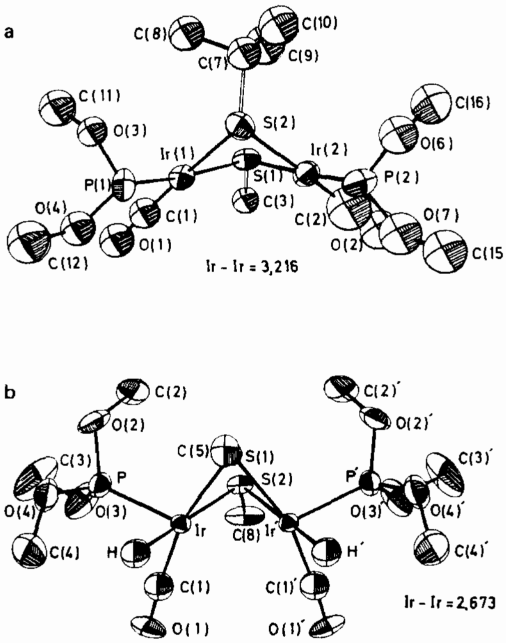


Fig. 4. Structural modifications of a dinuclear iridium compound through oxidation addition of molecular hydrogen.

The crystal structure has been obtained for the *cis* isomer of the phosphite derivative (Fig. 4). Together with the apical position of the phosphite ligand, the most salient feature is the short iridium–iridium distance (2.673 Å) in perfect agreement with the formation of a metal–metal bond.

From the high and probably almost identical values of the P–P coupling constants, the same situation can be inferred for the second isomer. Finally, *cis syn* endo and *trans syn* endo geometries were proposed for this pair of isomers and their dynamic equilibrium was attributed to a *cis–trans* isomerisation process.

TABLE II. Compared Spectroscopic Data for $[Ir(\mu\text{-}SBu^t)(CO)P(OBu^t)_3]_2$ and its 2:1 and 1:1 Hydrogen Adducts.[a]

	νCO cm^{-1}		$\delta\,^{31}P$ ppm/H_3PO_4	
$[Ir(\mu\text{-}SBu^t)(CO)P(OBu^t)_3]_2$	1958(VS)	1945(S)	78.77(s)	
$[Ir(\mu\text{-}SBu^t)(CO)P(OBu^t)_3(H)]_2$	2003(M)	1950(VS)	77.3(s, br)	51.2(t, br)
$[Ir(\mu\text{-}SBu^t)(CO)P(OBu^t)_3(H)_2]_2$	1990(VS)	1982(S)		54.2(t, br)

[a] s: singlet; t: triplet; br: broad.

As expected for metal–metal bonded complexes and following the previous study of semi-isostructural $[Fe(\mu\text{-}SR)(CO)_2L]_2$ complexes, it was possible to protonate the dihydrido diiridium complexes. In the cationic species $[(Ir(H)(\mu\text{-}SBu^t)(CO)(PA_3)_2H]^+$ thus obtained, the ^1H NMR spectra suggest the existence of both isomers as in the starting compounds and, together with the infra data, are consistent with a bridging position of added protons. The significant decrease of the P–P coupling constant emphasizes the similarity of the behaviour of the diiridium compounds and of the d^7–d^7 complexes [21] discussed above. It is interesting to notice that the protonation removed the dynamic equilibrium between isomers on the NMR time scale, as judged from the invariance of the spectra with temperature.

Coming back to the oxidative addition of molecular hydrogen, the case of the tertiobutylphosphite derivatives is of special interest [42], as, in contrast with the previously studied homologous compounds it adds, at first glance, at room temperature and normal pressure, two mol of hydrogen per mol of complex, leading therefore to a 2:1 adduct. This behaviour is similar to that observed by Wilkinson on $[Rh(\mu\text{-}Cl)(PPh_3)_2]_2$ [43], which adds also two mol of H_2 per mol of complex.

