

A FACILE SYNTHESIS OF COMPLEXES OF THE TYPE $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{L}_2\text{H}$ ($\text{L}_2 = \text{CHELATING PHOSPHINE}$)

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Summary

$\text{Ru}(\text{C}_5\text{H}_5)(\text{CO})_2\text{H}$, prepared in situ from $\text{Ru}_3(\text{CO})_{12}$, reacts with bisphosphines L_2 to give $\text{Ru}(\text{C}_5\text{H}_5)\text{L}_2\text{H}$ quantitatively [$\text{L}_2 = \text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$, $n = 2$ or 4 ; $\text{L}_2 = (R)\text{-Ph}_2\text{PCH}_2\text{CH}(\text{Me})\text{PPh}_2$].

A well-known feature of complexes of the type $\text{Ru}(\text{C}_5\text{H}_5)(\text{CO})_2\text{X}$ is that it is extremely difficult to replace both carbonyl ligands directly, and thus alternative complexes such as $\text{Ru}(\text{C}_5\text{H}_5)(\text{PPh}_3)_2\text{Cl}$ have become favoured synthons for cyclopentadienylruthenium complexes [1]. For example, the reported synthesis of $\text{Ru}(\text{C}_5\text{H}_5)(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{H}$ involves the displacement of the triphenylphosphine ligands from $\text{Ru}(\text{C}_5\text{H}_5)(\text{PPh}_3)_2\text{Cl}$ followed by reduction with LiAlH_4 [2]. However, we required a more direct route to such compounds and $\text{Ru}(\text{C}_5\text{H}_5)(\text{CO})_2\text{H}$ appeared to be an attractive precursor since it can be readily and rapidly prepared from $\text{Ru}_3(\text{CO})_{12}$ [3]; further, we reasoned that because of the labilizing effect of the hydrido ligand [4,5] this compound may be susceptible to double carbonyl substitution. In this communication we show that this is indeed the case, and that both carbonyl ligands in $\text{Ru}(\text{C}_5\text{H}_5)(\text{CO})_2\text{H}$ are readily replaced by a chelating phosphine to provide a "one-pot" synthesis of complexes of the type $\text{Ru}(\text{C}_5\text{H}_5)\text{L}_2\text{X}$ ($\text{L}_2 = \text{chelating phosphine}$, $\text{X} = \text{H}$, Cl , etc.) starting from $\text{Ru}_3(\text{CO})_{12}$.

Refluxing $\text{Ru}(\text{C}_5\text{H}_5)(\text{CO})_2\text{H}$ in heptane with a slight excess of a bisphosphine ligand L_2 gives $\text{Ru}(\text{C}_5\text{H}_5)\text{L}_2\text{H}$ quantitatively after 4 h ($\text{L}_2 = \text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$, $R\text{-}(+)\text{-Ph}_2\text{PCH}_2\text{CH}(\text{Me})\text{PPh}_2$) or after 14 h ($\text{L}_2 = \text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2$) *. This reactivity contrasts with that of $\text{Ru}(\text{C}_5\text{H}_5)(\text{CO})_2\text{Cl}$, which on refluxing in heptane for 24

* Satisfactory elemental analyses obtained for all new compounds.

h with an excess of 1,2-bis(diphenylphosphino)ethane gave a mixture consisting of 15% unreacted starting material and $\text{Ru}(\text{C}_5\text{H}_5)(\text{CO})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{Cl}$ as the only product; this illustrates the difficulty of replacing both carbonyl ligands in $\text{Ru}(\text{C}_5\text{H}_5)(\text{CO})_2\text{Cl}$. The fact that 1,4-bis(diphenylphosphino)butane requires a significantly longer reaction time than the 1,2-bisphosphines suggests that in addition to the labilizing effect of the hydrido ligand the chelate effect contributes to the facile displacement of both carbonyl ligands. This is confirmed by the reaction of $\text{Ru}(\text{C}_5\text{H}_5)(\text{CO})_2\text{H}$ with triphenylphosphine (Ru/P 1/4) in refluxing heptane; after 1 h $\text{Ru}(\text{C}_5\text{H}_5)(\text{CO})(\text{PPh}_3)\text{H}$ is formed, and no further reaction occurs upon refluxing for an additional 20 h.

