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The ambivalent behaviour of aryl-functionalized phosphines: coordination, hemilability and beyond

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Aryl-functionalized phosphines of the general composition $R_2P(CH_2)_n$(aryl) with bulky substituents R at the phosphorus atom react with olefin–rhodium(I) and –iridium(I) compounds to give complexes in which the phosphine behaves either as 2-electron or (2 + 6)-electron donor ligand. The aryl moiety is weakly coordinated and can be replaced by CO, acetonitrile or H_2 without breaking the metal–phosphorus bond. In some cases, the interaction of the phosphines with the rhodium or iridium centre leads to an insertion of the metal into one of the C–H bonds of the aryl group to afford a six-membered chelate ring system. This cyclometalation reaction not only proceeds under mild conditions but is also completely reversible as shown by addition reactions and labeling experiments. With the must bulky phosphine $tBu_2P(CH_2)_2C_6H_3$-2,6-Me_2, the isolation and structural characterization of a *cis*-configurated rhodium dicarbonyl *cis*-$[RhCl(PR_3)(CO)_2]$ and of an unprecedented dinuclear alkylrhodium(III) compound built up by two 14-electron $[RhCl_2(alkyl)(PR_3)]$ units has been achieved. Ruthenium(II) complexes with $tBu_2P(CH_2)_2C_6H_5$ and $tBu_2P(CH_2)_2OC_6H_5$ as ligands have been prepared from either $RuCl_3 \cdot 3H_2O$ or $[(\eta^6$-*p*-cymene)-$RuCl_2]_2$ as starting materials. From a five-coordinate $RuH(=C=CH_2)$ derivative, upon treatment with HBF_4, a cationic carbyneruthenium compound could be generated which is an active catalyst in olefin metathesis.

1. Introduction

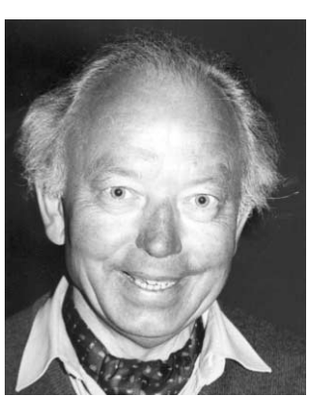
There is an increasing interest in the design of functionalized phosphines, which could behave as hemilabile ligands and, with the support of the weakly coordinating site, are thus able to stabilize a coordinatively unsaturated transition-metal centre.[1] While in most of the initial studies,[2] including those from our group,[3] phosphines containing ether, ester or olefinic functionalities were used, more recent investigations had focussed on ligands such as $Ph_2P(CH_2)_nXC_6H_4R$ being either 2-electron or (2 + 6)-electron donor moieties. As was shown, in particular, by Mirkin and co-workers, metal complexes derived from these ligands undergo novel η^6-arene/free arene exchange reactions with rates that are dependent on the electron richness of the arene, the polarity of the solvent and the presence of internal ether groups which can catalyze the reaction.[4]

Following our work on low-valent transition-metal complexes with P*i*Pr$_3$ as ligand, which led, for example, to the preparation of a series of metalla-cumulenes *trans*-$[MCl\{=C(=C)_nRR'\}(P$*i*$Pr_3)_2]$ (M = Rh, Ir; n = 1–4; R, R′ = H, alkyl, aryl),[5] we were tempted to find out whether with phosphines such as *i*$Pr_2P(CH_2)_n$(aryl) and *t*$Bu_2P(CH_2)_n$(aryl) (n = 2 or 3), both related in size to P*i*Pr$_3$, monomeric species $[MCl(PR_3)_2]$ are accessible and what their reactivity toward alkynes, diynes etc. is. In the course of these studies we found that apart from some similarities in the behaviour of P*i*Pr$_3$ and the aryl-functionalized phosphines, interesting differences exist among which the easy and reversible C–H activation of the aryl unit appears the most challenging. Moreover, the most bulky phosphine *t*$Bu_2P(CH_2)_2C_6H_3$-2,6-Me_2 with a triply substituted aryl functionality allowed for the first time the structural characterization of a *cis*-configurated rhodium dicarbonyl *cis*-$[RhCl(PR_3)(CO)_2]$ as well as the isolation of an unprecedented dinuclear alkylrhodium(III) compound built up by two 14-electron $[RhCl_2(alkyl)(PR_3)]$ units.

In this article, we summarize our work on the coordinating capabilities of bulky aryl-functionalized phosphines toward rhodium, iridium and ruthenium as metal centres. The potential of the new phosphines as supporting ligands in some catalytic reactions will be also briefly discussed.

2. Preparation of the ligands

A well-known procedure for the preparation of alkyldiphenylphosphines of the type $Ph_2P(CH_2)_nC_6H_5$ (n = 2, 3) consists of the reaction of $LiPPh_2$ or $KPPh_2$ with the respective benzene derivative $C_6H_5(CH_2)_nX$ (X = Cl, Br).[4] However, this method could not be applied for the diisopropyl- and di-*tert*-butylphosphine analogues since dialkylphosphides MPR_2 upon treatment



Helmut Werner

Helmut Werner was born 1934 in Mühlhausen in Thüringen. After obtaining his Diploma degree with Franz Hein at the University of Jena, he went to Munich to work for his PhD with Ernst Otto Fischer. Following postdoctoral work with Jack Richards at Caltech (Pasadena) and finishing his Habilitation at the Technical University in Munich, he joined the Faculty at the University of Zurich, Switzerland, where he became Professor of Chemistry in 1970. He returned to Germany at the end of 1975 to take up the chair of Inorganic Chemistry at the University of Würzburg. He was the Dean of the Faculty from 1987 to 1989 and the Chairman of an Interdisciplinary Research Unit from 1990 to 2001. He has been honoured by the awards of the Pacific West Coast Inorganic Lectureship (1987) by the American Chemical Society, the Alfred-Stock-Gedächtnispreis by the German Chemical Society (1988), the Centenary Medal and Lectureship by the Royal Society of Chemistry (1993), the Max-Planck-Forschungspreis (1994), the Paolo-Chini-Memorial Lectureship by the Italian Chemical Society (1995) and the Alexander-von-Humboldt/J. C. Mutis Award (1995). Since 1988, he has been a fellow of the Royal Society of Chemistry and of the Deutsche Akademie der Naturforscher Leopoldina.

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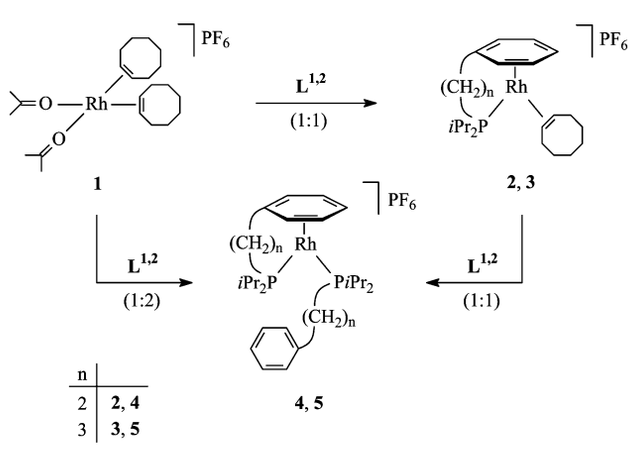
with alkylhalides R′X undergo a halide–metal exchange affording *via* reaction of MPR_2 with the intermediarily formed R_2PX the corresponding diphosphines P_2R_4.

