Synthesis and properties of five-co-ordinate complexes of ruthenium and osmium containing the bulky phosphine 1,2-bis(diisopropylphosphino)ethane (dippe). Crystal structure of [Ru(SPh)(dippe)$_2$]-[BPh$_4$] †

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The reaction of [RuCl$_2$(dippe)$_2$] [dippe = 1,2-bis(diisopropylphosphino)ethane] with NaBPh$_4$ in MeOH afforded the red-brown five-co-ordinate complex [RuCl(dippe)$_2$][BPh$_4$] **1**. In analogous fashion, the complex *cis*-[OsCl$_2$(dippe)$_2$] **2**, prepared by reaction of [NH$_4$]$_2$[OsCl$_6$] with dippe in refluxing 2-methoxyethanol, yielded the corresponding five-co-ordinate species [OsCl(dippe)$_2$][BPh$_4$] **3** upon treatment with NaBPh$_4$ in MeOH. Both complexes **1** and **3** react with PhSH furnishing the five-co-ordinate benzenethiolato derivatives [Ru(SPh)(dippe)$_2$][BPh$_4$] **4** and [Os(SPh)(dippe)$_2$][BPh$_4$] **5** respectively. The crystal structure of **4** has been determined, and shows that the complex cation adopts a distorted trigonal-bipyramidal geometry. With the exception of **4**, which is rigid on the NMR time-scale, the other five-co-ordinate complexes are stereochemically non-rigid, and in some instances undergo dynamic processes in solution which have been ascribed to interactions with the solvent. Whereas complexes **1** and **5** do not react with H$_2$, addition of H$_2$ to **3** yields the dihydrogen complex *trans*-[OsCl(H$_2$)(dippe)$_2$][BPh$_4$] **6**. The reaction of **4** with H$_2$ afforded the known five-co-ordinate hydride complex [RuH(dippe)$_2$][BPh$_4$], formed presumably by elimination of HSPh from an unstable thiolate–dihydrogen (or dihydride) complex, namely [Ru(SPh)(H$_2$)(dippe)$_2$][BPh$_4$].

Co-ordinatively unsaturated complexes of ruthenium and osmium have attracted much attention not only for their involvement in homogeneous catalytic processes, but also for providing transition-metal sites for the binding and activation of small molecules.[1–7] Bulky ligands are known to stabilise 16-electron species by increasing the steric crowding around the metal, allowing in some instances their isolation and study, both in solution and in the solid state. In this fashion, stable yet reactive 16-electron complexes of ruthenium and osmium containing bulky monodentate[1–3] or bidentate[4–8] phosphine ligands have been prepared and characterized. In recent years, our research group has taken advantage of the strong electron-releasing capabilities combined with the bulk of the phosphine 1,2-bis(diisopropylphosphino)ethane (dippe) for the preparation of co-ordinatively unsaturated complexes of iron[9] and ruthenium.[10] We have studied in detail the reactivity of the 16-electron ruthenium monohydride [RuH(dippe)$_2$][BPh$_4$] towards small molecules[10] and alk-1-ynes,[11] and now we have obtained a series of related five-co-ordinate complexes of ruthenium and osmium of the type [MX(dippe)$_2$][BPh$_4$] (M = Ru or Os; X = Cl or SPh). These compounds belong to a growing group of co-ordinatively unsaturated derivatives which in some instances have been shown to be active catalysts for organic transformations, such as the epoxidation of alkenes.[12] In this paper we report the synthesis and properties of these materials, as well as their interaction with dihydrogen.

Experimental

All synthetic operations were performed under a dry dinitrogen or argon atmosphere following conventional Schlenk or drybox techniques. Tetrahydrofuran, diethyl ether and light petroleum (b.p. 40–60 °C) were distilled from the appropriate drying agents. All solvents were deoxygenated immediately before use. 1,2-

Bis(diisopropylphosphino)ethane[13] and [RuCl$_2$(dippe)$_2$][10] were prepared according to reported procedures. The salt [NH$_4$]$_2$-[OsCl$_6$] was supplied by Aldrich. Infrared spectra were recorded in Nujol mulls on a Perkin-Elmer FTIR Spectrum 1000 spectrophotometer; NMR spectra were taken on Varian Unity 400 MHz or Varian Gemini 200 MHz equipment. Chemical shifts are given in ppm from SiMe$_4$ (^{1}H) or 85% H$_3$PO$_4$ (^{31}P-{^{1}H}). The phosphine protons for all the compounds appeared as a series of overlapping multiplets in the range δ 0.5–3, and were not assigned. Spectra simulation was carried out on a SUN workstation using the software included in the Varian Unity 400 MHz data processing system, which is based in the program LAOCOON.[14] Microanalyses were by Dr. Manuel Arjonilla at the CSIC, Instituto de Ciencias Marinas de Andalucía, or by the Servicios Científico, Técnicos, Universidad de Barcelona.

