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Preliminary communication

THE INSERTION OF CYCLOHEPTATRIENE AND CYCLOHEPTA-1,3-DIENE INTO THE Ru—H BOND OF $RuHCl(PPh_3)_3$ TO GIVE $Ru(\eta^5\text{-}C_7H_9)Cl(PPh_3)_2$ AND $Ru(\eta^3\text{-}C_7H_{11})Cl(PPh_3)_2$

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Summary

$RuHCl(PPh_3)_3$ reacts quantitatively with cycloheptatriene in CH_2Cl_2 at 35°C in 15 min to give $Ru(\eta^5\text{-}C_7H_9)Cl(PPh_3)_2$ and PPh_3. The major isomer adopts a conformation with inequivalent phosphorus ligands and no plane of symmetry through the C_7H_9 ligand, but rapid intramolecular scrambling with $\Delta G^{\ddagger} = 10.6$ kcal mol^{-1} results in an averaged ^1H, ^{13}C, and ^{31}P NMR spectrum at room temperature. $RuHCl(PPh_3)_3$ reacts with cyclohepta-1,3-diene to give initially $Ru(\eta^3\text{-}C_7H_{11})Cl(PPh_3)_2$, but in a subsequent reaction this is dehydrogenated to give $Ru(\eta^5\text{-}C_7H_9)Cl(PPh_3)_2$.

$RuHCl(PPh_3)_3$ is one of the most active homogeneous catalysts known for the hydrogenation of alk-1-enes [1]. The speed of hydrogenation is so high that kinetic studies analogous to those carried out on $RhCl(PPh_3)_3$ have been prevented because the limiting step is the rate of dissolution of H_2 in the solvent. The first stage of the reaction is believed to be the reaction of $RuHCl(PPh_3)_3$ with olefin to give $RuHCl(\eta^2\text{-olefin})(PPh_3)_2$, followed by insertion of the olefin into the Ru—H bond, giving $Ru(alkyl)Cl(PPh_3)_3$. Since the catalyst acts very quickly, it follows that each step of the catalytic pathway must also be fast. Despite the importance of this catalyst, there have been no reports of the isolation of an insertion product produced directly by the reaction of $RuHCl(PPh_3)_3$ with an olefin. It is known that $RuHCl(\eta^4\text{-norbornadiene})(PPh_3)_2$ reacts in the presence of CO to give I [5]. This lack of detectable products presumably arise from the instability of $Ru(alkyl)Cl(PPh_3)_3$. In order to stabilise the alkyl intermediate, cycloheptatriene was chosen as the olefin, as it is known that complexes of the type $Ru(\eta^5\text{-}C_7H_9)X(CO)_2$ (X = Br or I) [2], and $[Ru(\eta^5\text{-}C_7H_9)$-

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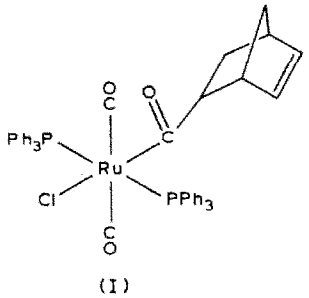
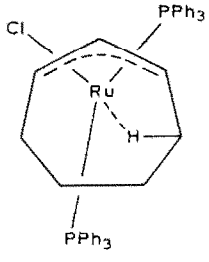
$(CO)_n\{P(OCH_2)_3CEt\}_{3-n}]^+$ (n = 1, 2) [3] are stable, the ruthenium—cycloheptadienyl bond being strengthened by additional bonding to the two olefins. The reaction between $RuHCl(PPh_3)_3$ and cycloheptatriene in CD_2Cl_2 was monitored by ^{31}P NMR spectroscopy. Cycloheptatriene was added to $RuHCl(PPh_3)_3$ at −60°C, but no reaction occurred. No significant reaction was detected until the solution was warmed to room temperature and above. A clean reaction occurs at 35°C, and is complete in 15 min to give PPh_3 and $Ru(\eta^5\text{-}C_7H_9)Cl(PPh_3)_2$ as the only products detected by ^{31}P NMR spectroscopy. The reaction was repeated on a preparative scale and the PPh_3 removed by washing with toluene to yield an analytically pure product. At room temperature, the ^1H, ^{13}C, and ^{31}P NMR spectra of the product are consistent with the products having an apparent plane of symmetry, but on cooling to −70°C, the spectra show the presence of a species with inequivalent phosphorus ligands and no plane of symmetry, at δ 31.9 and 22.6 ppm, $^2J(^{31}P,^{31}P)$ 25 Hz. The two inequivalent phosphorus nuclei undergo interconversion with $\Delta G^{\ddagger}$ 10.6 kcal mol^{-1}.