A convenient route to prepare the required phosphines iPr$_2$P(CH$_2$)$_2$C$_6$H$_5$ (**L**^{1}), iPr$_2$P(CH$_2$)$_3$C$_6$H$_5$ (**L**^{2}), tBu$_2$P(CH$_2$)$_2$C$_6$H$_5$ (**L**^{3}) and tBu$_2$P(CH$_2$)$_2$OC$_6$H$_5$ (**L**^{5}) proceeds *via* the trialkylphosphonium bromides [R$_2$PH(CH$_2$)$_n$C$_6$H$_5$]Br and [tBu$_2$PH(CH$_2$)$_2$OC$_6$H$_5$]Br. These intermediates are obtained by heating a mixture of HPR_2 with, respectively, C$_6$H$_5$(CH$_2$)$_n$Br and C$_6$H$_5$O(CH$_2$)$_2$Br for 24 h at 90 °C in the absence of solvent. After cooling, the purified phosphonium bromide is treated with a concentrated aqueous solution of NH_3 or KOH to give **L**^{1}, **L**^{2}, **L**^{3} and **L**^{5} as colorless viscous liquids in 78–89% yield. For the reaction of HPtBu$_2$ with C$_6$H$_5$O(CH$_2$)$_2$Br the temperature should not exceed 80 °C, since otherwise partial decomposition of the functionalized phenyl ether occurs.[6]

The preparation of the most bulky phosphine tBu$_2$P(CH$_2$)$_2$-C$_6$H$_3$-2,6-Me$_2$ (**L**^{4}) is somewhat different and occurs in three steps. The first consists in the formation of the Grignard reagent ClMg(CH$_2$)$_2$C$_6$H$_3$-2,6-Me$_2$, which reacts with tBuPCl$_2$ at 0 °C in THF to give ClP(tBu)(CH$_2$)$_2$C$_6$H$_3$-2,6-Me$_2$. Subsequent treatment of the chlorophosphine with a solution of tBuLi in pentane affords, after hydrolysis with degassed water, the product **L**^{4} in about 80% yield. While **L**^{4} similarly to the counterparts **L**$^{1–3}$ and **L**^{5} has been characterized by mass spectra and NMR spectroscopy, correct elemental analyses could only be obtained for the methylphosphonium salt prepared from **L**^{4} and CH_3I.[7]

3. Reactions of cationic olefinrhodium(I) complexes with L$^{1–3}$

The highly reactive bis(acetone)rhodium(I) derivative **1** is an appropriate starting material not only for the synthesis of compounds [(η^6-arene)(κ^2-iPr$_2$PCH$_2$PR$_2$)Rh]PF$_6$,[8] but also for that of the half-sandwich-type complexes **2**–**5** (Scheme 1). The success of the preparation of **2** and **3**, in which only one phosphine **L**^{1} or **L**^{2} is coordinated to rhodium, is strictly dependent on the reaction conditions. If these are not obeyed, mixtures of **2** and **4** or of **3** and **5** are obtained due to the lability of the Rh–C$_8$H$_{14}$ bond. X-Ray diffraction studies revealed that in compound **2**, in which the bridge between the arene and the iPr$_2$P unit is shorter than in **3**, the six-membered ring possesses a slightly inverse boat conformation with the *ipso*-carbon atom C1 and, to a smaller extent, the carbon atom C4 in *para* position being bent toward the metal center. As a consequence of the reduced strain, the arene ring in **3** is nearly planar and symmetrically coordinated to rhodium. Despite the conformational differences, the bond lengths Rh–P and Rh–C(olefin) in **2** and **3** are almost the same.[6] With regard to the structure of the bis(phosphine) complexes **4** and **5** in solution, it is important to note that in the temperature range between 295 and 363 K the



Scheme 1

^{1}H and ^{31}P NMR spectra are not temperature-dependent, which means that these molecules are rigid on the NMR time scale. This in contrast to the Ph$_2$P-containing compound [{η^6-*p*-FC$_6$H$_4$(CH$_2$)$_3$PPh$_2$-κ*P*}{*p*-FC$_6$H$_4$(CH$_2$)$_3$PPh$_2$-κ*P*}Rh]BF$_4$ reported by Mirkin and co-workers,[4] for which a fluxional behaviour in solution has been observed.

The cyclooctene ligand in the chelate complex **2** is displaced not only by **L**^{1} but also by ethene, maleicacid anhydride, ethyl propiolate and triisopropylstibine. Under an ethene atmosphere, compound **3** behaves similarly and affords the corresponding ethene derivative. All these reactions are rather slow, probably due to the fact that the metal center in the 18-electron starting materials is significantly shielded. The X-ray crystal structure analysis of [{η^6-C$_6$H$_5$(CH$_2$)$_3$PiPr$_2$-κ*P*}(C$_2$H$_4$)Rh]BF$_4$ revealed that the Rh–P distance and the bond angles of the cyclic RhPC$_4$ moiety are nearly identical with those of **3**.

Salts of the cation [{η^6-C$_6$H$_5$(CH$_2$)$_2$PtBu$_2$-κ*P*}(C$_8$H$_{14}$)Rh]$^+$ were obtained by using either compound **1** or the dimer [Rh(C$_8$H$_{14}$)$_2${μ-O$_2$S(O)CF$_3$}]$_2$ as the precursor. The anticipated lability of the Rh–C$_8$H$_{14}$ bond has been confirmed by the substitution reaction with ethyl propiolate which gives the corresponding alkyne complex in practically quantitative yield. While most of the relevant spectroscopic data of [{η^6-C$_6$H$_5$(CH$_2$)$_2$PtBu$_2$-κ*P*}(C$_8$H$_{14}$)Rh]PF$_6$ and [{η^6-C$_6$H$_5$(CH$_2$)$_2$-PiPr$_2$-κ*P*}(C$_8$H$_{14}$)Rh]PF$_6$ are quite similar, the stability of the tBu$_2$P-containing species in solution and in the solid state is enhanced compared with the iPr$_2$P counterpart, probably due to a better shielding of the metal by the more bulky *tert*-butyl groups.

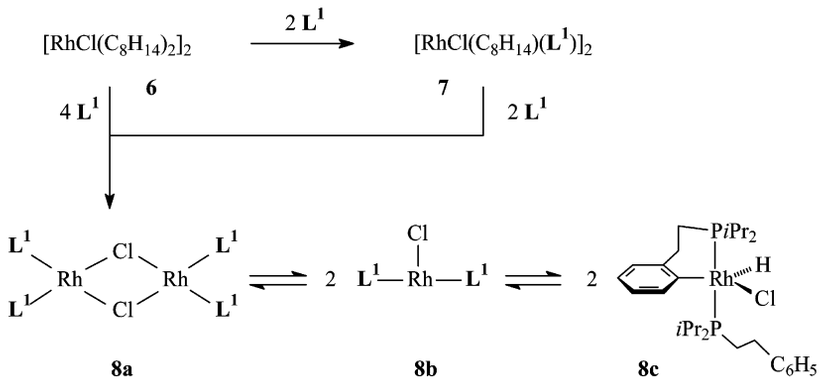
4. Reversible C–H activation at the aryl functionality

Under conditions analogous to those used for the preparation of [RhCl(PiPr$_3$)$_2$]$_2$,[9] the reaction of **6** with a twofold excess of **L**^{1} in pentane results in the formation of a yellow solid, the analytical composition of which corresponds to **7** (Scheme 2). The product is thermally not exceedingly stable and decomposes in solution at 10 °C in a few hours.