These new tetrahydrido compounds are well characterized by infrared spectra, and through simple and decoupled ^1H and ^{31}P spectra experiments. The proton data (τ_{H_a} = 15.98(dd); τ_{H_b} = 26.62(dd); $^2J_{H_aH_b}$ = 3.7 Hz; $^2J_{H_aP}$ = 21.3 Hz; $^2J_{H_bP}$ = 20.6 Hz) are consistent with a mutually *cis* position of the two hydrido ligands on each metal atom, as well as with a *cis* position thereof towards the phosphite ligands. In addition, more precise spectroscopic monitoring of the uptake of hydrogen has shown that a 1:1 adduct is an intermediate of the formation of the preceding 2:1 adduct.

The ^1H NMR spectra clearly demonstrate that the 1:1 adduct is *not symmetrical* with respect to the addition of molecular hydrogen, in significant contrast with the previously described series of dihydro complexes. One of its iridium atoms, namely Ir(III), has got the same coordination as both metal atoms in the tetrahydrido compound whereas the other one, namely Ir(I), is kept free from the oxidative addition of hydrogen. As a leading remark, it is of interest that whereas Ir(I) is allowed to add further hydrogen, the obtention of a symmetrical dihydride seems to be forbidden for this tertiobutylthiolato-bridged compound.

I.4 - General Patterns of the Oxidative Addition Reaction on Two Non-bonded Metal Atoms

The metal–metal bond formation through oxidative addition is adequately rationalized by standard electron counting. That is to say, if we consider a hydrido formulation for the studied symmetrical $[Ir(H)(\mu\text{-}SBu^t)(CO)(PA_3)]_2$ compounds, *i.e.* iridium-(II), d^7 atoms, we can expect the electron pairing accompanied by the observed metal–metal bond formation and diamagnetism.

In the same way, the addition of iodine on the same starting product $[Ir(\mu\text{-}SBu^t)(CO)(PA_3)]_2$ leads to diiodo adducts $[Ir(\mu\text{-}SBu^t)(I)(CO)(PA_3)]_2$ [44]. X-ray investigations showed a symmetrical structure in which each iridium reaches an almost square pyramidal coordinence completed by a short metal–metal distance (2.703 Å). In this compound, as well as in its isomer found in solution, the added iodine atom lies in the apical position. Once again the short iridium–iridium distance clearly suggests the formation of a metal–metal bond.

As far as the balance of the reaction is concerned, the analogy with the formation of a hydrido compound is obvious and the same electron counting rationalizes it satisfactorily. The equation b (scheme I) gives an adequate representation for such a variant of the oxidative addition reaction on a dimetal centre. Similar views, but devoted to other types of dinuclear geometries with other bridging ligands, can be introduced concerning reactions described in the literature [45]. A close analogy is now developed by Stobart, Atwood and co-workers on pyrazolyl-bridged iridium(I) dimer [46].

The above considerations in scheme I, as far as they concern the reactions of the diiridium compounds that we are studying, do not represent the kinetic pathway of the reactions. In contrast with the concerted mechanism which can be reasonably suggested for the hydrogen addition, it is indeed probable, as shown by the trapping effect of galvinoxide, that the addition of iodine is a radical process [44].

TABLE III. Infrared Data for the Compounds $Ir_2(\mu\text{-}SBu^t)_2(\mu\text{-}\eta^1\text{-}RC_2R)(CO)_2(PMe_3)_2$.

	νC=C* cm^{-1}	νCO** cm^{-1}		
A = CH_3; R = CO_2CH_3	1557	1995(s)	1972(m)	1955(m)
A = CH_3; R = CF_3	1554	1996(s)	1971(m)	1955(m)
A = C_6H_5; R = CO_2CH_3	1570	1005(s)	1980(m)	
A = CH_3; R = CF_3	1580	2010.1985***		

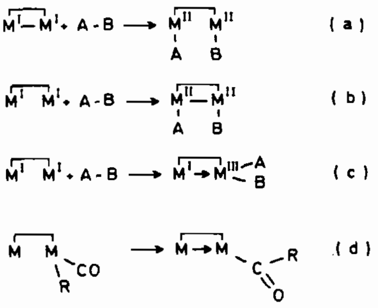
*CsBr pellet. **Hexadecane solution except***.

