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C—H Activation by dinuclear phosphine bridged complexes of rhodium, iridium, and ruthenium*

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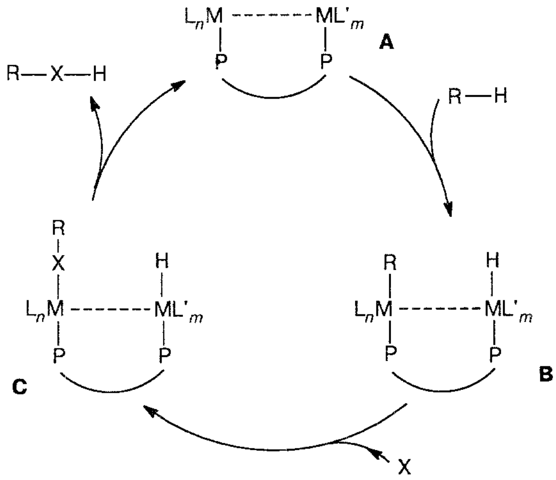
The possibility of activation of the C—H bond by dinuclear phosphine bridged complexes of rhodium, iridium, and ruthenium is considered.

Key words: dinuclear phosphine bridged complexes of Rh, Ir, and Ru.

Mononuclear organometallic complexes form the backbone of a great variety of industrially used homogeneous catalysts. In addition, many general concepts such as oxidative addition, reductive elimination, migratory insertion, oxidative coupling, *etc.* have been developed using mononuclear compounds. The question arises: can the same concepts also be applied to bi- and multinuclear species thus providing unprecedented chemical reactions and novel catalytic pathways?

With this concept in mind, we initiated a program focusing on dinuclear phosphine bridged complexes of type **A**, expecting that CH-bond activation would occur as shown in Scheme 1.

Scheme 1



In the first step R—H undergoes oxidative addition to the two metal atoms of complex **A** yielding product **B**. We assume that in this way — separating the two activating metal centers — reductive elimination of R—H is impeded thus favoring insertion of a further molecule X to give product **C**. The catalytic cycle is completed by reductive elimination of RXH. There have been many attempts to insert a molecule X into a monometallic complex formed by oxidative addition with splitting of a C—H bond, but reductive elimination of RH prevailed. We believe that the approach presented in Scheme 1 using oxidative addition of RH at two metal atoms makes it possible to prevent the reductive elimination of RH prior to insertion of molecule X.

In analogy to Bergman's[1] and Graham's[2] pioneering works, we decided to synthesize type **A** rhodium, iridium, and ruthenium complexes (Scheme 1). Various phosphine bridged complexes of rhodium with $R_2P-(CH_2)X-PR_2$ ligands have been reported in the literature.[3] To our knowledge, no iridium complexes have been reported. Regarding ruthenium, reference must be given to Meyer,[4] Singleton,[5] and Coleman.[6] Generally it can be stated that complexes of type **A** are rather rare.

We succeeded in the synthesis of 19 new iridium and rhodium complexes according to Scheme 2.[7]

Starting from a hexamethylbenzene—$RuCl_2$ complex, four ruthenium complexes have been prepared. The new iridium, rhodium and ruthenium complexes are listed in Table 1.

It is known that the rate of formation of complexes with chelating diphosphine ligands $R_2P(CH_2)_xPR_2$ depends considerably on the size of the diphosphine chelate ring.[8] The equilibrium in Scheme 3, in which one or two metal atoms are bonded to the phosphorus ligand, plays a key role here.

It has been established that the position of this equilibrium is metal-dependent.[9] For instance, the complex $Rh(CO)Cl[Bu_2{}^tP(CH_2)_{10}PBu_2{}^t]$ is dimeric whereas the analogous iridium complex has a monomeric struc-

