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FULL PAPER

Silver(I)-mediated isomerisation of *trans*-$[RuCl_2(P–P)_2]$ (P–P = four-membered ring chelate diphosphine ligand) to *cis*-$[\{Ru(P–P)_2(\mu\text{-}Cl)_2\}_nAg]^+$ species, and applications in stereoselective syntheses of *cis*- and *trans*-$[RuCl(L)(P–P)_2]^+$ (L = neutral ligand) †

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When complexes *trans*-$[RuCl_2(diphos)_2]$ (diphos = $(Ph_2P)_2C{=}CH_2$, $Ph_2PCH_2PPh_2$ or $Ph_2PNHPPh_2$) were treated with silver salts of poorly coordinating anions (*e.g.* $AgBF_4$, AgO_3SCF_3) in 1,2-dichloroethane halide abstraction was slow, even at reflux, and the reaction proceeded by an interesting mechanism involving a *trans* to *cis* isomerisation. At room temperature, a complex, characterized as $[RuCl(diphos)_2(\mu\text{-}Cl)Ag]^+$, forms. When heated to reflux for 5–10 min this reacts to give a mixture, which includes *cis*-$[RuCl_2(diphos)_2]$, and species of the type $[\{Ru(diphos)_2(\mu\text{-}Cl)_2\}_nAg]^+$ (n = 1 or 2) in which the exact coordination geometry at Ag^I is unknown. The reactions have been followed by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy, and electronic spectroscopy results also support the isomerisation. The ruthenium and silver K-edge EXAFS spectra of the solid isolated from the reaction of *trans*-$[RuCl_2(dppm)_2]$ and AgO_3SCF_3 lend support to this formulation; in particular, the best fit for the silver(I) environment includes coordination to one oxygen (from the $^-O_3SCF_3$; Ru–O 2.43 Å), two Cl (2.79 Å) and between one and two Ru (3.94 Å). Over 30–40 min at reflux, AgCl precipitates, the signals due to *cis*-$[RuCl_2(diphos)_2]$ disappear from the $^{31}P\text{-}\{^1H\}$ NMR spectra, those due to the $[\{Ru(diphos)_2(\mu\text{-}Cl)_2\}_nAg]^+$ mixture diminish, and new resonances, attributed to five-coordinate $[RuCl(diphos)_2]^+$, appear. This reaction has been investigated for stereoselective ligand substitution. Treatment of *trans*-$[RuCl_2(diphos)_2]$ with $AgBF_4$ or AgO_3SCF_3 in DCE in the presence of CH_3CN or CO yields exclusively *trans*-$[RuCl(L)(diphos)_2]^+$ (L = CH_3CN or CO), but treatment of *trans*-$[RuCl_2(diphos)_2]$ with $AgBF_4$ or AgO_3SCF_3 in DCE, *followed* by treatment with L, usually gave exclusively *cis*-$[RuCl(L)(diphos)_2]^+$ (L = CH_3CN or CO).

Introduction

The double bond of the diphosphine $(Ph_2P)_2C{=}CH_2$[1] (dppen) becomes activated towards nucleophilic addition when this ligand chelates to a metal centre, to an extent dependent upon the metal, oxidation state and co-ligands.[2–9] We have recently employed this chemistry with some success to prepare derivatives of the redox-active complex *trans*-$[RuCl_2(dppen)_2]$ *trans*-**1a** for anchoring to oxide supports,[10,11] and for electropolymerisation to afford a polypyrrole derivative.[12] However, in comparison with complexes $[MX_2(dppen)]$ (M = Pd, X = OAc; M = Pt or Pd, X = Cl or I),[5,7–9] *trans*-**1a** is rather unreactive. For example, although it will undergo reaction with an excess of primary amine to give *trans*-$[RuCl_2\{(Ph_2P)_2CHCH_2NHR\}_2]$, with one exception it proved unreactive towards carbanions, whereas complexes $[MX_2\{(Ph_2P)_2C{=}CH_2\}]$ readily add carbanions.[7–9] The exception is lithium acetylides, but these also displaced the chloride ligands to give *trans*-$[Ru(C{\equiv}CR)_2\{(Ph_2P)_2CHCH_2C{\equiv}CR\}_2]$ after work-up.[10] Earlier, we showed that the cationic complex $[Pt(dppen)_2]^{2+}$ was significantly more reactive to nucleophiles than neutral $[PtCl_2(dppen)]$.[9] We were therefore interested in the preparation and reactivity of cationic complexes such as $[RuCl(L)(dppen)_2]^+$, $[Ru(dppen)_2(L)_2]^{2+}$ (L = neutral ligand) and $[Ru(dppen)_3]^{2+}$.