[RuCl(dippe)$_2$][BPh$_4$] 1

A slurry of [RuCl$_2$(dippe)$_2$] (0.35 g, *ca.* 0.5 mmol) in MeOH was treated with an excess of solid NaBPh$_4$. A dark purplish brown microcrystalline precipitate was formed gradually. The mixture was stirred for *ca.* 15 min at room temperature. Then, the crystals were filtered off, washed with ethanol and light petroleum and dried *in vacuo*. Yield: 0.39 g, 80% (Found: C, 63.3; H, 8.63. Calc. for C$_{52}$H$_{84}$BClP$_4$Ru: C, 63.7; H, 8.57%). NMR (CDCl$_3$): ^{31}P-{^{1}H} δ (303 K) 59.0 (br s), 88.0 (br s, $\Delta\nu_{\frac{1}{2}}$ = 480 Hz); δ (223 K) 58.8 (t, $^2J_{PP}$ = 16.5 Hz), 92.8 (br s).

cis-[OsCl$_2$(dippe)$_2$] 2

To a solution of [NH$_4$]$_2$[OsCl$_6$] (0.5 g, 1.14 mmol) in 2-methoxyethanol (30 ml), dippe (1.2 ml, *ca.* 4 mmol) was added *via* syringe. A red solution was obtained, which was heated under reflux for 5 h. During this time, the colour changed to purple, and a yellow precipitate was formed. The mixture was cooled to room temperature. The yellow microcrystalline product was filtered off, washed with 2-methoxyethanol and

ethanol, and dried *in vacuo*. Yield: 0.67 g, 75% (Found: C, 43.1; H, 7.94. Calc. for $C_{28}H_{64}Cl_2OsP_4$: C, 42.8; H, 8.15%). NMR [$(CD_3)_2CO$]: ^{31}P-{^1H} A_2B_2 spin system: δ 5.9 (t), 12.8 (t, $^2J_{PP}$ = 16 Hz).

[OsCl(dippe)₂][BPh₄] 3

A yellow solution of complex **1** (0.15 g, *ca.* 0.19 mmol) in ethanol (12 ml) was treated with an excess of solid NaBPh₄. The mixture was stirred at room temperature for 30 min. A brown, crystalline precipitate was obtained, which was filtered off, washed with ethanol and light petroleum and dried *in vacuo*. Yield: 0.14 g, 70% (Found: C, 58.1; H, 7.91. Calc. for $C_{52}H_{84}$-BClOsP₄: C, 58.4; H, 7.86%). NMR (CD_2Cl_2): ^{31}P-{^1H} (298 K) δ 47.4 (br s), 34.0 (br s).

[Ru(SPh)(dippe)₂][BPh₄] 4

To a solution of complex **1** (0.15 g, *ca.* 0.15 mmol) in dichloromethane (15 ml), a few drops of thiophenol were added. The solution turned very dark. It was stirred at room temperature for 1 h. Some black-green solids deposited during this time. This material was filtered off using a frit. Addition of ethanol to the solution, concentration and cooling yielded a black-green microcrystalline precipitate, which was filtered off, washed with ethanol and light petroleum and dried *in vacuo*. All of the black-green solids were combined and extracted with hot acetone. The dark green solution was filtered and layered with ethanol. Slow diffusion afforded well formed dark green crystals, suitable for X-ray structure analysis. Yield: 0.11 g, 70% (Found: C, 65.9; H, 8.48. Calc. for $C_{58}H_{89}BP_4RuS$: C, 66.1; H, 8.45%). NMR [$(CD_3)_2CO$]: ^{31}P-{^1H} (303 K) δ 60.5 (t), 86.0 (t, $^2J_{PP}$ = 15.9 Hz). This compound was also obtained by treatment of [RuCl₂(dippe)₂] with HSPh and NaBPh₄ in ethanol or methanol. The dark green precipitate obtained in this way was recrystallized from hot acetone–ethanol, as described above.

[Os(SPh)(dippe)₂][BPh₄] 5

To a solution of complex **2** (0.1 g, *ca.* 0.13 mmol) in ethanol (20 ml), a few drops of thiophenol and an excess of solid NaBPh₄ were added. The mixture was refluxed for 2 h. Upon cooling to room temperature, a dark, almost black precipitate was obtained. It was filtered off, washed with ethanol and light petroleum and dried *in vacuo*. This compound was recrystallized by layering a concentrated acetone solution with ethanol. Slow diffusion afforded black crystals, which were filtered off, washed with light petroleum and dried *in vacuo*. Yield: 0.1 g, 67% (Found: C, 58.7; H, 7.63. Calc. for $C_{58}H_{89}BOsP_4S$: C, 59.1; H, 7.55%). NMR [$(CD_3)_2CO$]: ^{31}P-{^1H} (303 K) δ 39.6 (br s), 35.7 (s).

[OsCl(H₂)(dippe)₂][BPh₄] 6

Hydrogen was bubbled through a dichloromethane solution of complex **3** (0.1 g, 0.09 mmol), until it became colourless. Addition of ethanol, concentration and cooling to −20 °C afforded a white microcrystalline product which was filtered off, washed with light petroleum and dried *in vacuo*. Yield: 0.06 g, 62% (Found: C, 57.8; H, 7.94. Calc. for $C_{52}H_{86}BClOsP_4$: C, 58.2; H, 8.03%). NMR [$(CD_3)_2CO$]: ^1H δ (303 K) −13.83 (q, $^2J_{HP}$ = 12 Hz, OsH₂); δ (183 K) −13.99 (br s, OsH₂); T_1(min) = 55 ms at 211 K. ^{31}P-{^1H} δ (303 K) 34.8 (s); δ (183 K) 38.2 (br s, $\Delta\nu_{\frac{1}{2}}$ = 545 Hz).

