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Synthesis of the dicarbonyl ruthenium(0) triphosphole complex $[\mathrm{Ru(CO)_2\{\eta^5\text{-}P_3C_2Bu^t_2CH(SiMe_3)_2\}}]$ and its conversion into a tricarbonyl complex containing the novel 4-electron donor triphosphorus-ring system $\{\mathrm{CBu^tPP(H)CH(SiMe_3)_2CBu^tP(O)H}\}$

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Abstract

1,5-Cyclo-octadiene is readily displaced from $[\mathrm{Ru(\eta^4\text{-}COD)\{\eta^5\text{-}P_3C_2Bu^t_2CH(SiMe_3)_2\}}]$ to give the dicarbonyl complex $[\mathrm{Ru(CO)_2\{\eta^5\text{-}P_3C_2Bu^t_2CH(SiMe_3)_2\}}]$, which on treatment with water in the presence of CO is converted into a tricarbonyl complex containing the novel 4-electron donor triphosphorus-ring system $\{\mathrm{CBu^tPP(H)CH(SiMe_3)_2CBu^tP(O)H}\}$which has been structurally characterised. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Ruthenium; Triphosphole; Carbonyl complex

1. Introduction

Preferential displacement of the naphthalene ring rather than the 1,5-cyclo-octadiene ring by donor molecules occurs readily in the zerovalent ruthenium complex $[\mathrm{Ru(\eta^6\text{-}C_{10}H_8)(\eta^4\text{-}C_8H_{12})}]$ (**1**) [1]. The reaction involving CO, which is shown below in Fig. 1, affords the tricarbonyl complex **2**.

The 1,5-cyclo-octadiene ring can be displaced from **2** by butadiene, cycloheptadiene or cyclo-octatetraene to afford the corresponding diene ruthenium tricarbonyl complex [2–4]. We recently reported the 'arene-like' behaviour of the almost planar 1,2,4-triphosphole ring system $\mathrm{P_3C_2Bu^t_2CH(SiMe_3)_2}$ (**3**) and its ready displacement of naphthalene from the complex $[\mathrm{Ru(\eta^6\text{-}C_{10}H_8)(\eta^4\text{-}C_8H_{12})}]$ to give the yellow 1,2,4-triphosphole complex $[\mathrm{Ru(\eta^4\text{-}C_8H_{12})\{\eta^5\text{-}P_3C_2Bu^t_2CH(SiMe_3)_2\}}]$ (**4**) (Fig. 2) [5,6]. The single crystal X-ray diffraction study revealed an almost planar ligated triphosphole ring system acting as a 6-electron donor [5].

2. Results and discussion

By analogy with the behaviour of the naphthalene complex **1**, treatment of $[\mathrm{Ru(\eta^4\text{-}C_8H_{12})\{\eta^5\text{-}P_3C_2Bu^t_2\text{-}CH(SiMe_3)_2\}}]$ (**4**) with CO in toluene might be expected to displace the 1,2,4-triphosphole to afford the tricarbonyl complex $[\mathrm{Ru(CO)_3(\eta^4\text{-}C_8H_{12})}]$. However, because of the significantly stronger bonding of the 1,2,4-triphosphole ring to ruthenium centre in **4** compared with naphthalene in **1**, preferential displacement of the cyclo-octadiene results from reaction with dry CO with exclusive formation of the dicarbonyl complex $[\mathrm{Ru(CO)_2\{\eta^5\text{-}P_3C_2Bu^t_2CH(SiMe_3)_2\}}]$ (**5**) under mild conditions as shown in Fig. 3.