Our early efforts to prepare $[Ru(dppen)_3]^{2+}$, by treatment of *trans*-**1a** with two equivalents of AgOTf (TfO^- is triflate, $CF_3SO_3^-$) and one of dppen in 1,2-dichloroethane (DCE), eventually gave a complex mixture ($^{31}P\text{-}\{^1H\}$ NMR spectroscopic evidence). However, it was clear that some unusual chemistry was involved. Initially, no AgCl precipitate formed, although a reaction clearly occurred (colour change; several *cis*-$[RuX_2(dppen)_2]$ and other, broad, resonances seen in the $^{31}P\text{-}\{^1H\}$ NMR spectrum). Furthermore, other unusual products have been characterised from the reactions of $[RuCl_2(dppm)_2]$ with silver salts in the presence of CO.[13]

We have therefore investigated the reaction of complex *trans*-**1a** and related diphosphine complexes *trans*-$[RuCl_2(diphos)_2]$ (diphos = $Ph_2PCH_2PPh_2$, dppm, *trans*-**1b**; $Ph_2PNHPPh_2$, dppa, *trans*-**1c**; or dppe, *trans*-**1d**) with silver(I) salts in more detail. Preliminary accounts of this work,[14] and of the formation of related $[Ru(diphos)_3]^{2+}$,[15] have appeared. While our studies were in progress, Wolf and co-workers reported a similar case of *trans* to *cis* isomerisation of $[RuCl_2(dppm)_2]$, catalysed by CuCl.[16]

Experimental

Physical methods

Details of spectrometers used in this study were previously described.[10,17] Except where otherwise noted, the following standard conditions were employed for spectroscopic measurements: FAB mass spectra were recorded in 3-nitrobenzyl alcohol matrices using xenon bombardment, $^{31}P\text{-}\{^1H\}$ NMR spectra in 1,2-dichloroethane solution in a 10 mm diameter tube, using $CDCl_3$ in a coaxial 5 mm tube for locking, and ^1H NMR spectra using $CDCl_3$ solutions in 5 mm diameter tubes.

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† Electronic supplementary information (ESI) available: FAB-MS spectra of *cis*-**1a**/**2a** and *cis*-**1b**/**2b** mixtures. See http://www.rsc.org/suppdata/dt/b0/b009645h/

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Samples for EXAFS spectroscopy were lightly ground with BN in a pestle and mortar, and packed in aluminium sample holders between Sellotape windows. Data were collected at the ruthenium and silver K-edges using a liquid nitrogen-cooled cryostat, in transmission mode on Station 9.2 of the Daresbury Synchrotron Radiation Source. A Si(220) crystal monochromator, detuned to reject 50% of the incident signal to minimise harmonic contamination, was employed. Data were processed using the Daresbury program EXCALIB, the background was subtracted using EXBACK and the isolated EXAFS data were analysed by fitting a theoretical curve to the experimental k^3-weighted EXAFS spectra using EXCURV 98.[18] Theoretical fits were obtained by adding shells of backscattering atoms around the central absorber atom, and refining the Fermi energy E_f, the absorber–scatterer distances r, and the Debye–Waller factors, to minimise the R-factor. The number of scatterers, N, was taken as an integer value giving the best fit. Only shells giving a significant improvement in the R factor have been included in the final fits.