The preceding scheme of oxidative addition on a dimetal centre can be *mutatis mutandis* formally extended to unsaturated organic substrates. Thus, the binuclear iridium compounds $[Ir(\mu\text{-}SBu^t)(CO)PA_3]_2$ (A = OCH_3, C_6H_5, CH_3) react with different activated acetylenes R–C≡C–R (R = F_3C, $CH_3OC(O)$), giving diiridocyclobutene complexes [47] $Ir_2(\mu\text{-}SBu^t)_2(\mu\text{-}\eta^1\text{-}CF_3C_2CF_3)(CO)_2(PA_3)_2$.

In the case of the trimethylphosphine derivatives, the infrared (Table III) and NMR data show the existence of isomers due to the *cis* or *trans* positions of the carbonyl and phosphine ligands with respect to the dimetal centre.

Therefore, the magnetic equivalence of the R groups in the *trans* isomer is a clear indication for preferring a geometry for which Ir–Ir and C=C axes are parallel instead of being perpendicular, namely to choose a $\mu\text{-}\eta^1$ coordination of the acetylene ligand instead of a $\mu\text{-}\eta^2$ coordination, doubly σ bonded instead of doubly π bonded ligand. The crystal structure [48] of the analogous adduct of bis(cyclooctadiene)di-μ-pyrazolyl-diiridium with the hexafluoro but-2-yne perfectly confirms this bonding possibility and points out an Ir–Ir distance of 2.623 Å, suggesting the formation of a strong metal–metal interaction. As usual in the chemistry of mononuclear complexes, the reaction described can be considered as a two electron oxidative addition but occurring here on two metal atoms, leading us to suppose some electron pairing and metal–metal interactions*.

As a last example of oxidative addition occurring on thiolato-bridged d^8 iridium complexes, we have also initiated an investigation of the reaction of tetracyanoethylene with $[Ir(\mu\text{-}SBu^t)(CO)PA_3]_2$ (A = Me, Ph, OMe) [49]. This activated olefin irreversibly yields dinuclear 1:1 adducts $[Ir(\mu\text{-}SBu^t)(CO)PA_3]_2(C(CN)_2)_2$. In these compounds the added TCNE is bonded to one iridium atom only, and the environment of the iridium atoms is therefore of special interest. One of them is bonded to two sulphur atoms of the *tert-butyl thiolato* bridging groups, one carbon of a carbonyl, and *two carbons of tetracyanoethylene.* The other one is bonded to the two sulphur atoms of the bridging groups, to one carbon of the carbonyl and to two phosphorus atoms of the *two phosphite ligands.* The Ir–Ir separation has decreased to the value of 2.679 Å.



Scheme I. Some fundamental reactions of bridged dimetallic complexes. As far as the balance of the reactions only is concerned, the oxidative addition on a dimetal centre can be represented schematically by equations (a), (b) and (c) depending on the initial existence of a metal–metal bond (a) or not (b and c) (the brackets represent here some assembling ligands). The last equation (d)*, in an attempt to recognize and conceptualize the role of the metal–metal bonding in the fundamental reactions of polymetallic complexes, summarizes the most remarkable step of a metal-promoted alkyl migration recently reported by Collman *et al.* [61].

Taking into account the metal environment, it appears that iridium bonded to TCNE in an electron deficient d^6 centre, formally Ir(III) state, whereas the other iridium atom, formally Ir(I) state, is an electron rich d^8 centre. A heteropolar, dative homonuclear bond is thus required to explain the short Ir(I)–Ir(III) distance. Such metal–metal type of bonding has been recently suggested in other cases [38]. Its formation, as resulting from an oxidative addition, is schematized in Scheme I by equation c. The inexistence of such a phenomenon in the previously mentioned Rh(I)–Rh(III) compound is an interesting discrepancy which requires further investigation.

