Synthesis, characterization and reactivity of some mono- and dinuclear chlororuthenium complexes containing chelating ditertiary phosphines (P–P) with P–P:Ru = 1

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Abstract

Mixed-valence complexes of the type (P–P)ClRu(μ-Cl)$_3$RuCl(P–P), and the [RuCl(P–P)]$_2$(μ-Cl)$_2$ products formed by their reduction with H_2, are synthesized, where P–P is a chelating ditertiary phosphine $Ph_2P(CH_2)_nPPh_2$ (n = 3–6) or some related chiral analogues such as diop, chiraphos, dppcp, dpcycp, bdpp, binap, phenop or norphos (diop = $Ph_2PCH_2CHOCMe_2OCHCH_2PPh_2$; chiraphos = $Ph_2PCH(Me)CH(Me)PPh_2$; dppcp = $Ph_2PCH(CH_2)_3CHPPh_2$; dpcycp = $(C_6H_{11})_2PCH(CH_2)_3CHP(C_6H_{11})_2$; bdpp(skewphos) = $Ph_2PCH(Me)CH_2CH(Me)PPh_2$; binap = 2,2′-bis(diphenylphosphine)-1,1′-binaphthyl; phenop = $Ph_2PN(Et)CH(CH_2Ph)CH_2OPPh_2$; norphos = $Ph_2PCHCHCH{=}CHCH(CH_2)CHPPh_2$). The [RuCl(binap)]$_2$($\mu$-Cl)$_2$ species is also formed in solution by dissociation of PPh_3 from $RuCl_2$(binap)(PPh_3) which is synthesized by phosphine exchange with $RuCl_2(PPh_3)_3$. From the [RuCl(P–P)]$_2$(μ-Cl)$_2$ complex (P–P = $Ph_2P(CH_2)_4PPh_2$), a range of L(P–P)Ru(μ-Cl)$_3$RuCl(P–P) species is readily formed, where L includes an amine, acetone, *N,N*-dimethylacetamide, MeI, PhCN, CO, N_2 or H_2; the L = NEt_3 adduct is made also from $RuCl_2$(dppb)(PPh_3), while the corresponding dimethyl sulfoxide adduct (L = DMSO), **17e**, is synthesized directly from *cis*-$RuCl_2(DMSO)_4$ and the phosphine. $^{31}P\{^1H\}$ NMR data are presented for the Ru(II) species, while characterization of **17e** includes an X-ray crystallographic analysis that confirms the trichloro-bridged formulation. Crystal data are as follows: triclinic, $P\bar{1}$, a = 12.796(1), b = 14.559(1), c = 18.429(1) Å, α = 103.983(5), β = 99.634(6), γ = 99.634(6)°, Z = 2, R = 0.037 and R_w = 0.046 for 9088 reflections with $I \geq 3\sigma(I)$.

Introduction

Work from this laboratory in the late 1970s established that the key species in catalysis (particularly for asymmetric hydrogenations) using Ru complexes containing chelating bis(tertiary phosphine) ligands contained one such P–P ligand per Ru [1]. Subsequent work here [2, 3] and elsewhere [4–7] has amply demonstrated the spectacular success of such Ru(P–P) complexes, where P–P is a chiral phosphine (particularly diop or binap (Fig. 1)), for catalytic asymmetric hydrogenation of certain olefins and ketones.

The synthetic routes reported by other groups into 'Ru(P–P)' complexes have been generally via Ru^{II}(arene) precursors [4b], Ru^{II}(diene) precursors [4c, 5, 8] or $Ru^{II}(\eta^3$-allyl) derivatives [9]. Our synthetic work developed from the finding that the ruthenium(III) monodentate phosphine complexes $RuCl_3(PR_3)_2$ (R = Ph, *p*-tolyl) react with P–P ligands (either chiral or the non-chiral analogues $Ph_2P(CH_2)_nPPh_2$) to generate the mixed-valence triply chloro-bridged complexes $Ru_2Cl_5(P–P)_2$, eqn. (1) [10]. In donor solvents these dimers were found to disproportionate to Ru_2^{II} and Ru_2^{III} congeners, eqn. (2) [10, 11], while they could also be reduced by H_2 in the presence of a base to give Ru_2^{II} species, eqn. (3) [2].

$$4RuCl_3(PR_3)_2 + 4(P–P) \xrightarrow{H_2O} 2Ru_2Cl_5(P–P)_2 + OPR_3 + 7PR_3 + 2HCl \quad (1)$$

$$2Ru_2Cl_5(P–P)_2 \longrightarrow [RuCl_2(P–P)]_2(\mu\text{-}Cl)_2 + [RuCl(P–P)]_2(\mu\text{-}Cl)_2 \quad (2)$$

$$Ru_2Cl_5(P–P)_2 + 0.5H_2 \longrightarrow [RuCl(P–P)]_2(\mu\text{-}Cl)_2 + HCl \quad (3)$$

Reactions of these various dinuclear species with silver(I) salts led us to syntheses of cationic species such as $[Ru(P–P)(MeCN)]_2(\mu\text{-}Cl)_3^+$ and $RuCl(P–P)(solv)_3^+$ where $(solv)_3 = (MeCN)_3$ or η^6-toluene [2, 11].

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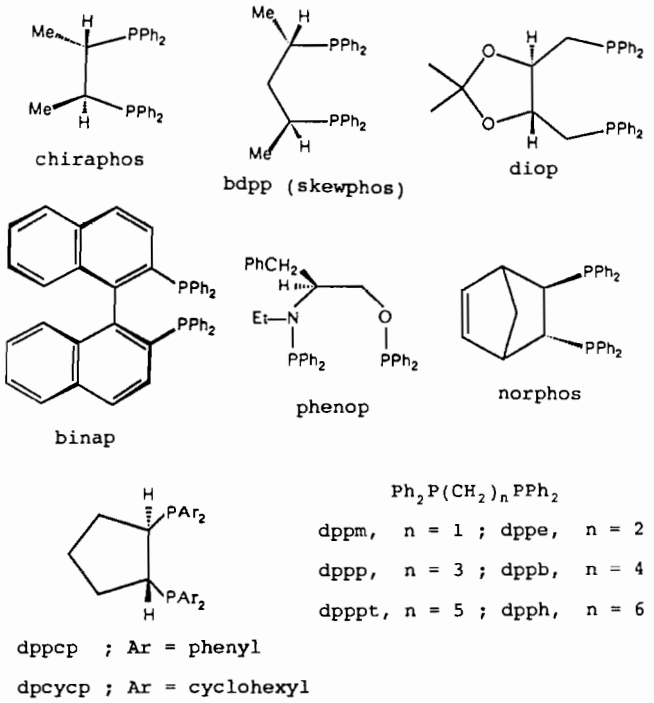


Fig. 1. Tertiary diphosphines used in the present work.

Our attempt to access coordinatively unsaturated 'Ru(H)(P–P)' species via treatment of *trans*-Ru(H)Cl(nbd)(dppb)* with H_2 was unsuccessful [12], but H_2 treatment of the dichloro-bridged ruthenium(II) species $[RuCl(P–P)]_2(\mu\text{-}Cl)_2$ in the presence of base did lead to isolation of such a moiety within the trimeric species $[Ru(H)Cl(P–P)]_3$ [2]. Monohydride species are plausible intermediates in catalytic hydrogenations using 'Ru(P–P)' catalysts [6].

In this paper we wish to report mainly on further details of the synthesis and characterization of the dinuclear mixed-valence and $[RuCl(P–P)]_2(\mu\text{-}Cl)_2$ species, and reactions of the latter with a variety of ligands L to give the trichloro-bridged species $L(P–P)Ru(\mu\text{-}Cl)_3$ RuCl(P–P); we have reported briefly elsewhere on the $L = \eta^2\text{-}H_2$ complex where P–P = dppb [13]. The known complexes $RuCl_2(dppb)(PPh_3)$ [14] and *cis*-$RuCl_2(DMSO)_4$ [15] are also shown to be useful precursors to the trichloro-bridged dinuclear species.

Abbreviations used: the phosphine abbreviations used are shown in Fig. 1; cod = 1,5-cyclooctadiene; Cp = pentamethylcyclopentadienyl; DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene; DMA = *N,N*-dimethylacetamide; DMSO = dimethyl sulfoxide; DMSO = S-bonded DMSO; nbd = 2,5-norbornadiene; PS (Proton Sponge) = 1,8-bis(dimethylamino)naphthalene; PVP = polyvinylpyridine; THF = tetrahydrofuran; TMS = tetramethylsilane. For NMR data, s = singlet, d = doublet, t = triplet, m = multiplet, br = broad.

Experimental

Materials

Spectral or reagent grade benzene, toluene, hexanes, THF and diethyl ether were refluxed with, and distilled from, Na/benzophenone under N_2. DMA was stirred with CaH_2 for at least 24 h, vacuum distilled at 35–40 °C, and stored under Ar in the dark. Dichloromethane, acetone, methanol, ethanol and 2-propanol were distilled after refluxing with the appropriate drying agents (P_2O_5 for CH_2Cl_2, anhydrous K_2CO_3 for acetone, and Mg/I_2 for the alcohols) [16]. All solvents were deoxygenated by freeze–pump–thaw cycles prior to use.

Deuterated solvents ($CDCl_3$, CD_2Cl_2, C_6D_6, toluene-d_8, acetone-d_6, CD_3CN, DMSO-d_6, methanol-d_4, 2-propanol-d_8 and D_2O) were obtained from Merck Frosst Canada Ltd. or Aldrich Chemical Co, and were dried if necessary over activated molecular sieves (Fisher: type 4 Å) before storing under Ar.

Purified Ar (H.P. grade), N_2 (U.S.P.), CO(C.P.) and H_2 (U.S.P.) were obtained from Union Carbide Ltd.; all were used without further purification except H_2, which was passed through an Engelhard Deoxo purifier to remove traces of O_2.