[RuH(dippe)₂][BPh₄] from the reaction of complex 4 with dihydrogen

Hydrogen was bubbled through a dichloromethane solution of complex **4** (0.1 g, *ca.* 1 mmol), until it became colourless. Then the bubbling was stopped. When the solution was placed under dinitrogen, it gradually turned yellow-orange. This process was accelerated by pumping *in vacuo*. Addition of ethanol, concen-

Table 1 Selected bond distances (Å) and angles (°) for [Ru(SPh)-(dippe)₂][BPh₄] with estimated standard deviations in parentheses

Ru(1)−S(1)	2.303(3)	Ru(1)−P(3)	2.309(3)
Ru(1)−P(1)	2.407(3)	Ru(1)−P(4)	2.422(3)
Ru(1)−P(2)	2.320(3)	S(1)−C(1)	1.79(1)
S(1)−Ru(1)−P(1)	79.5(1)	P(2)−Ru(1)−P(3)	92.7(1)
S(1)−Ru(1)−P(2)	129.0(1)	P(2)−Ru(1)−P(4)	101.0(1)
S(1)−Ru(1)−P(3)	136.9(1)	P(3)−Ru(1)−P(4)	82.1(1)
S(1)−Ru(1)−P(4)	97.4(1)	Ru(1)−S(1)−C(1)	129.3(4)
P(1)−Ru(1)−P(2)	82.9(1)	S(1)−C(1)−C(2)	123(1)
P(1)−Ru(1)−P(3)	98.4(1)	S(1)−C(1)−C(6)	119(1)
P(1)−Ru(1)−P(4)	176.0(1)		

tration and cooling to −20 °C yielded orange microcrystals of [RuH(dippe)₂][BPh₄], which were filtered off, washed well with light petroleum, in order to remove any traces of HSPh, and dried *in vacuo*. Yield: 0.08 g, 85%. This compound was not analysed, being identified by comparison of its ^1H and ^{31}P-{^1H} NMR spectra with those already reported by us.[10]

Experimental data for the crystal structure determination of complex 4

Crystal data. $C_{58}H_{89}BP_4RuS$, *M* = 1054.18, dark green crystal of dimensions 0.26 × 0.15 × 0.33 mm, monoclinic, space group $P2_1/c$ (no. 14), *a* = 18.468(9), *b* = 12.024(4), *c* = 26.658(7) Å, β = 106.56(3)°, *U* = 5674(4) Å³, *Z* = 4, D_c = 1.234 g cm⁻³, *F*(000) = 2248, μ = 4.51 cm⁻¹, minimum, maximum relative transmission 0.86, 1.00, *N* = 8533, N_{unique} = 6301 (R_{int} = 0.112), N_o = 4026 ($I > 3\sigma_I$), ρ_{max} +0.80, ρ_{min} −1.09 e Å⁻³. Lattice parameters and data were measured at 290 K on a Rigaku AFC-6S four-circle diffractometer, using Mo-Kα graphite-monochromated radiation (λ = 0.7107 Å); ω-scan method (5 < 2θ < 50°). Data reduction and application of Lorentz-polarization, absorption (ψ-scan method) and decay (−5.5%) corrections were carried out. The structure was solved by Patterson methods, and anisotropically refined by full-matrix least-squares methods for all non-hydrogen atoms. Most of the hydrogen atoms were included at idealised positions and not refined. 4026 Reflections having $I > 3\sigma(I)$ were used to refine 586 variables (reflection/parameter ratio 6.87) and converged at *R* = 0.061 and *R'* = 0.073 [$R = \Sigma||F_o| − |F_c||/\Sigma|F_o|$; $w = \sigma_F^{-2}$; $R' = (\Sigma w(|F_o| − |F_c|)^2/\Sigma w|F_o|^2)^{\frac{1}{2}}$], goodness of fit 1.83, maximum Δ/σ in final cycle was 1.14 (with shift less than 0.01 Å). All calculations were carried out using the TEXSAN[15] software system and ORTEP[16] for plotting on a VAX 3520 computer at the Servicio Central de Ciencia y Tecnología de la Universidad de Cádiz. Selected bond lengths and angles are listed in Table 1.

