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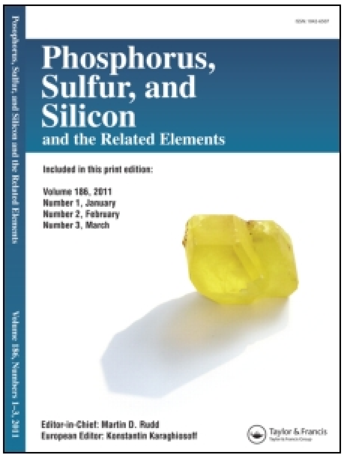

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NOVEL HYDROGEN TRANSFER REACTIONS TO THE LIGATED 1,2,4-TRIPHOSPHOLE IN $[Ru(\eta^4\text{-}C_8H_{12})\{\eta\text{-}P_3C_2Bu^t_2CH(SiMe_3)_2\}]$

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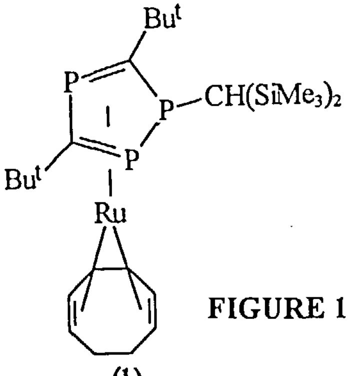
INTRODUCTION

As discussed in a recent preliminary publication[1], the complex $[Ru(\eta^4\text{-}C_8H_{12})\{\eta\text{-}P_3C_2Bu^t_2CH(SiMe_3)_2\}]$ (1) (C_8H_{12} = cycloocta-1,5-diene) was prepared by the reaction of $[Ru(\eta^6\text{-}C_{10}H_8)(\eta^4\text{-}C_8H_{12})]$ (2) ($C_{10}H_8$ = naphthalene) with the 1,2,4-triphosphole $P_3C_2Bu^t_2CH(SiMe_3)_2$ (3) (Fig. 1), illustrating the aromatic behaviour of (3).



(1)

FIGURE 1

Unexpectedly, complex (**1**) undergoes novel hydrogen transfer reactions. Under relatively mild conditions a hydrogen atom of the η^4-cycloocta-1,5-diene coligand migrates to the triphosphole ring to generate the new compound $[Ru(\eta^5\text{-}C_8H_{11})\text{-}\{\eta\text{-}P_3C_2\text{-}Bu^t_2H(CH(SiMe_3)_2)\}]$ (4), whose structure was established spectroscopically and by a single crystal X-ray diffraction study[1]. We now report that at more elevated temperature a further hydrogen transfer step occurs to afford $[Ru_2(\eta^5\text{-}C_8H_9)_2P_5(CH_2)_4\text{-}Bu^t_3CHSiMe_3SiMe_2]$ (5), whose structure was established by a single crystal X-ray diffraction study, and is discussed fully later.

RESULTS AND DISCUSSION

Heating a solution of (**1**) in tetrahydrofuran in the presence of PPh_3 leads to an unusual hydrogen migration from the η^4-ligated cycloocta-1,5-diene to the coordinated 1,2,4-triphosphole to afford the yellow ruthenium(II) complex $[Ru(\eta^5\text{-}C_8H_{11})\text{-}\eta\text{-}P_3C_2Bu^t_2\text{-}H(CH(SiMe_3)_2)\}]$ (4). The reaction occurs in the absence of PPh_3 and is complete after 72h, but can be significantly accelerated by addition of PPh_3. $^{31}P\{^1H\}$ nmr spectroscopy has been extensively used to monitor the progress of the reaction. Interesting changes in the $^{31}P\{^1H\}$ nmr spectrum of the reaction mixture were observed and the formation of the product (4) was shown by the steady decrease of the (1) resonances. This process probably involves an intramolecular hydrogen transfer because no intermediate compound was observed, although no deuterium labelling work was carried out to confirm this.