The following phosphines were used as supplied by Strem Chemicals, Inc: PPh_3, $P(p\text{-tolyl})_3$, $Ph_2P(CH_2)_nPPh_2$ ($n = 1$–6), *S,S*-chiraphos, *S,S*-bdpp, *R,R*-diop, *R*- and *S*-binap. *S*-Phenop [17a] and *R,R*-norphos [17b] were synthesized using the literature procedures, while the racemic forms of dppcp and dpcycp were synthesized by a reported method [18], but excluding the resolution step. The chiral and racemic diphosphines are illustrated in Fig. 1. Purity of the phosphines was ascertained by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy.

Triethylamine, di-n-butylamine and tri-n-butylamine (MCB products) were stirred over KOH and purified by distillation. PVP and DBU (Aldrich) were used as supplied; Proton Sponge (Aldrich) was purified by passing an n-pentane solution of the base through an alumina column, followed by concentration of the solution.

Ruthenium was obtained as $RuCl_3 \cdot 3H_2O$ on loan from Johnson Matthey Ltd (38–42% Ru).

Instrumentation

IR spectra were recorded on a Nicolet 5DX FT-IR machine as KBr pellets, or Nujol mulls between CsI plates, unless specified otherwise. UV–Vis spectra were recorded on a Perkin-Elmer 552A fitted with thermostatted cell compartments, using cells attached to Schlenk flasks.

The solution NMR spectra were recorded on a Bruker AC200 (200.1 MHz for ^1H, 81.0 MHz for ^{31}P), a Varian XL300 (300.0 MHz for ^1H, 121.4 MHz for ^{31}P), or a

Bruker WH400 (400.0 MHz for ^1H) FT-NMR spectrometer, using TMS and PPh_3 (*c.* −6 ppm with respect to 85% H_3PO_4 [19]) as external standards. All ^{31}P NMR shifts are reported with respect to 85% H_3PO_4, downfield being taken as positive.* Variable temperature NMR studies and various selective decoupling studies were conducted on Varian XL300, Bruker WH400 or Bruker AMX500 spectrometers. The ^{31}P NMR spectral simulations were performed on a Varian ADS4000 work station using Varian NMR spectral spin simulation software.

The magnetic susceptibilities of the $Ru_2Cl_5(P–P)_2$ complexes were determined by the solution NMR method at 20 °C using $CDCl_3$ solutions containing ~2%(vol./vol.) t-butanol [20].

Gas uptakes for stoichiometric or kinetic studies and gas solubility measurements were performed on a conventional constant-pressure, constant-temperature gas-uptake apparatus described elsewhere [21].

Ruthenium complexes

All synthetic reactions, unless specified otherwise, were carried out under an atmosphere of Ar, employing Schlenk techniques, as most of the complexes prepared are susceptible to oxidation by air, at least in solution. Elemental analyses were performed by P. Borda of this department.

The following complexes were prepared by literature methods: *cis*-$RuCl_2(DMSO)_4$ [15], $RuCl_2(PPh_3)_3$ [22], $Ru(H)Cl(PPh_3)_3 \cdot C_6H_6$ [23] and $RuCl_3(PR_3)_2(DMA)$ (R = Ph, *p*-tolyl) [10, 24, 25]. These complexes were analytically pure and the spectroscopic data (NMR, IR, UV–Vis) agreed with those in the literature [15, 22–26].

Dichloro(1,4-bis(diphenylphosphino)butane)(triphenylphosphine)ruthenium(II), $RuCl_2(dppb)(PPh_3)$ (1)

The reported ligand exchange reaction of $RuCl_2(PPh_3)_3$ with dppb was followed [14] except that, prior to addition of dry ethanol, the reactant CH_2Cl_2 solution was concentrated to ~5 ml by evacuation; the yields of **1** are increased from ~66% [14] to near quantitative. Sometimes, small amounts of the known complex $[RuCl_2(dppb)]_2(\mu\text{-dppb})$ [27] are present as evidenced by ^{31}P NMR spectroscopy [1a]; this CH_2Cl_2-insoluble impurity can be removed by filtration of the CH_2Cl_2 solution of **1** prior to the concentration stage. Low-temperature solution $^{31}P\{^1H\}$ NMR data for **1** agree with those in the literature [14], while solid state CP/MAS ^{31}P NMR spectra [28] will be reported elsewhere [29].

Dichloro(R-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl)(triphenylphosphine)ruthenium(II), $RuCl_2(R\text{-binap})(PPh_3)$ (2)

Complex **2** was prepared by stirring $RuCl_2(PPh_3)_3$ (0.12 g, 0.125 mmol) with 1 equiv. of the diphosphine in CH_2Cl_2 (15 ml) for 10 h under Ar. There was no perceptible change in the initial brown colour of the solution. Addition of diethyl ether (15 ml) following concentration of the solution to ~2 ml resulted in precipitation of an orange–brown solid. The mixture was stirred for 4 h, and the product was separated by filtration, washed with diethyl ether and hexane (5 ml of each), and dried under vacuum. Yield 0.13 g (81%). *Anal.* Calc. for $C_{62}H_{47}Cl_2P_3Ru$: C, 70.46; H, 4.48; Cl, 6.71. Found: C, 70.2; H, 4.6; Cl, 6.5%. Spectroscopic data for **2** are given in Table 1.

Dichloro-tri-μ-chloro-bis(bidentate phosphine)-diruthenium(II,III) complexes, $(P–P)ClRu(\mu\text{-}Cl)_3RuCl(P–P)$ or $Ru_2Cl_5(P–P)_2$ (3–15)

The previously reported title, mixed-valence compounds **3** (P–P = dppp), **4** (dppb), **5** (*R*,*R*-diop) and **6**

TABLE 1. $^{31}P\{^1H\}$ NMR data for $RuCl_2(R\text{-binap})(PPh_3)$ and the $[RuCl(P–P)]_2(\mu\text{-}Cl)_2$ complexes[a]

Complex	Chemical shifts δ (ppm)	$^2J(PP)$ (Hz)
$RuCl_2(R\text{-binap})(PPh_3)$ (2)	65.8, 56.1, 21.0[b]	
$Ru_2Cl_4(dppp)_2$ (16)	P_A 59.0, P_B 51.0	57.0
	(P_A 58.0, P_B 50.5	57.4) [c,d]
$Ru_2Cl_4(dppb)_2$ (17)	P_A 64.0, P_B 54.9	47.3
	(P_A 62.2, P_B 54.3	46.8) [c,e]
$Ru_2Cl_4(dpppt)_2$ (18)	P_A 55.8, P_B 42.3	35.0
$Ru_2Cl_4(R,R\text{-diop})_2$ (19)	P_A 50.7, P_B 47.5	46.1
	(P_A 50.0, P_B 47.1	46.4) [c]
$Ru_2Cl_4(S,S\text{-chiraphos})_2$ (20)	P_A 88.0, P_B 78.3,	38.2
	P_C 87.0, P_D 75.7	39.2
	(P_A 88.4, P_B 76.7,)	39.1 [c]
	(P_C 86.3, P_D 75.4)	39.1
$Ru_2Cl_4(S\text{-binap})_2$ (21)	P_A 75.6, P_B 5.6,	40.7
	P_C 58.7, P_D 58.1	42.5
$Ru_2Cl_4(R\text{-binap})_2$ (22)	P_A 75.8, P_B 5.8,	40.6
	P_C 58.6, P_D 58.2	43.2
$Ru_2Cl_4(S,S\text{-bdpp})_2$ (23)	64.5, 52.9	[f]

[a]In C_6D_6 at 20 °C (121.42 MHz), unless noted otherwise. [b]Multiplets of ABX pattern which is resolved at low temperatures [28, 29]. [c]In CD_2Cl_2 at −70 °C for **16**, **17** and **20**, and at 30 °C for **19** (32.4 MHz). [d]Incorrect data were given for **16** in ref. 2. [e]Spectrum of **17**, present in solution of $RuCl_2(dppb)(PPh_3)$, has been noted previously [14]. [f]Broad signals with unresolved coupling.

*The observed $^{31}P\{^1H\}$ chemical shifts for PPh_3 in $CDCl_3$, CD_2Cl_2, C_6D_6 and toluene-d_8, at 20 °C vs. aq. H_3PO_4 placed in a sealed inner capillary tube, ranged from −5.0 to −6.0 ppm.

(*S,S*-chiraphos) were prepared from the $RuCl_3(PR_3)_2$(DMA) (R = Ph or *p*-tolyl) precursors as described earlier using a 1:1 mixture of Ru(III) and P–P (refluxing in 150 ml hexane as a suspension under N_2 for 24 h) [10]. Product purity was generally improved by dissolving the isolated material in CH_2Cl_2 (~50 ml), filtering, concentrating the filtrate to ~10 ml, and adding Et_2O (~40 ml) for precipitation. The new complexes **7** (dpppt) and **8** (dpph) were synthesized in the same manner from the Ru(III) triphenylphosphine precursor, while **9** (*rac*-dppcp), **10** (*rac*-dpcycp), **11** (*S,S*-bdpp), **12** (*S*-binap), **13** (*R*-binap), **14** (*S*-phenop) and **15** (*R,R*-norphos) were made from the tris(*p*-tolyl)phosphine precursor. Magnetic moment data are given in BM; UV–Vis data were recorded at 20 °C in CH_2Cl_2 and are given as λ_{max} (nm) (ϵ in M^{-1} cm^{-1}) (sh = shoulder). The complexes all show an IR band in the 320–340 cm^{-1} range, characteristic of terminal Ru–Cl stretching.

$Ru_2Cl_5(dpppt)_2$ (7). Yield 60%. *Anal.* Calc. for $C_{58}H_{60}Cl_5P_4Ru_2$: C, 55.27; H, 4.80. Found: C, 55.7; H, 4.5%. μ_{eff} 2.20. λ_{max} 370sh (4415), 420sh (3810), 540sh (1170).

