Novel intramolecular hydrogen-atom transfer in an η^4-ligated cycloocta-1,5-diene η-1,2,4-triphosphole ruthenium(0) complex. Synthesis, crystal and molecular structures of $[Ru(\eta^4\text{-}C_8H_{12})\{\eta\text{-}P_3C_2Bu^t{}_2[CH(SiMe_3)_2]\}]$ and $[Ru(\eta^5\text{-}C_8H_{11})\{\eta\text{-}P_3C_2Bu^t{}_2H[CH(SiMe_3)_2]\}]$

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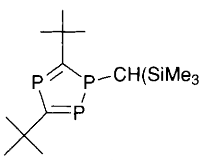
The first known ruthenium(0) complex of a 1,2,4-triphosphole is reported which undergoes a novel hydrogen migration reaction from the η^4-cycloocta-1,5-diene coligand on heating.

We recently reported[1] the first example of a 1,2,4-triphosphole **1** formed by alkylation of the aromatic $P_3C_2Bu^t{}_2$ ring anion. Compound **1** exhibits a variety of ligating behaviour, both as a 2e-donor, as in *trans*-$[PtCl_2(PEt_3)\{P_3C_2Bu^t{}_2[CH(SiMe_3)_2]\}]$, and as a 6e-donor, as in $[Fe_2(CO)_6\{P_3C_2Bu^t{}_2[CH(SiMe_3)_2]\}]$[1] Of special interest is the greatly enhanced aromatic behaviour of the 1,2,4-triphosphole ring system **1** compared with phospholes themselves, and in its complexes with $M(CO)_3$ fragments (M = Cr, Mo, W) the ligated ring is essentially planar.[2]



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We now describe a further illustration of the aromatic character of **1** in the ready formation of the yellow ruthenium(0) complex $[Ru(\eta^4\text{-}C_8H_{12})\{\eta\text{-}P_3C_2Bu^t{}_2[CH(SiMe_3)_2]\}]$ **2** by displacement of naphthalene from $[Ru(\eta^4\text{-}C_8H_{12})(\eta^6\text{-}C_{10}H_8)]$ ($C_{10}H_8$ = naphthalene) in acetonitrile.[3–5] The structure of **2**, which was elucidated by spectroscopic techniques† and by a single-crystal X-ray diffraction study‡ (Fig. 1 and Table 1), indicates that the triphosphole acts as a 6e-donor.

The 1,2,4-triphosphole ring in **2** is planar (Σ internal ring angles = 539.8°) with the saturated P(1) atom forming a significantly shorter bond [2.277(2) Å] to ruthenium than either of the sp^2-hybridised P atoms P(2) and P(3) [Ru–P av. 2.482(2) Å]. The P–C bond lengths within the ring average 1.754 Å, indicative of electron delocalisation, and the P–P bond length [2.124(2) Å] is comparable with P–P distances found in the sandwich compounds $[M(\eta^5\text{-}P_3C_2Bu^t{}_2)_2]$ (M = Fe, Cr, Ru) containing the planar aromatic $P_3C_2Bu^t{}_2$ ring anion.[6]