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Scheme 2

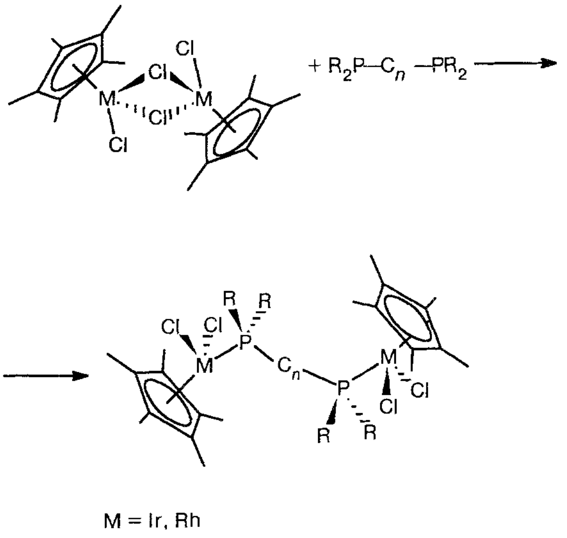


Table 1. Complexes of Ir, Rh, and Ru with $R_2P(CH_2)_xPR_2$ ligands

1	$[\mathrm{Cp^*IrCl_2}](\mu\text{-}\mathrm{P_2Me_2})$	12	$[\mathrm{Cp^*RhCl_2}]_2(\mu$-dmpm)
2	$[\mathrm{Cp^*IrCl_2}]_2(\mu$-dmpm)	13	$[\mathrm{Cp^*RhCl_2}]_2(\mu$-dmpe)
3	$[\mathrm{Cp^*IrCl_2}]_2(\mu$-dmpe)	14	$[\mathrm{Cp^*RhCl_2}]_2(\mu$-dmpp)
4	$[\mathrm{Cp^*IrCl_2}]_2(\mu$-dmpp)	15	$[\mathrm{Cp^*RhCl_2}]_2(\mu$-dppm)
5	$[\mathrm{Cp^*IrCl_2}]_2(\mu$-dmpbe)	16	$[\mathrm{Cp^*RhCl_2}]_2(\mu$-dppp)
6	$[\mathrm{Cp^*IrCl_2}]_2(\mu$-dppm)	17	$[\mathrm{Cp^*RhCl_2}]_2(\mu$-dpp(b)
7	$[\mathrm{Cp^*IrCl_2}]_2(\mu$-dppe)	18	$[\mathrm{Cp^*RhCl_2}]_2(\mu$-dpppe)
8	$[\mathrm{Cp^*IrCl_2}]_2(\mu$-dppp)	19	$[\mathrm{Cp^*RhCl_2}]_2(\mu$-dpph)
9	$[\mathrm{Cp^*IrCl_2}]_2(\mu$-dpp(b)	20	$[(\eta^6\text{-}\mathrm{C_6Me_6})\mathrm{RuCl_2}]_2(\mu$-dmpm)
10	$[\mathrm{Cp^*IrCl_2}]_2(\mu$-dpppe)	21	$[(\eta^6\text{-}\mathrm{C_6Me_6})\mathrm{RuCl_2}]_2(\mu$-dmpe)
11	$[\mathrm{Cp^*IrCl_2}]_2(\mu$-dpph)	22	$[(\eta^6\text{-}\mathrm{C_6Me_6})\mathrm{RuCl_2}]_2(\mu$-dmpp)
		23	$[(\eta^6\text{-}\mathrm{C_6Me_6})\mathrm{RuCl_2}]_2(\mu$-dmph)

Note: The following abbreviations are used:
Cp* = pentamethylcyclopentadienyl,
dmpm = $\mathrm{Me_2P{-}(CH_2){-}PMe_2}$,
dppe = $\mathrm{Ph_2P{-}(CH_2)_2{-}PPh_2}$,
dmpe = $\mathrm{Me_2P{-}(CH_2)_2{-}PMe_2}$,
dppp = $\mathrm{Ph_2P{-}(CH_2)_3{-}PPh_2}$,
dmpp = $\mathrm{Me_2P{-}(CH_2)_3{-}PMe_2}$,
dppb = $\mathrm{Ph_2P{-}(CH_2)_4{-}PPh_2}$,
dmph = $\mathrm{Me_2P{-}(CH_2)_6{-}PMe_2}$,
dpppe = $\mathrm{Ph_2P{-}(CH_2)_5{-}PPh_2}$,
dpph = $\mathrm{Ph_2P{-}(CH_2)_6{-}PPh_2}$,
dppm = $\mathrm{Ph_2P{-}(CH_2){-}PPh_2}$,
dmpbe = $\mathrm{Me_2P{-}(C_6H_4){-}PMe_2}$.