$Ru_2Cl_5(dpph)_2$ (8). Yield 60%. *Anal.* Calc. for $C_{60}H_{64}Cl_5P_4Ru_2$: C, 55.93; H, 5.01. Found: C, 55.5; H, 5.0%.

$Ru_2Cl_5(dppcp)_2$ (9). Yield 70%. *Anal.* Calc. for $C_{58}H_{56}Cl_5P_4Ru_2$: C, 55.45; H, 4.49. Found: C, 55.1; H, 4.5%. μ_{eff} 2.03. λ_{max} 380sh (2550), 515 (2210), 659 (425).

$Ru_2Cl_5(dpcycp)_2$ (10). Yield 30%. *Anal.* Calc. for $C_{58}H_{104}Cl_5P_4Ru_2$: C, 53.39; H, 8.03; Cl, 13.59. Found: C, 53.5; H, 8.0; Cl, 14.0%. λ_{max} 350 (5225), 430sh (2840), 525 (3590).

$Ru_2Cl_5(S,S\text{-}bdpp)_2$ (11). Yield 80%. *Anal.* Calc. for $C_{58}H_{60}Cl_5P_4Ru_2$: C, 55.27; H, 4.80. Found: unacceptable, C being typically 2.3% low.

$Ru_2Cl_5(S\text{-}binap)_2 \cdot H_2O$ (12). Yield 85%. *Anal.* Calc. for $C_{88}H_{64}Cl_5P_4Ru_2 \cdot H_2O$: C, 64.34; H, 4.05; Cl, 10.79. Found: C, 64.6; H, 4.3; Cl, 10.6%. The presence of H_2O was confirmed from IR and NMR spectra. μ_{eff} = 1.90. λ_{max} 405sh (4980), 660 (815).

$Ru_2Cl_5(R\text{-}binap)_2 \cdot H_2O$ (13). Yield 65% using half-scale. *Anal.* Calc. (see **12**). Found: C, 64.3; H, 4.2%. μ_{eff} 1.82. λ_{max} 405sh (5210), 660 (1135).

$Ru_2Cl_5(R,R\text{-}norphos)_2$ (14). Yield 50%. *Anal.* Calc. for $C_{62}H_{56}Cl_5P_4Ru_2$: C, 57.08; H, 4.30; Cl, 13.62. Found: C, 56.7; H, 4.5; Cl, 13.8%. μ_{eff} 2.01. λ_{max} 410 (4150), 520sh (2150).

$Ru_2Cl_5(S\text{-}phenop)_2$ (15). *S*-Phenop is insoluble in hexane, and thus 30 ml benzene were added to the hexane suspension to solubilize the ligand. Yield 55%. *Anal.* Calc. for $C_{70}H_{70}N_2O_2Cl_5P_4Ru_2$: C, 57.02; H, 4.78; N, 1.90. Found: C, 57.5; H, 5.0; N, 1.6%. μ_{eff} 2.16. λ_{max} 340sh (4950), 440sh (1485).

Dichloro-di-μ-chloro-bis(bidentate phosphine)-diruthenium(II) complexes, $[RuCl(P\text{–}P)]_2(\mu\text{-}Cl)_2$ or $Ru_2Cl_4(P\text{–}P)_2$ (16–23)

$Ru_2Cl_4(dppp)_2 \cdot H_2O$ (16). Complex **3** (1.0 g, 0.81 mmol) in DMA (30 ml) was stirred under H_2 for 24 h. The resulting dark brown solution was concentrated to 5 ml, dry MeOH (40 ml) added and the mixture stirred for 3 h under H_2. The orange product was filtered, washed with MeOH (2×5 ml) and diethyl ether (10 ml), and vacuum dried. The solid sometimes contained nitrogen present as DMA impurity which could be removed by recrystallization from CH_2Cl_2–diethyl ether. Yield 75%. *Anal.* Calc. for $C_{54}H_{52}P_4Ru_2 \cdot H_2O$: C, 54.65; H, 4.59; Cl, 11.95. Found: C, 54.7; H, 4.8; Cl, 11.9%.

$Ru_2Cl_4(dppb)_2 \cdot H_2O$ (17). Complex **4** was used as precursor in a synthesis corresponding to that given above for **16**. Yield 90%. *Anal.* Calc. for $C_{56}H_{56}Cl_4P_4Ru_2 \cdot H_2O$: C, 55.36; H, 4.81; Cl, 11.70. Found: C, 55.4; H, 5.0, Cl, 11.5%.

$Ru_2Cl_4(dpppt)_2$ (18). Prepared according to the procedure given for **16**, but using **7** as precursor (on half-scale). Yield 80%. *Anal.* Calc. for $C_{58}H_{60}Cl_4P_4Ru_2$: C, 56.87; H, 4.94. Found: C, 57.5; H, 5.2%.

$Ru_2Cl_4(R,R\text{-}diop)_2$ (19). Complex **5** (1.0 g, 0.75 mmol) was added to a rigorously deoxygenated benzene or toluene suspension (30 ml) of PVP (2.5 g) and the mixture stirred under 1 atm H_2 for 24 h. The orange–brown solution obtained after filtering off the insoluble polymer was concentrated to ~5 ml. Addition of dry hexane (40 ml) followed by stirring for a few hours yielded **19** as a brown solid which was filtered off, washed with hexane (20 ml) and vacuum dried. Yield 85%. *Anal.* Calc. for $C_{62}H_{64}O_4Cl_4P_4Ru_2$: C, 55.53; H, 4.81; Cl, 10.57. Found: C, 55.7; H, 5.0; Cl, 10.8%.

$Ru_2Cl_4(S\text{-}S\text{-}chiraphos)_2$ (20). As described for **19**, but from **6**. Yield 80%. *Anal.* Calc. for $C_{56}H_{56}Cl_4P_4Ru_2$: C, 56.20; H, 4.72; Cl, 11.85. Found: C, 56.2; H, 4.9; Cl, 11.6%. The acetone adduct $Ru_2Cl_4(chiraphos)_2$-(acetone) was obtained by addition of acetone (5 ml) to the concentrated orange–brown solution, prior to precipitation by addition of hexane. Yield 75%. *Anal.* Calc. for $C_{59}H_{62}OCl_4P_4Ru_2$: C, 56.46; H, 4.94; O, 1.28;

Cl, 11.32. Found: C, 56.3; H, 4.9; O, 1.4; Cl, 11.3%. IR (cm^{-1}): 1624 ν(CO), coordinated acetone.

$Ru_2Cl_4(S\text{-}binap)_2$ (21). As described for **19**, but from **12** using 1/5th scale. Yield 90%. *Anal.* Calc. for $C_{88}H_{64}Cl_4P_4Ru_2$: C, 66.50; H, 4.06; Cl, 8.92. Found: C, 66.2; H, 4.2; Cl, 8.8%.

$Ru_2Cl_4(R\text{-}binap)_2$ (22). As described for **19**, but from **13** using 1/5th scale. Yield 80%. *Anal.* Calc. (see **21**). Found: C, 65.9; H, 4.5%.

$Ru_2Cl_4(S,S\text{-}bdpp)_2$ (23). With the procedure described for **19**, the precursor **11** showed no reaction with H_2, even after heating the mixture at 60 °C for 4 days; the toluene remained colourless and **11** remained undissolved. After 2 months at 20 °C, the toluene had become yellow, but most of **11** remained in suspension. After filtration, the filtrate was evaporated to dryness and the residue dissolved in CH_2Cl_2 (2 ml); addition of Et_2O (10 ml) precipitated an orange solid which was filtered, washed with Et_2O, and vacuum dried. Yield 8%. *Anal.* Calc. for $C_{58}H_{60}Cl_4P_4Ru_2$: C, 56.87; H, 4.94. Found: 56.0; H, 5.2%.

The $^{31}P\{^1H\}$ data for **16–23** are given in Table 1.

Chloro-tri-μ-chloro(ligand L)bis(1,4-bis-(diphenylphosphino)butane)diruthenium(II) complexes, L(dppb)Ru(μ-Cl)$_3$RuCl(dppb), 17a–17e

L = NEt_3; $Ru_2Cl_4(dppb)_2(NEt_3)$ (17a). Complex **17** (0.2 g, 0.17 mmol) was stirred with excess NEt_3 (0.5 ml, 3.6 mmol) in benzene or toluene (10 ml) for 6 h. Some orange solid precipitated; further precipitation was induced by adding hexanes (20 ml). The product was washed with ethanol and hexanes, and dried under vacuum. Yield 85%. Alternatively, **17a** can be prepared from complex **1** and NEt_3 in the same manner (~90% yield). *Anal.* Calc. for $C_{62}H_{71}NCl_4P_4Ru_2$: C, 57.37; H, 5.51; N, 1.08; Cl, 10.92. Found: C, 57.3; H, 5.6; N, 1.0; Cl, 10.7%. ^1H NMR ($CDCl_3$, 20 °C), δ: 3.20 (br m, 6H, $-NCH_2-$), 1.08 (br m, 9H, $-NCH_2CH_3$).

L = NH^nBu_2; $Ru_2Cl_4(dppb)_2(NH^nBu_2)$ (17b). (a) From **17**, as described above for **17a**, but using NH^nBu_2 instead of NEt_3. (b) Complex **1** (0.20 g, 0.23 mmol) was refluxed in benzene/hexane (1:4, 20 ml) as a suspension with NH^nBu_2 or N^nBu_3 (2 ml) for 3 h under N_2. After concentration of the solution to ~5 ml and addition of hexane (40 ml), the orange–brown product was filtered off, washed with ethanol and hexane, and vacuum dried. Yield 70%. *Anal.* Calc. for $C_{64}H_{75}NCl_4P_4Ru_2$: C, 57.97; H, 5.70; N, 1.06. Found: C, 57.7; H, 5.5; N, 1.0%. IR (cm^{-1}): 1572 δ(N–H). ^1H NMR ($CDCl_3$, 20 °C), δ: 2.87 (br m, 4H, $-NCH_2-$), 1.62 (m, 4H, $-NCH_2CH_2-$), 1.34 (m, 4H, $-CH_2CH_3$), 0.97 (t, 6H, $-CH_2CH_3$).