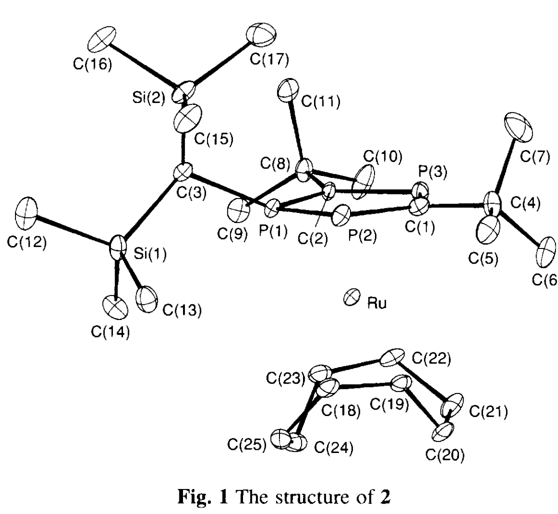


Fig. 1 The structure of **2**

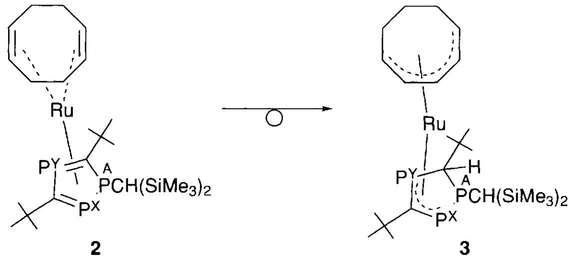
Heating a solution of **2** in tetrahydrofuran unexpectedly leads to an unusual hydrogen migration from the η^4-ligated cycloocta-1,5-diene to the coordinated 1,2,4-triphosphole to afford the yellow ruthenium(II) complex $[Ru(\eta^5\text{-}C_8H_{11})\{\eta\text{-}P_3C_2Bu^t{}_2H[CH(SiMe_3)_2]\}]$ **3** (Scheme 1).§ The reaction can be monitored by changes in the $^{31}P\{^1H\}$ NMR spectrum and no P-containing species other than **2** and **3** were detected. The reaction is complete after 72 h but can be significantly accelerated in the presence of PPh_3.

Confirmation of the molecular structure of **3** comes from a single-crystal X-ray diffraction study (Fig. 2 and Table 2) which reveals several interesting features: (*i*) the ruthenium is η^5-ligated to the five co-planar C atoms [C(18)–C(22)] of the cyclooctadienyl C_8H_{11} ring system; (*ii*) the metal is bonded to

Table 1 Selected bond lengths (Å) and angles (°) for **2**[a]

Ru–P(1)	2.277(2)	Ru–P(2)	2.490(2)
Ru–P(3)	2.475(2)	Ru–C(1)	2.349(7)
Ru–C(2)	2.316(6)	Ru–C(18)	2.181(7)
Ru–C(19)	2.173(6)	Ru–C(22)	2.161(7)
Ru–C(23)	2.170(7)	Ru–M(1)	1.809(7)
Ru–M(3)	2.049(7)	Ru–M(2)	2.062(7)
P(1)–C(2)	1.746(6)	P(1)–C(3)	1.835(6)
P(1)–P(2)	2.124(2)	P(3)–C(1)	1.740(7)
P(3)–C(2)	1.765(6)	P(2)–C(1)	1.766(7)
M(1)–Ru–M(3)	138.0(3)	M(1)–Ru–M(2)	135.2(3)
M(3)–Ru–M(2)	85.4(3)	C(2)–P(1)–C(3)	124.8(3)
C(2)–P(1)–P(2)	104.1(2)	C(3)–P(1)–P(2)	120.8(2)
C(1)–P(3)–C(2)	100.4(3)	C(1)–P(2)–P(1)	94.5(2)
C(4)–C(1)–P(3)	116.5(5)	C(4)–C(1)–P(2)	119.2(5)
P(3)–C(1)–P(2)	124.2(4)	C(8)–C(2)–P(1)	124.5(4)
C(8)–C(2)–P(3)	118.7(4)	P(1)–C(2)–P(3)	116.6(4)

[a] M(1) is the centroid of the P_3C_2 ring, M(2) is the midpoint of the C(18)–C(19) bond and M(3) is the midpoint of the C(22)–C(23) bond.



Scheme 1

the planar four-atom P(2)P(3)C(2)P(1) framework with the Ru–P(2) (σ^3-P) bond distance 2.303(1) Å being significantly shorter than either of the Ru–P(1) (σ^2, λ^3-P) and Ru–P(3) (σ^2, λ^3-P) bond lengths [2.441(2), 2.456(2) Å respectively]; (*iii*) there is an 8.1° angle between the two planes described in (*i*) and (*ii*); and (*iv*) although, as expected, there is no interaction between the saturated C(1) atom and the Ru centre, the C atom C(11) of the *C*H(SiMe$_3$)$_2$ group attached to P(2) lies only slightly out of the P(2)P(3)C(2)P(1) plane.