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*Interestingly, the very recent example [48] of 1,2-addition of an alkyl halide across two adjacent metal atoms gives only a very small contraction of the Ir–Ir distance from 3.216 Å in the bis(cyclooctadiene)di-μ-pyrazolyl-diiridium to 3.112 Å in its adducts.

*Not presented during the EUCHEM Conference Venice.

I.5 - A Tentative Description for a Concerted Mechanism for the Metal to Metal Migration of the Hydrogen Ligand

It would be unpardonable, under estimation of the trend of entropy, to admit *a priori* the direct formation of the $Ir(\mu\text{-}SBu^t)(H)(CO)(PA_3)_2$ complex through a perfectly symmetrical activation state. It is much more probable that an initial attack of the molecular hydrogen occurs on one of the metal centres, and the non-symmetrical $Ir(H)_2(CO)(POBu^t_3)(\mu\text{-}SBu^t)_2Ir(CO)(POBu^t_3)$ is a good model of what really occurs in the general case. Therefore, *if we admit an intramolecular process*, a phase of *migration* of one hydrogen ligand from one metal atom to the other is requested. It is our present opinion that in a compound like $Ir^{III}(H_2)(CO)(PA_3)(\mu\text{-}SBu^t)Ir^{I}(CO)(PA_3)$ the 'pinching' mode of deformation around the S–S axis could be favored by the effect of some dative bonding interaction between d^6 and d^8 centres (following equation c, scheme I). The configuration of the complex obtained by such a process would be close to that drawn in Fig. 5, on the ground of a metal–metal distance decreasing to *ca.* 2.7 Å. This story is probably not a bad heuristic exercise, but more seriously it points out the factors which *could have* some influence on the facility of the pinching, namely on the weight and steric hindrance of the terminal ligands and on the *flexibility* of the bridging ligands. Work is in progress in this field.

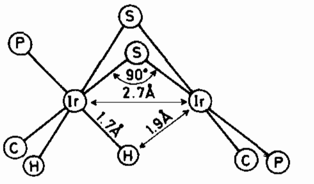


Fig. 5. Suggested structure of the transition state in the postulated metal–metal migration process.

II. Reactivity of Coordination Ligands: Alkenes and Alkynes Bonded to Two Metallic Centres

The preceding studies contribute to the knowledge of the now conventional chapter of the 'fundamental reactions of complexes', broadening this concept to the case of bimetallic complexes. Similarly we thought of studying the 'reactivity of coordinated ligands' when such a complexation implies a dimetal centre.

The study was comparatively carried out on derivatives *with a metal–metal bond* such as $[Ir(\mu\text{-}SBu^t)(CO)L]_2(\mu_2\text{-}\eta^1\text{-}RCCR)$ and on derivatives *without such a bond* such as $[Fe(\mu\text{-}SMe)(CO)_2L]_2(\mu_2\text{-}\eta^1\text{-}RCCR)$ and $[Fe(\mu\text{-}SMe)(CO)_2L]_2(\mu_2\text{-}\eta^1\text{-}F_2CCF_2)$.

The chemistry of bridging alkyne $\mu_2\text{-}\eta^1$ bonded to two metal centres is a recent and growing field of interest [50]. Protonation giving bridged vinyl compounds has been the most studied reaction [50a–e]. In the cases where the two metals are connected by a metal–metal bond, two modes of reaction have been found; one in which the alkyne group has been transformed into a vinyl or a carbenoid complex [50a]; the other in which an intermediate containing a bridging hydride has been isolated [50e]. This intermediate then rearranges to a cationic bridged vinyl complex.