L = acetone; $Ru_2Cl_4(dppb)_2(acetone)\cdot acetone$ (17c). Complex **17** (0.2 g, 0.17 mmol) was dissolved in acetone/CH_2Cl_2(1:1, 10 ml) and reprecipitated by addition of Et_2O (40 ml). Yield 70%. *Anal.* Calc. for $C_{59}H_{62}OCl_4P_4Ru_2\cdot C_3H_6O$: C, 56.71; H, 5.22; O, 2.44; Cl, 10.82. Found: C, 56.5; H, 5.1; O, 2.6; Cl, 10.6%. IR (cm^{-1}): 1705 ν(CO), solvate C_3H_6O; 1645 ν(CO), coordinated C_3H_6O.

L = CO; $Ru_2Cl_4(dppb)_2(CO)$ (17d). (a) Gaseous formaldehyde, generated by heating paraformaldehyde at 180 °C under a slow stream of Ar, was bubbled through a CH_2Cl_2 solution (30 ml) of **17** (0.50 g, 0.41 mmol). After 10 min, the solution was concentrated to a red oil to which 30 ml of benzene were added; the solution was stirred for 16 h under Ar and filtered through Celite to remove some 'polymeric' material. Concentration of the filtrate to ~10 ml precipitated the orange product which was filtered, washed with hexane and dried under vacuum. (b) **17** (0.25 g, 0.21 mmol) was stirred with excess CH_3CHO or PhCHO (0.5 ml) at 50 °C for 24 h; concentration of the solution to ~5 ml, followed by addition of hexane (30 ml), gave **17d**. (c) Complex **1** (0.20 g, 0.23 mmol) was reacted in benzene (20 ml) at 50 °C with an equimolar amount of $Mo(CO)_6$ for 24 h under Ar. Concentration of the resultant greenish yellow solution to ~5 ml followed by addition of hexane (30 ml) precipitated **17d**. Yields 60–85% for methods (a) and (b), 90% for (c). *Anal.* Calc. for $C_{57}H_{56}OCl_4P_4Ru_2$: C, 55.89; H, 4.61; Cl, 11.58. Found: C, 56.2; H, 4.8; Cl, 11.4%. IR (cm^{-1}): 1977 ν(CO).

L = DMSO; $Ru_2Cl_4(dppb)_2(DMSO)$ (17e). Some dppb (0.15 g, 0.35 mmol) was added to a solution of *cis*-$RuCl_2(DMSO)_4$ (0.17 g, 0.35 mmol) in CH_2Cl_2:acetone (1:1, 20 ml) and the mixture stirred for 8 h under Ar. The original yellow solution instantly turned orange and further changed slowly to a greenish brown suspension. The bright green solid ($Ru_2Cl_4(dppb)_3$ [27]) was filtered off (~7 mg) and washed with CH_2Cl_2 (5 ml). The orange–yellow filtrate was reduced to ~5 ml, Et_2O (25 ml) added and the mixture stirred for 8 h. The resulting orange suspension was filtered to remove small amounts of **17** (~8 mg). The bright orange filtrate was refrigerated for a week to afford dark orange–red crystals of **17e**. Yield 75%. *Anal.* Calc. for $C_{58}H_{62}OCl_4P_4Ru_2S$: C, 54.63; H, 4.90; Cl, 11.12. Found: C, 54.7; H, 5.1; Cl, 11.0%. IR (cm^{-1}): 1090 ν(SO). Complex **17e** was also characterized crystallographically (see below).

The $^{31}P\{^1H\}$ data for **17a–17e** are summarized in Table 2.

X-ray crystallographic analysis of $Ru_2Cl_4(dppb)_2(DMSO)\cdot 0.67Et_2O\cdot 0.33CH_2Cl_2$

Crystallographic data appear in Table 3. The final unit-cell parameters were obtained by least-squares on 2 sin θ/λ values for 25 reflections with $2\theta = 38.8$–$48.2°$. The intensities of three standard reflections, measured every hour of X-ray exposure time throughout the data collection, showed only small random variations. The data were processed (using locally written computer programs for data processing and locally modified versions of those given in ref. 30) and corrected for Lorentz and polarization effects and absorption (numerical integration, 104 sampling points). A total of 14845 unique reflections was collected on an Enraf-Nonius CAD4F diffractometer, those 9088 having $I \geqslant 3\sigma(I)$ being employed in the solution and refinement of the structure.

The structure was solved by conventional heavy atom methods, the coordinates of the Ru, Cl, S and P atoms of the metal complex being determined from the Patterson function and those of the remaining non-hydrogen atoms from subsequent difference Fourier syntheses. A region of asymmetric unit was found to contain superimposed Et_2O and CH_2Cl_2 solvent molecules. The total occupancy at this site was assumed to be 1.0; the relative amounts of the two components present was initially estimated from relative Fourier peak heights and the occupancy factors for the two components were adjusted during the course of the refinement to yield approximately equal thermal parameters for the atoms involved. In the final stages of the refinement the occupancy factors for the solvent molecules were fixed and the non-hydrogen atoms of these molecules were refined with isotropic thermal parameters. All non-hydrogen atoms of the binuclear metal complex were refined with anisotropic thermal parameters and the hydrogen atoms of the metal complex were fixed in idealized positions ($C(sp^2)$–H = 0.97, $C(sp^3)$–H = 0.98 Å, $U_H \propto U_{\text{bonded atom}}$). Neutral atom scattering factors and anomalous dispersion corrections for all atoms were taken from ref. 31. Final atomic coordinates and equivalent isotropic thermal parameters ($U_{eq} = 1/3$ trace U_{diag}), and selected bond lengths and angles appear in Tables 4–6, respectively. See also 'Supplementary material'.

TABLE 2. $^{31}P\{^1H\}$ NMR data for the [L(dppb)Ru(μ-Cl)$_3$RuCl(dppb)] complexes[a]

Complex, L	Chemical shifts, δ (ppm)	^2J(PP) (Hz)
17a, NEt_3	48.3, s[b]	
17b, NH^nBu_2	48.2, s[b]	
L = Proton Sponge[c]	48.4, s	
L = DBU[c]	44.8, s	
17c, Me_2CO[d]	P_A 52.8, P_B 51.5,	43.7
	P_C 50.1, P_D 48.7	38.4
17d, CO	P_A 53.8, P_B 53.3,	45.2
	P_C 46.9, P_D 33.1	29.6
17e, DMSO	P_A 53.6, P_B 50.6,	43.8
	P_C 41.6, P_D 28.9[e]	32.1
17f, DMA[c]	P_A 53.5, P_B 52.2,	43.6
	P_C 52.7, P_D 50.7[f]	39.6
17g, MeI[c]	P_A 52.6, P_B 51.7,	43.4
	P_C 48.6, P_D 41.8	36.7
17h, PhCN	P_A 52.6, P_B 51.8,	42.1
	P_C 50.3, P_D 44.7	36.5
17i, N_2[c]	P_A 54.4, P_B 53.5	45.1
	P_C 46.6, P_D 36.8	32.1
17j, H_2[c]	P_A 53.7, P_B 53.2,	44.4
	P_C 53.8, P_D 38.3	33.8

[a]At 20 °C (121.42 MHz) in $CDCl_3$ for the amine and MeI adducts, and in C_6D_6 for all the other adducts. [b]Unchanged from 20 to −60 °C. [c]Formed *in situ* from $Ru_2Cl_4(dppb)_2$ (**17**). [d]For the chiraphos analogue at −90 °C in CD_2Cl_2 (32.4 MHz), δ 56.8, 77.1 (J 37.8 Hz), 82.6, 76.4 (J 34.2 Hz). [e]Essentially identical shifts and J values were measured in $CDCl_3$ and DMSO-d_6. [f]In $CDCl_3$, shifts were *c.* 1–3 ppm to higher field with essentially the same J values.

Results and discussion

The mixed-valence, trichloro-bridged $Ru_2Cl_5(P\text{–}P)_2$ *complexes*

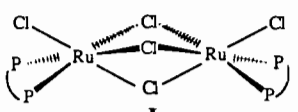
Refluxing a hexane suspension of $RuCl_3(PR_3)_2$ (R = Ph or *p*-tolyl) with equimolar amounts of the appropriate diphosphines affords the corresponding formally mixed-valence dinuclear complexes, $Ru_2Cl_5(P\text{–}P)_2$, as air-stable red-brown or yellow-brown powders, eqn. (1). In addition to the complexes **3–6** reported earlier [10], respectively containing dppp, dppb, *R,R*-diop and *S,S*-chiraphos, new analogous complexes incorporating the diphosphines dpppt (**7**), dpph (**8**), *rac*-dppcp (**9**), *rac*-dpcycp (**10**), *S,S*-bdpp (**11**), *S*- and *R*-binap (**12, 13**) and *R,R*-norphos (**14**), and the aminophosphinephosphinite ligand *S*-phenop (**15**), have been prepared. The nature of the syntheses, with both reactant and product complexes being present as suspensions, and the very low solubility of some of the products in CH_2Cl_2 and other common organic solvents, posed difficulties in recrystallization/reprecipitation procedures and elemental analyses were sometimes marginal (e.g. for **7, 8** and **15**) and in one case (**11**) unacceptable. The binap derivatives **12** and **13** analyze well for the presence of monohydrated species, and IR and NMR reveal qualitatively the presence of uncoordinated H_2O. The solution magnetic moments, measured when possible, are in the range 1.8–2.2 BM,

TABLE 3. Crystallographic data for **17e**[a]