The identity of **5** was confirmed by (i) the observation of the parent ion in the mass spectrum and peaks corresponding to successive loss of two CO ligands; and (ii) by its characteristic $^{31}\mathrm{P}\{^1\mathrm{H}\}$-NMR spectrum, which consisted of three doublet of doublet resonances at δ 91.9 ($J_{\mathrm{P-P'}} = 22.1$, $J_{\mathrm{P-P''}} = 34.0$ Hz), δ 56.2 ($J_{\mathrm{P-P'}} = 296.2$, $J_{\mathrm{P-P''}} = 34.0$ Hz), and δ -0.9 ($J_{\mathrm{P-P'}} = 296.2$, $J_{\mathrm{P-P''}} = 34.0$ Hz) ppm. Confirmation of **5** as a dicarbonyl complex came from the synthesis of the fully ^{13}CO labelled complex when the reaction was repeated using ^{13}CO. The $^{31}\mathrm{P}\{^1\mathrm{H}\}$-NMR spectrum of

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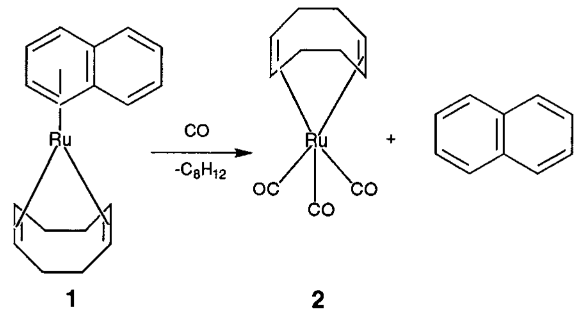


Fig. 1.

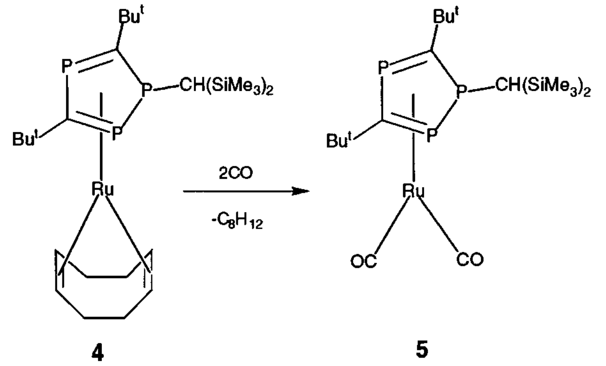


Fig. 3.

$[Ru(^{13}CO)_2\{\eta^5\text{-}P_3C_2Bu^t_2CH(SiMe_3)_2\}]$ is similar to that of **5** but the resonances at 56.2 and −0.9 ppm are now observed as doublets of doublets of triplets having $J_{P-C} = 17.8$ and 5.2 Hz, respectively, indicating that each phosphorus is coupled to two equivalent ^{13}C nuclei. This triplet splitting is observed even in the presence of an excess of ^{13}CO indicating that the species in solution is exclusively the dicarbonyl complex **5**. The $^{13}C\{^1H\}$-NMR spectrum of $[Ru(^{13}CO)_2\{\eta^5\text{-}P_3C_2Bu^t_2CH(SiMe_3)_2\}]$ in the carbonyl region exhibited a broad resonance at 195.2 ppm and its IR spectrum in pentane solution shows six ν(C=O) bands around 2000 cm^{-1} rather than the two expected for the static C_1 structure. Taken together these observations suggest that the carbonyls may reside in several different co-ordination environments and **5** may exist as a mixture of isomers. By analogy with **4** the dicarbonyl complex **5** is also likely to contain an almost planar 'aromatic' triphosphole ring.

Interestingly, **5** reacts instantly with a few drops of water in benzene under CO to afford the novel tricarbonyl complex $[Ru(CO)_3\{\eta^5\text{-}CBu^tPP(H)CH(SiMe_3)_2\text{-}CBu^tP(O)H\}]$ (**6**) which can also be made directly from **4** in 80% yield using moist CO directly from a cylinder (Fig. 4).

The structure of **6**, which was established by a single-crystal X-ray diffraction study, contains three coordinated CO ligands and the formal incorporation of one water molecule into the ligated 1,2,4-triphosphole generating the novel $(Bu^t)CPP(H)CH(SiMe_3)_2CBu^tP(O)H$ ring system. Only one of the two original unsaturated phosphorus atoms in the triphosphole ring (P(A)) remains two-coordinate and the other two phosphorus atoms P(B) and P(C) are each now attached to a hydrogen atom; P(B) is also doubly bonded to the oxygen atom. The metal is bound to the new ring only via phosphorus P(A) and the two carbon atoms of the heterocycle. P(C) and P(A) can be thought of as partners in a zwitterion.

