

METAL BASICITY AS A SYNTHETIC TOOL IN ORGANOMETALLIC CHEMISTRY

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Abstract - Transition metal complexes of the type C_5R_5MLL' and $C_6R_6M'LL'$ ($R = H, Me$; $M = Co, Rh$; $M' = Ru, Os$; $L = L' = PR_3, P(OR)_3$ and $L = PR_3, L' = CO, CNR, C_2H_3R, C_2R_2$ etc.) behave like metal bases and react with an electrophile to form a new metal-to-element bond. After having studied the reactivity of the bis(phosphine) and bis(phosphite) complexes, we have recently focussed our attention on reactions of the mono(phosphine) compounds containing isonitriles, olefins or alkynes as the ligand L' . The reactions in particular with Brönsted acids, methylating agents and heteroallenes are discussed, and the formation of metallocyclic rings is emphasized.

INTRODUCTION

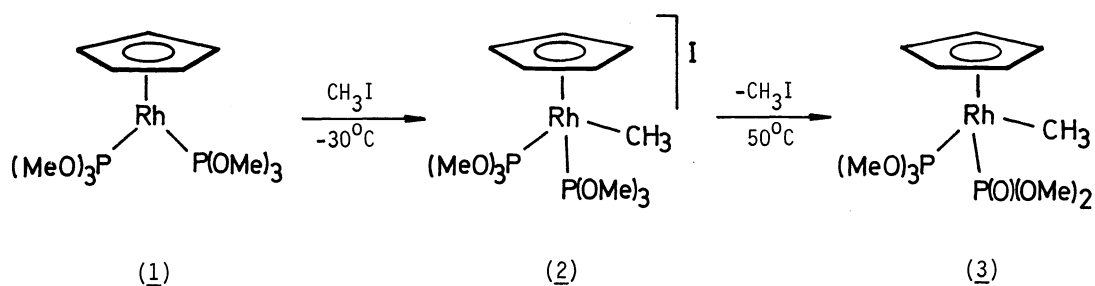
The term "metal basicity" has become popular since Shriver (1) published his review on this topic in 1970. In the foregoing decade it was mainly the work of Vaska (2) which indicated that various reactions of d^8 metal complexes of the type $[RhL_2L'X]$ and $[IrL_2L'X]$ (in particular, $L = PPh_3, L' = CO, X = Cl, Br$ etc.) with substrates such as $HCl, CH_3I, O_2, SO_2, BF_3, C_2(CN)_4$ etc. can be generally considered as Lewis base-Lewis acid reactions. As the central metal atom serves as an electron-pair donor, the complexes are called "metal bases".

Recent work in our laboratory has been concerned with the Lewis-basic behaviour of another type of d^8 metal complexes, namely those in which the metal is coordinated to a five- or six-membered aromatic ring C_nH_n (or C_nMe_n) and to two two-electron donor ligands L and L' . Provided that at least one of the ligands L or L' is a good donor, for example a trialkylphosphine or a trialkylphosphite, these complexes react with an electrophile to form a new metal-to-element bond. It should be mentioned that cyclopentadienylmetal compounds such as $C_5H_5M(CO)PR_3$ ($M = Co, Rh, Ir$) and $C_5H_5Rh(PPh_3)L$ ($L = PPh_3, C_2H_4$) have already been used by Graham's and Yamazaki's groups (3, 4) as starting materials, particularly for reactions with methyl iodide and other alkyl halides. In our own work, trimethylphosphine and trimethylphosphite have been employed as strong donor ligands, and we have mainly used the complexes $C_nR_nM(PMe_3)_2, C_nR_nM[P(OMe)_3]_2$ and $C_nR_nM(PMe_3)L$ with $L = CO, CS, CNR, C_2H_4, C_2H_3R, C_2R_2$ as metal bases.

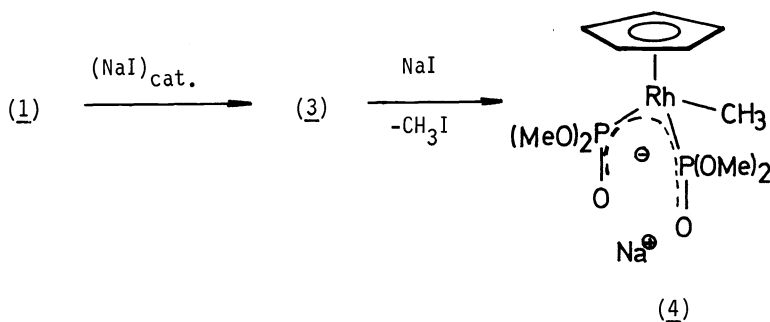
I. THE CYCLOPENTADIENYL BIS(PHOSPHITE) COMPLEXES

During studies on the synthesis of the "supersandwiches" $(C_5H_5)_2Co_3[P(O)(OR)_2]_6$ ($R = Me, Et$) (Ref.5) we observed that the starting complexes $C_5H_5Co[P(OR)_3]_2$ and also their rhodium analogues react with Brönsted acids and with methyl iodide even at temperatures below $-20^\circ C$ to form salts of the cations $[C_5H_5ME(P(OR)_3)_2]^+$ ($E = H, CH_3$) (Ref.6). In the case of compound 2, a further reaction occurs, which by elimination of methyl iodide, yields an

isomer 3 of the starting complex 1.



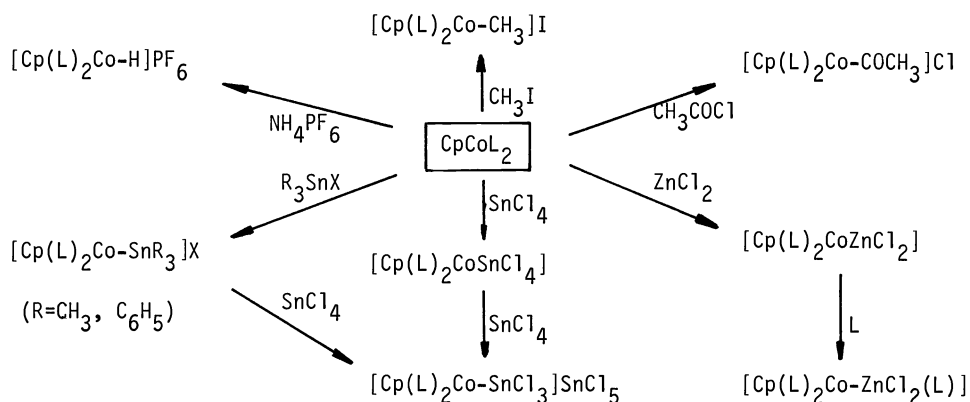
The same rearrangement of 1 to 3 occurs with catalytic amounts of NaI. If, however, the bis(phosphite) complex 1 is treated with alkali metal iodides MI (M = Li, Na, K) in a 1:1 molar ratio, the corresponding bis(phosphonate) compounds $\text{C}_5\text{H}_5\text{RhCH}_3[\text{P}(\text{O})(\text{OMe})_2]_2\text{M}$ (4) are formed, which in solution presumably exist as contact ion-pairs rather than dissociated ions (Ref.7).



