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DIENE AND DIENYL COMPLEXES OF TRANSITION ELEMENTS

VII *. CARBONYLCHLOROBIS(DIMETHYLPHENYLPHOSPHINE)-(η^3-PENTADIENYL)RUTHENIUM

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Summary

The reaction between $[\{Ru(CO)Cl_2(PMe_2Ph)_2\}_2]$ and $SnBu_3(C_5H_7)$ in chloroform yields the η^3-pentadienyl complex $[Ru(CO)Cl(\eta^3\text{-}C_5H_7)(PMe_2Ph)_2]$. The ^1H NMR spectra are reported and discussed.

Introduction

Abel and Moorhouse have used the allyltin reagents $SnMe_3(C_3H_5)$ and $SuBu_3(C_3H_5)$ to convert halogeno complexes into η^3-allyl complexes [2]. The corresponding pentadienyl compounds $SnMe_3(C_5H_7)$ and $SnBu_3(C_5H_7)$ have been employed by Seyferth [3] and by us [4] to prepare $Mn(\eta^5\text{-}C_5H_7)(CO)_3$ and $Re(\eta^5\text{-}C_5H_7)(CO)_3$, respectively. Mawby and coworkers have shown that the dimeric ruthenium complex $[\{RuCl_2(CO)(PMe_2Ph)_2\}_2]$ reacts with $SnBu_3(C_3H_5)$ to afford the η^3-allyl compound $[Ru(CO)Cl(\eta^3\text{-}C_3H_5)(PMe_2Ph)_2]$ in 60% yield [5]. In this paper we describe the reaction of tributylpentadienyltin with the ruthenium dimer. In principle this could yield either an η^5-pentadienyl complex $[RuCl(\eta^5\text{-}C_5H_7)(PMe_2Ph)_2]$ or an η^3-pentadienyl derivative $[Ru(CO)Cl(\eta^3\text{-}C_5H_7)(PMe_2Ph)_2]$. In the event the latter compound was produced. η^3-Pentadienyl complexes of nickel [6] have recently been described, and we have prepared complexes of rhodium [1], iridium [7], manganese [8] and molybdenum [8] which contain this ligand.

Results and discussion

When a solution of the dimer $[\{Ru(CO)Cl_2(PMe_2Ph)_2\}_2]$ in chloroform was stirred with tributylpentadienyltin for 2 h at 40°C, a smooth reaction occurred to

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* For part VI see ref. 1.

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yield the η^3-pentadienyl complex $[Ru(CO)Cl(\eta^3\text{-}C_5H_7)(PMe_2Ph)_2]$ (I). The product was isolated as a pale cream powder after chromatography on alumina and crystallisation from light petroleum. The progress of the reaction was monitored by infrared spectroscopy. No evidence was obtained for the formation of η^1-pentadienyl intermediates. Although indirect evidence for such intermediates was presented by Mawby, he similarly, did not observe them directly by spectroscopy.

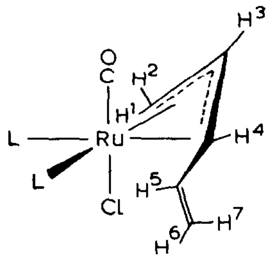
The structure and stereochemistry of I are assigned on the basis of NMR spectra. The ^1H NMR spectrum is complicated by the presence of extensive coupling to ^{31}P. Accordingly a spectrum was measured in which the ^{31}P nuclei were decoupled. This spectrum shows seven widely separated bands with equal intensities corresponding to seven inequivalent hydrogen nuclei. Assignments are made on the basis of coupling constants, double resonance experiments and by analogy with spectra of other η^3-pentadienyl complexes. In particular the uncoordinated vinyl group is indicated by resonances at 6.07δ (doublet of triplets,H^5), 5.20δ (doublet of doublets, H^7) and 4.96δ (doublet of doublets, H^6). Moreover a band at 1620 cm^{-1} in the infrared spectrum in chloroform solution shows the presence of a free carbon–carbon double bond.

In the phosphorus-decoupled spectrum, the methyl substituents of the phosphine ligands give rise to two sets of signals, a singlet at 1.75δ and another pair of singlets at 1.58 and 1.44δ. This shows that the two ligands are not equivalent, suggesting that they adopt a mutually *cis* configuration. Moreover the two methyl groups in one of the ligands must be in different environments; this could reflect the asymmetry of the η^3-pentadienyl system in comparison with the analogous allyl complex, reported by Mawby, in which the spectrum shows only two methyl resonances with very similar chemical shifts.