II.1 - Protonation of Metal–Metal Bonded Organodimetallic Compounds

The di-iridacyclobutene complexes $Ir_2(\mu\text{-}SR)_2(\mu\text{-}\eta^1\text{-}RC_2R)(CO)_2(PA_3)_2$ were supposed to admit (see above) some metal–metal bonding interaction and therefore, as well as in the case of other d^7–d^7 complexes (in particular di-iron complexes), some reactions of protonation were expected. The quite complex study [51] of their protonation by trifluoro acetic (XH) acid leads us to isolate a number of compounds and to draw the network of their reactions (Fig. 6). These reactions may be interpreted as *successions of oxidative additions and reductive*

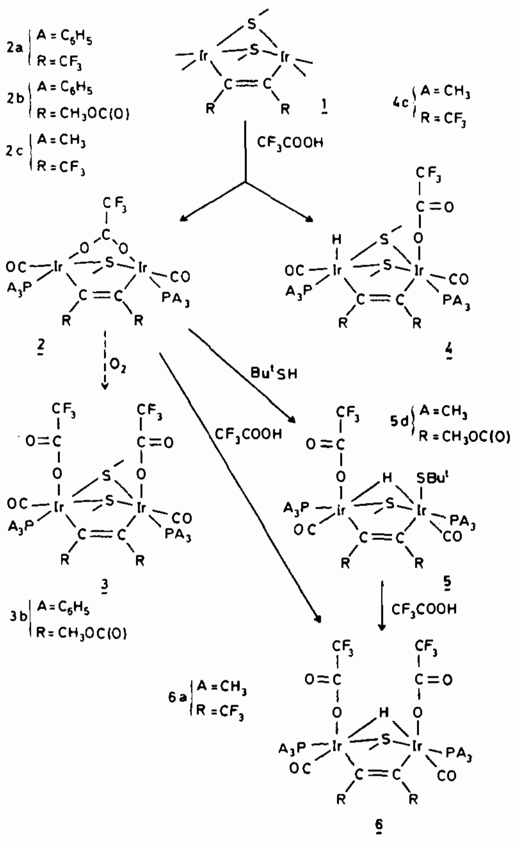


Fig. 6. Protonation of a series of $\mu_2\text{-}\eta^1$ alkyne bridged di-iridium(II) complexes.

eliminations which result in changes in the *coordination numbers* of the metallic atoms and in the nature of the *bridging ligands.*

The whole reaction scheme shows a tendency to spontaneous rearrangements leading to a re-building of the metal–metal bond. Thus the change for compounds where a 3-electron bridging ligand (X or SR) is replaced by a one-electron bridging ligand (H) (formally leading to a 17-electron configuration for each Ir atom), seems to show that *the formation of a metal–metal bond may be a noticeable drawing force in that case.*

It is also to be noted that no reactivity of the alkyne is observed. Such a result may be explained assuming a primary attack on the metal–metal bond. Such an attack has been observed [52] on $Pt_2\mu\text{-}\eta^{-}\text{-}(CF_3C_2CF_3)(cod)_2$ which gives cationic bridged hydrides (which further rearrange to form diplatinum bridged vynil species) by protonation. Some confirmation of this proposal can be drawn from the absence of pathway from *4* to *2a*. More precisely this observation precludes the possibility for *4* to be an intermediate from *1* to *2a*. It is therefore tempting to propose an intermediate protonated cation, leading either to *4* by further addition of acetate, or to *2a* by elimination of a tert butyl thiol, followed by the addition of acetate. For these various reasons, crystallographic scrutiny is also requested on compounds *2, 5* and *6*. Compound *3* is an artifact obtained when traces of oxygen are present.

II.2 - Hydrogenation of Alkynes Bonded to Dimetal Centres

The reactions of the hydrogen with various di-iridacyclobutene complexes have been studied by Mathieu [53]; they are very complicated and their products difficult to isolate. These products have been in a first approach monitored spectroscopically (Infrared and NMR). On the other hand, the compounds *3, 4, 6, 7,* and *8* of Fig. 7 have been isolated indirectly using easy-to-measure amounts of formic acid as hydrogenating reagent, and fully characterized by spectroscopic methods. Finally, products 4, 7 and 8 were recognized in the direct hydrogenation pathway. The network of the reactions of Fig. 7 is like the result of successive oxidative addition of molecular hydrogen (giving an Ir(III)–Ir(III) state), then elimination of tert butylthiol (coming back to an Ir(II)–Ir(II) state), then addition of hydrogen (Ir(III)–Ir(III)). Compound *2* is proposed as an intermediate in the formation of *3* and *4*; compound *6*, which was isolated by starting from the dicarboxylate derivative, is a model for the proposed monobridged intermediate *5*.