The reaction of 4 (M = Na) with HCl in benzene yields the complex $\text{C}_5\text{H}_5\text{RhCH}_3[\text{P}(\text{O})(\text{OMe})_2]_2\text{H}$ (5) in which a chelate ligand containing a POHOP hydrogen bridge is present. Compound 5 reacts with thallium acetylacetonate to produce $\text{C}_5\text{H}_5\text{RhCH}_3[\text{P}(\text{O})(\text{OMe})_2]_2\text{Tl}$ (6). This compound can be used as starting material for the synthesis of the tri- and tetranuclear complexes $\{\text{C}_5\text{H}_5\text{RhCH}_3[\text{P}(\text{O})(\text{OMe})_2]_2\}_n\text{M}$ (n = 2 : M = Co, Zn; n = 3 : M = Fe, Al). The bis(phosphonate)-rhodium anion serves as chelating ligand to the central metal in a completely similar manner to that of the related anions $\text{C}_5\text{H}_5\text{M}[\text{P}(\text{O})(\text{OMe})_2]_2^-$ (M = Ni, Pd), which have been recently prepared in our laboratory (Ref.8).

II. THE CYCLOPENTADIENYL BIS(PHOSPHINE) COMPLEXES

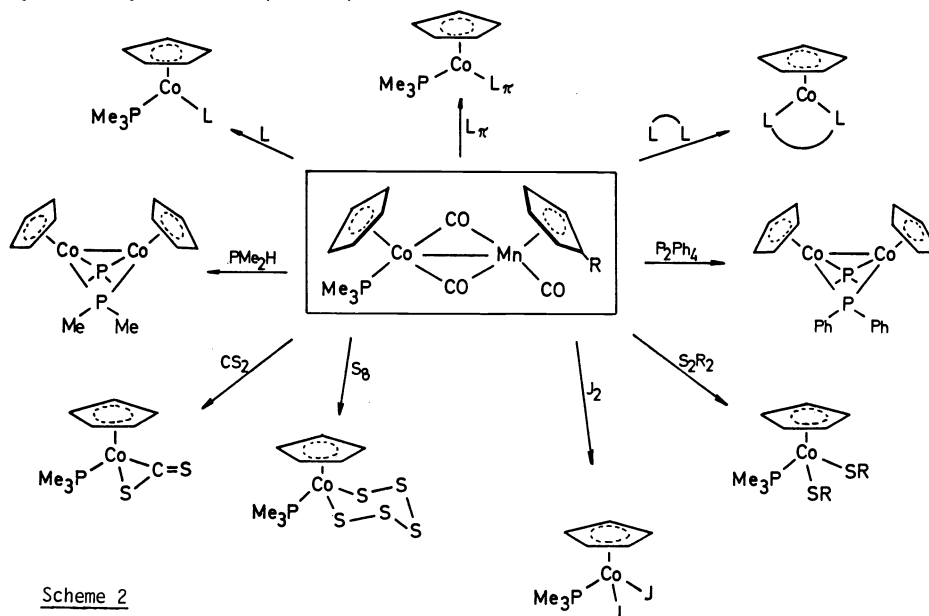
As trialkylphosphines are generally considered to be stronger donor and weaker acceptor ligands than trialkylphosphites, the electron density at the metal in complexes such as $\text{C}_5\text{H}_5\text{M}(\text{PMe}_3)_2$ and $\text{C}_5\text{H}_5\text{M}(\text{PET}_3)_2$ (M = Co, Rh) should be higher than in those containing $\text{P}(\text{OMe})_3$ and $\text{P}(\text{OEt})_3$ rather than PMe_3 and PET_3 as ligands. This seems to be true. The cobalt compounds $\text{C}_5\text{H}_5\text{Co}(\text{PMe}_3)_2$ (7) and $\text{C}_5\text{H}_5\text{Co}(\text{PET}_3)_2$ (8) which are readily accessible from $\text{Co}(\text{PR}_3)_3\text{Cl}$ and TlC_5H_5 (Ref.9 and 10), can be protonated even with methanol to form the cations $[\text{C}_5\text{H}_5\text{CoH}(\text{PR}_3)_2]^+$. The strong metal basicity particularly of complex 7 has been further demonstrated by the reactions which are summarized in Scheme 1 (Ref.9 and 11).



Scheme 1 (Cp = C₅H₅, L = PMe₃)

An interesting result was observed when we tried to prepare heterodinuclear complexes containing cobalt-to-metal bonds by the reaction of the base 7 with Lewis acidic species ML_n (e.g. Cr(CO)₅, Fe(CO)₄, Mn(CO)₂C₅H₅) where the metal only contains 16 electrons in its valence shell. By using C₅H₅Mn(CO)₂THF (or (C₅H₄Me)Mn(CO)₂THF) as the substrate, we indeed obtained a dinuclear complex but of composition C₅H₅(PMe₃)Co(μ-CO)₂Mn(CO)C₅H₄R (9) instead of C₅H₅(PMe₃)₂CoMn(CO)₂C₅H₄R as we had expected (Ref.12). It has been shown by the X-ray structural analysis (Ref.13) that this complex (R = CH₃) contains two unsymmetrical CO bridges (with shorter Mn-C and longer Co-C distances) which may explain why 9 is so reactive towards a whole range of electrophiles as well as nucleophiles. In all the reactions which are summarized in Scheme 2, besides the corresponding cobalt complex the cyclopentadienylmanganese tricarbonyl (C₅H₄R)Mn(CO)₃ is formed which serves as a "ligand" for the coordinatively unsaturated C₅H₅Co(PMe₃) fragment (Ref.12-14).