Compound	$Ru_2Cl_4(dppb)_2(DMSO)\cdot 0.67Et_2O\cdot 0.33CH_2Cl_2$
Formula	$C_{58}H_{62}Cl_4OP_4Ru_2S\cdot 0.67C_4H_{10}O\cdot 0.33CH_2Cl_2$
Formula weight	1352.60
Color, habit	yellow–orange prism
Crystal size (mm)	$0.20\times 0.30\times 0.55$
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	12.796(1)
b (Å)	14.559(1)
c (Å)	18.429(1)
α (°)	103.983(5)
β (°)	95.036(6)
γ (°)	99.634(6)
V (Å^3)	3255.0(4)
Z	2
ρ_c (g/cm^3)	1.380
$F(000)$	1383.88
Wavelength (Å)	0.71073
μ (cm^{-1})	8.13
Transmission factors	0.761–0.872
Scan type	ω–2θ
Scan range (° in ω)	$0.85+0.35\tan\theta$
Scan rate (°/min)	2.0–20.0
Data collected	$-h, \pm k, \pm l$
$2\theta_{max}$ (°)	55
Crystal decay	negligible
No. unique reflections	14845
No. reflections with $I\geqslant 3\sigma(I)$	9088
No. variables	663
R	0.037
R_w	0.046
GOF	1.45
Max Δ/σ (final cycle)	0.41
Residual density (e/Å^3)	1.30 (near Ru)

[a]Temperature 294 K, Enraf-Nonius CAD4-F diffractometer, Mo Kα radiation ($\lambda K_{\alpha 1}=0.70930$, $\lambda K_{\alpha 2}=0.71359$ Å), graphite monochromator, takeoff angle 2.7°, aperture $(2.0+\tan\theta)\times 4.0$ mm at a distance of 173 mm from the crystal, scan range extended by 25% on both sides for background measurement, $\sigma^2(I)=C+2B+[0.04(C-B)]^2$ (S = scan rate, C = scan count, B = normalized background count), function minimized $\Sigma w(|F_o|-|F_c|)^2$ where $w=4F_o^2/\sigma^2(F_o^2)$, $R=\Sigma||F_o|-|F_c||\Sigma|F_o|$, $R_w=(\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2)^{1/2}$, and $GOF=[\Sigma(|F_o|-|F_c|)^2/(m-n)]^{1/2}$. Values given for R, R_w and GOF are based on those reflections with $I\geqslant 3\sigma(I)$.

consistent with one unpaired electron per molecule. The structures are considered analogous to that previously determined crystallographically for the *S,S*-chiraphos complex **6** [10]. The UV–Vis spectra in CH_2Cl_2 are all similar with absorption maxima or shoulders in the 370, 450 and 520 nm regions and, by analogy with analysis of UV–Vis and near-IR data reported earlier for **3–6** [10], all the trichloro-bridged species, illustrated in **I**, are best formulated as valence-delocalized class III A systems [32].



I

DMA solutions of the $Ru_2Cl_5(P\text{–}P)_2$ complexes absorb 0.5 ± 0.05 mol equiv. of H_2 at 1 atm H_2 and 30 °C, the stoichiometry being consistent with eqn. (4).

$$Ru_2Cl_5(P\text{–}P)_2+0.5H_2 \longrightarrow Ru_2Cl_4(P\text{–}P)_2+H^+ +Cl^- \quad (4)$$

The dinuclear Ru_2^{II} species can be isolated as the neutral species (see below) or as the ionic compounds $[DMAH^+][Ru_2Cl_5(P\text{–}P)_2^-]$, where $DMAH^+$ is the amide protonated at the oxygen atom [33]. The mechanistic aspects of the H_2-reduction process in DMA, and isolation of the ionic species [2, 34] will be published elsewhere [35].

The dichloro-bridged $[RuCl_2(P\text{–}P)]_2$ complexes

The dinuclear Ru_2^{II} species are formed from the respective $Ru_2Cl_5(P\text{–}P)_2$ complex by H_2-reduction in the presence of base, which is needed to neutralize the HCl regenerated, eqn. (4). DMA solvent can play

TABLE 4. Final positional (fractional $\times 10^4$; Ru, Cl, P, S $\times 10^5$) and isotropic thermal parameters ($U \times 10^3$ Å^2) with e.s.d.s. in parentheses

Atom	x	y	z	U_{eq}/U_{iso}
Ru(1)	23098(2)	39241(2)	24199(2)	31
Ru(2)	44051(2)	28214(2)	21969(2)	30
Cl(1)	27687(8)	24681(7)	27268(6)	37
Cl(2)	42465(8)	44823(7)	29259(5)	36
Cl(3)	30744(8)	32144(7)	13065(5)	38
Cl(4)	58139(9)	35609(8)	16247(6)	47
P(1)	21230(10)	53395(8)	21172(7)	43
P(2)	6141(9)	31461(8)	18432(6)	38
P(3)	44571(9)	13776(8)	14110(6)	37
P(4)	54493(9)	25354(8)	31382(6)	40
S	18208(2)	44453(8)	35647(6)	41
O(1)	960(2)	5005(2)	3667(2)	56
C(1)	792(5)	5525(4)	1774(4)	71
C(2)	−167(5)	5365(4)	2181(4)	78
C(3)	−919(4)	4389(4)	1876(3)	62
C(4)	−567	3589(3)	2183(3)	50
C(5)	5798(4)	1231(3)	1175(3)	50
C(6)	6723(4)	1556(4)	1823(3)	67
C(7)	6692(4)	1136(4)	2483(3)	70
C(8)	5829(4)	1341(4)	2998(3)	58
C(9)	2924(5)	5129(4)	4253(3)	57
C(10)	1461(5)	3489(4)	4006(3)	64
C(11)	2856(4)	5577(3)	1351(3)	48
C(12)	3904(4)	5455(4)	1355(3)	58
C(13)	4508(5)	5653(4)	803(4)	77
C(14)	4070(7)	5954(4)	224(4)	84
C(15)	3034(6)	6063(4)	188(3)	79
C(16)	2429(5)	5892(4)	755(3)	68
C(17)	2681(5)	6454(3)	2871(3)	57
C(18)	3755(5)	6773(4)	3051(4)	77
C(19)	4165(7)	7604(5)	3617(5)	108
C(20)	3555(10)	8111(6)	4004(5)	128
C(21)	2479(10)	7817(6)	3843(6)	148
C(22)	2012(6)	6989(4)	3262(5)	110
C(23)	269(4)	2914(3)	817(2)	47
C(24)	−707(4)	2316(4)	476(3)	60
C(25)	−1023(5)	2128(4)	−282(4)	74
C(26)	−375(6)	2514(5)	−715(3)	81
C(27)	595(5)	3128(4)	−403(3)	69
C(28)	902(4)	3324(4)	369(3)	53
C(29)	336(3)	1897(3)	1919(3)	48
C(30)	−253(4)	1636(4)	2466(3)	65
C(31)	−402(5)	679(5)	2519(4)	86
C(32)	8(5)	13(5)	2033(5)	96
C(33)	567(5)	264(4)	1492(4)	82
C(34)	742(4)	1203(4)	1437(3)	64
C(35)	3729(3)	1201(3)	469(2)	42
C(36)	2803(4)	522(4)	188(3)	55
C(37)	2239(4)	477(4)	−500(3)	71
C(38)	2600(5)	1102(5)	−917(3)	73
C(39)	3528(5)	1774(4)	−645(3)	64
C(40)	4094(4)	1833(4)	39(3)	54
C(41)	3908(4)	226(3)	1617(3)	44
C(42)	3150(4)	175(3)	2092(3)	58
C(43)	2771(5)	−675(4)	2280(3)	67
C(44)	3124(5)	−1488(4)	1973(4)	70
C(45)	3846(5)	−1467(4)	1485(4)	82
C(46)	4240(5)	−632(4)	1298(3)	68
C(47)	6723(3)	3362(4)	3542(3)	50
C(48)	6959(4)	4250(4)	3412(3)	62
C(49)	7940(5)	4877(5)	3717(3)	87
C(50)	8682(5)	4589(6)	4145(4)	94
C(51)	8471(5)	3699(6)	4285(4)	92
C(52)	7502(4)	3103(5)	3992(3)	73
C(53)	4773(3)	2579(4)	3987(3)	47
C(54)	4862(4)	3441(4)	4628(3)	57
C(55)	4298(5)	3491(5)	5138(3)	69
C(56)	3647(5)	2686(6)	5200(4)	86
C(57)	3542(5)	1830(6)	4677(4)	87
C(58)	4094(5)	1773(4)	4073(3)	69
Cl(5)[a]	8466(31)	7633(26)	3285(21)	432(17)
Cl(6)[a]	9634(30)	8202(27)	4493(23)	591(22)
O(2)[b]	7206(34)	7482(35)	2695(25)	477(23)
C(59)[b]	7161(25)	8293(28)	3114(19)	271(14)
C(60)[b]	7305(31)	9451(31)	3672(23)	387(19)
C(61)[b]	7511(42)	6803(41)	2205(30)	437(31)
C(62)[b]	6785(24)	6370(22)	2408(18)	257(13)
C(63)[a]	9241(66)	8508(56)	3744(48)	335(35)

[a]Occupancy factor 0.33. [b]Occupancy factor 0.67.