Another example of a succession of oxidative addition and reductive elimination reactions related to the preceding one is offered starting from the dihydro compound $[Ir(\mu\text{-}SBu^t)(CO)(PA_3)(H)]_2$ (A = OMe and Me) and reacting with hexafluorobutyne [54]. The product of this reaction (clearly identified by spectroscopic methods) can be described as the juxtaposition of dihydro and alkyne adducts of Vaska's complex associated through thiolato bridges, namely as a dissymmetrical Ir(III)–Ir(III) dinuclear complex $(PA_3)(CO)(H)_2Ir(\mu\text{-}SBu^t)_2Ir(C_4F_6)CO(PA_3)$. When R = OMe, the loss of H_2 induces a new molecular rearrangement leading to the symmetrical diiridacyclobutene compound previously obtained by direct reaction. It is quite probable that the first step of the reaction of the symmetrical dihydro compounds with the activated acetylene requires the dissymmetrical dihydro compounds as intermediates. Such a form could well be the intermediate of the dynamic equilibrium between *cis* and *trans* isomers of the symmetrical compound.

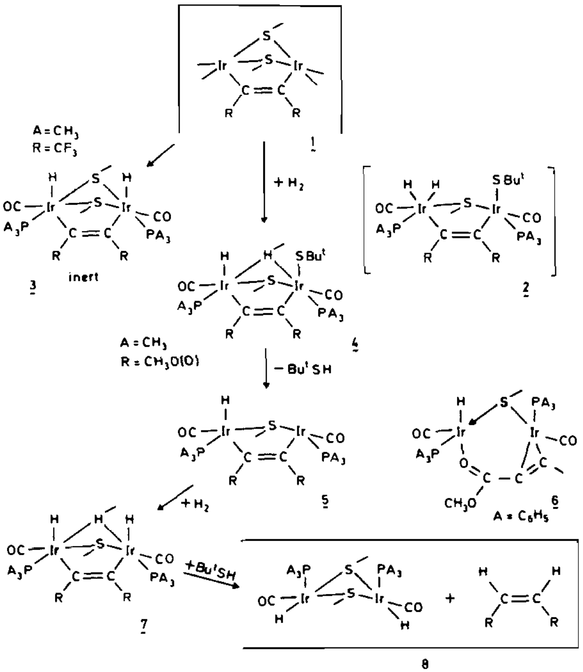
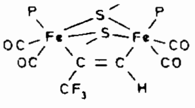


Fig. 7. Pathway 1–4–7–8 for the hydrogenation of $\mu_2\text{-}\eta^1$ alkyne ligand and isolated products 3–8 in the reaction of formic acid on the dinuclear complexes.

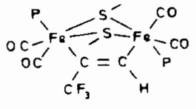
II.3 - Protonation of Non Metal–Metal Bonded Organodimetallic Compounds

It has been shown by Mathieu [55] that the reactions of $Fe(\mu\text{-}SMe)(CO)_2(PMe_3)_2RCCR$ complexes with the electrophilic proton and carbocation lead to vinylic species. Especially, the molecular structure [56] of the cation $[(\mu\text{-}SCH_3)Fe(CO)(PMe_3)_2]_2\text{-}(CH_3COOCCHCOOCH_3)^+$ shows the vinylic group to be σ-bonded to one iron atom through one carbon of the double bond, and to be bonded through the oxygen of the ester group in α position towards the carbon to the second iron atom. Then, the hydrogen is in a *trans* position towards this ester moiety.