Compound **6** was further characterised by $^{31}P\{^1H\}$-, ^1H-NMR, and mass and IR spectroscopy. The mass spectrum of **6** shows the expected parent ion (m/z = 594) and a peak corresponding to loss of the two CO groups (m/z = 538) from the molecular ion. The IR spectrum in the carbonyl region exhibited the expected three bands (2059, 1996 and 1968 cm^{-1}) which are comparable with those observed for other complexes of the type $[Ru(CO)_3(\eta^4\text{-diene})]$ [4,7,8]. An additional sharp band at 1157 cm^{-1} can be assigned to the ν(P=O) stretching vibration.

The $^{31}P\{^1H\}$-NMR spectrum of **6** consists of the anticipated [ABX] spin system (δ P(C) 11.1; δ P(B) 6.8; δ P(A) −126.8 ppm), exhibiting a large one-bond coupling constant between P(A) and P(C) ($^1J_{P(A)-P(C)} =$ 299.2 Hz) and smaller two-bond couplings ($^2J_{P(B)-P(C)}$ = 90.6, $^2J_{P(A)-P(B)} = 21.6$ Hz). The ^1H-NMR

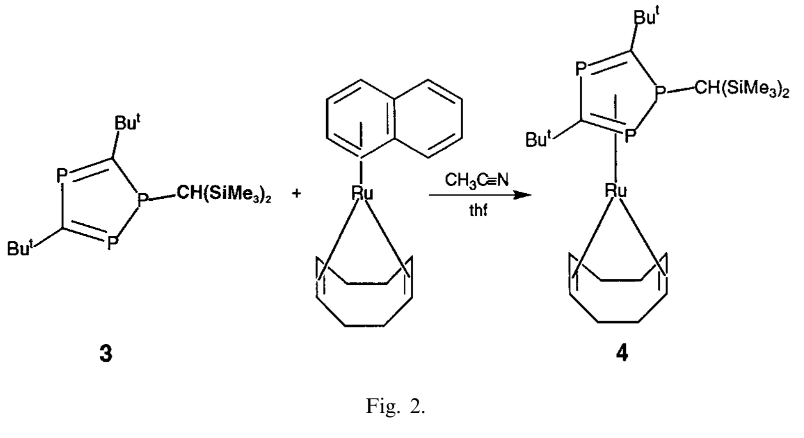
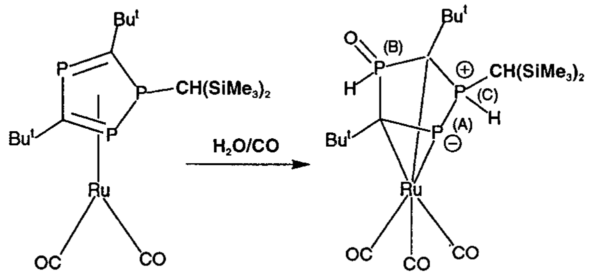


Fig. 2.



5 **6**

Fig. 4.

spectrum of **6** confirms that the observed solid-state structure is retained in solution, exhibiting (i) the expected two resonances at δ 0.32 and δ 0.46 ppm corresponding to the two nonequivalent trimethylsilyl groups (intensity 9H each); (ii) resonances at δ 1.32 and δ 1.34 ppm for the likewise nonequivalent *tert*-butyl groups (intensity 9H each); (iii) a resonance at δ 1.85 ppm corresponding to $CH(SiMe_3)_2$ (1H); and (iv) doublet of doublet resonances at δ 7.89 and δ 7.85 ppm which can be assigned to P(O)*H* and P*H*, respectively, due to the characteristic one-bond $^{31}P–^{1}H$ coupling constants ($^{1}J_{H-P(C)} = 478.7$, $^{1}J_{H-P(B)} = 541.0$ Hz), which are similar in magnitude to those found in other phosphonium and phosphoryl compounds.