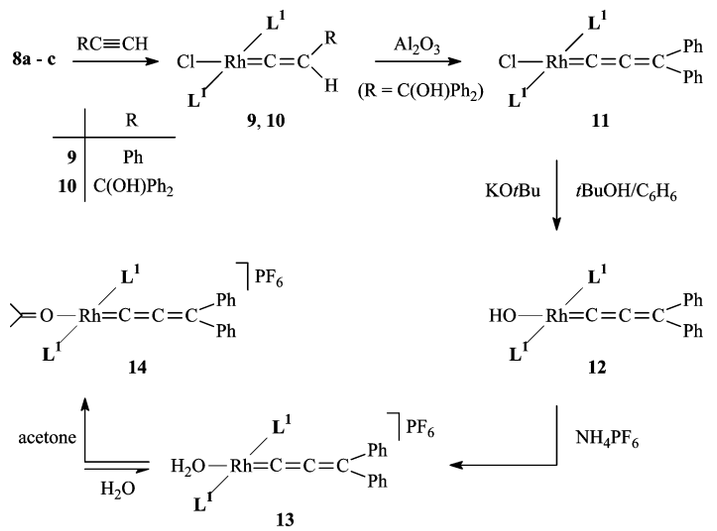
Treatment of **6** with four instead of two equivalents of **L**^{1} generates a red solution, from which, after recrystallization from pentane at low temperatures, a red air-sensitive solid can be isolated. Although the elemental analysis of the solid is in good agreement with a ratio of Rh : Cl : **L**^{1} = 1 : 1 : 2, the ^{1}H and ^{31}P NMR spectra indicate that the product is a mixture of three compounds but not solely a rhodium(I) complex with two intact phosphine ligands **L**^{1} per metal atom. At room temperature, besides the expected dimer **8a** compound **8c** is the dominating species which displays in the high-field region of the ^{1}H NMR spectrum a signal at δ −19.89 that is typical for a hydridorhodium complex. Both the splitting of this signal (being a doublet of doublets of doublets) and the appearance of two resonances in the ^{31}P NMR spectrum suggest that **8c** is an analogue of compound **16** (see Scheme 4) which has been characterized by X-ray crystallography.[10]

The third species observed in solution possibly is the monomer **8b**. It is characterized by a single doublet resonance in the ^{31}P NMR spectrum, the chemical shift and the ^{31}P–^{103}Rh coupling constant of which are quite similar to those of the counterpart [RhCl(PCy$_3$)$_2$].[11] As shown in Scheme 2, there are two ways to stabilize the 14-electron monomer **8b** either by dimerization or by C–H activation, the latter being a reversible process. In both cases, the monomer approaches a situation in which each rhodium centre formally possesses a 16-electron count.

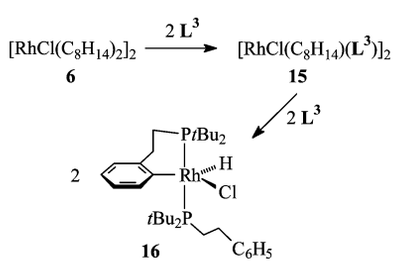
The assumption that compounds **8a** (which has been characterized crystallographically) and **8c** are in equilibrium with the monomer **8b** is supported by the reactivity of the solution containing the mixture of **8a**, **8b** and **8c** with various substrates. With CO the carbonyl complex *trans*-[RhCl(CO)(**L**^{1})$_2$] is



Scheme 2



Scheme 3



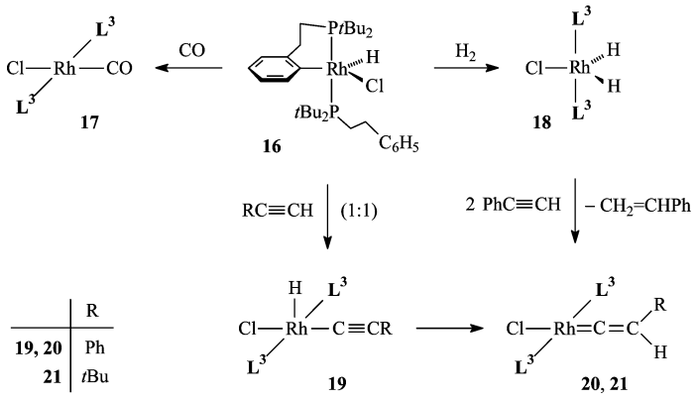
Scheme 4

formed, while with C_2H_4 the related ethene compound *trans*-[RhCl(C_2H_4)($\mathbf{L^1}$)$_2$] is obtained. In each case, the yield of the isolated product is *ca*. 90%. The ethene derivative reacts with H_2 to give mainly the dihydride [$RhH_2Cl(\mathbf{L^1})_2$], for which in analogy to [$RhH_2Cl(P{i}Pr_3)_2$] a trigonal-bipyramidal structure can be proposed.[10]

The outcome of the reactions of **8a**–**c** with phenylacetylene and the propargylic alcohol HC≡CC(OH)Ph_2 is summarized in Scheme 3. The rearrangement of the alkyne to the isomeric vinylidene probably occurs *via* coordination and intramolecular oxidative addition as was shown by monitoring the reaction in an NMR tube. The conversion of **10** to **11** followed the methodology which we had already applied for the Rh($P{i}Pr_3$)$_2$ counterpart.[12] The subsequent steps from **11** to **12** and further to **13** and **14** indicate that the metallacumulene unit is rather inert and not attacked by basic and acidic substrates.

The more bulky functionalized phosphine $\mathbf{L^3}$ behaves in some respects similarly, but in others differently, compared with $\mathbf{L^1}$. Thus, while treatment of the starting material **6** with two equivalents of $\mathbf{L^3}$ gives the expected chloro-bridged dimer **15**, the reaction of **1** with $\mathbf{L^3}$ in the molar ratio of 1 : 4 does not lead to a mixture of products but affords the aryl(hydrido) compound **16** in 85% isolated yield (Scheme 4). This species, probably formed by an intramolecular C–H activation, can also be prepared stepwise from [RhCl(C_2H_4)$_2$]$_2$ and excess $\mathbf{L^3}$ *via* the isolable dimer [RhCl(C_2H_4)($\mathbf{L^3}$)]$_2$ as an intermediate. As confirmed by an X-ray crystal structure analysis of **16**, the coordination geometry around the rhodium centre corresponds to a distorted trigonal bipyramid with the two phosphorus atoms in the apical positions. The two Rh–P bond lengths are slightly longer than in the related, more symmetrical chelate complex [RhHCl(tBu$_2$PCH$_2$C$_6$H$_3$CH$_2$PtBu$_2$-κ^3*P*,*C*,*P*)] reported by Kaska and co-workers.[13] The P–Rh–P axis of **16** is significantly bent (160.18(5)°), which could be due both to steric hindrance between the phosphine substituents and the strain of the chelate ring. The conformation of the six-membered ring corresponds to a boat form, the rhodium and the CH_2 carbon atom next to the ring being the top and the end of the boat.[10]

The results regarding the reactivity of **16** toward CO, H_2 and terminal alkynes are summarized in Scheme 5. The reactions not only proceed under mild conditions and give the products in good to excellent yields, but also support the assumption that in solution the cyclometallated compound **16** is in equilibrium with the (non-detected) monomeric species [RhCl($\mathbf{L^3}$)$_2$]. Both the carbonyl complex **17** and the vinylidene analogue **20** are noteworthy insofar as the NMR spectra indicate that they are fluxional in solution. At 223 K (**17**) or 233 K (**20**), three sets of signals for the ^{31}P nuclei are observed which are assigned to three different rotamers. These rotamers differ by the orientation of the phosphine substituents along the P–Rh–P axis, thereby the most bulky *t*-butyl groups probably playing the dominant role. A similar fluxional behaviour has been detected for the compounds *trans*-[RhCl(CO)(PtBu$_2$R)$_2$] (R = H, Me, Et, *n*Pr, *n*Bu, Ph)[14] as well as for the half-sandwich-type complexes [(η^6-arene)OsR$_2$(PHtBu$_2$)] (R = H, Me),[15] and in both cases has also been studied by ^{31}P NMR spectroscopy.