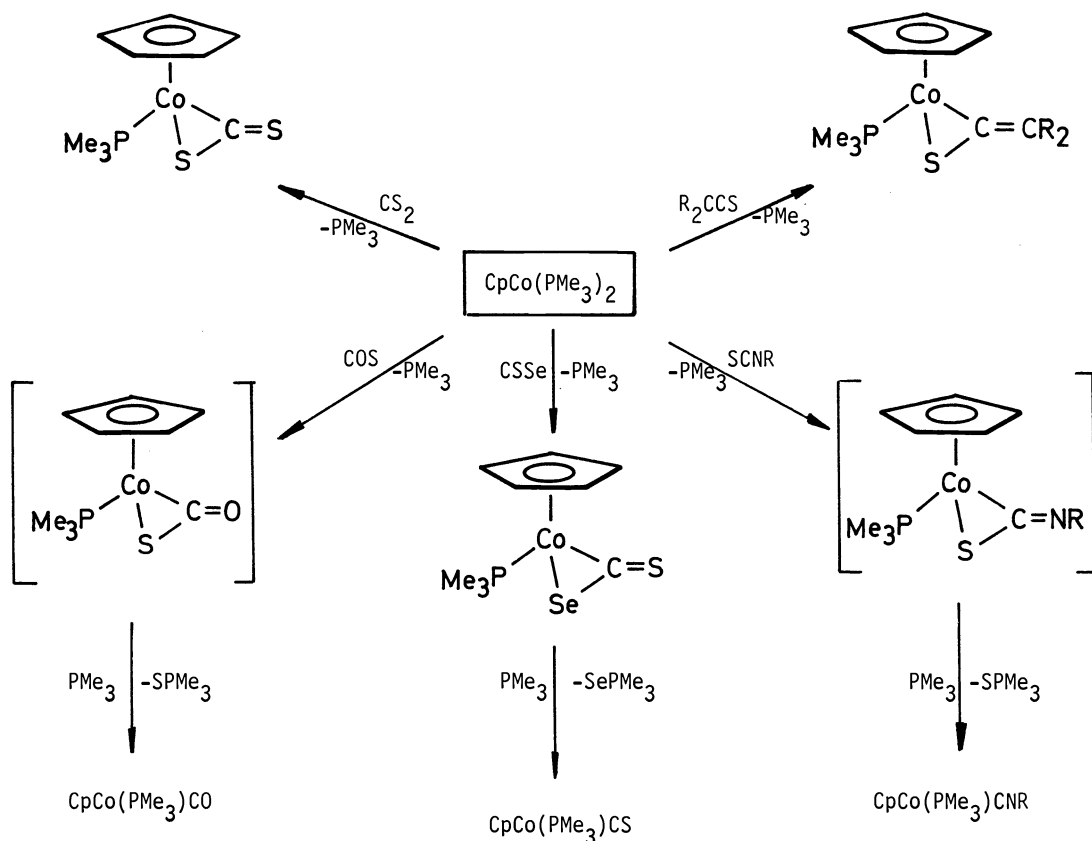
An alternative route to prepare compound 9 uses C₅H₅Co(PMe₃)CO as the starting material (Ref.15), which has already been shown by us to behave as a Lewis base in the reactions with alkyl and acyl halides (Ref.16).



Scheme 2

(L = PMe₃, PPh₃, P(OMe)₃, P(OPh)₃; L_π = C₂H₃CN, cis- and trans-C₂H₂(COOMe)₂, C₂H₂(CO)₂O, C₂Ph₂;
 L_π L = C₂H₄(PPh₂)₂, nor-C₇H₈; R = Me, CH₂Ph, Ph)

The carbondisulfidecobalt complex shown in Scheme 2 is not only formed from 9 and CS_2 but also in practically quantitative yields from 7 and CS_2 (Ref.17). The mechanism of this reaction is best explained by a nucleophilic attack of the metal center of 7 at the electrophilic carbon atom of CS_2 . The carbon atoms of other heteroallenes, for example COS , CSSe , SCNR and $\text{R}_2\text{C}=\text{C}=\text{S}$, are also attacked by the bis(phosphine) complex 7 (see Scheme 3) (Ref.18-20). Using this method the thiocarbonyl $\text{C}_5\text{H}_5\text{Co}(\text{PMe}_3)\text{CS}$ and the isonitrile compounds $\text{C}_5\text{H}_5\text{Co}(\text{PMe}_3)\text{CNR}$ ($\text{R} = \text{Me}, \text{Ph}$) were synthesized. Whereas there is only indirect evidence for the formation of the $\text{Co}(\eta^2\text{-SCNR})$ complex (e.g., the reaction of this intermediate with a second molecule of isothiocyanate to form the metallocycle $\text{C}_5\text{H}_5(\text{PMe}_3)\text{CoSC}(\text{NR})\text{SC}(\text{NR})$; see Ref.19), the $\text{Co}(\eta^2\text{-CSSe})$ complex has been isolated and characterised (Ref.18). Its clean reaction with PMe_3 or PPh_3 to give the thiocarbonyl $\text{C}_5\text{H}_5\text{Co}(\text{PMe}_3)\text{CS}$ and SePR_3 (and not the selenocarbonyl $\text{C}_5\text{H}_5\text{Co}(\text{PMe}_3)\text{CSe}$ and SPR_3) supports the structural proposal for $\text{C}_5\text{H}_5\text{Co}(\text{PMe}_3)(\eta^2\text{-CSSe})$ shown in the scheme.