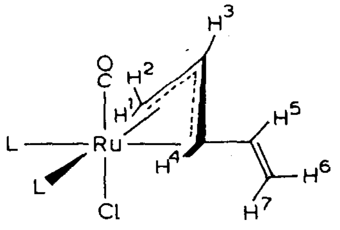
In the spectrum without phosphorus decoupling the methyl resonances appear as doublets with coupling constants $^4J(P\text{–}Ru\text{–}C\text{–}H)$ of about 9 Hz. The values of the $^4J(P\text{–}H)$ coupling constants are useful in defining the stereochemistry of the complex, by comparison with Mawby's study. Phosphorus is strongly coupled to protons H^1, H^2 and H^4, but the coupling to the protons of the uncoordinated vinyl group is small.

Two possible structures for complex I, (A and B) are considered, of which the latter B is thought to be the more likely.

The assignment of an *anti*-configuration to the proton H^4 (B) is suggested by the NMR measurements, but is by no means certain. In contrast to observations on tricarbonyltrimethylphosphine η^3-pentadienyl manganese, for which a *syn*-configuration for H^4 and an *anti*-vinyl group have been established by X-ray crystallography [9], proton H^4 in the spectrum of I resonates to high field of H^3. The magnitude of the coupling constant $J(H^3H^4)$, ca. 11 Hz, is suggestive of a *trans* arrangement. Moreover, the similar values (both 5.8 Hz) of the coupling constants $J(^{31}P\text{–}H^1)$ and $J(^{31}P\text{–}H^4)$, to the corresponding *trans* phosphorus nucleus and the absence of coupling to the *cis* phosphorus nucleus in both cases, indicate similar dispositions for both hydrogen atoms (see below). In contrast the *syn* proton H^2 couples with both phosphorus nuclei. These results are similar to those reported by Mawby for the complex $[Ru(CO)_2Cl(\eta^3\text{-}C_3H_5)(PMe_2Ph)]$ [5]. The very small coupling to the central proton of the η^3-allyl group, H^3, suggests that the allyl group is oriented as shown, away from the bulky chlorine atom, as found by X-ray crystallography for the complex $[Ru(CO)_2Cl(\eta^3\text{-}C_3H_5)(PMe_2Ph)]$ [10].



(A)



(B)

(L = PMe_2Ph)

Experimental

All reactions were carried out under dry nitrogen using Schlenk tube techniques. The complex *cis*-$[RuCl_2(CO)_2(PMe_2Ph)_2]$ was converted into $[\{RuCl_2(CO)(PMe_2Ph)_2\}_2]$ as described in the literature [11,12]. Microanalyses were by Butterworth Laboratories. NMR spectra (250 MHz) were recorded on a Bruker WM-250 spectrometer at King's College, University of London.

Preparation of the complex $[Ru(CO)Cl(\eta^3\text{-}C_5H_7)(PMe_2Ph)_2]$

A solution of $[\{RuCl_2(CO)(PMe_2Ph)_2\}_2]$ (0.36 g, 0.38 mmol) in chloroform (90 cm^3) was stirred with tributylpentadienyltin [4] (0.41 g, 1.14 mmol) at 40°C for 3.5 h. The pale yellow solution was evaporated to dryness and the residue chromatographed on alumina, using chloroform as eluant. A yellow oil was obtained which was crystallised from light petroleum and dried in vacuo. The product was a pale cream powder (0.16 g, 41%), m.p. 127°C decomp. Anal. Found: C, 51.52; H, 5.90. $C_{22}H_{29}ClOP_2Ru$ calcd.: 52.02; H, 5.76%.

^1H NMR (Multiplicities of signals refer to ^{31}P decoupled spectrum); 2.24δ(dt), H^1; 2.83δ(d), H^2; 4.83δ(td), H^3; 3.67δ(t), H^4; 6.07δ(dt), H^5; 4.96δ(dd), H^6; 5.20δ(dd), H^7; 7.36δ(m), 7.47δ(m), Ph; 1.44δ(s), 1.58δ(s), 1.75δ(s), Me.

$J(H^1H^3)$ 12.2; $J(H^2\ H^3)$ 7.8; $J(H^3\ H^4)$ ~ 11; $J(H^4\ H^5)$ ~ 11; $J(H^5\ H^6)$ 10.3; $J(H^5\ H^7)$ 17.0; $J(H^6\ H^7)$ 1.8 Hz;

$J(PH^1)$ 5.8; $J(PH^4)$ 5.8; $J(PH^5)$ 1.5; $J(PH^6)$ 0.8; $J(PH^7)$ 0.8 Hz.

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