Scheme 5

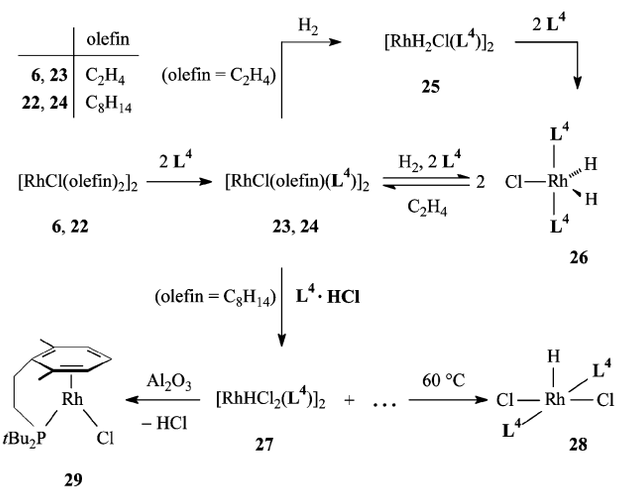
To find out whether by abstracting the hydride or the chloro ligand from **16** a four-coordinate cation of composition $[RhX(C_6H_5CH_2CH_2PtBu_2\text{-}\kappa P)(C_6H_4CH_2CH_2PtBu_2\text{-}\kappa C,P)]^+$ could be generated, the reactivity of the cyclometallated complex **16** toward acids and $AgPF_6$ has been studied. With gaseous HCl, an almost instantaneous reaction of **16** takes place which does not lead, however, to the elimination of H_2 but instead to the addition of the substrate to the metal centre and the formation of $[RhHCl_2(\mathbf{L}^3)_2]$. Upon addition of NEt_3 to a solution of this compound in benzene, the precursor **16** is regenerated. From **16** and one half equivalent of HBF_4 two products are formed which have been separated and characterized analytically. One is the hydrido complex $[RhHCl_2(\mathbf{L}^3)_2]$ and the other an ionic compound of the formal composition $[Rh(\mathbf{L}^3)_2]BF_4$, the corresponding PF_6^- salt being accessible from **16** and $AgPF_6$. As it was shown by an X-ray diffraction study,[10] the structure of chelating part of the cation $[Rh(\eta^6\text{-}C_6H_5CH_2CH_2PtBu_2\text{-}\kappa P)]^+$ is quite similar to that of compound **2** in which the coordination sphere is completed by cyclooctene instead of a monodentate phosphine.

5. Some surprising results with the most bulky phosphine L^4

After we found that in the reactions of the starting material **6** with $\mathbf{L}^1$ and $\mathbf{L}^3$ the insertion of the metal occurs exclusively into the phenyl C–H bond situated in *ortho*-position to the $CH_2CH_2PR_2$ substituent, we became eager to see what the behaviour of a phosphine such as $\mathbf{L}^4$ is where the two ring carbon atoms next to the β-phosphinoethyl moiety are blocked by methyl groups. We had in mind the elegant work by Milstein and co-workers illustrating that the pincer-type ligand $C_6H\text{-}1,3\text{-}(CH_2PtBu_2)_2\text{-}2,4,6\text{-}Me_3$ reacts even at room temperature with the olefin compound **1** by C–C bond cleavage to give the five-coordinate methylrhodium(III) complex $[RhCl(CH_3)\{C_6H\text{-}2,4\text{-}(CH_2PtBu_2)_2\text{-}3,5\text{-}Me_2\text{-}\kappa^3P,C,P\}]$.[16]

Treatment of both **6** and the corresponding ethene derivative **22** with a twofold excess of $\mathbf{L}^4$ affords the dinuclear compounds **23** and **24** (Scheme 6). The ^{31}P NMR spectrum of **23** reveals that only one species is present which, as the X-ray crystal structure analysis confirmed, is the isomer containing the two ethene and the two phosphine ligands in *trans* disposition.[7] In contrast, the ^{31}P NMR spectrum of **24** displays two resonances (both doublets) indicating that the *trans*- as well as the *cis*-isomer of the chloro-bridged complex is formed. The dominating species is the *trans*-isomer which, as in the case of **23**, seems to be thermodynamically preferred.

The attempted conversion of **23**, under a hydrogen atmosphere in order to eliminate and hydrogenate the olefin, with two equivalents of $\mathbf{L}^4$ to give either the monomer $[RhCl(\mathbf{L}^4)_2]$ or the dimer $[RhCl(\mathbf{L}^4)_2]_2$, affords the dihydrido complex **26** in practically quantitative yield. Since each of the ^1H NMR and the ^{31}P NMR spectra of **26** displays only one resonance, there is



Scheme 6

no doubt that the hydrido as well as the phosphine ligands are stereochemically equivalent. With regard to the mechanism of formation of **26**, we assume that in the initial step an oxidative addition of H_2 followed by the elimination of ethane takes place. This assumption is supported by the observation that upon stirring a solution of **23**, in the absence of $\mathbf{L}^4$, under a H_2 atmosphere a hydridorhodium(III) compound is generated which presumably is the dimer **25**. Since this species is stable only in the presence of excess hydrogen, it has been characterized by IR and NMR spectroscopy. Addition of two equivalents of $\mathbf{L}^4$ to a solution of **25** in CH_2Cl_2 yields exclusively the dihydrido complex **26**. With excess ethene, **26** reacts in pentane at room temperature to regenerate the dimer **23**. This reaction is rather slow and after replacing the ethene for a H_2 atmosphere, the mixture of **23** and $\mathbf{L}^4$ is re-converted to **26**.[7]

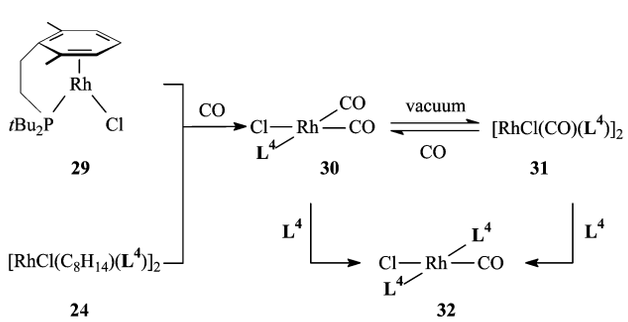
While both **23** and **24** are fairly inert toward $\mathbf{L}^4$, the cyclooctene derivative **24** reacts with the phosphonium salt $\mathbf{L}^4\cdot$HCl in the molar ratio of 1 : 2 to give a mixture of products which mainly consists of about equal amounts of $\mathbf{L}^4\cdot$HCl and a new compound that probably is the chloro(dihydrido)rhodium(III) complex **27** (see Scheme 6). Warming the solution containing $\mathbf{L}^4\cdot$HCl and **27** in benzene for 2 h at 60 °C leads to the formation of the monomer **28** which has been isolated as an orange air-stable solid in 71% yield. The elimination of HCl from **28** with NEt_3, undertaken in the hope to generate $[RhCl(\mathbf{L}^4)_2]_n$ ($n = 1$ or 2), affords instead the novel half-sandwich-type complex **29**. Since **29** like $[HNEt_3]Cl$ is only sparingly soluble in benzene, it could not be completely separated from the ammonium salt and was thus initially only characterized by spectroscopic means.