With a dissymetrical alkyne like CF_3CCH, the study is both more complex and more interesting, due to the existence of the disubstituted compound $Fe_2(\mu\text{-}SMe)_2(CO)_2(PMe_3)_2CF_3CCH$ in solution in three isomeric forms in equilibrium at room temperature. Two of these forms are largely predominant.



Isomer I



Isomer II

Isomer I reacts with trifluoroacetic acid to yield a purple primary product which slowly gives the $\sigma-\pi$ bonded vinylic structure. The intermediate purple product seems to exhibit a very unusual mode of bonding of the vinylic moiety which makes it look like a *carbocationic bridged alkylidene complex* [55].

Through protonation of isomer (II) with trifluoroacetic acid, a monoaceto molecular compound with a dissymetrical structure is isolated, where the proton is linked to the carbon of the C–H group of the alkyne.

The differences observed in the reactivity may be due to the nature of the ligands in a *trans* position towards the carbons of the alkyne, *i.e.* phosphines in isomer (I), carbon monoxide in isomer (II). The difference between the π-accepting abilities of these ligands should result in a shift of the attacking site of the proton.

II.4 - Rearrangement of the Doubly σ Bonded Tetrafluoroethylene into a CF–CF₃ Carbene Bridge, then into a Terminal Perfluoromethyl Carbyne Ligand [57]

The insertion of tetrafluoroethylene into the Fe–Fe of the dinuclear complex $[\mu(SCH_3)Fe(CO)_3]_2$ is photochemically induced. When the temperature of the reaction is stabilized at 20 °C, the major product is the yellow dinuclear species $\mu(SCH_3)_2\mu(C_2F_4)$-$Fe_2(CO)_6$ *1*, where C_2F_4 bridges the Fe atom with two σ(C–Fe) bonds, while the C–C bond is parallel to the Fe–Fe axis. When the temperature is higher, *i.e.* 35 °C, the product is the red dinuclear species $\mu(SCH_3)_2\mu(FCCF_3)Fe_2(CO)_6$ *2*, which contains a $CF-CF_3$ carbene bridge. It is possible by heating *1* to obtain *2*, and a mechanism for this reaction is proposed (Fig. 8) based in part on a study of the action of BF_3 on *1*. The action of BF_3 on the disubstituted derivative of *2* with trimethylphosphine, affords $\mu(SCH_3)_2Fe_2(CO)_3(PCH_3)_3)_2(CCF_3)$ BF_4 (*7*), which may be a perfluoromethylcarbyne complex.

The crystal structure determination (Fig. 9) of both compounds *1* and *2* leads to values of the Fe–Fe distance (respectively 3.311 Å and 2.963 Å) compatible with the absence of a metal–metal bond.

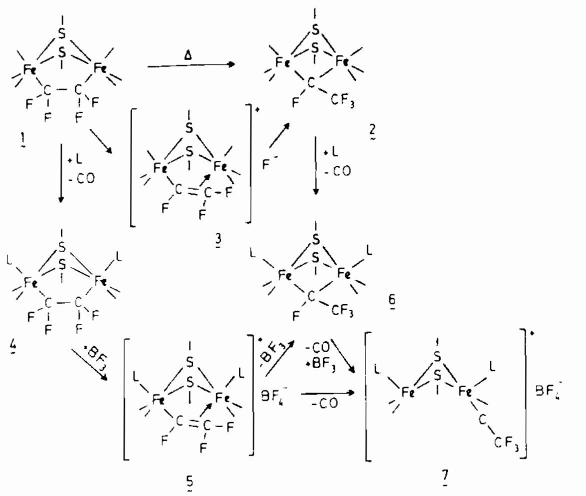


Fig. 8. Proposed mechanism of a rearrangement of the C_2F_4 bridging group to give a trifluoromethylfluoromethylene bridge, then a terminal perfluoromethyl carbyne ligand.

