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# THE SYSTEMATIC SYNTHESIS OF NOVEL BRIDGED DIRUTHENIUM CATIONS CONTAINING CYCLOPENTADIENYL AND BIDENTATE AMINE LIGANDS. THE CRYSTAL AND MOLECULAR STRUCTURE OF $[\{(\eta^5\text{-}C_5H_5)Ru(1,10\text{-phenanthroline})\}_2(\mu\text{-dppm})](PF_6)_2 \cdot CH_2Cl_2$ (dppm = bis(diphenylphosphino)methane)

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## Summary

The labile cation $[(\eta^5\text{-}C_5H_5)Ru(1,10\text{-phen})(ethanol)]^+$ (phen = phenanthroline) undergoes a substitution reaction with bis(diphenylphosphino)methane (dppm) to give $[(\eta^5\text{-}C_5H_5)Ru(1,10\text{-phen})(\eta^1\text{-dppm})]^+$ and $[\{(\eta^5\text{-}C_5H_5)Ru(1,10\text{-phen})\}_2(\mu\text{-dppm})]^{2+}$, and with $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(\eta^1\text{-dppm})Cl]$, $[(\eta^5\text{-}C_5H_5)Ru(dppm)(\eta^1\text{-dppm})]PF_6$ and $[Fe(CO)_4(\eta^1\text{-dppm})]$ to give unsymmetrical $\mu$-dppm complexes. The X-ray crystal structure of $[\{(\eta^5\text{-}C_5H_5)Ru(1,10\text{-phen})\}_2(\mu\text{-dppm})](PF_6)_2 \cdot CH_2Cl_2$ has been determined.

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There are relatively few rational synthetic routes for the assembly of dinuclear transition metal complexes from mononuclear precursor fragments. One of the potentially most attractive routes involves the use of pendant [1,2] or incipient-pendant functionality [3,4] to draw the two metal centres together, but only a few relevant complexes containing suitable uncoordinated functionality and only a few suitable receptor complexes are available. We recently reported the synthesis of a number of classes of new cyclopentadienylruthenium(II) complexes [5,6]. We now report on the use of one of these series, $[(\eta^5\text{-}C_5H_5)Ru(diamine)Cl]$ (where diamine represents a range of ligands typified by 1,10-phenanthroline and 2,2'-bipyridine), in a rare example [cf. ref. 2] of the systematic synthesis of bimetallic complexes containing single bridging diphosphine ligands, reactions which involve as intermediates the novel, highly reactive, receptor and pendant-functionality systems $[(\eta^5\text{-}C_5H_5)Ru(diamine)(solvent)]^+$ and $[(\eta^5\text{-}C_5H_5)Ru(diamine)(\eta^1\text{-diphosphine})]^+$.

The electron-rich complex $[(\eta^5\text{-}C_5H_5)Ru(1,10\text{-phen})Cl]$ (**1**; phen = phenanthroline) [6] undergoes facile chloride-ligand replacement in ethanol to give $[(\eta^5\text{-}C_5H_5)Ru(1,10\text{-phen})(ethanol)]^+$ (**2**), which may be isolated in association with

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large counterions, such as hexafluorophosphate, as orange, air-stable, crystals *. The ethanol ligand in **2** is exceptionally labile towards ligand replacement [7] and, in its reactions **2** is reminiscent of the versatile and highly reactive manganese(I) complex $[(\eta^5\text{-}C_5H_5)Mn(CO)_2(THF)]$, which has found extensive application in organometallic chemistry [8,9]. Surprisingly, though, **2** is remarkably different from $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2(\text{methanol})]^+$, which exists in an equilibrium with $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$ in methanol [10], and which to date has shown only limited synthetic potential [10].