Synthetic chemistry

All reactions were carried out under nitrogen or argon atmospheres using Schlenk techniques. The ligands dppm and dppe were purchased from Aldrich and used as received, and dppen[1] and dppa[19] were prepared by literature methods. Ruthenium(III) chloride hydrate (41–43% Ru) was a loan from Johnson-Matthey. Silver(I) and thallium(I) salts were purchased from Aldrich and used as received. Complexes *trans*-[RuCl$_2$(diphos)$_2$] (diphos = dppen, *trans*-**1a**;[10] dppm, *trans*-**1b**;[20] dppa, *trans*-**1c**;[21] or dppe, *trans*-**1d**[22]) were conveniently prepared in 80–95% yield from [RuCl$_2$(PPh$_3$)$_3$][23] using the method published for *trans*-**1a**.[10] Complexes *cis*-[RuCl$_2$(diphos)$_2$] (diphos = dppen, *cis*-**1a**;[10] or dppm, *cis*-**1b**[20]) were prepared by thermal isomerisation of the *trans* isomers. [OsCl$_2$(dppm)$_2$] (*cis* and *trans* isomers) were prepared by a literature method.[20] Although methods are given mainly for tetrafluoroborate salts, in all cases except where noted the corresponding triflate salt could be prepared similarly.

***cis*-[RuCl$_2$(dppa)$_2$], *cis*-1c.** Complex *trans*-**1c** (2.0 g, 2.12 mmol) was dissolved in the minimum volume of DCE. The solution was refluxed for 20 h, then allowed to cool to room temperature. Hexane (100 cm^3) was added slowly, with scratching, and the bright yellow product filtered off and dried *in vacuo*. Yield 1.95 g, 98%. Found: C, 59.73; H, 4.37; N, 2.81%. $C_{48}H_{42}Cl_2N_2P_4Ru\cdot0.5C_2H_4Cl_2$ requires C, 59.31; H, 4.47; N, 2.82%. FAB-MS data: *m/z* 942 (100), M$^+$; 907 (42), [M − Cl]$^+$; and 893 (27%), [M − Cl − HCl]$^+$. ^{31}P-{^{1}H} NMR: δ +62.8 and +37.2 ('virtual' t's, AA′XX′, $|J_{AX} + J_{AX'}|$ 76 Hz). Selected ^{1}H NMR: δ 8.1–6.6 (40 H, m's, aromatic) and +3.65 (2H, s, br; NH).

***trans*-[RuCl(dppen)$_2$(μ-Cl)Ag]BF$_4$, *trans*-2a.** To complex *trans*-**1a** (0.15 g, 0.16 mmol) dissolved in 1,2-dichloroethane (DCE; 40 cm^3) was added AgBF$_4$ (0.034 g, 0.175 mmol) at room temperature. The mixture was stirred for 1 h. The volume was then reduced to 20 cm^3 *in vacuo* and the product precipitated by addition of hexanes (20 cm^3). The yellow-green solid was filtered off and dried *in vacuo*. Yield 0.135 g, 75%. Found: C, 54.77; H, 4.18%. $C_{52}H_{44}AgBCl_2F_4P_4Ru$ requires C, 53.87; H, 3.82%. FAB-MS data: *m/z* 964 (100), [RuCl$_2$(dppen)$_2$]; and 929 (95%), [RuCl(dppen)$_2$]. ^{31}P-{^{1}H} NMR: δ +9.52 (s).

***trans*-[RuCl(dppm)$_2$(μ-Cl)Ag]OTf, *trans*-2b.** Prepared similarly from complex *trans*-**1b** and AgOTf in 57% yield. Found: C, 52.17; H, 3.86%. $C_{51}H_{44}AgCl_2F_3O_3P_4RuS$ requires C, 51.14; H, 3.70%. FAB-MS data: *m/z* 940 (28), [RuCl$_2$(dppm)$_2$]; and 905 (100%), [RuCl(dppm)$_2$]. ^{31}P-{^{1}H} NMR: δ + 13.97 (s). The corresponding tetrafluoroborate salt, with essentially identical spectroscopic properties, was similarly prepared in 70% yield using AgBF$_4$.