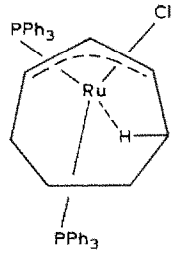
When $RuHCl(PPh_3)_3$ is treated with cyclohepta-1,3-diene, the behaviour is initially similar, with the reaction proceeding steadily in CD_2Cl_2 at 35°C to give $Ru(\eta^3\text{-}C_7H_{11})Cl(PPh_3)_2$ and PPh_3. The $Ru(\eta^3\text{-}C_7H_{11})Cl(PPh_3)_2$ was characterised only in solution. The ^{31}P NMR spectrum shows two doublets at δ 63.9 and 33.5 ppm with $^2J(^{31}P,^{31}P)$ 33 Hz. The ^1H NMR spectrum shows a single "agostic" hydrogen at δ −7.8 ppm. This chemical shift is similar to that already reported for the "agostic" hydrogen at δ −8.2 ppm in the static $[Ru(\eta^3\text{-}C_7H_{11})\text{-}\{P(OMe)_2Ph\}_3]^+$ at 183 K [4]. No dynamic process occurs until there is the well documented hydrogen migration around the ring with $\Delta G^{\ddagger}$ (ca. 17.1 kcal mol^{-1} at 20°C. The usual metal exchange between the "agostic" hydrogen and the equivalent on the other side of the cycloheptenyl ring is not observed. In $[Ru(\eta^3\text{-}C_7H_{11})(PR_3)_3]^+$, this process is of very low energy, being frozen out only at 183 K when $PR_3 = P(OMe)_2Ph$ [6]. This difference can be rationalised if the stereochemistry is such that the two sides of the ring are inequivalent, with the "agostic" hydrogen *trans* to chloride and the corresponding hydrogen on the other side of the ring *trans* to PPh_3 or vice versa as in II or III. This interpretation is consistent with the observation of two inequivalent ^{31}P nuclei at room temperature. Attempts to form pure $Ru(\eta^3\text{-}C_7H_{11})Cl(PPh_3)_2$ in solution failed due to its conversion to $Ru(\eta^5\text{-}C_7H_9)Cl(PPh_3)_2$ before all the $RuHCl(PPh_3)_3$ is consumed. This occurred even if a stoichiometric quantity of C_7H_{10}



(I)



(II)



(III)

is used in the reaction, and approximately half the $RuHCl(PPh_3)_3$ is unconsumed. It is assumed that the $Ru(\eta^3\text{-}C_7H_{11})Cl(PPh_3)_2$ reacts with cyclohepta-1,3-diene to give $Ru(\eta^5\text{-}C_7H_9)Cl(PPh_3)_2$ and cycloheptene. This is analogous with the reaction between $[RuH(cod)(PMe_2Ph)_3]^+$ and C_7H_{10} to give both $[Ru(\eta^3\text{-}C_7H_{11})(PMe_2Ph)_3]^+$ and $[Ru(\eta^5\text{-}C_7H_9)(PMe_2Ph)_3]^+$ [7].

This is the first successful isolation of products from the direct reaction of $RuHCl(PPh_3)_3$ with an olefin. In contrast, there are numerous examples of the insertion of olefins into other ruthenium—hydride bonds, e.g., $RuHCl(CO)(PPh_3)_2$ reacts with $CH_2{=}CHCO_2R$ to give $Ru(CH_2CH_2CO_2Me)Cl(CO)(PPh_3)_2$ [6], and $[RuH(1,5\text{-}cod)(PMe_2Ph)_3]^+$ reacts with 1,3-dienes to give $[Ru(\eta^3\text{-}enyl)(PMe_2Ph)_3]^+$ [7]. Preliminary work indicates that there is a similar, but slower reaction with 1,3-cyclooctadiene, and investigations of similar reactions are in hand.

$Ru(\eta^5\text{-}C_7H_9)Cl(PPh_3)_2$ was examined as a hydrogenation catalyst, but proved to be ineffective. The ready formation of this compound thus provides a mechanism for the poisoning of the hydrogenation catalyst $RuHCl(PPh_3)_3$.

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