Treatment of **2** with bis(diphenylphosphino)methane (dppm) (mole ratio 1/1) in ethanol at 0 ° C gave a single cationic product $[(\eta^5\text{-}C_5H_5)Ru(1,10\text{-phen})(\eta^1\text{-dppm})]^+$, which was isolated as the hexafluorophosphate salt **3**. Complex **3** has been characterized by a combination of elemental analysis and NMR spectroscopy. In particular, the $^{31}P\{^1H\}$ NMR spectrum, which shows two doublet resonances at $\delta$ 44.58 and $-25.08$ ($J$(PCP) 74 Hz), identifies the monodentate coordination mode of the dppm ligand. However, in boiling ethanol solution and using a 2/1 ratio of **2** to dppm, a second cationic product, characterized as $[\{(\eta^5\text{-}C_5H_5)Ru(1,10\text{-phen})\}_2(\mu\text{-dppm})](PF_6)_2$ (**4**) was isolated. The $^{31}P\{^1H\}$ NMR spectrum in this case shows only the expected singlet, at $\delta$ 49.39 ppm, for the two equivalent coordinated phosphorus atoms. Most significantly, **4** was also synthesized in high yield by treatment of **2** with an equimolar amount of **3** in boiling ethanol solution.

These observations are noteworthy in that such facile single dppm bridge formation in the absence of other bridging ligand systems or a metal–metal bond is exceptionally rare [2]. In order to elucidate the factors which facilitate bridge formation in these systems, and thus to assess the utility of the $\{(\eta^5\text{-}C_5H_5)Ru(\text{diamine})\}$ fragment as a precursor for unsymmetrical and heterometallic complexes, the X-ray crystal structure of **4** (as the dichloromethane solvate) has been determined **. The most salient features of the cation of **4** (Fig. 1) are (i) the very long Ru ··· Ru internuclear distance of 6.445(1) Å, (ii) the relatively large P–C–P angle subtended by the bridging dppm (133.1(3)° compared with the P–C–P range of 114.4(4) to 118.7(6)° for monodentate dppm ligands [12]), and (iii) the approximate *cis* conformation adopted with respect to the Ru ··· Ru (or P ··· P) vector. These features reflect an accommodation within the cation of the steric requirements of the two ruthenium atoms and their associated ligands, as well as reduced phenyl–phenyl steric interactions between rings on opposite phosphorus atoms (leaving shortest phenyl ··· phenyl distances of C(121) ··· C(212) 3.242(10) and C(121) ··· H(212) 2.70(1) Å), and minimized $C_5H_5$ ··· $C_5H_5$ contacts (H(53) ··· H(63) 2.60(1) Å). It is thus apparent that the relatively small volume

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* Satisfactory elemental analyses, $^1H$ NMR and where appropriate, $^{31}P\{^1H\}$ NMR spectra, were obtained for all compounds.

** *Crystal data*: $C_{60}H_{50}Cl_2F_{12}P_4N_4Ru_2$, $M = 1452.01$; triclinic, space group $P1$, $a$ 10.439(5), $b$ 15.614(4), $c$ 18.990(2) Å, $\alpha$ 68.21(1), $\beta$ 81.86(2), $\gamma$ 87.79(3)°, $U = 2844.6$ Å$^3$, $Z = 2$, $D_c = 1.695$ Mg m$^{-3}$, $F(000) = 1456$, Enraf–Nonius CAD4F diffractometer, Mo-$K_\alpha$ radiation, $\lambda$ 0.71069 Å, $\mu$(Mo-$K_\alpha$) 0.728 mm$^{-1}$. Crystals: orange-red plates grown from $CH_2Cl_2$/EtOH solution. The structure was solved by conventional heavy atom methods and was refined by least squares methods with unit weights using SHELX [11] to give a current $R = 0.0583$ for 7530 reflections with $F_0 \geqslant 4\sigma(F_0)$.
The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any requests should be accompanied by the full literature citation for this communication.

