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Preliminary communication

Addition of allyl halides and other addenda molecules to some cationic derivatives of rhodium(I)

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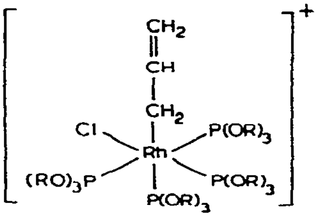
The oxidative addition reactions of allyl halides to neutral rhodium(I) and iridium(I) derivatives are well documented[1]. No such reactions have been reported for cationic complexes of these metals, however. This communication reports the addition of allyl chloride to the cations, $Rh[P(OR)_3]_4^+$ ($R = CH_3, C_2H_5, i\text{-}C_3H_7$)[2] and $Rh[P(OR)_3]_5^+$ ($R = CH_3, C_2H_5$)[3].

Treatment of $Rh[P(OCH_3)_3]_5B(C_6H_5)_4$ with neat allyl chloride gave along with $\{RhCl(\pi\text{-}C_3H_5)[P(OCH_3)_3]_3\}$ $B(C_6H_5)_4$, a second product characterised as $\{Rh(\pi\text{-}C_3H_5)[P(OCH_3)_3]_4\}$ $[B(C_6H_5)_4]_2$ and shown conductimetrically to be a 1/2 electrolyte in acetone. This unusual dicationic complex is not only the major product of the above reaction but is the sole product if the reaction is performed in methanol. In contrast, treatment of $Rh[P(OC_2H_5)_3]_5B(C_6H_5)_4$ with neat allyl chloride yielded only $\{RhCl(\pi\text{-}C_3H_5)[P(OC_2H_5)_3]_3\}$ $B(C_6H_5)_4$. The dicationic complex, $\{Rh(\pi\text{-}C_3H_5)[P(OC_2H_5)_3]_4\}$ $[B(C_6H_5)_4]_2$, is again the sole product if this reaction is performed in methanol.

The four-coordinate derivatives, $Rh[P(OR)_3]_4B(C_6H_5)_4$ ($R = CH_3, C_2H_5$), give $\{Rh(\pi\text{-}C_3H_5)[P(OR)_3]_4\}$ $[B(C_6H_5)_4]_2$ on treatment with allyl chloride in methanol as observed for their five-coordinate analogues. This contrasts with the behaviour of $Rh[P(O\text{-}i\text{-}C_3H_7)_3]_4B(C_6H_5)_4$ which affords the chloro-complex, $\{RhCl(\pi\text{-}C_3H_5)[P(O\text{-}i\text{-}C_3H_7)_3]_3\}$ $B(C_6H_5)_4$, on reaction with allyl chloride in methanol.

The nature of the bonding of the allyl groups in these rhodium(III) derivatives could not be ascertained from the NMR data as the resonances associated with C_3H_5 occur in the same region as those corresponding to the ligand protons, $P{-}O{-}CH_{\overline{n}}$. It as assumed however that both $\{Rh(C_3H_5)[P(OR)_3]_4\}^{2+}$ and $\{RhCl(C_3H_5)[P(OR)_3]_3\}^+$ are six-coordinate and thus the allyl groups are necesssarily π-bonded to the metal atom in these cations. The absence of peaks in the region of 1610 cm^{-1} in the IR spectra of these derivatives is consistent with this proposal.

The formation of the cations, $\{RhCl(\pi\text{-}C_3H_5)[P(OR)_3]_3\}^+$ and $\{Rh(\pi\text{-}C_3H_5)[P(OR)_3]_4\}^{2+}$, is readily explained in terms of a mechanism involving the σ-allyl species (I) as an intermediate. The olefinic group in (I) effects displacement of the chloride to afford $\{Rh(\pi\text{-}C_3H_5)[P(OR)_3]_4\}^{2+}$ or replacement of a tertiary phosphite ligand to form $\{RhCl(\pi\text{-}C_3H_5)[P(OR)_3]_3\}^+$. The observation that the cation, $\{Rh(\pi\text{-}C_3H_5)[P(OR)_3]_4\}^{2+}$, is formed more readily in an ionizing solvent such as methanol is consistent with the proposed mechanism. The inability to isolate σ-allyl derivatives of the type, $\{RhCl(\sigma\text{-}C_3H_5)[P(OR)_3]_4\}B(C_6H_5)_4$ is attributed to their high intramolecular reactivity.



(I)

The reactions of the cationic derivatives, $Rh[P(OCH_3)_3]_4B(C_6H_5)_4$ and $Rh[P(OCH_3)_3]_5B(C_6H_5)_4$, with other addenda molecules have also been studied. For instance, carbon monoxide was observed to react with $Rh[P(OCH_3)_3]_4B(C_6H_5)_4$ to give the five-coordinate derivative, $\{Rh(CO)[P(OCH_3)_3]_4\}B(C_6H_5)_4$ ($\nu(CO) = 1974\ cm^{-1}$) in high yield. Treatment of $Rh[P(OCH_3)_3]_4B(C_6H_5)_4$ with hydrogen results in the formation of the dihydride, *cis*- $\{Rh[P(OCH_3)_3]_4H_2\}B(C_6H_5)_4$ ($\nu(RhH) = 1975\ cm^{-1}$, broad); this reaction is reversible in contrast to the corresponding reaction involving $Rh[P(n\text{-}C_4H_9)_3]_4B(C_6H_5)_4$. The action of bromine on $Rh[P(OCH_3)_3]_5B(C_6H_5)_4$ gave a mixture of *cis* and *trans*-$\{Rh[P(OCH_3)_3]_4Br_2\}B(C_6H_5)_4$, which were separated by fractional crystallisation. Interestingly *cis*- $\{Rh[P(OCH_3)_3]_4Br_2\}B(C_6H_5)_4$ is obtained by reacting *trans*- $\{Rh[P(OCH_3)_3]_4HBr\}B(C_6H_5)_4$ with excess HBr in ethanol. This latter complex is the initial product in the reaction of $Rh[P(OCH_3)_3]_5B(C_6H_5)_4$ with HBr. Methyl iodide reacts with $Rh[P(OCH_3)_3]_4B(C_6H_5)_4$ to yield $\{Rh[P(OCH_3)_3]_4MeI\}B(C_6H_5)_4$.

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