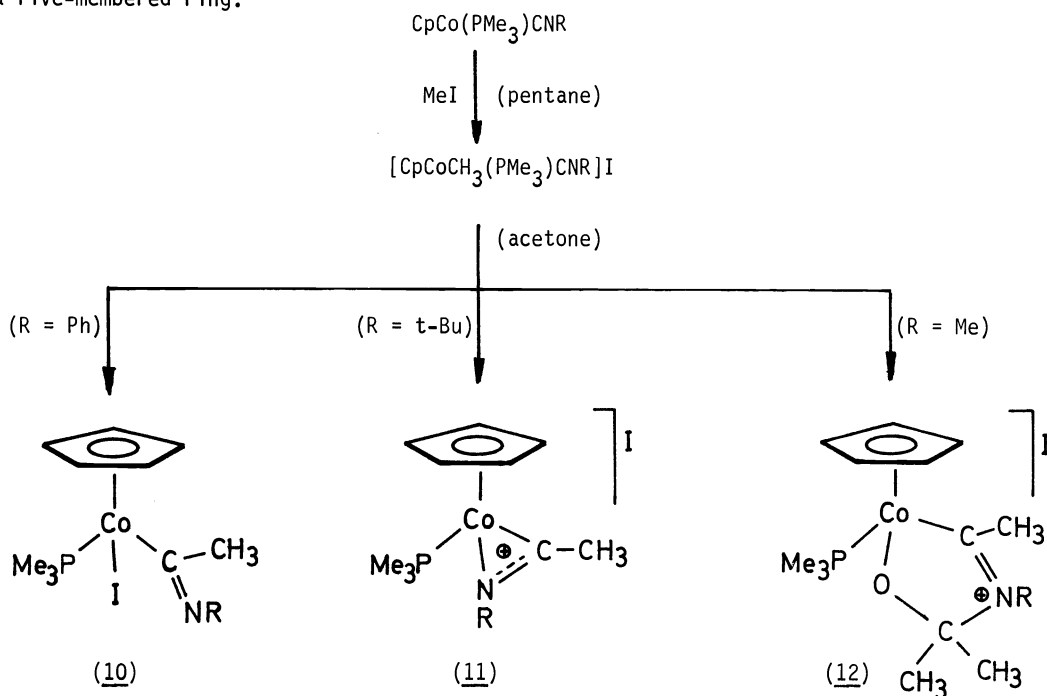


Scheme 3 ($\text{Cp} = \text{C}_5\text{H}_5$)

III. THE CYCLOPENTADIENYL MONO(PHOSPHINE) COMPLEXES

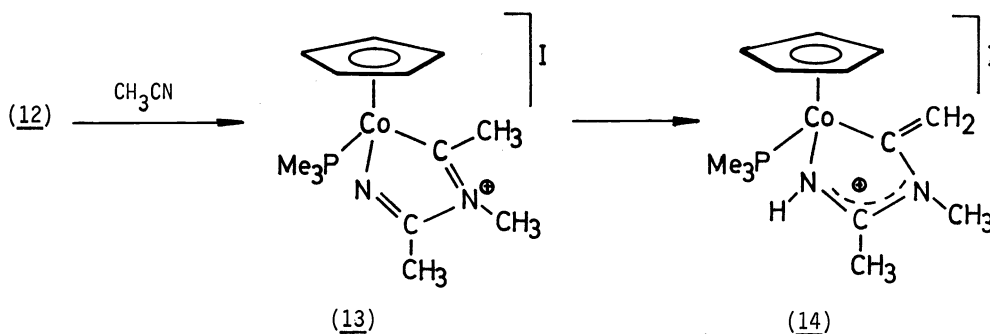
The mono(phosphine) complexes of cobalt and rhodium, mainly of the general composition $\text{C}_5\text{H}_5\text{M}(\text{PR}_3)\text{L}$ ($\text{R} = \text{Me}, \text{Et}, \text{i-Pr}$) are all weaker metal bases than the corresponding bis(phosphine) compounds. Since it is not possible in this short account to give a comprehensive view on the chemistry of the complexes $\text{C}_5\text{H}_5\text{M}(\text{PR}_3)\text{L}$, only some, mostly unpublished, results on the behaviour of the compounds with $\text{L} = \text{CNR}, \text{C}_2\text{H}_3\text{R}$ and C_2R_2 which have been obtained in our group during the last two years will be reported.

The carbonyl complex $C_5H_5Co(PMe_3)CO$ reacts with methyl iodide via the intermediate $[C_5H_5Co-CH_3(PMe_3)CO]I$ to yield the cobalt acetyl $[C_5H_5CoCOCH_3(PMe_3)I]$ (Ref.16). In the reactions of the isocyanide complexes $C_5H_5Co(PMe_3)CNR$ ($R = Me, t-Bu, Ph$) with MeI in pentane, the first step is analogous to that of the reaction of $C_5H_5Co(PMe_3)CO$ and the primary product is $[C_5H_5CoCH_3(PMe_3)CNR]I$ which is formed by nucleophilic attack of the metal base at the carbon atom of the alkyl halide. When these salts are dissolved in acetone, a fast reaction occurs which leads to different products, depending on the group R of the isocyanide (see Scheme 4). Whereas the phenylisocyanide complex behaves as expected and produces the neutral acylimino compound 10, the t-butyliisocyanide complex forms the ionic complex 11 in which the acylimino ligand is *dihapto*-bonded (Ref.19). It is possibly due to steric reasons that the methylisocyanide complex reacts by methyl migration from the cobalt to the isocyanide carbon atom and subsequent [3+2]-cycloaddition to form the heterocyclic compound 12 containing a five-membered ring.



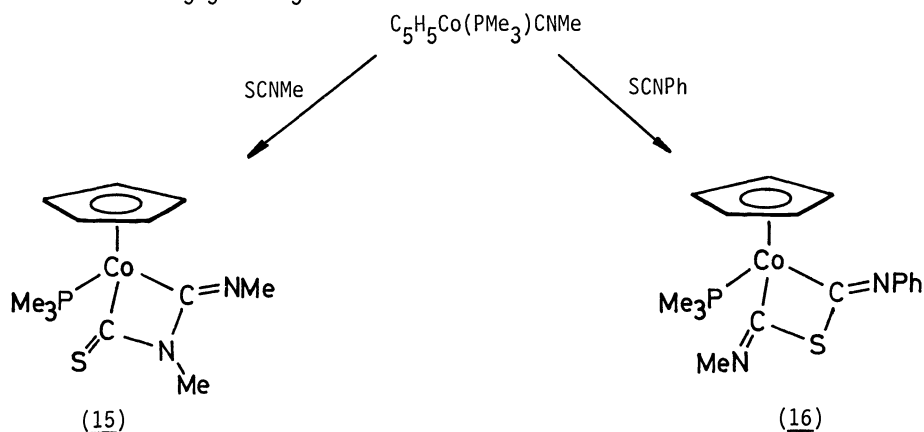
Scheme 4

In the reaction of 12 with MeCN, the acetone is displaced and the new heterocycle 14 is obtained. It seems possible that the initial product formed in this reaction is the compound 13 which rapidly rearranges to yield the tautomeric complex 14. The X-ray structural analysis has shown that there is a relatively small difference in the HN-CMe and MeC-NMe bond lengths indicating that the positive charge in the NCN fragment of the ring should be delocalized (Ref.21). Complex 14 is also obtained by dissolving $[C_5H_5CoCH_3(PMe_3)CNR]I$ in acetonitrile.