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Results and Discussion

While studying the interaction of [RuCl₂(dippe)₂] with alk-1-ynes, we eventually isolated a dark brown crystalline material from the reaction of this compound with NaBPh₄ in MeOH. The microanalysis of this material was consistent with the formation of the five-co-ordinate 16-electron complex [RuCl-(dippe)₂][BPh₄] **1**. The ^{31}P-{^1H} NMR spectrum of this compound in CDCl₃ at 303 K (Fig. 1) consists of two very broad resonances (*ca.* 480 Hz half-width) centred at δ 59 and 88 respectively. These signals broaden considerably, and eventually merge into the baseline of the spectrum when the temperature is raised to 328 K, whereas they sharpen when the temperature is lowered. At 223 K, the signal at higher field resolves into a triplet, $^2J_{PP}$ = 16.5 Hz, although the other resonance remains rather broad and unresolved. This pattern corresponds to a partially resolved A_2B_2 spin system, being consistent with a trigonal-bipyramidal structure, having the chloride ligand at an equatorial position, and the bidentate dippe ligands spanning
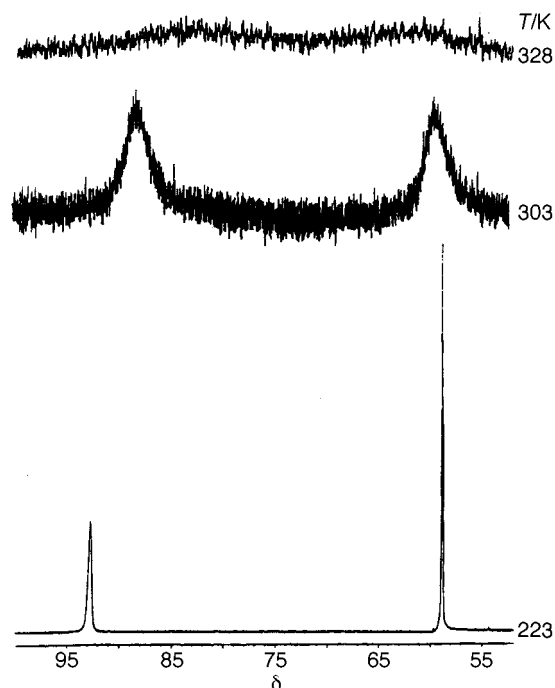
Fig. 1 Variable-temperature ^{31}P-{^1H} NMR spectra of complex **1** in $(CD_3)_2CO$

axial and equatorial positions. The temperature-dependence of NMR spectra arises from the lack of stereochemical rigidity normally associated with five-co-ordinate species.[17] A similar pattern has been reported for the related complexes [RuCl-(dppe)$_2$][PF$_6$][4] and [RuX(dcpe)$_2$][PF$_6$] [X = Cl, Br or I; dppe = 1,2-bis(diphenylphosphino)ethane; dcpe = 1,2-bis(dicyclohexylphosphino)ethane].[5] However, it is interesting to note that the ^{31}P-{^1H} NMR spectrum of the five-co-ordinate monohydride [RuH(dippe)$_2$][BPh$_4$] displays only one broad resonance which sharpens when the temperature is lowered becoming a singlet.[10] This was interpreted in terms of a square-pyramidal structure for this complex cation, having the hydride ligand in the apical position. This is the favoured geometry in the case of five-co-ordinate d^6 metal complexes,[18] hence the change to a trigonal-bipyramidal structure for complexes of the type [MX(diphos)$_2$]$^+$ (M = Ru or Os; X = halide; diphos = bidentate diphosphine)[4–6] might be attributed to the differences in both electronic and steric properties of halide ligands in comparison with hydride. As happened with [RuH(dippe)$_2$]$^+$, no spectral evidence for significant agostic interactions has been detected in the case of complex **1**, nor in any other of the five-co-ordinate derivatives described in this work.

The *cis* isomer of the complex *cis*-[OsCl$_2$(dippe)$_2$] **2** has been selectively obtained in good yields by reaction of [NH$_4$]$_2$[OsCl$_6$] with dippe in refluxing 2-methoxyethanol, the *trans* isomer not being observed irrespective of the reaction conditions, at variance with other related osmium phosphine complexes, for which *cis/trans* isomerization is achieved by suitable control of temperature and reaction times. In a fashion analogous to that for [RuCl$_2$(dippe)$_2$], **2** also dissociates one chloride ligand in methanol or ethanol solution yielding the five-co-ordinate cation [OsCl(dippe)$_2$]$^+$, which was isolated as the tetraphenylborate salt **3**. The ^{31}P-{^1H} NMR spectrum of this compound in CD$_2$Cl$_2$ is very similar to that of **1**, consisting of two broad resonances at δ 34.0 and 47.4, indicative of a trigonal-bipyramidal structure for this complex cation also. The broad resonances do not resolve into triplets as expected when the temperature is lowered. The signals remain broad at 183 K, and a new, broad resonance arises at δ 5.1. If the spectrum is recorded in a better donor solvent, such as $(CD_3)_2CO$, the observed pattern is very similar, except that one sharper, more intense resonance appears at δ 4.2 even at room temperature,
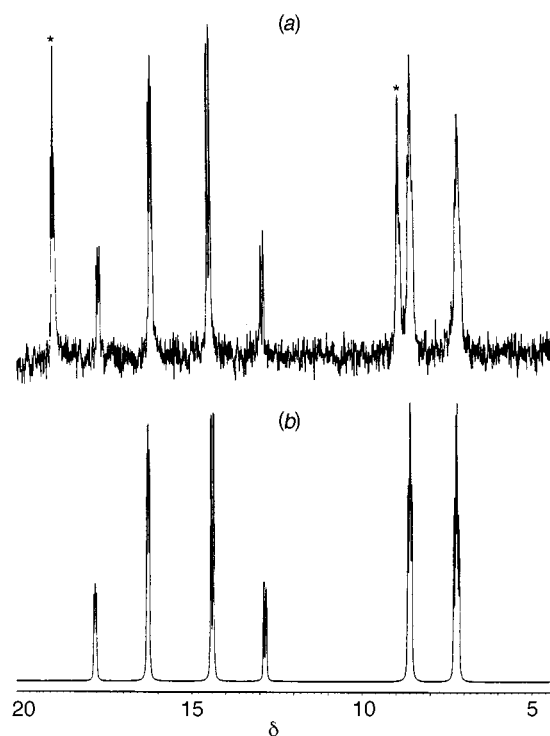