A clean method to obtain **29** as an analytically pure compound was found on an unexpected route. While attempting to separate the mixture of $\mathbf{L}^4\cdot$HCl and **27** by column chromatography on Al_2O_3, we observed that from the yellow material a

green fraction could be eluted with CH_2Cl_2 which did contain complex **29**. Conductivity measurements confirmed that this compound in nitromethane is a non-electrolyte. By taking into consideration that to the best of our knowledge neutral compounds of the general composition [(η^6-arene)Rh(PR_3)X] (X = halide) are unknown,[17] the isolation of **29** illustrates quite convincingly the supportive influence of the functionalized phosphine $\mathbf{L^4}$ for the formation of neutral half-sandwich-type arenerhodium(I) derivatives.

Owing to the coordinative capabilities of $\mathbf{L^{1-3}}$ and the counterparts $Ph_2P(CH_2)_2C_6H_4R$, we assumed that in compound **29** the chelating phosphine $\mathbf{L^4}$ is coordinated in a hemilabile fashion and thus the η^6-bonded arene could be substituted by CO. Although we were aware of the fact that rhodium(I) complexes of the type *cis*-[RhCl(PR_3)($CO)_2$] have been reported by various authors to be key intermediates in the reactions of [RhCl$(CO)_2]_2$ with PR_3 and of [RhCl(CO)(PR_3)$]_2$ with CO,[18] none of these dicarbonyl species had been identified crystallographically.

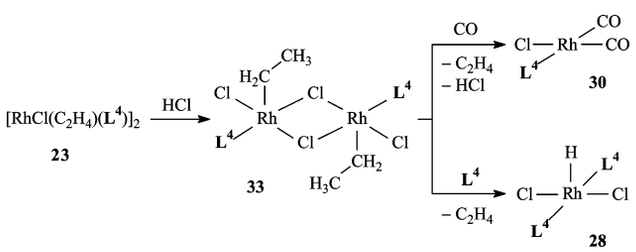
The reactions of both **29** and **24** with CO in pentane or dichloromethane are very fast indeed and afford in a few seconds a yellow compound, the ^{31}P NMR spectrum of which displays a single resonance. This would be in agreement with the presence of the dicarbonyl **30** (Scheme 7). However, after evaporation of the solvent *in vacuo* a yellow air-stable product is isolated which owing to the spectroscopic data is a mixture of the *cis*- and *trans*-isomers of dimer **31**. This dimer could be converted to the target molecule **30**, if it is treated in pentane with carbon monoxide and the solvent is not removed in vacuo but in a stream of CO. Using this methodology, compound **30** has been isolated as a light yellow air-stable solid in 95% yield.[7] As indicated by the IR spectrum (showing two CO stretching vibrations in KBr at 2086 and 1999 cm^{-1}), the two CO ligands are in different environments and this has been substantiated by an X-ray diffraction investigation. As expected, the coordination geometry around rhodium is square planar with bond angles P–Rh–Cl and P–Rh–C that are slightly larger, and bond angles C–Rh–Cl and C–Rh–C that are slightly smaller than 90°. The effect of the sterically demanding phosphine is obvious. The most noteworthy feature, however, is the difference in the two Rh–C bond lengths [1.826(2) *vs*. 1.9112(19) Å] which clearly reflects the *trans* influence of the phosphine. Both **30** and **31** react with $\mathbf{L^4}$ to give the monocarbonyl compound **32**, the ^{31}P NMR spectrum of which indicates that the two phosphine ligands are *trans*-disposed.[7]



Scheme 7

The reaction of **23** with HCl, initially undertaken to generate the five-coordinate dichloro(hydrido) complex [$RhHCl_2(C_2H_4)$-($\mathbf{L^4}$)], furnished a surprising result. After passing a slow stream of dry HCl through a suspension of **23** in CH_2Cl_2 for 10 s, an orange air-sensitive solid could be isolated, the elemental analysis of which was in agreement with the expected composition [$RhHCl_2(C_2H_4)(\mathbf{L^4})$]. However, the ^{1}H NMR spectrum of the compound shows no signals for hydridic and olefinic hydrogens but resonances indicating the presence of an ethyl group in the molecule. The ^{13}C NMR spectrum equally displays two signals at δ 23.7 and 24.6 assigned to CH_2 and CH_3 carbon atoms.

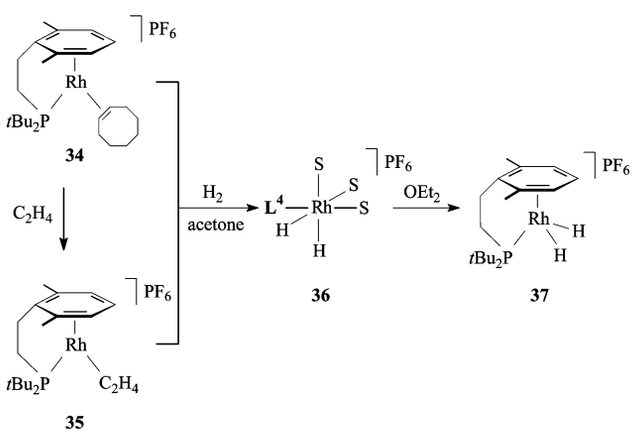
That in fact a Rh–C_2H_5 moiety is part of the unexpected product **33**, has been confirmed by an X-ray crystal structure analysis. A shown in Scheme 8, a dinuclear rhodium(III) complex is formed which is built up by two 14-electron [$RhCl_2(C_2H_5)(\mathbf{L^4})$] fragments. These fragments are linked by two bridging chlorides which are unsymmetrically situated between the two metal centres. Since the two terminal chlorides lie exactly and the two phosphorus atoms nearly in the plane of the Rh_2Cl_2 ring, the coordination geometry around both rhodium atoms can be best described as square-pyramidal with the C_2H_5 ligand in the apical position. The ethyl groups of the two fragments are located *trans* to each other, *i.e.*, on opposite sides of the Rh_2Cl_2 plane. We note that independent from our work, Budzelaar, Gal and co-workers reported the preparation and structural characterization of an analogue of **33** containing a bulky β-diiminato ligand instead of one chloro ligand and phosphine $\mathbf{L^4}$, two phenyl instead of two ethyl groups and two bridging bromides. In contrast to **33**, this complex was obtained from the 14-electron rhodium(I) precursor [Rh(β-diiminate)-(C_8H_{14})] and bromobenzene by oxidative addition.[19]



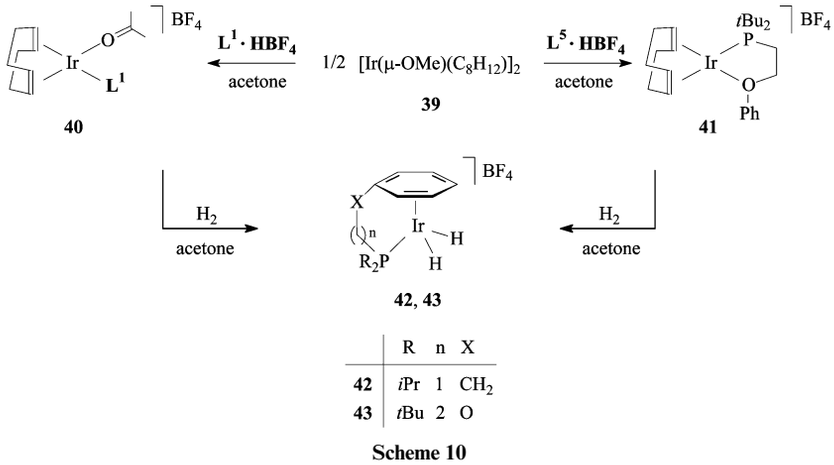
Scheme 8

The reactivity of the dinuclear ethylrhodium(III) derivative **33** is quite unusual. Treatment of **33** with $\mathbf{L^4}$ does not lead to the formation of the mononuclear five-coordinate compound [$RhCl_2(C_2H_5)(\mathbf{L^4})_2$] but affords the monohydrido complex **28** instead. This result can be explained by postulating that in solution an equilibrium between a (possibly monomeric) Rh(C_2H_5) and a RhH(C_2H_4) isomer exists and that **28** is formed from the latter by olefin/phosphine exchange. The same ethene-(hydrido)rhodium(III) intermediate is probably also involved in the formation of **30** from **33** and CO which, according to reaction control by NMR spectrsocopy, proceeds quantitatively. Careful investigation of the gas phase indicated that ethene as well as HCl were eliminated.