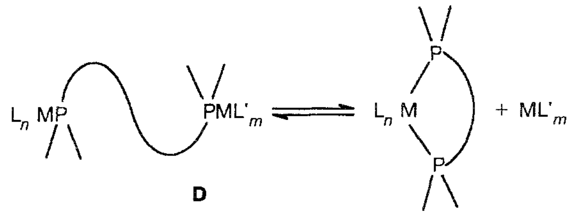
ture. With $\mathrm{Ph_2P(CH_2)_xPPh_2}$ ligands monomeric chelate complexes are commonly formed with $x = 2$, while when $x = 1$, 3, or 4 dimeric derivatives are also obtained. Apparently the geometry and the reactivity of these species depend on the strain in the chelate ring, the flexibility, and the electronic properties of the diphosphine.

To confirm the structures, X-ray analyses of complexes **2—5**, **13**, **21**, and **23** were carried out. The metal—metal distances are as follows (Å):

2	$[\mathrm{Cp^*IrCl_2}]_2$dmpm	6.65
3	$[\mathrm{Cp^*IrCl_2}]_2$dmpe	7.33
4	$[\mathrm{Cp^*IrCl_2}]_2$dmpp	8.42
5	$[\mathrm{Cp^*IrCl_2}]_2$dmpbe	8.20
13	$[\mathrm{Cp^*RhCl_2}]_2$dmpe	8.20
21	$[(\eta^6\mathrm{C_6Me_6})\mathrm{RuCl_2}]_2(\mu$-dmpe)	8.45
23	$[(\eta^6\text{-}\mathrm{C_6Me_6})\mathrm{RuCl_2}]_2(\mu$-dmph)	11.32

Obviously, no metal—metal bonding exists. On the contrary, the metals are separated by long distances favoring a bridging structure as shown in Schemes 2 and 3.

Scheme 3



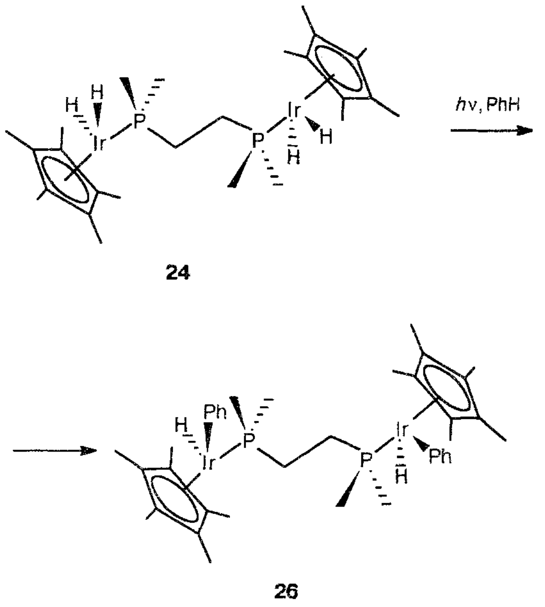
Attempts to bring the metals closer together by shortening the P—P distances (complex **2**) or lengthening them (complex **4**), or by creating a cisoide conformation (complex **5**) failed. The use of $\mathrm{Me_2P{-}(CH_2)_x{-}PMe_2}$ chelate phosphine ligands leads only to dimeric structures without metal—metal bonding.

C—H bond activation in methane, benzene, and cyclohexane

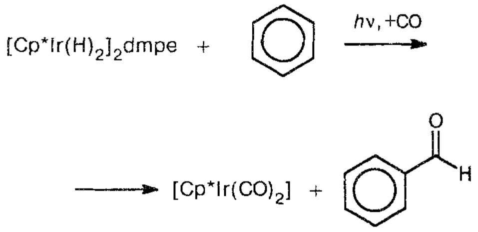
Dinuclear phosphine bridged complexes of iridium and rhodium are very similar to those of Bergman[1] and Graham[2] who applied them as hydrides to activate C—H bonds. In view of this, complexes $[\mathrm{Cp^{*+}IrCl_2}]_2$dmpe (**3**) and $[(\eta^6\text{-}\mathrm{C_6Me_6})\mathrm{RuCl_2}]_2$dmpe (**20**) were chosen. Reduction with $\mathrm{Li(Et_3BH)}$[Super-Hydride] or $\mathrm{NaBH_4/Pr^iOH}$ yielded hydrides $[\mathrm{Cp^*Ir(H)_2}]_2$dmpe (**24**) and $[(\eta^6\text{-}\mathrm{C_6Me_6})]\mathrm{Ru(H)_2}]_2$dmpe (**25**), which are extremely sensitive towards moisture or air. Crystals for structure determination could not be obtained but the hydrides were unequivocally characterized spectroscopically.[7]

The iridium complex **24** and the ruthenium complex **25** were photolyzed (500 W mercury lamp) in the presence of methane, neopentane, cyclohexane, and benzene in a pressure vessel made of quartz. Only with benzene and cyclohexane was C—H activation observed. The experiments must be carried out under a nitrogen atmosphere (pressure 5—10 Bar) to obtain characterizable products. With benzene, complex **24** quantitatively yielded complex **26**, as shown spectroscopically (Scheme 4).