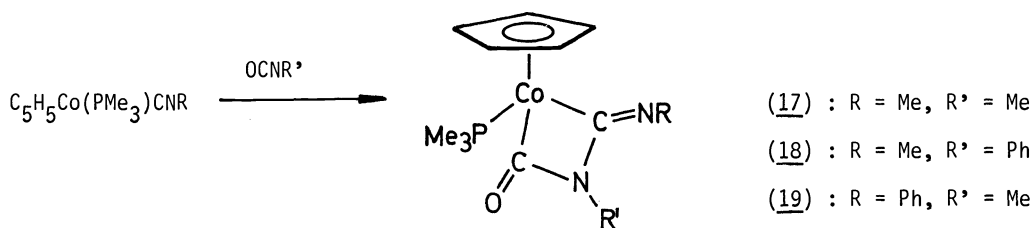


Acetone displacement from 12 occurs not only with MeCN (and with other nitriles such as PhCN and $\text{CH}_2=\text{CHCN}$) but also with isothiocyanates and carbondisulfide. In each of these reactions, a new five-membered heterocyclic ring is formed (Ref.22). Whether the product retains the Co-CMe=NMe unit or whether a rearrangement takes place to form the tautomer with an exocyclic $\text{C}=\text{CH}_2$ double bond depends on the particular substrate. The common property of all these heterocycles is that they can be readily protonated, either at the $\text{C}=\text{CH}_2$ or another exocyclic $\text{C}=\text{S}$ or $\text{C}=\text{NR}$ bond.

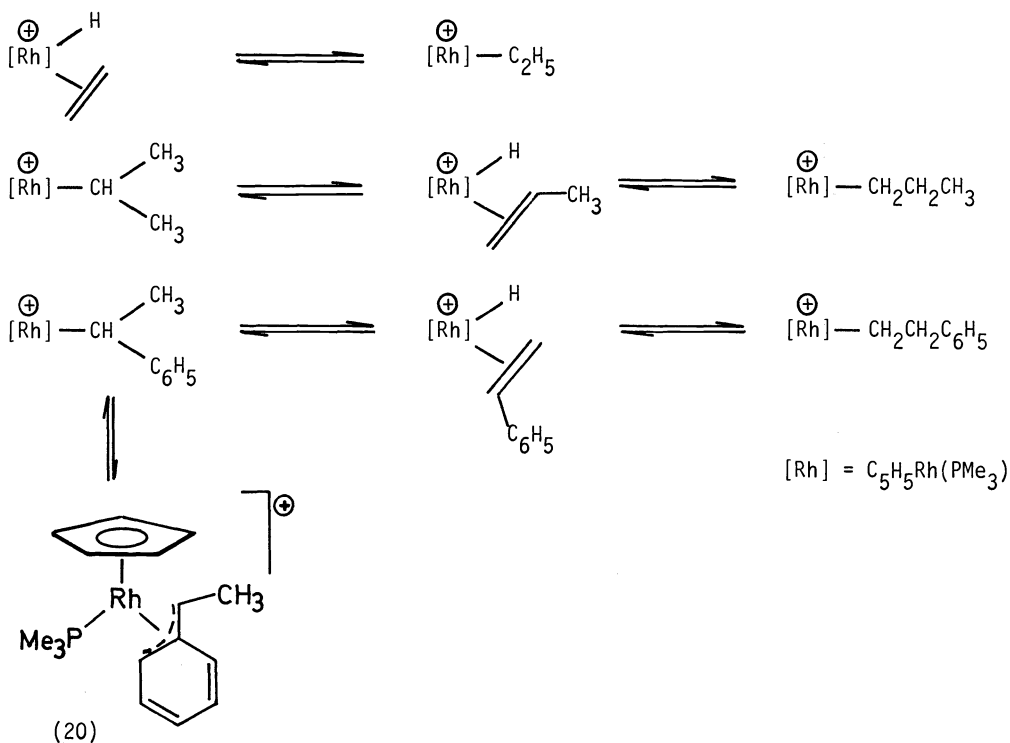
The metal basicity of the starting isocyanide complexes $\text{C}_5\text{H}_5\text{Co}(\text{PMe}_3)\text{CNR}$ has also been demonstrated in the reactions with isothiocyanates SCNR' . Attack of the metal on the electrophilic carbon atom of the isothiocyanate leads to the formation of a four-membered ring with the sulfur atom either in a cyclic or an exocyclic position. Up to now the two complexes shown in Scheme 5 have been characterised by an X-ray structural analysis (Ref.23). It is interesting to note that compound 16 is not only obtained from $\text{C}_5\text{H}_5\text{Co}(\text{PMe}_3)\text{CNMe}$ and SCNPh but also from $\text{C}_5\text{H}_5\text{Co}(\text{PMe}_3)\text{CNPh}$ and SCNMe .



Whereas methyl- and phenylisocyanates do not react at ambient temperatures with $\text{C}_5\text{H}_5\text{Co}(\text{PMe}_3)_2$ (7) and thus behave differently from SCNMe and SCNPh , both isocyanates smoothly undergo cycloaddition reactions with $\text{C}_5\text{H}_5\text{Co}(\text{PMe}_3)\text{CNR}$ leading to the complexes 17 - 19 (Ref.22). In this case there is no evidence that a second type of product with a CoCOC four-membered ring is formed.