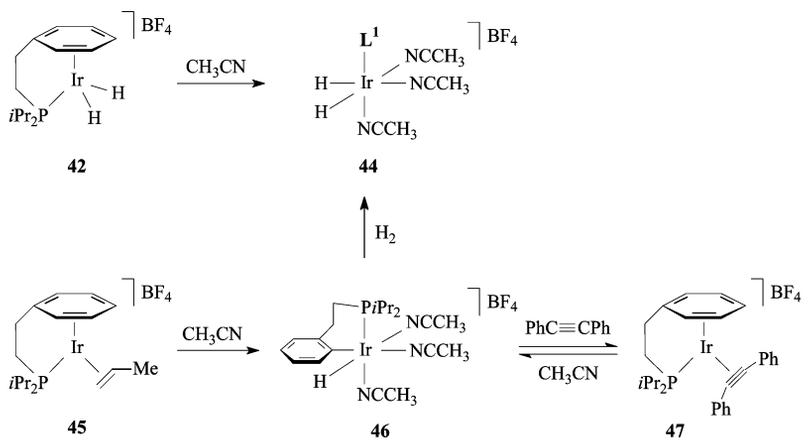
On a similar route as shown in Scheme 1 for compounds **2** and **3**, the half-sandwich-type complex **34** is generated from **1** and $\mathbf{L^4}$. The cyclooctene ligand is not firmly bound and can be smoothly replaced by ethene to give **35** (Scheme 9). In acetone under a hydrogen atmosphere, both **34** and **35** can be converted stepwise to the dihydridorhodium(III) derivative **37**, which is a



Scheme 9



Scheme 10



Scheme 11

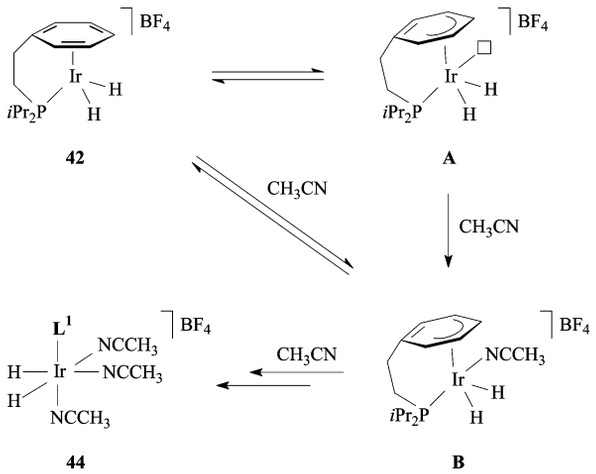
light brown, moderately air-stable solid that can be stored under argon at −20 °C for a few days. As an intermediate the tris(solvato) compound **36** is formed that has been characterized by ^{1}H and ^{31}P NMR spectroscopy. It is stable under hydrogen for hours but rearranges, after replacing the H_2 atmosphere for argon, slowly to the chelate complex [{η^6-2,6-$Me_2C_6H_3(CH_2)_2P$*t*Bu_2-κ*P*}(acetone)Rh]PF_6.[7]

6. Iridium(I) and iridium(III) complexes derived from L^1 and L^5 as ligands

In contrast to the half-sandwich-type rhodium compound **2**, the iridium counterpart [{η^6-$C_6H_5(CH_2)_2P$*i*Pr_2-κ*P*}(C_8H_{14})-Ir]PF_6 (**38**) is rather inert. Under an ethene atmosphere, it reacts very slowly by olefin exchange to generate the corresponding ethene complex [{η^6-$C_6H_5(CH_2)_2P$*i*Pr_2-κ*P*}(C_2H_4)Ir]PF_6 to a maximum amount of *ca.* 30%. In the presence of hydrogen, no reaction of **38** takes place. However, both the required dihydrido compound **42** and the analogue **43** containing L^5 as ligand are accessible from the methoxy-bridged dimer **39** as the precursor. As shown in Scheme 10, this dimer can be transformed to the 1,5-cyclooctadiene–metal intermediates **40** and **41**, which react with H_2 in acetone at room temperature to give the half-sandwich-type complexes **42** and **43** in 79–87% yield. After repeated recrystallization from acetone–diethyl ether, they are isolated as white solids which for a short time can be even handled in air.[20]

Upon treatment with ethene or propene, **42** as well as **43** behave as H_2 carriers and afford the olefin complexes [(η^6-L^n-κ*P*)(CH_2=CHR)Ir]PF_6 (*n* = 1, 5; R = H, Me) plus one equivalent of the alkane. The reactions of **43** are significantly slower than those of **42** and, to achieve a quantitative conversion, a temperature of 50 °C has to be employed. As the NMR spectra indicate, the structure of the olefin complexes is similar to that of the rhodium counterparts and this has been confirmed by the X-ray crystal structure analysis of the stilbene derivative [(η^6-L^1-κ*P*){(*Z*)–PhCH=CHPh}Ir]PF_6.[20] This compound has been obtained either from [(η^6-L^1-κ*P*)(CH_2=CHMe)Ir]PF_6 and *Z*-stilbene or from **42** and diphenylacetylene. In the presence of excess C_2Ph_2, the stilbene ligand is smoothly replaced and the corresponding π-alkyne complex [(η^6-L^1-κ*P*)(PhC≡CPh)Ir]-PF_6 is formed. Although the reactions of this complex and of the olefin analogues [(η^6-L^n-κ*P*)(CH_2=CHR)Ir]PF_6 with H_2 to give **42** and **43** are rather slow, the dihydrido compounds are good catalysts for the hydrogenation of unsaturated substrates.[21]

The reaction of **42** with excess acetonitrile leads to a partial opening of the chelate bond and affords the six-coordinate dihydridoiridium(III) complex **44** in 87% isolated yield (Scheme 11). Both the ^{1}H and ^{13}C NMR spectra of **44** display two signals for the CH_3CN protons and carbon atoms indicating that the acetonitrile ligands are stereochemically inequivalent. In analogy with [$IrH_2(NCCH_3)_3(P$*i*$Pr_3)$]BF_4,[22] we assume that also for the cation of **44** the *fac* configuration is preferred. A kinetic study with CD_3CN as the substrate revealed a rate law that is first order in the concentration of **42** and first order in the concentration of CD_3CN. From these data we conclude, that either the primary and rate-determining step consists of the direct attack of the nitrile ligand to the metal centre or an equilibrium between **42** and a coordinatively unsaturated intermediate **A** exists (see Scheme 12). If this equilibrium is fast and the subsequent addition of acetonitrile to the free coordination site is slow, a second-order rate law would equally result. In this context we note, that a η^6-to-η^4 slippage has been discussed for the ligand exchange reactions of (η^6-arene)-chromium tricarbonyls with different arenes,[23] and has been proved for the formation of [(η^5-C_5Me_5)Ir(η^4-C_6Me_6)] from [(η^5-C_5Me_5)Ir(η^6-C_6Me_6)]$^{2+}$ as the precursor.[24]