Interestingly, further heating compound (4) in boiling dekalin results in a hydrogen transfer reaction, from the η^5-coordinated cyclooctadienyl ring to form a new polyphosphorus system affording the orange η^5-trihydropentalenyl complex $[Ru_2(\eta^5\text{-}C_8H_9)_2P_5(CH_2)_4Bu^t_3\text{-}CHSiMe_3SiMe_2]$ (5) with loss of one P atom, one Bu^t group and one $CH(SiMe_3)_2$ fragment. The conversion of compound (4) into the trihydropentalenyl complex (5) may proceed by ring closure of the cyclooctadienyl ring in (4) involving loss of two hydrogens from the η^5-coordinated cyclooctadienyl group. The first step probably involves transannular carbon-carbon bond formation resulting in a η^5-ligated ruthenium cyclooctadienyl intermediate and the elimination of two hydrogen atoms which transfer to the η^5-$(P_3C_2Bu^t_2H(CH(SiMe_3)_2)$ ring. The structure of complex (5) clearly shows the formation of three P-CH_2-Bu^t groups, which obviously derive from the $P_3C_2Bu^t_2H(CH(SiMe_3)_2)$ ring system. It seems likely that as the hydrogen transfer reaction proceeds, the resulting saturated ring system is unable to satisfy the electron requirements of the ruthenium centre. The formation of the dinuclear ruthenium product (5) must therefore be a result of activation of one of the Me groups in -$CH(SiMe_3)_2$ side chain with elimination of Bu^tP and $CH(SiMe_3)_2$ fragments and generation of the very unusual $Bu^tCH_2P(CH_2SiMe_2CH(SiMe_3)$-$PP(PCH_2Bu^t)_2$ ligand bonded to two η^5-$(C_8H_9)Ru$ fragments.

Each of the trihydropentalenyl rings (C_8H_9) donates five electrons to the metal centres Ru(1) and Ru(2). The P(A), P(D) and P(E) contribute in total five electrons to the Ru(1) while P(A), P(C), P(D) and P(E), which are bonded to Ru(2), donate a total of five electrons from their lone pairs. Thus each ruthenium atom in (5) attains an 18 valence-electron configuration.

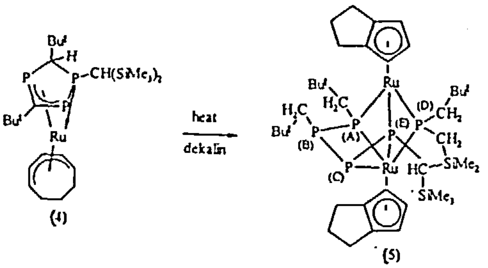


FIGURE 2 Synthesis of compound (5).

Although such hydrogen transfer reactions are unprecedented in complexes containing unsaturated organophosphorus ring systems, related hydrogen transfer reactions have been studied in several organometallic ruthenium systems. Several complexes containing the unstable polyolefin pentalene have been obtained from reactions between ruthenium carbonyl complexes and cyclic hydrocarbons such as cyclooctatetraene or cyclododeca-1,5,9-triene.[4-6] A single crystal X-ray diffraction study of (5) revealed the molecular structure shown in Fig. 3,

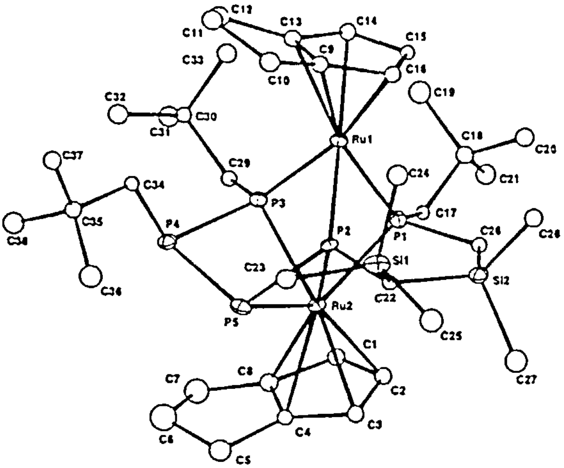


FIGURE 3

which contains two ruthenium atoms ligated to two trihydropentalenyl rings. There are five sets of Ru-C(ring) distances for each ruthenium atom. The averages of the carbon-carbon bond lengths of the η^5- coordinated trihydropentalenyl rings (1.44 Å) is comparable with other pentalenyl-transition metal complexes.[7,8] The P(2)-P(5), P(3)-P(4) and P(4)-P(5) bond distances (2.125(6), 2.225(6) and 2.183(6) Å, respectively) lie in the range expected for a P-P single bond.[2,3,9-11] The P(1)-C(17), P(1)-C(26), P(2)-C(22), P(3)-C(29) and P(4)-C(34) bond distances (1.85(2), 1.85(2), 1.83(2), 1.86(2) and 1.86(2) Å, respectively) are all typical for P-C single bonds.

The Ru(1) is bonded to three different phosphorus atoms and the Ru(1)-P(1), Ru(1)-P(2) and Ru(1)-P(3) bond lengths (2.327(5), 2.300(4) and 2.340(5) Å, respectively) are longer than Ru(2)-P bond distances in which the metal is bonded to four phosphorus atoms, Ru(2)-P(1), Ru(2)-P(2), Ru(2)-P(3) and Ru(2)-P(5) (2.361(5), 2.390(4), 2.387(5) and 2.412(4) Å, respectively). There is no interaction between the phosphorus atom P(4) with either Ru(1) and Ru(2).

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