TABLE 5. Selected bond lengths (Å) with e.s.d.s in parentheses

Ru(1)–Cl(1)	2.469(1)	P(2)–C(29)	1.836(5)
Ru(1)–Cl(2)	2.495(1)	P(3)–C(5)	1.840(4)
Ru(1)–Cl(3)	2.429(1)	P(3)–C(35)	1.836(4)
Ru(1)–P(1)	2.305(1)	P(3)–C(41)	1.847(4)
Ru(1)–P(2)	2.305(1)	P(4)–C(8)	1.847(5)
Ru(1)–S	2.244(1)	P(4)–C(47)	1.832(5)
Ru(2)–Cl(1)	2.418(1)	P(4)–C(53)	1.846(5)
Ru(2)–Cl(2)	2.517(1)	S–O(1)	1.474(3)
Ru(2)–Cl(3)	2.492(1)	S–C(9)	1.788(5)
Ru(2)–Cl(4)	2.399(1)	S–C(10)	1.792(5)
Ru(2)–P(3)	2.261(1)	C(1)–C(2)	1.508(8)
Ru(2)–P(4)	2.257(1)	C(2)–C(3)	1.524(8)
P(1)–O(1)	3.433(3)	C(3)–C(4)	1.527(7)
P(1)–C(11)	1.831(5)	C(5)–C(6)	1.531(7)
P(1)–C(17)	1.851(5)	C(6)–C(7)	1.491(8)
P(2)–C(4)	1.842(4)	C(7)–C(8)	1.537(7)
P(2)–C(23)	1.839(5)		

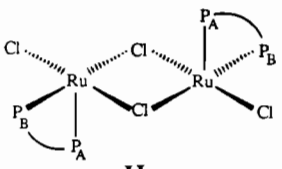
the role of the base [33], but more convenient is the use of polyvinylpyridine (PVP) because this base and its hydrochloride salt are simply removed by filtration at the end of the reaction with H_2 in benzene or toluene solution. The dppp (**16**) and dppb (**17**) complexes are isolated as monohydrates, and indeed the complexes generally are hygroscopic (and air-sensitive) in the solid state. Satisfactory elemental analyses, including chlorine in some cases, were obtained for most of the complexes, although the bdpp complex (**23**) was low in carbon (like its precursor **11**), while the *R*-binap species **22** was somewhat low in carbon; however, the *S*-binap complex (**21**) gave good analytical data. The dpppt species (**18**) gives a rather high C analysis. The

TABLE 6. Selected bond angles (°) with e.s.d.s in parentheses

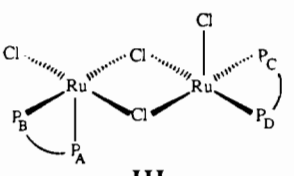
Cl(1)–Ru(1)–Cl(2)	78.25(3)	O(1)–P(1)–C(11)	174.7(2)
Cl(1)–Ru(1)–Cl(3)	78.46(3)	O(1)–P(1)–C(17)	75.2(2)
Cl(1)–Ru(1)–P(1)	172.23(4)	C(11)–P(1)–C(17)	100.5(2)
Cl(1)–Ru(1)–P(2)	93.62(4)	Ru(1)–P(2)–C(4)	120.4(2)
Cl(1)–Ru(1)–S	91.86(4)	Ru(1)–P(2)–C(23)	120.3(2)
Cl(2)–Ru(1)–Cl(3)	80.80(3)	Ru(1)–P(2)–C(29)	111.0(1)
Cl(2)–Ru(1)–P(1)	94.73(4)	C(4)–P(2)–C(23)	101.2(2)
Cl(2)–Ru(1)–P(2)	169.35(4)	C(4)–P(2)–C(29)	101.6(2)
Cl(2)–Ru(1)–S	91.94(4)	C(23)–P(2)–C(29)	98.9(2)
Cl(3)–Ru(1)–P(1)	97.29(4)	Ru(2)–P(3)–C(5)	114.5(1)
Cl(3)–Ru(1)–P(2)	90.90(4)	Ru(2)–P(3)–C(35)	112.5(1)
Cl(3)–Ru(1)–S	168.87(4)	Ru(2)–P(3)–C(41)	122.0(2)
P(1)–Ru(1)–P(2)	92.93(4)	C(5)–P(3)–C(35)	100.9(2)
P(1)–Ru(1)–S	91.68(4)	C(5)–P(3)–C(41)	103.6(2)
P(2)–Ru(1)–S	95.23(4)	C(35)–P(3)–C(41)	100.6(2)
Cl(1)–Ru(2)–Cl(2)	78.78(3)	Ru(2)–P(4)–C(8)	118.8(2)
Cl(1)–Ru(2)–Cl(3)	78.23(3)	Ru(2)–P(4)–C(47)	119.6(2)
Cl(1)–Ru(2)–Cl(4)	163.48(4)	Ru(2)–P(4)–C(53)	111.6(1)
Cl(1)–Ru(2)–P(3)	102.24(4)	C(8)–P(4)–C(47)	102.3(2)
Cl(1)–Ru(2)–P(4)	94.23(4)	C(8)–P(4)–C(53)	100.4(2)
Cl(2)–Ru(2)–Cl(3)	79.18(3)	C(47)–P(4)–C(53)	101.0(2)
Cl(2)–Ru(2)–Cl(4)	88.45(4)	Ru(1)–S–O(1)	120.8(1)
Cl(2)–Ru(2)–P(3)	172.71(4)	Ru(1)–S–C(9)	112.6(2)
Cl(2)–Ru(2)–P(4)	95.12(4)	Ru(1)–S–C(10)	112.7(2)
Cl(3)–Ru(2)–Cl(4)	89.18(4)	O(1)–S–C(9)	105.6(2)
Cl(3)–Ru(2)–P(3)	93.92(4)	O(1)–S–C(10)	104.9(2)
Cl(3)–Ru(2)–P(4)	171.26(4)	C(9)–S–C(10)	97.5(3)
Cl(4)–Ru(2)–P(3)	89.13(4)	P(1)–O(1)–S	70.9(1)
Cl(4)–Ru(2)–P(4)	97.34(4)	C(1)–C(2)–C(3)	115.4(5)
P(3)–Ru(2)–P(4)	92.00(4)	C(2)–C(3)–C(4)	113.6(4)
Ru(1)–Cl(1)–Ru(2)	86.69(3)	P(2)–C(4)–C(3)	117.1(3)
Ru(1)–Cl(2)–Ru(2)	84.01(3)	P(3)–C(5)–C(6)	117.3(3)
Ru(1)–Cl(3)–Ru(2)	85.93(3)	C(5)–C(6)–C(7)	120.5(5)
Ru(1)–P(1)–O(1)	65.75(6)	C(6)–C(7)–C(8)	118.0(4)
Ru(1)–P(1)–C(11)	114.2(1)	P(4)–C(8)–C(7)	117.2(4)
Ru(1)–P(1)–C(17)	115.1(2)		

$Ru_2Cl_5(dpph)_2$ complex **8** failed to undergo reduction by H_2; the other mixed valence complexes **9, 10, 14** and **15** have not yet been tested for reactivity toward H_2.

The $^{31}P\{^1H\}$ NMR data (Table 1) leave no doubt as to the identity of these dichloro-bridged complexes. The AB pattern noted previously for **16** and **17** [2], and now seen for **18**, is consistent with a bridged structure with two square pyramids sharing a basal edge (**II**), analogous to that proposed for $[RuCl_2(PR_3)_2]_2$ [25, 26, 36]. Incorporation of chirality in to the phosphine gives 2AB quartets of equal intensity because the P_As (and P_Bs) of **II** are now inequivalent.



II



III

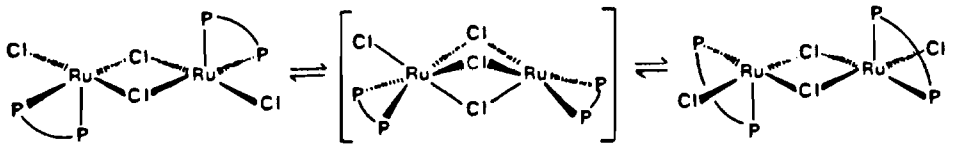
The spectrum for **20** is shown in Fig. 1 of our earlier publication [2], while the dimeric formulation was confirmed by a molecular weight determination of 1100 (calc. 1196) using the Signer method [37]. The $^{31}P\{^1H\}$ NMR spectra of the *S*- and *R*-binap derivatives (**21** and **22**) are essentially identical, and differ from the spectrum of **20** in the resonance position of one of the P atoms (labelled P_B). By comparison with reported data for other square pyramidal Ru complexes containing apical/basal pairs of phosphines [14, 26], the resonances of **21** and **22** at ~76 and 6 ppm could be assigned to an apical/basal (P_A/P_B) pair within a structure such as **III**; the remaining two resonances around 58 ppm would then correspond to P_C and P_D, *cis* in a basal plane. Crystallographic data are needed to distinguish unambiguously between **II** and **III**.

A structure such as **II** probably interconverts readily to its diastereomer via the process shown in Scheme 1, involving a triply-chloride-bridged intermediate, a species which is readily formed (see below). Thus, an alternative explanation for the presence of two AB patterns, involving degeneracy of the diastereotopic pair of phosphines on the two Ru centres and the existence of inequivalent diastereomers, is considered highly unlikely.

As noted earlier [2], the *R,R*-diop complex **19** gives only a single AB pattern in the $^{31}P\{^1H\}$ NMR spectrum, and this probably results from the larger, more flexible ring size (versus chiraphos) giving two coincidentally degenerate AB quartets (binap, like diop, gives seven membered chelate rings, but the $-PPh_2$ moieties are attached to sp-carbons within a more rigid backbone). The relatively impure *S,S*-bdpp complex **23** gave broad, unresolved $^{31}P\{^1H\}$ signals which could conceal one or two AB quartets.

The $^{31}P\{^1H\}$ spectra of $[RuCl_2(P\text{–}P)]_2$, P–P = dppb [14] and diop [38], were first observed with *in situ* species formed as a result of partial dissociation of PPh_3 from the corresponding $RuCl_2(P\text{–}P)(PPh_3)$ complexes. Analogous data have just been published for the system with P–P = biphemp [2,2'-dimethyl-6,6'-bis(diphenylphosphino)biphenyl], where the *in situ* $[RuCl_2(biphemp)]_2$ species is an extremely effective enantioselective catalyst for mono- or bis-hydrogenation of diketones [39]. Of interest, these authors were unable to synthesize $RuCl_2(binap)(PPh_3)$ (**2**) by the same phosphine exchange method reported here (see below).