The hydrido complexes $\text{C}_5\text{H}_5\text{Ru}(\text{L}_2)\text{H}$ are air-stable for weeks in the solid-state and therefore are convenient model compounds for studying the chemistry of the ruthenium-hydride bond. If an unsymmetrical chelating phosphine is used then this synthesis provides a ready access to hydrido complexes containing a chiral ruthenium centre as illustrated herein in the case of $\text{Ru}(\text{C}_5\text{H}_5)((R)\text{-Ph}_2\text{PCH}_2\text{CH}(\text{Me})\text{PPh}_2)\text{H}$. Alternatively, they can be rapidly and quantitatively converted by chlorinated solvents into the corresponding chloro complexes $\text{Ru}(\text{C}_5\text{H}_5)\text{L}_2\text{Cl}$ which in turn have proved to be valuable precursors to a wide range of cyclopentadienylruthenium complexes [2].

Experimental

[1,2-Bis(diphenylphosphino)ethane](cyclopentadienyl)hydridoruthenium

Freshly cracked cyclopentadiene (3 ml) was added to a refluxing solution of $\text{Ru}_3(\text{CO})_{12}$ (300 mg, 0.47 mmol) in heptane (80 ml) under nitrogen and the reflux was continued until the infrared spectrum of the mixture indicated that all the $\text{Ru}_3(\text{CO})_{12}$ had been converted into $\text{Ru}(\text{C}_5\text{H}_5)(\text{CO})_2\text{H}$ (ca. 1.5 h). 1,2-Bis(diphenylphosphino)ethane (617 mg, 1.55 mmol) was then added and the mixture refluxed for a further 4 h. The solution was then allowed to cool to room temperature and pale yellow crystals deposited. These were filtered off, washed with heptane (5 ml) and dried in vacuo to yield pure $\text{Ru}(\text{C}_5\text{H}_5)[\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2]\text{H}$ (618 mg, 78%). A

TABLE 1
INFRARED, NMR AND MASS SPECTROMETRIC DATA

	$\nu(\text{Ru-H})^a$	$^1\text{H NMR}^b$		$^{31}\text{P}(^1\text{H})^b$	M^+
		C_5H_5	Ru-H		
$\text{Ru}(\text{C}_5\text{H}_5)(\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2)\text{H}$	1905	4.76	-13.22(t) (J 34) ^c	93.3	566(40) ^d
$\text{Ru}(\text{C}_5\text{H}_5)(\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2)\text{H}$	1908	4.41	-12.18(t) (J 33) ^c	44.22	594(55) ^d
$\text{Ru}(\text{C}_5\text{H}_5)((R)\text{-Ph}_2\text{PCH}_2\text{CH}(\text{Me})\text{PPh}_2)\text{H}$	1897	4.60	-13.28(dd) ^e (J 33) ^c	103.8(d) ^f ; 85.6(d) ^f ; (J 59) ^g 98.2(d) ^h ; 77.3(d) ^h ; (J 65) ^g	580(90) ^d

^a KBr. ^b δ Scale, recorded in C_6D_6 . ^c $J(^{31}\text{P}-^1\text{H})$ in Hz. ^d Intensity relative to the most abundant ion in the mass spectrum. ^e The signals of the two diastereoisomers overlap. ^f Major diastereoisomer (82%). ^g $J(^{31}\text{P}-^{31}\text{P})$ in Hz. ^h Minor diastereoisomer.

further crop (0.125 mg) of product was obtained by concentrating the filtrate to ca. 20 ml and then cooling the solution to 0°C.

Other complexes of the type $\text{Ru}(\text{C}_5\text{H}_5)_2\text{L}_2\text{H}$ were prepared using an identical procedure and the appropriate chelating phosphine L_2 .

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