2.1. Molecular structure of $[Ru(CO)_3\{\eta^5\text{-}CBu^tPP(H)CH(SiMe_3)_2CBu^tP(O)H\}]$ *(6)*

X-ray quality crystals of **6** were obtained by recrystallisation from a mixture of petroleum ether (60–80°C) and toluene, and the molecular structure of **6** is shown in Fig. 5 together with selected bond lengths and bond angles. The ruthenium atom is bound to the three-atom P(2)–C(1)–C(2) fragment with the Ru-plane distance equal to 1.761 Å and the C(1)–Ru–P(2), C(2)–Ru–C(1) and C(2)–Ru–P(2) bond angles are 78.2, 71.8 and 46.0°, respectively. The Ru–P(2) bond distance of 2.415(3) Å is significantly longer than the ruthenium–phosphorus bonds in **4** which range from 2.34 to 2.39 Å, which argues a diminished bonding interaction between the Ru centre and the two-coordinate phosphorus nucleus of **6** than that between Ru and the phosphorus donors of **4,** which are members of an aromatic ring. As expected, there is no interaction between the ruthenium and the other two phosphorus atoms P(1) and P(3), which are phosphonium and phosphoryl centres, respectively. In the saturated part of the ring the P(1)–P(2) distance of 2.173(4) Å lies in the range expected for P–P single bonds. The sum of the bond angles around the uncoordinated phosphorus atoms P(1) and P(3) are 337.5 and 336.7°, respectively. The P(1)–C(1), P(2)–C(2), P(3)–C(1) and P(3)–C(2)

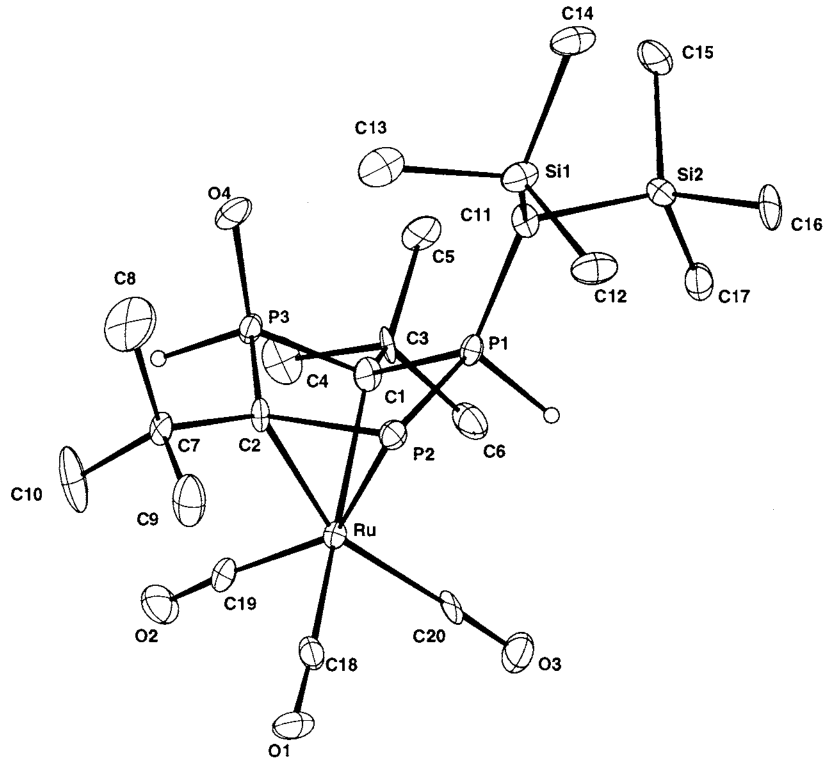


Fig. 5. Molecular structure of $[Ru(CO)_3\{\eta^5CBu^tPP(H)CH(SiMe_3)_2CBu^tP(O)H\}]$ (**6**). Selected bond lengths (Å) and bond angles (°): P(1)–P(2) 2.173(4), P(2)–C(2) 1.817(11), P(3)–C(2) 1.771(11), P(3)–C(1) 1.788(13),P(1)–C(1) 1.833(11); P(2)–(P1)–C(1) 95.3(4), P(1)–P(2)–C(2) 95.1(4), P(2)–C(2)–P(3) 115.6(6), C(1)–P(3)–C(2) 95.7(5), P(2)–P(1)–C(11) 120.3(4), P(1)–C(1)–P(3) 120.3(4), C(1)–P(1)–C(11) 121.9(5).

bond lengths (1.833(11), 1817(11), 1.788(13) and 1.771(11) Å, respectively) are also typical for P–C single bonds. The new ring system may therefore be considered as a four electron donor (via P(2) and the two carbon atoms C(1) and C(2)) resulting in an optimum 18 valence electron configuration for ruthenium.