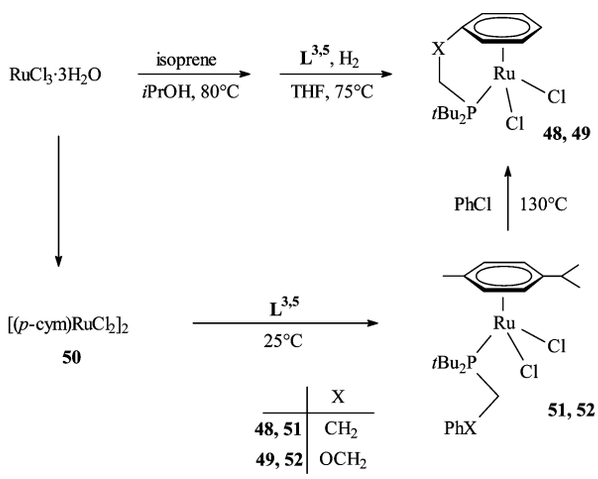
Scheme 12

In contrast to **42**, the half-sandwich-type complex **45** reacts with acetonitrile not only by substitution of the olefin and displacement of the arene ring but also by insertion of the metal into one of the C–H bonds of the C_6H_5 unit.[20] The X-ray crystal structure analysis of the product **46** showed that the coordination geometry around the iridium centre corresponds to a distorted octahedron, the *cis* bond angles P–Ir–C, N–Ir–C, P–Ir–N and N–Ir–N lying between 84.34(12) and 100.38(9)°. Two of the Ir–N distances are nearly identical while the third one for the acetonitrile *trans* to hydride is somewhat elongated. The six-membered chelate ring of **46** possesses a boat conformation, which is quite analogous to the structure of the rhodium compound **16**.

The cyclometalated compound **46** is formed not only from **45** but also from **47** upon treatment with excess acetontrile in acetone. If this reaction is monitored by $^{31}P\{^1H\}$ NMR spectroscopy, the yield of **46** is nearly 100%. However, if the solvent and other volatile substrates are removed in vacuo, the π-alkyne complex **47** is partly regenerated. Addition of a ten-fold excess of C_2Ph_2 to the solution of **46** in acetone affords **47** quantitatively. That the insertion of the metal into one of the arene C–H bonds is completely reversible, is also supported by the observation that the reaction of **46** with H_2 in acetone gives the dihydrido compound **44** in good yield. Since with D_2 instead of H_2 the bis(deuterido) derivative $[IrD_2(NCCH_3)_3(\mathbf{L^1})]BF_4$ is generated up to at least 95%, we assume that both the reactions of **46** with diphenylacetylene and with hydrogen take place *via* the 16-electron species $[Ir(\mathbf{L^1})(NCCH_3)_3]^+$ which appears to be the kinetically favored isomer of **46**.

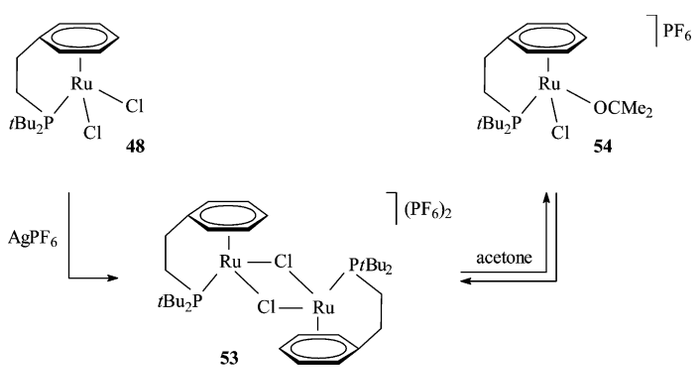
7. Ruthenium(II) complexes with L^3 and L^5 as monodentate and chelating ligands

Following the observation that $RuCl_3{\cdot}3H_2O$ can be converted with PCy_3, isoprene and H_2 in a one-pot reaction to the hydrido-(dihydrogen) complex $[RuHCl(H_2)(PCy_3)_2]$,[25] the starting material $RuCl_3{\cdot}3H_2O$ was also treated with the functionalized phosphines $\mathbf{L^3}$ and $\mathbf{L^5}$. However, instead of the anticipated compounds $[RuHCl(H_2)(\mathbf{L^n})_2]$ (n = 3, 5) the half-sandwich-type complexes **48** and **49** (Scheme 13) were generated as the dominating species. An alternative route, which affords **48** and **49** without any by-products, consists of the conversion of the dimer **50** to the monomeric (*p*-cymene)ruthenium(II) derivatives **51** and **52** which upon heating in chlorobenzene furnish the target molecules nearly quantitatively.[26] This clean intramolecular substitution is noteworthy insofar as the corresponding reaction of **50** with $C_6H_5(CH_2)_3PPh_2$ gives the half-sandwich-type compound $[\{\eta^6\text{-}C_6H_5(CH_2)_3PPh_2\text{-}\kappa P\}RuCl_2]$ in only moderate yield.[27] It seems that the bulkiness of the *tert*-butyl substituents at phosphorus facilitates the displacement of the *p*-cymene ligand and also hinders side-reactions such as the *inter*molecular attack of the phenyl ring of a second molecule of **51** or **52** to the metal centre.



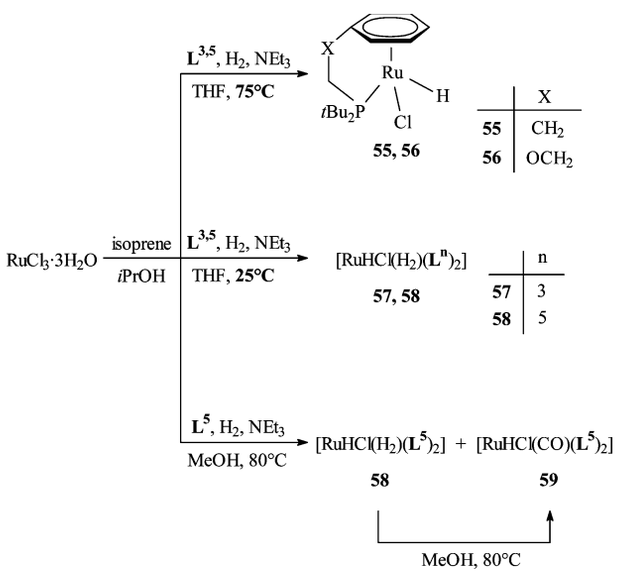
Scheme 13

The dichloro compound **48** reacts with one equivalent of $AgPF_6$ in acetone to give an orange-yellow solution from which, upon addition of pentane, the PF_6^- salt of the dicationic species **53** can be isolated (Scheme 14). If this salt is dissolved in acetone, the chloro bridges of **53** are split and the monomeric complex **54** is formed. The reaction is completely reversible since after removal of the solvent the dinuclear precursor **53** is regenerated quantitatively. The related acetonitrile compound $[\{\eta^6\text{-}C_6H_5(CH_2)_2PtBu_2\text{-}\kappa P\}(NCMe)RuCl]PF_6$, the molecular structure of which has been confirmed crystallographically, is significantly more stable and can be prepared either from **48** and $AgPF_6$ in CH_2Cl_2–CH_3CN or from **53** and acetonitrile. The ^1H NMR spectra of $[\{\eta^6\text{-}C_6H_5(CH_2)_2PtBu_2\text{-}\kappa P\}(NCMe)\text{-}RuCl]PF_6$ and the PMe_3 counterpart display five resonances for the C_6H_5 ring protons and the ^{13}C NMR spectra six signals for the corresponding ring carbon atoms indicating, in agreement with the presence of a chiral centre in the cations, all the CH units of the phenyl ring are stereochemically different.[26]