Fig. 2 Real (*a*) and simulated (*b*) ^{31}P-{^1H} NMR spectra of complex **3** in CD$_3$CN, corresponding to *cis*-[OsCl(NCCD$_3$)(dippe)$_2$]$^+$. The peaks marked * are attributed to *cis*-[Os(NCCD$_3$)$_2$(dippe)$_2$]$^{2+}$. Simulation parameters: ABCD spin system, δ_A 2732.2, δ_B 2234.5, δ_C 1164.9, δ_D 1392.0 Hz; J_{AB} = 252.5, J_{AC} = 5.8, J_{AD} = 9.5, J_{BC} = 12.3, J_{BD} = 2.4, J_{CD} = 11.0 Hz

together with broad signals at δ 34.2 and 47.6. This behaviour was not observed for the homologous ruthenium complex **1**. Rigo and co-workers[5] have found for complexes of the type [MX(dcpe)$_2$]$^+$ (M = Ru or Os; X = halide) that at low temperatures the solvation equilibrium (1) becomes important. Loss

$$[MX(dcpe)_2]^+ + solv \rightleftharpoons [MX(solv)(dcpe)_2]^+ \quad (1)$$
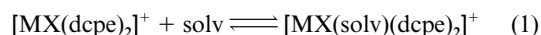
and addition of the solvent molecule may cause the equivalence of the phosphorus atoms on the NMR time-scale. A similar explanation may hold in our case, and hence the observed resonance near δ 5 could be attributed to a solvated species in equilibrium with the five-co-ordinate cation [OsCl(dippe)$_2$]$^+$. If the solvent is itself a good ligand, such as acetonitrile, then the equilibrium shifts completely to the corresponding 18-electron six-co-ordinate adduct. Thus, the ^{31}P-{^1H} NMR spectrum of **3** in CD$_3$CN is completely different to those obtained using CD$_2$Cl$_2$ or $(CD_3)_2CO$, consisting of a series of complex multiplets characteristic for *cis* octahedral species of the type *cis*-MXYL$_4$. This observation is consistent with the fact that in this case the actual species observed by NMR spectroscopy is the complex *cis*-[OsCl(NCCD$_3$)(dippe)$_2$][BPh$_4$]. The observed pattern in the ^{31}P-{^1H} NMR spectrum was reproduced by computer simulation assuming an ABCD spin system with the parameters shown in Fig. 2. Apart from the multiplets attributable to *cis*-[OsCl(NCCD$_3$)(dippe)$_2$]$^+$, two triplets at δ 19.1 and 8.9, $^2J_{PP}$ = 7.3 Hz, are also observed in the ^{31}P-{^1H} NMR spectrum. These two signals correspond to an A$_2$B$_2$ spin system, and have been tentatively assigned to the complex *cis*-[Os(NCCD$_3$)$_2$-(dippe)$_2$]$^{2+}$ formed *in situ* upon dissociation of the chloride ligand from *cis*-[OsCl(NCCD$_3$)(dippe)$_2$]$^+$. No attempt was made to isolate these species as solids.

Both complexes **1** and **3** react with HSPh in dichloromethane yielding dark solutions from which dark green or black crystals of the thiolate complexes [M(SPh)(dippe)$_2$][BPh$_4$] (M = Ru **4** or Os **5**) were respectively obtained. These compounds were also prepared by reaction of [MCl$_2$(dippe)$_2$] (M = Ru or Os) with
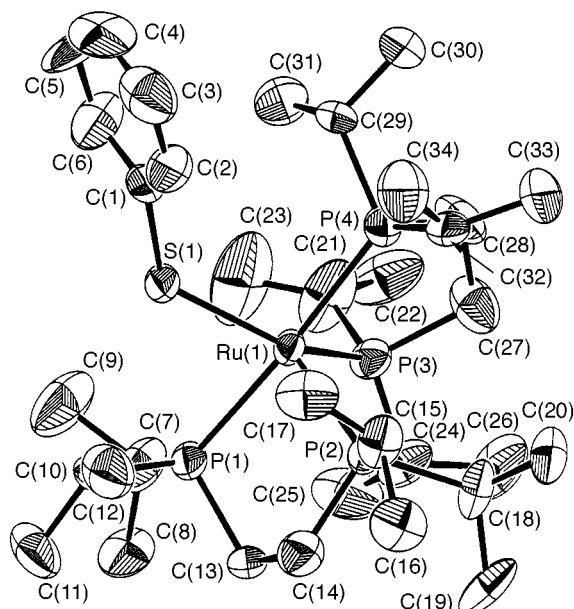
Fig. 3 An ORTEP drawing of the cation [Ru(SPh)(dippe)$_2$]$^+$ with 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity

HSPh in methanol or ethanol in the presence of NaBPh$_4$. Both materials are air stable in the solid state, and they do not display any band near 2500 cm^{-1} in their IR spectra which may be ascribed to ν(SH), this being consistent with the formulation as thiolate rather than thiol complexes. The ^{1}H NMR spectrum of both compounds shows a series of multiplets in the aromatic region apart from those due to the [BPh$_4$]$^-$ anion, which correspond to the protons of the phenyl ring of the benzenethiolate ligand. The ^{31}P-{^{1}H} NMR spectrum of **4** at room temperature consists of two well resolved triplets at δ 86.0 and 60.5, $^2J_{PP}$ = 15.9 Hz, being similar to that of compound **1** at 223 K. The spectrum does not change when the temperature is lowered, whereas the triplets become broad signals when the temperature is raised. These spectral data suggest a trigonal-bipyramidal structure for the complex cation, this being stereochemically rigid on the NMR time-scale, at variance with **1**. This may be attributed to the increased bulk of the benzenethiolate ligand compared to chloride, which may increase the energy of the barrier to atom scrambling. The crystal structure of **4** was determined by single-crystal X-ray crystallography, which represents, as far as we are aware, the first structural report of a five-co-ordinate ruthenium thiolate complex. An ORTEP view of the complex cation [Ru(SPh)(dippe)$_2$]$^+$ is shown in Fig. 3. Selected bond lengths and angles are listed in Table 1. The co-ordination around the ruthenium atom can be described as distorted trigonal-bipyramidal. The bidentate dippe ligands span axial and equatorial positions, with bite angles P(1)–Ru(1)–P(2) and P(3)–Ru(1)–P(4) of 82.9(1) and 82.1(1)° respectively. The benzenethiolate group lies at the equatorial position, with a Ru(1)–S(1) bond distance of 2.303(3) Å, which is significantly short compared to the values found in other ruthenium–thiolate complexes such as *trans*-[Ru(SPh)$_2$(dmpe)$_2$] [2.472(1) and 2.466(1) Å; dmpe = 1,2-bis(dimethylphosphino)ethane],[19] or [(C$_5$H$_5$)Ru(SPh)(dippe)] [2.420(4) Å].[20] This indicates that Ru–S π bonding may occur to a significant extent in this complex, at variance with what happens to related complexes having chloride ligands instead of thiolate. For these complexes, if there is Ru–Cl π bonding it is usually of the same order as that observed in 18-electron halide complexes.[4] In our case, this π interaction might also contribute to the stereochemical rigidity observed for the complex cation. The Ru(1)–S(1)–C(1) angle of 129.3(4)° suggests sp^2 hybridization for the sulfur atom, which is also consistent with the possibility of Ru–S π bonding in this complex. As has been observed for the complexes
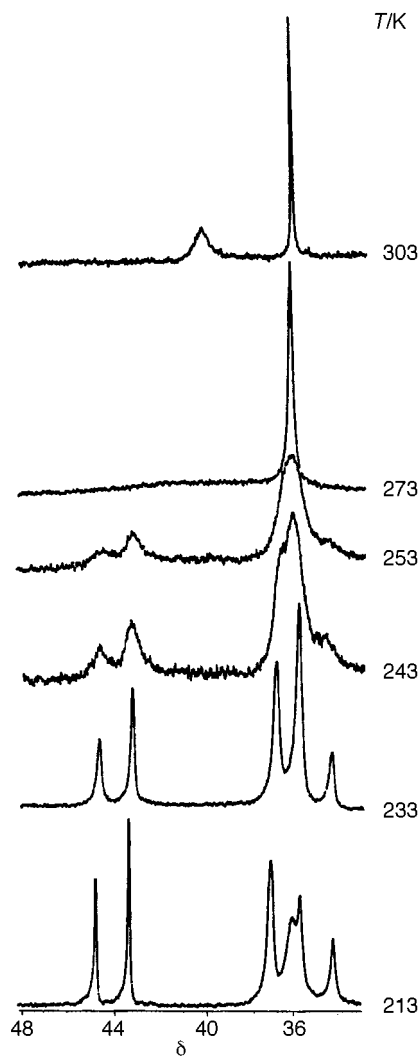

Fig. 4 Variable-temperature ^{31}P-{^{1}H} NMR spectra of complex **5** in (CD$_3$)$_2$CO

[RuCl(dppe)$_2$]$^+$ and [RuCl(dcpe)$_2$]$^+$, the major distortion from the regular trigonal bipyramidal geometry in [Ru(SPh)-(dippe)$_2$]$^+$ is a change from trigonal to a 'Y' shape in the equatorial plane, in which the two equatorial Ru–P bonds form the top of the 'Y', with a reduced P(2)–Ru(1)–P(3) angle of 92.7°. The 'Y' itself is distorted, due to the unequal angles S(1)–Ru(1)–P(2) [129.0(1)°] and S(1)–Ru(1)–P(3) [136.9(1)°]. The origin of these distortions from the regular geometry has been theoretically explained, and no further comments will be made.[4,21] All other bond lengths and angles, including the [BPh$_4$]$^-$ anion, are in the expected range, being unexceptional. As happens in solution, no evidence for agostic interactions in the solid-state structure was found either.