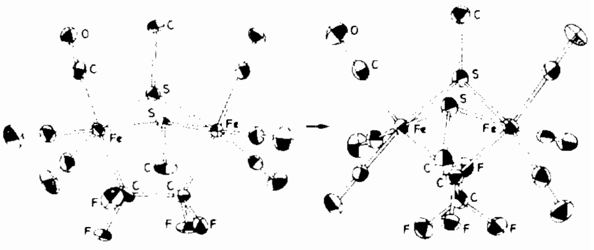


Fig. 9. The transformation of the μ_2-η^1 form into a carbene bridge form of C_2F_4.

The fluorine migration in mononuclear complexes is a rather well established reaction [58]. In the present case, it supposes the abstraction of an ion-like fluoride in intermediate *3*. This abstraction is easier in the presence of a fluoride ion abstractor and leads to the isolation of the product *5* when starting with phosphine derivative *4*. This product when left at room temperature transforms into compound *7* which, from spectroscopic data, could be *the first example of a perfluoroalkyl carbyne complex.*

III. Prospects for Heterobimetallic Compounds with New Assembling Ligands

Some published results show a possibility of activation of organic groups through the cooperative action of two different metallic centres (see for instance [16] and [62]). In that case, the organic group is initially bonded to one of the metallic centres and the two centres do not belong to the same complex.

A further step towards direct activation of small molecules may be thought of with complexes having assembling ligands which associate distinct metallic centres.

This approach focuses therefore on the choice of ligands liable to carry out such an association. A possible strategy consists of using bifunctional ligands, each extremity of which has different affinities for such or such metallic centre (soft or hard bonding capacity for instance).

III.1 - Heterometallic Complexes Deriving from Li^+*-*$C_5H_4(CH_2)_nPPh_2^-$ *Bifunctional Ligands (n = 0, 1, 2)*

As recently shown by Mathey *et al.* [15a–d], it is possible, starting from $C_5H_5(CH_2)_nPPh_2$ compounds, to get ligands with phosphine and cyclopentadienyl functionalities, when wrenching a proton by means of butyl-lithium. The length of the carbon chain bonding the two functional sites is *a priori* an important variable which will allow the modification of the interaction between the metallic centres bonded to the two functional sites.

Taking advantage of the reactivity of the cyclopentadienyl site during the first reaction step, we carried out syntheses of complexes with a potentially usable tertiary phosphine site [59]. This verified when n = 2; heterobimetallic complexes associating Titanium(IV) with Rhodium(I) or Molybdenum(0), then Zirconium(IV) with Rhodium(I) or Molybdenum(0) have been prepared and the study of their properties is in progress.

III.2 - Synthesis and Reactivity of Homo and Heterobimetallic Complexes Deriving from Ligands with Tertiary Phosphine and Alkyl Amine Functionalities

The bidentate dissymetrical molecule Ph_2P–CH_2–NEt_2 (diphenylphosphinodiethylaminoethane (p.a.m.)) exemplifies another case of ligand with soft and hard ends, respectively.

The p.a.m. ligand proves to be an efficient assembler allowing the synthesis with palladium(II) and platinum(II) of (b) type dinuclear complexes which reversibly fix carbon monoxide [60]. The p.a.m. also forms dinuclear compounds with Pt(I) and Rh(I), as well as a mixed Rh–Pd compound.

IV. Conclusion

The involvement of metal–metal bonds making or breaking in the fundamental reactions like protonation, oxidative addition, 1,2-migration is clearly demonstrated in numerous examples. Evidence of their participation in the reactions of coordinated ligands is more difficult to assess, but in such cases it is the greater choice of coordination modes for these ligands which makes the reactions of dinuclear compounds specific.

Implications of the participation of the metal–metal bonding are now to be searched in the field of homogeneous catalysis.

Acknowledgements

The author wishes to express his gratitude to his co-workers who have performed the works described above and whose names appear in the references listed below. He particularly thanks Drs. R. Mathieu and A. Maisonnat for reading the manuscript and helpful discussions.

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