One representation of the bonding between the P$_3$C$_2$Bu$^t{}_2$H[CH(SiMe$_3$)$_2$] ring and ruthenium in **3** is to consider it as a 5e-donor involving an η^3-1,3-diphosphaallyl component (3e-donor), augmented by an η^1-interaction (2e-donor) from the σ^3-P centre.

It seems likely that the hydrogen-transfer reaction from one ring to the other in the formation of **3** from **2** proceeds *via* the ruthenium centre, and the first step must involve rearrangement of the η^4-ligated cycloocta-1,5-diene to the η^4-bonded cycloocta-1,3-diene isomer prior to the hydrogen transfer. The role of PPh$_3$ may be to accelerate this isomerisation step possible *via* an η^2-monoalkene intermediate.

No previous examples of this type of hydrogen migration have been reported; however, hydrogen migration is known to occur in protonation reactions of [(η^6-cycloocta-1,3,5-triene)(η^4-cycloocta-1,5-diene)]ruthenium, which affords [RuH(η^5-C$_8$H$_{11}$)$_2$]$^+$, and on subsequent treatment with PMePh$_2$ loses cycloocta-1,3-diene.[7–9] In acetone, [RuH(η^5-C$_8$H$_{11}$)$_2$]$^+$ undergoes partial isomerisation by hydrogen transfer to the cationic complex [Ru(η^5-C$_8$H$_{11}$)(η^4-1,3-C$_8$H$_{12}$)]$^+$; likewise, [RuH(η-C$_8$H$_{12}$)L$_3$]$^+$ salts (L = tertiary phosphine) isomerise to agostic hydride metal complexes [Ru(η^3-C$_8$H$_{13}$)L$_3$]$^+$ *via* a double bond migration that occurs within the initial product of hydrogen transfer to the coordinated cyclooctadiene.[10,11]

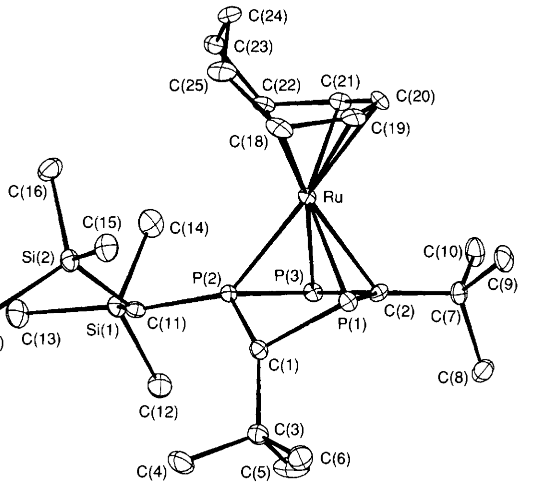


Fig. 2 The structure of **3**

Table 2 Selected bond lengths (Å) and angles (°) for **3**

Ru–P(1)	2.441(2)	Ru–P(2)	2.303(1)
Ru–P(3)	2.456(2)	Ru–C(2)	2.238(4)
Ru–C(18)	2.203(5)	Ru–C(19)	2.166(4)
Ru–C(20)	2.220(5)	Ru–C(21)	2.174(5)
Ru–C(22)	2.239(5)	P(1)–C(2)	1.778(5)
P(1)–C(1)	1.893(5)	P(2)–C(1)	1.821(5)
P(2)–C(11)	1.834(5)	P(2)–P(3)	2.150(2)
P(3)–C(2)	1.803(4)		
C(2)–P(1)–C(1)	103.7(2)	C(1)–P(2)–C(11)	114.0(2)
C(1)–P(2)–P(3)	107.2(2)	C(11)–P(2)–P(3)	120.1(2)
C(2)–P(3)–P(2)	89.0(2)	C(3)–C(1)–P(2)	126.1(3)
C(3)–C(1)–P(1)	119.0(3)	P(2)–C(1)–P(1)	93.3(2)
C(7)–C(2)–P(1)	120.7(3)	C(7)–C(2)–P(3)	119.9(3)
P(1)–C(2)–P(3)	119.1(3)		