The room-temperature ^{31}P-{^{1}H} NMR spectrum of the osmium derivative **5** consists of one rather sharp resonance at δ 35.7, and one broad signal at δ 39.6 (Δν$_½$ = 95 Hz), which may correspond to an unresolved A$_2$B$_2$ spin system, indicative of a trigonal-bipyramidal structure as in the case of compound **4**. However, when the temperature is lowered, the spectrum changes considerably, as shown in Fig. 4. At 273 K, the signal at δ 39.6 becomes so broad that it merges into the baseline, whereas the resonance at 35.7 increases its half-width. At 253 K, the signal at δ 39.6 splits into two broad doublets, one of them overlapping with the broad resonance centred at δ 37.6. At 213 K, the latter signals splits also into two broad resonances. This spectrum has been reproduced by computer simulation assuming an ABCD spin system, using the parameters shown in Fig. 5. This suggests that the four phosphorus atoms of the phosphine ligands become non-equivalent at low temperature.
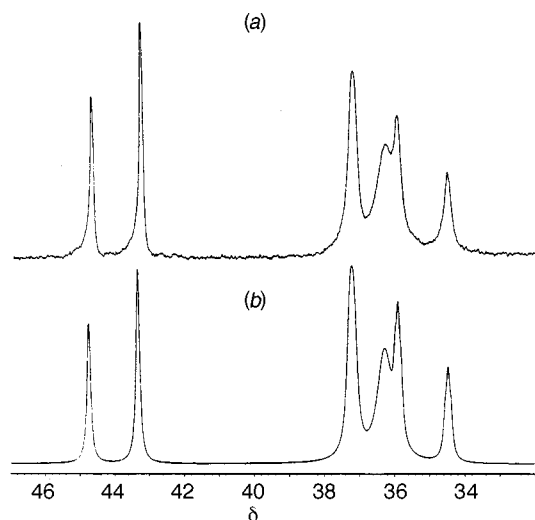
Fig. 5 Real (*a*) and simulated (*b*) ^{31}P-{^{1}H} NMR spectra of complex **5** at 213 K in (CD$_3$)$_2$O. Simulation parameters: ABCD spin system, δ_A 7122.4, δ_B 5708.2, δ_C 6025.6, δ_D 5876.6 Hz; $J_{AB} = 230$, $J_{AC} \approx J_{AD} = 0$, $J_{BC} = 12$, $J_{BD} = 15$, $J_{CD} = 20$ Hz

A similar behaviour has been reported for the octahedral complexes *trans*-[RuX(CO)(dcpe)$_2$][BPh$_4$] (X = Cl, Br or I), for which the ^{31}P-{^{1}H} NMR spectra change from one sharp singlet at room temperature, as expected, to a complex ABCD pattern at 153 K.[5] This has been interpreted in terms of restriction in the ligand motion due to the bulkiness of the cyclohexyl substituents, which leads to the non-equivalence of the four phosphorus atoms. Something similar may happen in our case, in which **5** adopts a distorted trigonal-bipyramidal structure instead of octahedral. In fact, we have already shown that the four phosphorus atoms in the solid-state structure of complex **4** are not equivalent, due to the Y-distortions in the equatorial plane, and also due to the particular arrangement of the benzenethiolate ligand.

The reactivity of complexes **1**, **3**, **4** and **5** towards dihydrogen has been studied. No reaction was observed when dihydrogen was bubbled through a dichloromethane solution of **1**, at variance with the related complexes [RuCl(dcpe)$_2$][BPh$_4$] and [RuCl(dppe)$_2$][PF$_6$], which furnish the corresponding dihydrogen adducts [RuCl(H$_2$)(dcpe)$_2$][BPh$_4$][7] and [RuCl(H$_2$)(dppe)$_2$]-[PF$_6$][4] respectively. If a dihydrogen adduct such as [RuCl(H$_2$)-(dippe)$_2$][BPh$_4$] is formed in the reaction mixture, it must be a labile species, elusive to isolation. We have already noted that the hydrido(dihydrogen) complex [RuH(H$_2$)(dippe)$_2$][BPh$_4$] was a labile species, being stable only under a H$_2$ atmosphere. Under dinitrogen, argon or *in vacuo* the H$_2$ ligand was released to yield the five-co-ordinate monohydride [RuH(dippe)$_2$][BPh$_4$].[10] At variance with **1**, the homologous osmium complex **3** reacts with 1 atm (= 101 325 Pa) of H$_2$ in dichloromethane yielding colourless crystals of the dihydrogen complex [OsCl(H$_2$)(dippe)$_2$]-[BPh$_4$] **6**. This compound can also be obtained by reaction of the *cis*-dichloroosmium complex **2** with H$_2$ and NaBPh$_4$ in methanol, in good yields. No band attributable to v(OsH) is observed in its IR spectrum. The hydridic protons appear in the ^{1}H NMR spectrum as one quintet at δ −13.83, resulting from the coupling to four equivalent phosphorus atoms. When the temperature is lowered, the quintet becomes a broad, unresolved signal. The formulation of **6** as a 'non-classical' hydride complex was established upon longitudinal relaxation time (T_1) measurements for the dihydrogen resonance.[22] From the determination of T_1 at four different temperatures, a minimum T_1 value of 55 ms at 211 K [400 MHz, (CD$_3$)$_2$CO] was obtained, upon least-squares fit of the T_1 *versus* T data to a quadratic function. This value is fully consistent with the presence of one dihydrogen ligand attached to osmium, comparing well with the minimum T_1 values (at 400 MHz) found for the