Scheme 14

Ruthenium(II) complexes with one hydride and the functionalized phosphine $\mathbf{L^3}$ or $\mathbf{L^5}$ either as chelating or merely *P*-bonded ligand are also accessible from $RuCl_3 \cdot 3H_2O$ as the starting material. The procedure to prepare the chloro(hydrido) compounds **55** and **56** (Scheme 15) is different to that of the dichloro derivatives **51** and **52** only insofar as the *in situ* generated intermediate $[(\eta^3{:}\eta^3\text{-}C_{10}H_{16})RuCl_2]_2$ is treated with the phosphine in methanol or boiling THF under a hydrogen atmosphere in the presence of one equivalent of NEt_3. In both cases, the yield of of the chelate complex is nearly quantitative. The reaction of the intermediate $[(\eta^3{:}\eta^3\text{-}C_{10}H_{16})RuCl_2]_2$ with $\mathbf{L^3}$ or $\mathbf{L^5}$ and NEt_3 in THF under H_2 at room temperature affords the five-coordinate hydrido(dihydrogen) compounds **57** and **58** in moderate to good yields. However, by treating the intermediate $[(\eta^3{:}\eta^3\text{-}C_{10}H_{16})RuCl_2]_2$ with $\mathbf{L^5}$ and H_2 in methanol under reflux, a mixture of **58** and **59** is formed. Stirring this mixture in methanol at 80 °C for 6 h generates the hydrido(carbonyl) complex **59** exclusively.



Scheme 15

In contrast to the coordinatively unsaturated compound **59**, which reacts with CO by addition to give $[RuHCl(CO)_2(\mathbf{L^5})_2]$ and with acetylene by insertion to afford $[Ru(CH{=}CH_2)Cl(CO)(\mathbf{L^5})_2]$, the hydrido(chloro) complex **55** is inert towards acetylene and $HC{\equiv}CC(OH)Ph_2$. If, however, the reaction of **55** with the substituted propargyl alcohol is carried out in the presence of an equimolar amount of HBF_4 in diethyl ether, the cationic ruthenium allenylidene **60a** is obtained in practically quantitative yield. Treatment of the dichloro derivative **48** with $HC{\equiv}CC(OH)Ph_2$ and one equivalent of $AgPF_6$ in acetone affords the corresponding PF_6^- salt **60b** (Scheme 16). The preparation of the analogous complex **61** with $\mathbf{L^5}$ as ligand proceeds on the same route. Quite unexpectedly, the cations of both **60a**,**b** and **61** are catalytically inactive in olefin metathesis. This is surprising insofar as recently the groups of Dixneuf and Fürstner reported that the related (*p*-cymene)ruthenium(II) compound $[(\eta^6\text{-}p\text{-cym})RuCl(=C{=}C{=}CPh_2)(PCy_3)]^+$ catalyzes, although at higher temperatures, the ring-closure of α,ω-dienes.[28]

Active catalysts for ROMP (Ring Opening Metathesis Polymerization) of cyclooctene were generated upon treatment of solutions of the vinylidene complexes $[RuHCl(=C{=}CH_2)(\mathbf{L^n})_2]$ (n = 3, 5) in CH_2Cl_2 with an ethereal solution of HBF_4 at −78 °C. Under these conditions, the carbyneruthenium cations $[RuHCl(\equiv CCH_3)(OEt_2)(\mathbf{L^n})_2]^+$ are formed and have been characterized by NMR spectroscopy.[26] They are near relatives of the cation $[RuHCl(\equiv CCH_3)(OEt_2)(PCy_3)_2]^+$, that catalyzes not only ROMP of cyclooctene but also the cross-olefin metathesis of cyclopentene with methyl acrylate to give unsaturated carboxylic acid esters.[29]

In ROMP of cyclooctene, the carbyneruthenium cations containing $\mathbf{L^3}$ and $\mathbf{L^5}$ as ligands are even more active than the well-known Grubbs carbene $[RuHCl(=CHPh)(PCy_3)_2]$. Under identical conditions, the polymerization of C_8H_{14} with $[RuHCl(\equiv CCH_3)(OEt_2)(\mathbf{L^5})_2]BF_4$ as catalyst in dichloromethane/diethyl ether at room temperature is finished after *ca.* 8 min whereas with the carbene complex in the same period of time only *ca.* 15% of the olefin is polymerized. A reasonable explanation for the remarkable difference in rate is that the dissociation of one phosphine ligand, being the rate-determining step in the catalysis with $[RuHCl(=CHPh)(PCy_3)_2]$,[30] proceeds much faster in the case of the carbyneruthenium cation which in general is more labile than the neutral ruthenium carbene.

8. Concluding remarks

The work summarized in this article illustrates that the functionalized phosphines $R_2P(CH_2)_2$(aryl) and $R_2P(CH_2)_2X$(aryl) (X = CH_2, O) with two bulky substituents R at the phosphorus atom coordinate to rhodium, iridium and ruthenium both as 2-electron and (2 + 6)-electron donor ligands. However, the even more interesting facet is that the bonding capabilities of the phosphines used in our studies go beyond the $\mathbf{L^n}$-κ*P* and η^6-$\mathbf{L^n}$-κ*P* coordination modes. As has been shown by the generation of the five-coordinate rhodium(III) complex **8c** and the isolation of the related compounds **16** and **46**, the interaction of the phosphines $\mathbf{L^1}$ and $\mathbf{L^3}$ with the rhodium or iridium centre can lead to an insertion of the metal into one of the C–H bonds of the aryl group of the phosphine to give a new six-membered chelate ring system. This cyclometalation reaction appears to be not only an energetically favored process but it is also reversible which is convincingly shown by the formation of various complexes derived from **8c**, **16** and **46** as well as by some labeling experiments. In the case of M = Rh, the formation of these complexes presumably proceed *via* the 14-electron intermediates $[RhCl(\mathbf{L^n}\text{-}\kappa P)_2]$ with the C–H activated isomer representing the resting state. This assumption could be important for catalytic reactions but this has to be proven by further investigations.

Acknowledgements

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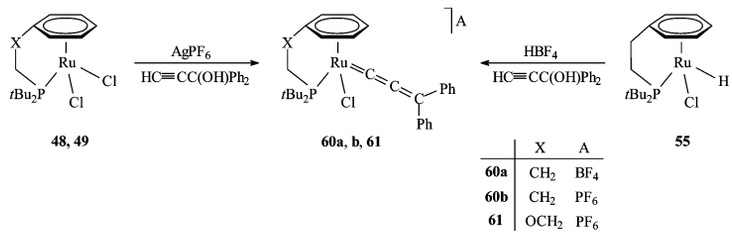

Scheme 16

reported. Moreover, I highly appreciate the collaboration with Justin Wolf and with the group of Professor Luis A. Oro, in particular with Eduardo Sola, Marta Martín and Fernando Lahoz, who were most influential in developing the iridium chemistry with the functionalized phosphines as ligands. The constant and unbureaucratic financial support by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is also gratefully acknowledged.

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