The thermodynamic stability of the 5e-donor ligand P$_3$C$_2$Bu^{t}H[CH(SiMe$_3$)$_2$] in **3** is noteworthy, suggesting that **1** may react directly with a variety of transition-metal hydrides to form other complexes of this general type, and this possibility is currently under investigation.

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Footnotes

† 62% yield. ^{31}P{^{1}H} (C$_6$D$_6$): δ −82.5 [P^A, dd, ^1J(P^{A}P^X) 494.5, ^2J(P^{A}P^Y) 31.5 Hz], 60.4 [P^Y, dd, ^2J(P^{Y}P^A) 30.8, ^2J(P^{Y}P^X) 44.8 Hz], 75.0 [P^X, dd, ^1J(P^{X}P^A) 494.2, ^2J(P^{X}P^Y) 45.0 Hz].

‡ *Crystal data* **2**: C$_{25}$H$_{49}$P$_3$RuSi$_2$, M = 599.8, monoclinic, space group $P2_1/c$ (no. 14), a = 16.474(5), b = 9.784(4), c = 18.756(6) Å, β = 97.84(2)°, U = 2995(2) Å^3, Z = 4, D_c = 1.33 g cm^{-3}, F(000) = 1264. Monochromated Mo-Kα radiation λ = 0.71073 Å, T = 173 K. Data were collected on an Enraf-Nonius CAD 4 diffractometer using a crystal of 0.30 × 0.25 × 0.10 mm. A total of 5433 unique reflections were measured for $2 < \theta < 25°$ of which 3641 had $I > 2\sigma(I)$. The structure was solved by direct methods using SHELX86 and refined on F^2 with all non-H atoms anisotropic. H atoms were included in riding mode with U_{iso} = 1.2 U_{eq}(C) or 1.5 U_{eq}(C) for methyl groups. The final residuals were $R1$ = 0.058 [for $I > 2\sigma(I)$] and $wR2$ = 0.145 (for all data).

3: C$_{25}$H$_{49}$P$_3$RuSi$_2$, M = 599.8, triclinic, space group $P\bar{1}$ (no. 2), a = 9.297(6), b = 9.919(4), c = 17.904(6) Å, α = 77.88(3), β = 88.21(4), γ = 67.79(4)°, U = 1492.4(12) Å^3, Z = 2, D_c = 1.34 g cm^{-3}. F(000) = 632. Monochromated Mo-Kα radiation λ = 0.71073 Å, T = 173 K. Data were collected on an Enraf-Nonius CAD 4 diffractometer using a crystal of 0.40 × 0.40 × 0.20 mm. A total of 5240 unique reflections were measured for $2 < \theta < 25°$ of which 4737 had $I > 2\sigma(I)$. The structure was solved by direct methods using SHELX86 and refined on F^2 with all non-H atoms anisotropic. H atoms were included in riding mode with U_{iso} = 1.2 U_{eq}(C) or 1.5 U_{eq}(C) for methyl groups. The final residals were $R1$ = 0.058 [for $I > 2\sigma(I)$] and $wR2$ = 0.169 (for all data). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/281.

§ 33% yield. ^{31}P{^{1}H} (C$_6$D$_6$): δ −130.9 [P^A, dd, ^1J(P^{A}P^X) 374.0, ^2J(P^{A}P^Y) 25.0 Hz], −18.8 [P^Y, dd, J(P^{Y}P^A) 24.5, ^2J(P^{Y}P^X) 15.6 Hz], 1.6 [P^X, dd, ^1J(P^{X}P^A) 374.1, ^2J(P^{X}P^Y) 15.6 Hz].

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