3. Experimental

Standard procedures for the manipulation of air-sensitive materials were employed. Unless otherwise indicated, all manipulations were carried out at ambient temperature under an atmosphere of dry nitrogen gas using standard Schlenk, syringe and high vacuum-line techniques, with glassware that had been flame-dried in vacuo prior to use. Solvents were dried, freshly distilled under a blanket of dinitrogen and degassed prior to use. IR spectra were recorded, as nujol mulls or in pentane solution, on a Perkin–Elmer 1720-FTIR spectrometer and were calibrated relative to polystyrene. Mass spectra were recorded at the University of Sussex by Dr A. Abdul-Sada, using a Fison Instruments-VG Autospec. Complex **4** was made according to the literature method [6]. Solution NMR spectra were recorded on Bruker ACP-250, DPX-300 or AMX-500 instruments at ambient probe temperature. Coupling constants (J) are given in Hz, and chemical shift data (δ) in ppm are relative to the residual proton chemical shift of the deuterated solvent and external $P(OMe)_3$ (141.00 ppm with respect to H_3PO_4 at 0.00 ppm).

3.1. *[Ru(CO)$_2${η^5-P$_3$C$_2$Bu$^t_2$CH(SiMe$_3$)$_2$}]* (**5**)

Treatment of a toluene solution of $[Ru(\eta^4\text{-}C_8H_{12})\{\eta^5\text{-}P_3C_2Bu^t_2CH(SiMe_3)_2\}]$ with 99.997% CO (Praxair) (or the boil-off from frozen CO) gave a quantitative yield of yellow crystals of **5** from petroleum ether. ^{1}H-NMR (d_6-benzene, 300.00 MHz): δ 1.37 and 1.25 (s, 18H, Bu^t), 0.30 and 0.23 (s, 18H, SiMe_3), 0.27 (m, 1H, CH). ^{31}P{^{1}H}-NMR (d_6-benzene, 121.42 MHz): δ 91.9 (dd, 1P, $J_{\mathrm{P-P'}} = 22.1$, $J_{\mathrm{P-P''}} = 34.0$ Hz), 56.2 (dd, 1P, $J_{\mathrm{P-P'}} = 296.2$, $J_{\mathrm{P-P''}} = 34.0$ Hz), -0.9 (dd, 1P, $J_{\mathrm{P-P'}} = 296.2$, $J_{\mathrm{P-P''}} = 34.0$ Hz). IR (pentane): v 2071 (s), 2056 (sh), 2022 (s), 2005 (s), 1975 (s), 1959 (s) cm^{-1}. MS: m/z (%) 548 (75) [M$^+$], 520 (17) [M$^+$ $-$CO], 492 (70) [M$^+$ $-$2CO], 477 (30), 417 (22), 390 (15), 300 (60), 73 (100). $[Ru(^{13}CO)_2\{\eta^5\text{-}P_3C_2Bu^t_2CH(SiMe_3)_2\}]$. Synthesis as above using ^{13}CO-^{31}P{^{1}H}-NMR (d_6-benzene, 121.42 MHz): δ 91.8 (m, 1P, $J_{\mathrm{P-P'}} = 22.0$, $J_{\mathrm{P-P''}} = 34.0$ Hz), 56.1 (ddt, 1P, $J_{\mathrm{P-P'}} = 296.2$, $J_{\mathrm{P-P''}} = 34.0$, $J_{\mathrm{P-C}} = 17.8$ Hz), -1.1 (ddt, 1P, $J_{\mathrm{P-P'}} = 296.2$, $J_{\mathrm{P-P''}} = 34.0$, $J_{\mathrm{P-C}} = 5.2$ Hz). ^{13}C{^{1}H}-NMR (d_6-benzene, 75.33 MHz): δ 195.2 (br m). $[Ru(CO)_3\{\eta^5\text{-}CBu^tPP(H)CH(SiMe_3)_2CBu^tP(O)H\}]$ **6** (see below) can be synthesised from $[Ru(CO)_2\{\eta^5\text{-}P_3C_2Bu^t_2CH(SiMe_3)_2\}]$ **5** by adding a few drops of water to a solution of the latter in d_6-benzene under CO. The reaction is complete within the time of mixing.