The orange–brown solutions of the $Ru_2Cl_4(P\text{–}P)_2$ complexes reveal UV–Vis absorption maxima typically at 365–385 nm (ϵ = 3000–5000 M^{-1} cm^{-1}) and at 450–470 nm (ϵ = 500–1800 M^{-1} cm^{-1}); the spectra are also somewhat solvent dependent, the absorption maximum varying within the ranges just noted (e.g. for **20** in toluene, acetone and DMA; a spectrum of **17** in DMSO is given in Fig. 6 of ref. 10). Complex **20** obeys Beer's Law in DMA from about 10^{-4} to 10^{-2} M. In coordinating



II

Scheme 1. Interconversion between diastereomers of $Ru_2Cl_4(P\text{–}P)_2$ complexes.

solvents such as acetone, DMA or DMSO, the species are almost certainly present as the triply-chloride-bridged species L(P–P)Ru(μ-Cl)$_3$RuCl(P–P), L = solvent (see below). The $Ru_2Cl_4(P\text{–}P)_2$ complexes isolated as monohydrates (**16** and **17**) on dissolution in C_6D_6 or CD_2Cl_2 for NMR measurements certainly do not exist as the (μ-Cl)$_3$ species with L = H_2O; however, the possibility that **16** and **17** exist as such in the solid state cannot be ruled out at this stage. The $Ru_2Cl_4(dppb)_2$(DM*S*O) complex (**17e**) is shown crystallographically *and* by solution NMR to exist as a (μ-Cl)$_3$ species (see below), while the analogous acetone complex **17c** contains both coordinated acetone (within the (μ-Cl)$_3$ structure) and an acetone solvate (see below).

Addition of 1 equiv. of the appropriate P–P ligand go the orange–brown solutions of the $[RuCl_2(P\text{–}P)]_2$ species containing dppb (**17**) and *R,R*-diop (**19**) generates the phosphine-bridged, dinuclear species $[RuCl_2(P\text{–}P)]_2(\mu(P\text{–}P))$ [1, 27].

The $RuCl_2(P\text{–}P)(PPh_3)$ complexes

One objective of the current work was to develop syntheses of 'Ru(P–P)' species (see 'Introduction'), and phosphine displacement reactions, for example eqn. (1), were an obvious strategy to pursue. It is now clear that the choice of the Ru precursor and solvent used are crucial. Reaction in hexane of 1 equiv. of P–P with $RuCl_3(PR_3)_2$ precursors yields the mixed-valence $Ru_2Cl_5(P\text{–}P)_2$ complexes (see above). However, reaction of $RuCl_3(PPh_3)_2$(DMA) with 1 equiv. of dppb in DMA affords $RuCl_3$(dppb)(DMA) as the initial product from a reaction time of ~16 h [28, 29]; over longer reaction periods (4 days), the bright green mixed-phosphine complex $RuCl_2$(dppb)(PPh_3) (**1**) is obtained. The following reaction sequence is envisaged:

$$RuCl_3P_2(DMA) \xrightarrow[-2P]{dppb} RuCl_3(dppb)(DMA) \xrightarrow{P/H_2O}$$

(P = PPh_3)

$$Ru_2Cl_4(dppb)_2 \xrightarrow{P} RuCl_2(dppb)(P)$$

17 **1**

The reduction step to **17** is again attributed to PPh_3 in the presence of water, presumably via $Ru_2Cl_5(P\text{–}P)_2$ (cf. eqn. (1)). The insolubility of $Ru_2Cl_5(P\text{–}P)_2$ in hexane presumably accounts for formation of this mixed valence species in this solvent. Support of the above sequence comes from the observation that **17** reacts rapidly with PPh_3 to form **1**.

The mixed-phosphine complex **1** is more readily made from an exchange reaction using $RuCl_2(PPh_3)_3$ and dppb in CH_2Cl_2 [14], see 'Experimental', and we isolated the binap analogue $RuCl_2$(*R*-binap)(PPh_3) (**2**) via a similar procedure. The *R,R*-diop analogue was synthesized previously in this laboratory by refluxing stoichiometric amounts of $RuCl_2(PPh_3)_3$ and diop in hexane [38]. Reaction of $RuCl_2(PPh_3)_3$ with dppm, dppe, dppp, chiraphos or bdpp yields a mixture of the unreacted precursor, free PPh_3 and the *trans*-$RuCl_2(P\text{–}P)_2$ complexes, readily identified by $^{31}P\{^1H\}$ singlet resonances [14, 28, 29].

As well documented [1a, 14, 38, 39], the mixed-phosphine complexes dissociate in solution with partial loss of PPh_3, eqn. (5), and the low temperature $^{31}P\{^1H\}$ NMR spectra (Table 1, footnotes b and e) reveal the AB pattern(s) of the $Ru_2Cl_4(P\text{–}P)_2$ products (see above), the signal for free PPh_3, and the ABX pattern of the $RuCl_2(P\text{–}P)(PPh_3)$ species, which are square-pyramidal with *trans* chlorides, PPh_3, and one phosphorus of the P–P ligand, in the basal plane. Further details on the chemistry of the mixed-phosphine complexes, as well as solid state ^{31}P studies on these and the closely related $RuCl_2(PPh_3)_3$ complex [28], will be published elsewhere [29].

$$2RuCl_2(P\text{–}P)(PPh_3) \longrightarrow Ru_2Cl_4(P\text{–}P)_2 + 2PPh_3 \qquad (5)$$

The trichloro-bridged [(L)(dppb)Ru(μ-Cl)$_3$RuCl(dppb)] complexes

The coordinatively unsaturated $Ru_2Cl_4(P\text{–}P)_2$ complexes readily add an extra, single ligand L to form the trichloro-bridged, coordinatively saturated, title complexes, eqn. (6).

$$Ru_2Cl_4(P\text{–}P)_2 \overset{L}{\rightleftharpoons} L(dppb)Ru(\mu\text{-}Cl)_3RuCl(dppb) \qquad (6)$$

Reported are the isolation procedures and NMR data for the dppb complexes with L = NEt_3 (**17a**), NH^nBu_2 (**17b**), acetone (**17c**), CO (**17d**) and DM*S*O (**17e**), as well as structural data for **17e**. The acetone adduct of the chiraphos complex is also described here. *In situ* species with L = DMA, Proton Sponge, DBU, PhCN or MeI, are formed also from $Ru_2Cl_4(dppb)_2$ (**17**).

The acetone adducts are readily synthesized, and are more stable to air-oxidation than the $Ru_2Cl_4(P\text{–}P)_2$ species, while having essentially the same catalytic hydrogenation activity [2, 28, 29, 34, 35]. The amine adducts, which can also be synthesized using **1** as precursor (see eqn. (5)), show ^1H NMR signals of reversibly coordinating amine (see below); for example, **17a** has the methylene and methyl signals at 3.20 and 1.08 ppm, respectively, shifted from the 2.39 and 0.95 ppm positions of free NEt_3. The di-n-butylamine adduct **17b** is formed as expected using NH^nBu_2 reagent, but also surprisingly using N^nBu_3; however, such de-alkenylation of amines in the presence of transition metal complexes is well documented [40]. The Ru_2Cl_4 (*R*-binap)$_2$(NEt_3) complex prepared from the $[RuCl_2(cod)]_n$ precursor [41] is presumably analogous to **17a**.

Attempts to synthesize **17d** from direct reaction of **1** or **17** with CO were unsuccessful, an isolated product probably being a mixture of $RuCl_2(dppb)(CO)_2$ and unidentified monocarbonyls [28]. However, use of aldehydes or $Mo(CO)_6$ as a source of CO provided effective routes for synthesis of the dinuclear monocarbonyl of interest; such decarbonylation reactions of aldehydes [42] and $Mo(CO)_6$ [43] are well known.

The DMSO adduct **17e** is synthesized by addition of 1 equiv. of dppb to *cis*-$RuCl_2(DMSO)_4$. A small amount of $Ru_2Cl_4(dppb)_3$ [27] is also formed but this is readily filtered off, and dark red crystals of **17e** are isolated in good yield from the orange filtrate as an Et_2O/CH_2Cl_2 solvate (0.67:0:33 per molecule as evidenced by X-ray crystallographic analysis). The isolated, vacuum dried product analyzed correctly for the non-solvated form.

The IR band at 1090 cm^{-1} ν(SO) is consistent with S-bonded sulfoxide [44]. The structure (Fig. 2) reveals the dinuclear, trichloro-bridged formulation, with S-bonded DMSO at one of the Ru atoms; selected bond lengths and angles are listed in Tables 5 and 6, respectively.

The geometry about each Ru in **17e** is irregular octahedral. The bond distances Ru(1)–S (2.244 Å), S–O (1.474 Å) and Ru(1)–Cl(3) (2.429 Å) for the bridging chloride *trans* to DMSO, are comparable to those found in *cis*-$RuCl_2(DMSO)_4$ (av. 2.276, 1.485 and 2.435 Å, respectively [45]) and *fac*-$[RuCl_3(DMSO)_3]^-$ complexes (average 2.262, 1.477 and 2.426 Å, respectively [46]), which also contain S-bonded sulfoxides *trans* to a chloride ligand. The slight shortening of the Ru–S bond of **17e** is likely because of the reduced *trans* influence of the bridging chloride as compared to that of a terminal Cl. While the respective Ru(1)–P(1,2) and Ru(2)–P(3,4) bond lengths of 2.305 and 2.26 Å (av. ~2.28 Å) are within normal range found for Ru(II) tertiary phosphine complexes [2, 47–49], the difference between the two sets is indicative of the different environments about the Ru(II) centres. The Ru–Cl bond length for the bridging chlorides which are *trans* to phosphorus (av. 2.493 Å) is longer than the Ru(2)–Cl(1) distance (2.418 Å), where Cl(1) is *trans* to the terminal chloride Cl(4). The stronger *trans* influence of phosphine, compared to chloride, clearly results in a weaker and consequently longer bond. Two regular octahedra sharing one face have a bridging angle θ of 70.5° (given by cos $\theta/2 = 2/3$) [48]. In this complex the average bridging angle (∠Ru-Cl-Ru) is 85.54°, implying that the two Ru atoms are further apart than they would be in a regular cofacial bioctahedron. Indeed, the distance between the ruthenium centres (3.35 Å) is well outside the range (2.28–2.95 Å) usually observed for a Ru–Ru bond [50].