Scheme 4



Scheme 5



Complex **26** could be unambiguously characterized spectroscopically. Interestingly, if the reaction is carried out under 3.5 Bar CO, benzaldehyde is formed in a stoichiometric reaction according to Scheme 5.

With cyclohexane, two products **27** amd **28** (ratio 1:4) are formed in a yield of 50% according to Scheme 6. It was not possible to separate these two complexes.

The activation of benzene was also possible with complex **25** as shown in Scheme 7.

The formation of complex **29** could be confirmed spectroscopically. Simultaneous insertion of CO yielded benzaldehyde.

The results of this work confirm that activation of C—H bonds is possible by dinuclear phosphine bridged complexes. However, no unusual reactions were observed supporting Scheme 1. Evidently, it must be concluded that each metal atom in these complexes acts independently.

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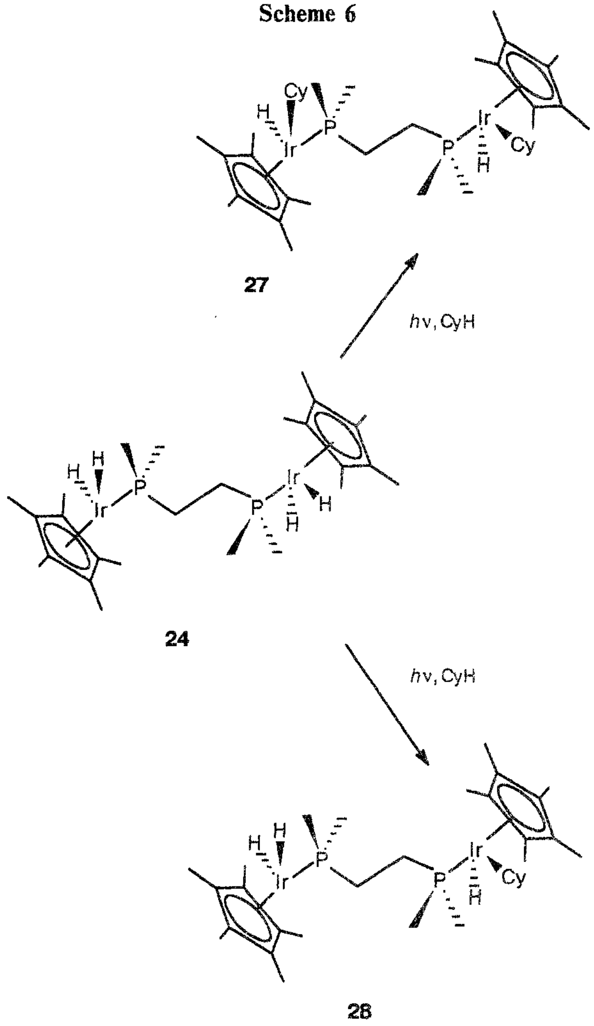
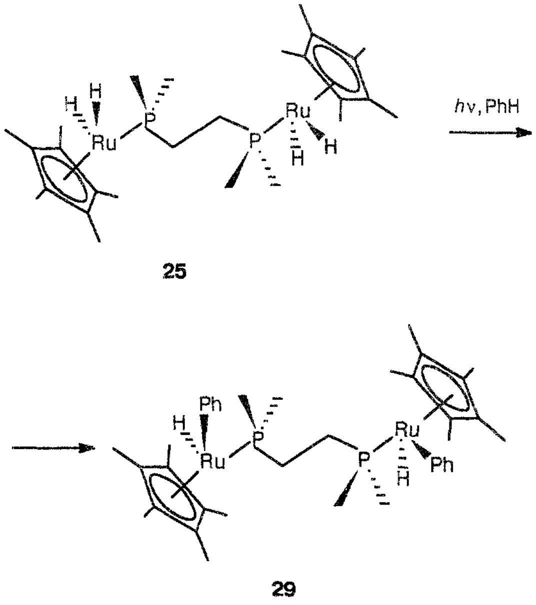
Scheme 6



Scheme 7



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