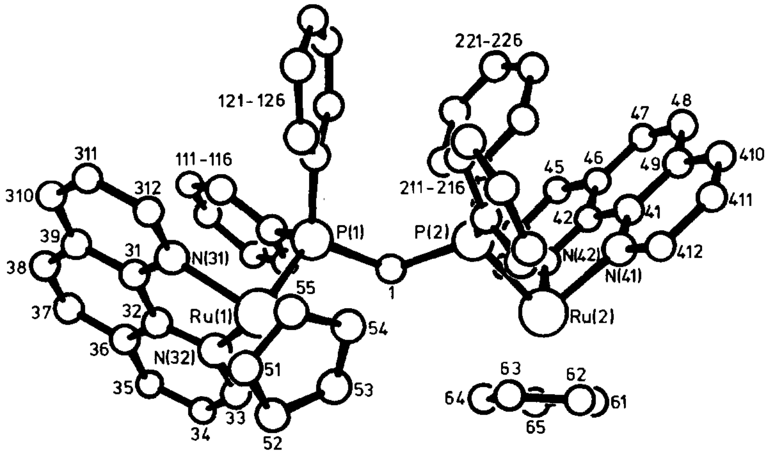

Fig. 1. A perspective view of the cation of 4 (hydrogen atoms omitted for clarity) showing the atom numbering scheme. Unaccompanied numbers refer to carbon atoms. Selected bond lengths (Å) and angles (°): Ru(1)···Ru(2) 6.445(1), Ru(1)–P(1) 2.316(2), Ru(2)–P(2) 2.324(2), Ru(1)–N(31) 2.093(7), Ru(1)–N(32) 2.096(5), Ru(2)–N(41) 2.090(6), Ru(2)–N(42) 2.093(6), Ru–C(cp) mean 2.180(10), P(1)–C(1) 1.860(8), P(2)–C(1) 1.843(8), Ru(1)–P(1)–C(1) 111.4(2), Ru(2)–P(2)–C(1) 110.7(2), P(1)–C(1)–P(2) 133.1(3).

requirements of the cyclopentadienyl and 1,10-phenanthroline ligands in **4** are largely the reason for the accommodation of the dppm phosphorus atoms and their associated phenyl substituents in the coordination sphere of the ruthenium atoms. This probably accounts for the previous lack of success in preparing related complexes [12] with a single bridging dppm ligand, and also suggests that the differences in the reactivity of **2** and $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru(PPh}_3)_2\text{(methanol)}]^+$ [10] are largely steric in origin.

In order to explore the applicability of **2** as a receptor complex for pendant dppm functionality of a more sterically congested kind, the reactions of **2** with the complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru(PPh}_3)(\eta^1\text{-dppm)Cl}]$ [13] $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru(dppm)}(\eta^1\text{-dppm)}]\text{PF}_6$ [13] and $[\text{Fe(CO)}_4(\eta^1\text{-dppm)}]$ [2] were examined. In all three cases rapid reaction occurred within minutes in boiling ethanol to give, after anion exchange with $\text{NH}_4\text{PF}_6$, high yields of the novel unsymmetrical dppm bridged complexes $[\{(\eta^5\text{-C}_5\text{H}_5)\text{Ru(PPh}_3)\text{Cl}\}\{(\eta^5\text{-C}_5\text{H}_5)\text{Ru(1,10-phen)}\}(\mu\text{-dppm})]\text{PF}_6$ (**5**), $[\{(\eta^5\text{-C}_5\text{H}_5)\text{Ru(dppm)}\}\{(\eta^5\text{-C}_5\text{H}_5)\text{Ru(1,10-phen)}\}(\mu\text{-dppm})](\text{PF}_6)_2$ (**6**), and $[\{\text{Fe(CO)}_4\}\{(\eta^5\text{-C}_5\text{H}_5)\text{Ru(1,10-phen)}\}(\mu\text{-dppm})]\text{PF}_6$ (**7**), respectively. It is noteworthy that the synthesis of **5** proceeds without the formation of by-products arising from $\text{PPh}_3$ transfer or chloride ligand replacement [13].

In conclusion, the lability of the ethanol ligand in $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru(diamine)(ethanol)}]^+$, in conjunction with the modest steric demands of the cyclopentadienyl and diamine ligands within the coordination sphere of the ruthenium atom, underlies a remarkable pattern of reactivity which has been illustrated here in terms of novel, rational, synthetic routes to symmetrical and unsymmetrical diruthenium complexes and also to heterobimetallic systems. Further implications of this pattern of reactivity will be discussed elsewhere.

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