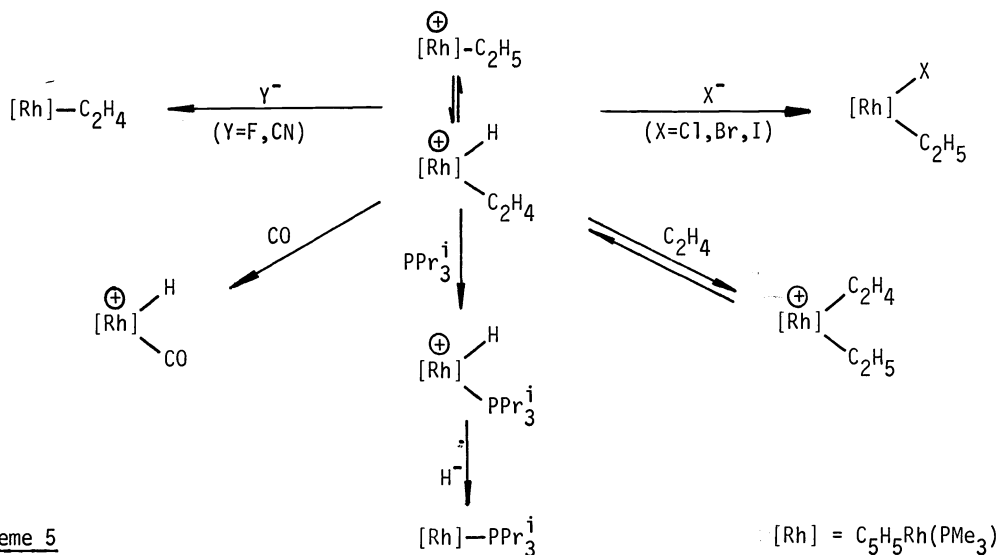


Mono(phosphine) olefin complexes $\text{C}_5\text{H}_5\text{Rh}(\text{PR}_3)_2\text{C}_2\text{H}_3\text{R}'$ have been prepared for $\text{PR}_3 = \text{PMe}_3$, PMe_2Ph , PPr_3^i and $\text{R}' = \text{H}$, Me, Ph (Ref.24 and 25). They react with acids, for example HBF_4 , and with methyl iodide to form cations containing Rh-H and Rh- CH_3 bonds, respectively. In these methylrhodium(III) cations the metal-to-olefin bond is rather labile and thus the olefin can be displaced by various nucleophiles such as phosphines or iodide. In some cases olefin displacement also occurs in the reactions of the hydrido(olefin) cations $[\text{C}_5\text{H}_5\text{RhH}(\text{PR}_3)_2\text{C}_2\text{H}_3\text{R}']^+$ although the reactivity of these species is primarily determined by the equilibrium with the corresponding alkyl compounds. On the basis of variable-temperature n.m.r. measurements and deuteration experiments, for $\text{PR}_3 = \text{PMe}_3$ the following equilibria have been established:



The product isolated from the reaction of $\text{C}_5\text{H}_5\text{Rh}(\text{PMe}_3)_2\text{C}_2\text{H}_3\text{Ph}$ and NH_4PF_6 is the PF_6^- -salt of the cation 20 in which the X-ray structural analysis shows that the η^3 -benzyl ligand is coordinated in the syn-configuration (Ref.25).

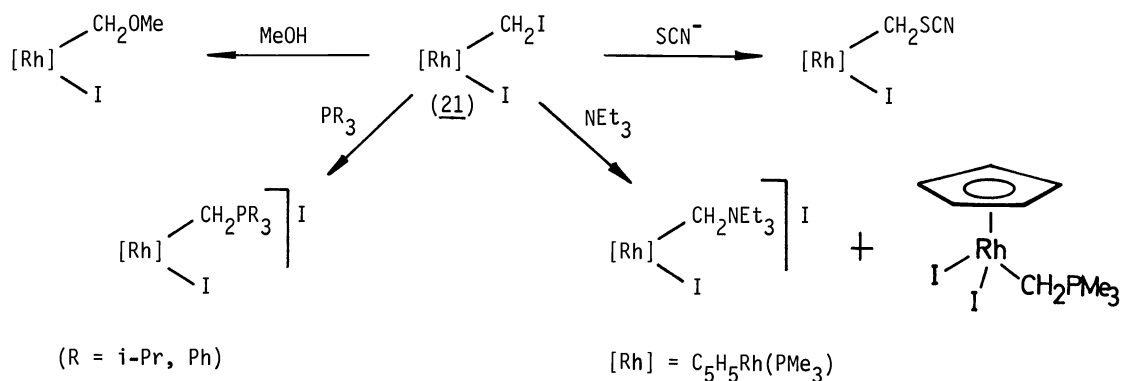
Some examples demonstrating the reactivity of the ethylene(hydrido) cation are summarized in Scheme 5.



Scheme 5

The starting ethylenrhodium complex $\text{C}_5\text{H}_5\text{Rh}(\text{PMe}_3)_2\text{C}_2\text{H}_4$ not only reacts with methyl iodide but also with CH_2I_2 and CH_2ClI . Whereas the complex $[\text{C}_5\text{H}_5\text{RhCH}_3(\text{PMe}_3)_2\text{C}_2\text{H}_4]\text{I}$ can be isolated in the reaction with MeI , the corresponding salt-like compounds $[\text{C}_5\text{H}_5\text{RhCH}_2\text{X}(\text{PMe}_3)_2\text{C}_2\text{H}_4]\text{I}$ ($\text{X} = \text{Cl}, \text{I}$) are obviously very unstable and, therefore, the complexes $[\text{C}_5\text{H}_5\text{RhCH}_2\text{X}(\text{PMe}_3)_2\text{I}]$ are obtained formed by nucleophilic displacement of the ethylene with the iodide ion. The

iodomethyl compound 21 is rather reactive towards nucleophilic substrates (see Scheme 6) and has been employed, for example, to prepare some novel ylido-rhodium(III) complexes which might be difficult to obtain by other routes.