The structure of **17e** is shown schematically in **IV**, which may be compared with that for the mixed-valence complex $Ru_2Cl_5(S,S\text{-chiraphos})_2$ (**6**) of structure type **I** studied previously [2].

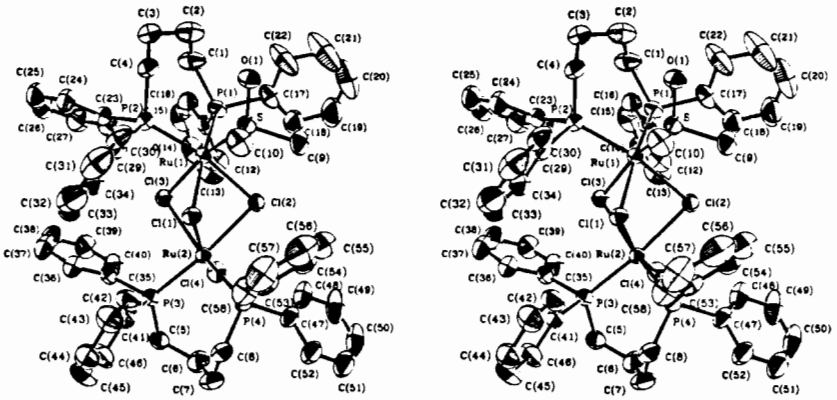
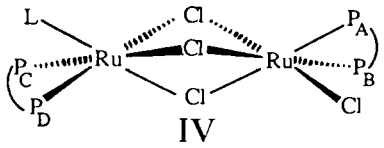


Fig. 2. An ORTEP stereoview of the $Ru_2Cl_4(dppb)_2(DMSO)$ molecule; 50% probability thermal ellipsoids are shown for the non-hydrogen atoms.



IV

Despite the different oxidation states at the Ru centres, the corresponding bond lengths and angles are very similar; however, compared to the highly symmetric **6** (**I**) which has a near two-fold axis through a bridging chloride, **17e** has one of the octahedra rotated by $\pm 120°$ about the Ru–Ru vector and the positioning of the diphosphines is unsymmetrical. The analogous thiocarbonyl complex $(CS)(PPh_3)_2Ru(\mu\text{-}Cl)_3RuCl(PPh_3)_2$ [47b] also shows a similar unsymmetrical arrangement of PPh_3 ligands.

The ambient temperature $^{31}P\{^1H\}$ spectra of solutions of **17c–17e** consist of two independent AB quartet patterns of equal integral intensity (Table 2), consistent with the unsymmetrical solution structure typified by **IV**, and shown in the solid state for **17e**; the inequivalence of all four P atoms implies the absence of a dissociation/re-association of the adduct ligand L (eqn. (6) and Scheme 1), or at least such a process must be slow on the NMR time-scale. The $^{31}P\{^1H\}$ NMR spectrum of the isolated acetone adduct **17c** shows also the AB quartet of the precursor $Ru_2Cl_4(dppb)_2$ (**17**) at ~25% of the intensity, implying reversible dissociation of L; no L dissociation is seen for the CO and DMSO adducts. Of the two AB quartets of **17c–17e**, the relatively lower field pattern is insensitive to the nature of L ($\delta_{AB} = 52 \pm 2$ ppm, $^2J_{AB} = 43 \pm 2$ Hz) and is therefore assigned as shown to the $(\mu\text{-}Cl)_3RuCl(P\text{–}P)$ portion of the molecule; the other set of signals varies with the nature of L ($\delta_{CD} = 33$–53 ppm, $^2J_{CD} = 29$–40 Hz) and is attributed to the L(P–P)Ru fragment.

Addition of about a 100-fold excess of DMA or MeI to solutions of **17** results in partial conversion to *in situ* species **17f** and **17g** which again show $^{31}P\{^1H\}$ spectra (Table 2) typical of $L(dppb)Ru(\mu\text{-}Cl)_3RuCl(dppb)$ species. The amide ligand is presumably bonded via the O atom as in all documented cases of metal amide complexes [33, 51]. Methyl iodide more commonly undergoes oxidative addition at a transition metal centre [52], but recently complexes containing metal←IMe moieties have been characterized including $Cp^*Ru(dppe)(MeI)^+$ [53]. From a reaction of **17** with PhCN in CH_2Cl_2, we have isolated a product which gives a single AB pattern in the $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$, 20 °C; $\delta_A = 48.8$, $\delta_B = 45.2$ ppm, $^2J_{AB} = 35.7$ Hz); coordinated nitrile is seen at 2238 cm^{-1} in the IR, and proton intensities in the ^1H NMR spectrum show the presence of one PhCN per Ru–dppb unit. The data are consistent with a $[RuCl(dppb)(PhCN)]_2(\mu\text{-}Cl)_2$ formulation with the phosphines of a dppb ligand being inequivalent (one *trans* to μ-Cl, and one *trans* to PhCN); analogous $[RuCl(PPh_3)_2(RCN)]_2(\mu\text{-}Cl)_2$ complexes (R = Me, Ph) are known [54]. The $^{31}P\{^1H\}$ NMR spectrum also shows an additional pair of AB quartets of ~15% total integral intensity that are assigned to the $(PhCN)(dppb)Ru(\mu\text{-}Cl)_3RuCl(dppb)$ species (**17h**) (Table 2), presumably formed by loss of nitrile from the bis(nitrile) species.

For the sake of completeness, Table 2 includes also the $^{31}P\{^1H\}$ data for the $L = N_2$ and $L = \eta^2\text{-}H_2$ complexes which we have described previously [13]. Two sets of $^{31}P\{^1H\}$ AB patterns have been observed for complexes of the type $(L)(PR_3)_2Ru(\mu\text{-}Cl)_3RuCl(PR_3)_2$, analogous to **17c–17j** but containing two monodentate phosphines instead of dppb, where L = CO [55], CS [47b, 56], PF_3 [57], DMA [58] and acetone [58]; the $L = N_2$ complex has also been synthesized [59].

Of interest, the NEt_3 and NH^nBu_2 adducts **17a** and **17b**, which do contain only one amine per $Ru_2Cl_4(dppb)_2$ unit as evidenced by elemental analysis and integrations of the ^1H NMR signals, give only a singlet in the $^{31}P\{^1H\}$ NMR spectra even at −60 °C (Table 2); this must result from rapid reversible dissociation of the amine and recoordination to either Ru centre which results in scrambling of all four P atoms. The 'non-nucleophilic' bases Proton Sponge and DBU are also considered to form corresponding *in situ* dinuclear species with amine coordinated at one Ru, as judged by $^{31}P\{^1H\}$ NMR data (Table 2).

Finally it should be noted that the synthesis of the DMSO adduct **17e** from the easily available *cis*-$RuCl_2(DMSO)_4$ precursor provides an attractive route to the potentially catalytic 'Ru(P–P)' complexes, but unfortunately it is not a general route. Corresponding reactions of *cis*-$RuCl_2(DMSO)_4$ with 1 equiv. of dppm and dppe give partial conversion to the known, yellow complexes *cis*-$RuCl_2(dppm)_2$ and a 1:1 mixture of *cis*- and *trans*-$RuCl_2(dppe)_2$, respectively [14, 60]; addition of excess diphosphine results in complete conversion to the $RuCl_2(P\text{–}P)_2$ species. Reaction of *cis*-$RuCl_2(DMSO)_4$ with 1 equiv. of *S,S*-bdpp, using the experimental procedure described for isolation of **17e**, gives a roughly 3:2 mixture of $(DMSO)(bdpp)Ru(\mu\text{-}Cl)_3RuCl(bdpp)$ and *trans*-$RuCl_2(S,S\text{-}bdpp)_2$. The DMSO adduct was identified by $^{31}P\{^1H\}$ NMR (C_6D_6, 20 °C, 2 sets of AX patterns: $\delta_A(ppm) = 65.3$, $\delta_B = 54.2$, $^2J(PP) = 51.0$ Hz; $\delta_C = 49.6$, $\delta_D = 30.9$, $^2J(PP) = 40.1$ Hz) by analogy to data for **17e** (Table 2), and IR (1089 cm^{-1}), ν(SO) of DMSO), while the *trans*-$RuCl_2(S,S\text{-}bdpp)_2$ complex which shows a $^{31}P\{^1H\}$ singlet at δ 9.2 ppm (C_6D_6, 20 °C) has been characterized crystallographically [28, 61]. The reactivity of bidentate phos-

phines with *cis*-$RuCl_2(DMSO)_4$ shows a clear trend of giving solely $RuCl_2(P–P)_2$ complexes with dppm and dppe (which form four- and five-membered rings, respectively), a mixture of $RuCl_2(P–P)_2$ and dinuclear '$RuCl_2(P–P)$' species with bdpp (six-membered ring), and almost entirely the dinuclear species with dppb (seven-membered ring).

Conclusions

Practical synthetic routes to Ru complexes containing one chelating, ditertiary phosphine (P–P) per metal are described. The complexes include: mononuclear $RuCl_2(P–P)(PPh_3)$ species; dinuclear, trichloro-bridged mixed valence $Ru_2Cl_5(P–P)_2$ species; dinuclear, dichloro-bridged $Ru_2Cl_4(P–P)_2$ species; and dinuclear, trichloro-bridged $Ru_2Cl_4(P–P)_2L$ species where L may be a wide variety of donor ligands. The systems containing chiral P–P ligands are of importance because of their ability to effect catalytic asymmetric hydrogenation of olefinic and carbonyl groups, which has been documented elsewhere and shown to be of wider application than that of related rhodium systems.

Supplementary material

Tables of hydrogen atom parameters, anisotropic thermal parameters, complete lists of bond lengths and angles, torsion angles, and measured and calculated structure factor amplitudes for the structure of **17e** are available on request from the authors.

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