3.2. *[Ru(CO)$_3${η^5-CBu^{t}PP(H)CH(SiMe$_3$)$_2$CBu^{t}P(O)H}]* (**6**)

CO from a cylinder was bubbled through a solution of $[Ru(\eta^4\text{-}C_8H_{12})\{\eta^5\text{-}P_3C_2Bu^t_2CH(SiMe_3)_2\}]$ (390 mg, 0.65 mmol) in toluene (7 ml) for 4 h at 40°C and the solvent was evaporated in vacuo. The light yellow residue was washed with petroleum ether (60–80°C) to give a white solid (310 mg, 80%). The product was identified on the basis of ^{31}P{^{1}H}-, ^{1}H-NMR, IR spectroscopy and mass spectroscopy. Recrystallisation from petroleum ether (60–80°C) and toluene, gave needle-like colourless crystals (m.p.(dec.) = 125–126°C). Anal. Calc. for $C_{20}H_{39}O_4P_3RuSi_2$: C, 40.4, H, 6.6. Found: C, 39.2, H, 6.7. ^{31}P{^{1}H}-NMR (121.4 MHz, d_1-chloroform): δ -126.8 (dd, P(A), $^1J_{\mathrm{P(A)-P(C)}} = 299.2$, $^2J_{\mathrm{P(A)-P(B)}} = 21.6$ Hz), 6.8 ppm (dd, P(B), $^2J_{\mathrm{P(B)-P(A)}} = 21.6$, $^2J_{\mathrm{P(B)-P(C)}} = 90.6$ Hz), 11.1 ppm (dd, P(C), $^1J_{\mathrm{P(C)-P(A)}} = 299.2$, $^2J_{\mathrm{P(C)-P(B)}} = 90.6$ Hz). ^{1}H-NMR (250.2 MHz, d_1-chloroform): δ 0.32 and 0.46 (s, 9H, SiMe_3), 1.32 and 1.34 (s, 9H, Bu^t), 1.85 (m, 1H, CH), 7.89 (dd, 1H, P(O)H, $^1J_{\mathrm{H-P(B)}} = 541.0$, $^3J_{\mathrm{H-P(C)}} = 1.9$ Hz), 7.85 (dd, 1H, PH, $^1J_{\mathrm{H-P(C)}} = 478.7$, $^3J_{\mathrm{H-P(B)}} = 27.0$ Hz). IR (nujol mull): v(C=O) 2059 (s), 1996 (sh), 1968 (s); v(P=O), 1157 (s) cm^{-1}. MS: m/z (%) 594 [M$^+$] (37), 538 [M$^+$ $-$2CO] (64), 73 (100).

3.3. *Crystal structure*

Empirical formula, $C_{20}H_{39}O_4P_3RuSi_2$; $M_r = 593.7$; $T = 173(2)$ K; monoclinic $P2_1/c$ (no. 14), $a = 7.222(2)$, $b = 19.283(3)$, $c = 20.034(6)$ Å; $\beta = 98.19(2)°$; $V = 2761.5(12)$ Å^3; $Z = 4$; $D_{\mathrm{calc.}} = 1.43$ Mg m^{-3}; $F(000) = 1232$. Data were collected on a crystal of size 0.40 × 0.05 × 0.05 mm using an Enraf–Nonius CAD4 diffractometer, $\lambda = 0.71073$ Å, in the θ range 2–20°. A total of 2556 independent reflections were collected, 1926 with $I > 2\sigma I$. The structure was solved using Direct Methods and refined using full matrix least squares on all F^2. The final R indices were $R_1 = 0.056$, $wR_2 = 0.127$ for $I > 2\sigma I$ and $R_1 = 0.093$, $wR_2 = 0.146$ for all data.

Acknowledgements

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