Scheme 6

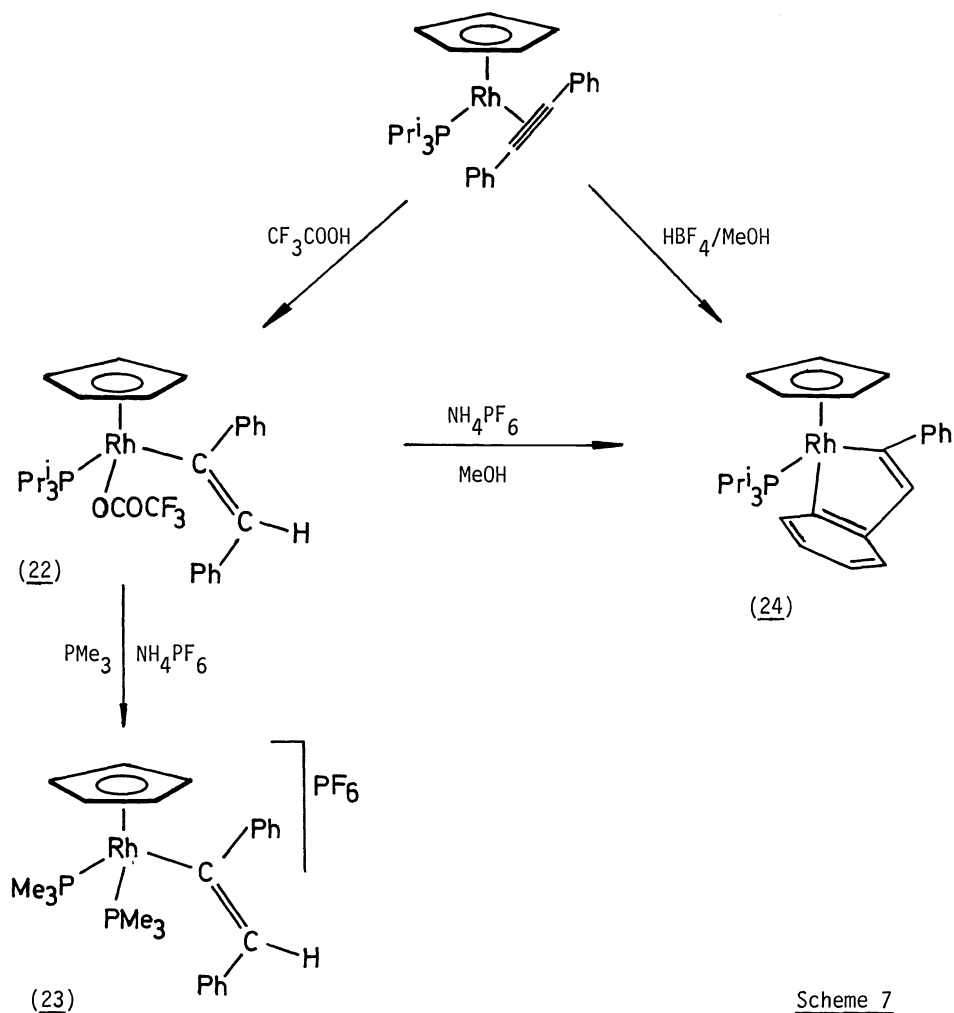
It is particularly noteworthy that in the reaction of 21 with NEt₃ besides the nucleophilic substitution (to form the RhCH₂NEt₃ complex and iodide ion) a rearrangement occurs leading to an isomer of the starting material (Ref.26). A similar rearrangement occurs when salts of the cation [C₅H₅RhCH₂I(PMe₃)₂]⁺ are treated with NEt₃. In this case, there is good evidence that the isomerization according to



proceeds intramolecularly with the formation of a four-center transition state (Ref.27).

The mono(phosphine) alkynerhodium complexes C₅H₅Rh(PPrⁱ₃)C₂R₂ are also readily protonated but in contrast to the reactions of the analogous alkene compounds C₅H₅Rh(PR₃)C₂H₄ (R = Me, i-Pr) with acids, the initially formed alkyne(hydrido) cations seem to be very unstable. The first product isolated in the reaction of C₅H₅Rh(PPrⁱ₃)C₂Ph₂ with CF₃COOH is the metalated trans-stilbene derivative 22 which on further reaction with PMe₃ in presence of NH₄PF₆ yields the PF₆⁻ salt 23 containing a very stable Rh-CPh=CHPh bond. When HBF₄ is used instead of CF₃COOH and methanol as the solvent, the protonation of C₅H₅Rh(PPrⁱ₃)C₂Ph₂ leads directly to the metallacyclopentadiene complex 24 which is also formed in practically quantitative yields from 22 and NH₄PF₆ in methanol (Scheme 7). The X-ray structural analysis shows that the rhodacyclopentadiene ring is not completely planar and can not be considered as a delocalised π-electron system (Ref.28).

In the protonation reaction of the 2-butyne complex C₅H₅Rh(PPrⁱ₃)C₂Me₂ both hydrogen migration from the metal to the alkyne and subsequent rearrangement occurs which leads to the formation of the cationic 1-methylallyl complex [C₅H₅Rh(PPrⁱ₃)(1-MeC₃H₄)]⁺. The PF₆⁻ salts of both syn- and anti-isomers have been isolated (Ref.28).

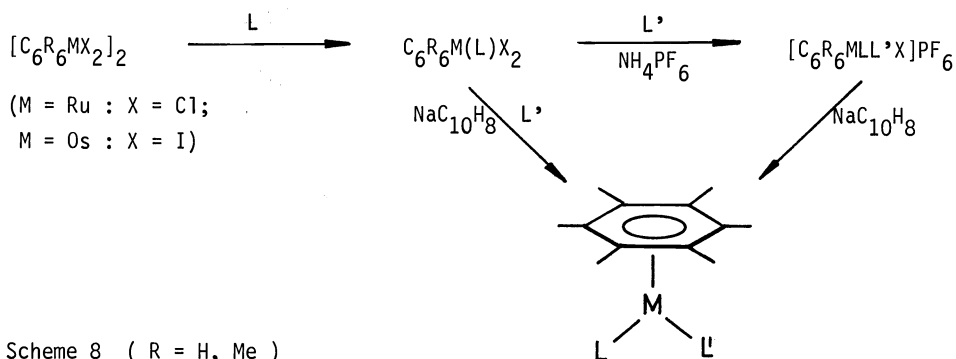


Scheme 7

IV. ARENERUTHENIUM AND ARENEOSMIUM COMPLEXES

The final part of this account deals with the reactivity of the Lewis basic areneruthenium(0) and osmium(0) complexes $\text{C}_6\text{R}_6\text{MLL}'$ in which R is H or Me, L is PR_3 or P(OR)_3 and the other ligand L' is either a phosphine, a phosphite, an olefin or a CO molecule. Based on HMO calculations it has been predicted by Albright and Hoffmann (29) that the bonding in $\text{C}_6\text{R}_6\text{MLL}'$ ($\text{M} = \text{Fe}, \text{Ru}, \text{Os}$) and $\text{C}_5\text{R}_5\text{M}'\text{LL}'$ ($\text{M}' = \text{Co}, \text{Rh}, \text{Ir}$) should be very similar.

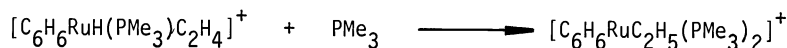
The synthesis of the complexes $\text{C}_6\text{H}_6\text{RuL}_2$ ($\text{L} = \text{PMe}_3, \text{P(OMe)}_3$), $\text{C}_6\text{H}_6\text{Ru(PMe}_3)\text{L}$ ($\text{L} = \text{PMe}_2\text{Ph}, \text{P(OMe)}_3, \text{C}_2\text{H}_4$), $\text{C}_6\text{Me}_6\text{Ru(PMe}_3)\text{CO}$, $\text{C}_6\text{H}_6\text{OsL}_2$ ($\text{L} = \text{PPh}_3, \text{P(OMe)}_3$) and $\text{C}_6\text{H}_6\text{Os(PMe}_3)\text{L}$ ($\text{L} = \text{C}_2\text{H}_4, \text{C}_3\text{H}_6, \text{CO}$) which usually proceeds through a reduction, is outlined in Scheme 8 (Ref.30 - 34).