Scheme 1
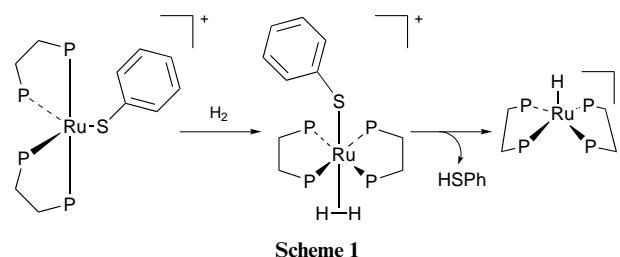
related osmium–dihydrogen complexes: [OsCl(H$_2$)(dcpe)$_2$]$^+$ (50 ms)[7] and [OsCl(H$_2$)(depe)$_2$]$^+$ [60 ms; depe = 1,2-bis(diethylphosphino)ethane].[4] From T_1(min) it is possible to estimate the H−H separation, assuming either fast or slow spinning of the dihydrogen ligand.[22] Thus, the calculated H−H bond distances are 1.0 Å in the case of fast rotation, and 1.3 Å if we assume slow or no rotation. These values fall in the range expected for dihydrogen complexes (below 1.6 Å). The ^{31}P-{^{1}H} NMR spectrum of **6** displays one sharp singlet at room temperature, suggesting a *trans* arrangement of the phosphine ligands. When the temperature is lowered, the signal broadens gradually. At 183 K it is so broad that it merges into the baseline. The rapid spinning of the dihydrogen ligand causes the equivalence of the phosphorus atoms at room temperature. When the temperature is lowered, this motion is slowed, leading to the observed broadening of the signal and eventually to the non-equivalence of the phosphorus atoms at lower temperature. A similar behaviour has been observed for [OsCl(H$_2$)(dcpe)$_2$]$^+$.

When dihydrogen was bubbled through a dark green solution of **4** in dichloromethane or acetone, the solution became colourless. When the solution was placed under dinitrogen or argon during work-up, the colour changed to yellow-orange. Addition of ethanol, concentration and cooling to −20 °C afforded orange microcrystals of [RuH(dippe)$_2$][BPh$_4$]. The isolation of this material suggests that an unstable dihydrogen (or dihydride) benzenethiolate complex is formed first, and this eliminates HSPh yielding the monohydride [RuH(dippe)$_2$]$^+$, according to Scheme 1. The orange ruthenium monohydride is known to add dihydrogen to give the labile colourless hydrido(dihydrogen) complex [RuH(H$_2$)(dippe)$_2$]$^+$, this being responsible for the colour change sequence observed in the reaction mixture. Very recently, Morris and co-workers[23] have shown the occurrence of a tautomeric equilibrium between hydride–thiol and dihydrogen–thiolate tautomers. This sort of equilibrium is possibly involved in our system, although the thiol ligand would be released from the hydride–thiol tautomer, namely [RuH(HSPh)(dippe)$_2$]$^+$, yielding the monohydride as final product. Benzenethiolate–dihydrogen ruthenium complexes such as [Ru(SPh)(H$_2$)(dmpe)$_2$]$^+$ have also been postulated as intermediates in the course of the reaction of *cis*-[RuH$_2$(dmpe)$_2$] with HSPh.[19] In this particular case, [Ru-(SPh)(H$_2$)(dmpe)$_2$]$^+$ seems to eliminate H$_2$ rather than HSPh, to yield the five-co-ordinate intermediate complex [Ru(SPh)-(dmpe)$_2$]$^+$, formally analogous to **4**, albeit not detected. Addition of PhS$^-$ to this intermediate affords a mixture of *cis*/*trans*-[Ru(SPh)$_2$(dmpe)$_2$] as the final isolated and characterized products of the reaction.[19]

On the other hand, stable thiolato–dihydrogen complexes such as [RuH(SR)(H$_2$){P(C$_6$H$_{11}$)$_3$}$_2$] (R = C$_6$H$_{11}$, Ph or Bu^t) have been reported by Chaudret and co-workers.[24] At variance with **4**, no reaction was observed when H$_2$ was bubbled through dichloromethane solutions of **5**, this compound being recovered quantitatively upon work-up of the reaction mixture.

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