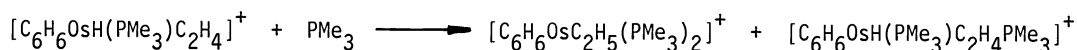
Scheme 8 (R = H, Me)

The strongly basic character of the metal atom in the arene complexes is demonstrated by the reactions with Brönsted acids and methyl iodide which lead to the corresponding cations containing stable M-H and M-CH₃ bonds. In spite of the various similarities in the behaviour of the cations $[C_6R_6MR'LL']^+$ and $[C_5R_5M'R'LL']^+$ (M = Ru, Os; M' = Co, Rh; R' = H, CH₃) towards nucleophilic as well as electrophilic substrates, there are also some notable differences, for example in the reactions of the ethylene(hydrido) and ethylene(methyl) complexes with trimethylphosphine.

The cyclopentadienylrhodium cation $[C_5H_5RhH(PMe_3)C_2H_4]^+$ reacts with excess PMe_3 by elimination of cyclopentadiene to yield a mixture of cationic ethylene(phosphine) rhodium(I) complexes (Ref.26). Under similar conditions, ethylene is inserted into the metal-to-hydride bond of the corresponding benzeneruthenium cation $[C_6H_6RuH(PMe_3)C_2H_4]^+$ to form the ethyl compound (Ref.31).



In the reaction of the benzeneosmium cation $[C_6H_6OsH(PMe_3)C_2H_4]^+$ with PMe_3 , the formation of the ethyl compound is accompanied by the formation of a β-substituted alkyl(hydrido) complex resulting from nucleophilic attack of the phosphine at the ethylene ligand (Ref.33).

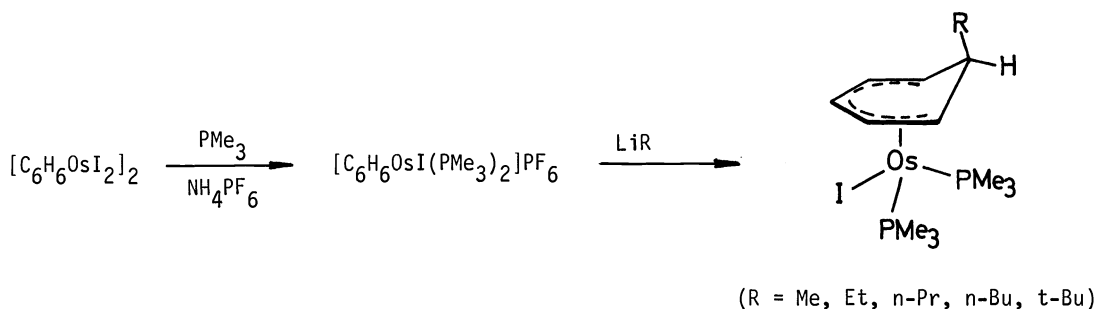


In our opinion, the difference in behaviour towards PMe_3 between the two ethylene(hydrido) cations may be explained by the fact that the ruthenium compound is observed to be in equilibrium with the ethylruthenium complex, whereas the corresponding osmium compound $[C_6H_6OsH(PMe_3)C_2H_4]^+$ is the only species detectable by ¹H n.m.r. spectroscopy and deuteration experiments in solution.

The methyl(olefin) cations $[C_6H_6MCH_3(PMe_3)C_2H_3R]^+$ (M = Ru, R = H; M = Os, R = H, Me) also react under rather mild conditions with trimethylphosphine. The hope, however, that during these reactions a migration of the methyl group from the metal to the olefin could occur, was not fulfilled. In the methyl(propene) osmium complex, olefin displacement takes place and $[C_6H_6OsCH_3(PMe_3)_2]^+$ is formed in quantitative yields. The reaction of the ethylene complexes $[C_6H_6MCH_3(PMe_3)C_2H_4]^+$ with PMe_3 give the β-phosphinoethyl cations $[C_6H_6MCH_3(PMe_3)C_2H_4PMe_3]^+$ as the sole products (Ref.31 and 33). These cations are remarkably stable and do not eliminate the olefin even on heating to produce the compounds $[C_6H_6MCH_3(PMe_3)_2]^+$. The tendency to form such β-substituted ethylmetal cations is even

greater, at least for $M = Ru$, when the dicationic complex $[C_6H_6Ru(PMe_3)_2C_2H_4]^{2+}$, prepared from $[C_6H_6RuC_2H_5(PMe_3)_2]^+$ by hydride abstraction with CPh_3^+ , is treated with nucleophiles. Using this method, the PF_6 salts of the cations $[C_6H_6Ru(PMe_3)_2C_2H_4PR_3]^{2+}$ ($R = Me, i-Pr, Ph$), $[C_6H_6Ru(PMe_3)_2C_2H_4P(OR)_3]^{2+}$ ($R = Me, Ph$) and $[C_6H_6Ru(PMe_3)_2C_2H_4P(O)(OMe)_2]^+$ have been obtained (Ref.35).

Following the investigations of the metal basicity of the d^8 complexes $C_5R_5ML_2$, C_5R_5MLL' ($M = Co, Rh$) and $C_6R_6M^*L_2$, $C_6R_6M^*LL'$ ($M = Ru, Os$), current activities are directed to related d^6 systems. It has not yet been possible to prepare stable hydridomanganese or methylmanganese cations $[C_5H_5MnRL_3]^+$ ($R = H, Me; L = PMe_3, P(OMe)_3$) by reacting $C_5H_5MnL_3$ with protonating and methylating reagents (Ref.36). It is possible, however, to obtain stable cationic hydridoosmium complexes $[(C_6H_6R)OsHI(PMe_3)_2]^+$ from $(C_6H_6R)OsI(PMe_3)_2$ and HPF_6 in acetone solution (Ref.37). The synthesis of the ringsubstituted cyclohexadienyl-osmium(II) compounds proceeds as follows:



The exo-position for $R = n-Bu$ has been confirmed by an X-ray structural analysis (Ref.38). The reason that the cyclohexadienyl complexes are prone to electrophilic attack of the proton at the metal is probably due to the strong donor properties of the trimethylphosphine ligands, which cause even osmium(II) to become a center of metal basicity.

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