***cis*-[{Ru(dppen)$_2$(μ-Cl)$_2$}$_n$Ag]BF$_4$ (mixture of n = 1 or 2 species), *cis*-2a.** To complex *trans*-**1a** (0.30 g, 0.31 mmol) in DCE (50 cm^3) was added AgBF$_4$ (0.06 g, 0.31 mmol). The mixture was brought to reflux and stirred for 10 min. The reaction mixture was then examined by ^{31}P-{^{1}H} NMR spectroscopy at 25 °C; see Results and Discussion section. A yellow-green solid could be isolated by reducing the volume to 20 cm^3 *in vacuo*, and precipitating with hexanes (10 cm^3). Yield 60–70% based on Ru (assuming 1 : 1 Ru:Ag). Found: C, 55.13; H, 4.12%. $C_{52}H_{44}AgBCl_2F_4P_4Ru$ requires C, 53.87; H, 3.82% (some variability; a typical example is quoted). FAB-MS data: *m/z* 2037 (4), [{Ru(dppen)$_2$(μ-Cl)$_2$}$_2$Ag]$^+$; 964 (22), [RuCl$_2$(dppen)$_2$]; and 929 (65%), [RuCl(dppen)$_2$]. ^{31}P-{^{1}H} NMR: pairs of singlets at δ +16.89, −5.92; +15.23, −4.62; +13.80, −3.61 respectively.

***cis*-[{Ru(dppm)$_2$(μ-Cl)$_2$}$_n$Ag]BF$_4$ (mixture of n = 1 or 2 species), *cis*-2b.** Prepared similarly from complex *trans*-**1b** and AgBF$_4$ in DCE solution. Characterised *in situ* by ^{31}P-{^{1}H} NMR spectroscopy. Yellow-green solid isolated as for *cis*-**2a**. Yield 70%. FAB-MS data: *m/z* 1990 (10), [{Ru(dppm)$_2$(μ-Cl)$_2$}$_2$Ag]$^+$; 940 (14), [RuCl$_2$(dppm)$_2$]; and 905 (100%), [RuCl(dppm)$_2$]. ^{31}P-{^{1}H} NMR: pairs of triplets at δ *ca.* +0.4, −27.48; +0.4, −26.02; +0.4, −24.76 ($|J_{AX} + J_{AX'}|$ all 73 Hz). The corresponding triflate salt, with essentially identical spectroscopic properties, was similarly prepared using AgOTf.

***cis*-[{Ru(dppa)$_2$(μ-Cl)$_2$}$_n$Ag]BF$_4$ (mixture of n = 1 or 2 species), *cis*-2c.** Yellow-green solid, prepared similarly, from *trans*-**1c**. Yield 73%. FAB-MS data: *m/z* 1992 (3), [{Ru(dppa)$_2$(μ-Cl)$_2$}$_2$Ag]$^+$; 942 (100), [RuCl$_2$(dppa)$_2$]; and 907 (23%), [RuCl(dppa)$_2$]. ^{31}P-{^{1}H} NMR: pairs of triplets at δ *ca.* +63.0, +34.50; +63.0, +36.57; +63.0, +38.50.

Attempted synthesis of [RuCl(dppen)$_2$]BF$_4$ 3a. To complex *trans*-**1a** (0.23 g, 0.24 mmol) in DCE (50 cm^3) was added AgBF$_4$ (0.047 g, 0.24 mmol) at reflux. After 40 min, the solution was allowed to cool to room temperature, and then filtered through Keiselguhr. The volume was reduced to 20 cm^3 *in vacuo*. The product was precipitated by addition of hexanes (10 cm^3). The dark red solid was filtered off and dried *in vacuo*. Yield 0.18 g. FAB-MS data: *m/z* 964 (10), residual [RuCl$_2$(dppen)$_2$] species; and 929 (100%), [RuCl(dppen)$_2$]. Electronic spectrum (cm^{-1}) (DCE, 1 mM Ru): 14,080 and 21,280 (sh). ^{31}P-{^{1}H} NMR: δ +21.64, −0.13 (br, s); weak peaks due to *cis*-**2a** species.

Attempted syntheses of [RuCl(dppm)$_2$]BF$_4$ 3b and of [RuCl(dppa)$_2$]BF$_4$ 3c. The same procedure was followed, using complexes *trans*-**1b** and *trans*-**1c** respectively. Neither **3b** nor **3c** could be isolated free of *cis*-**2b** or *cis*-**2c** respectively. Spectroscopic data for **3b**: electronic spectrum (cm^{-1}) (DCE, 1 mM Ru) 19,300; ^{31}P-{^{1}H} NMR δ: +6.21 and −20.58 (br, t's, $|J_{AX} + J_{AX'}|$ 70 Hz). Spectroscopic data for **3c**: electronic spectrum (cm^{-1}) (DCE, 1 mM Ru) 19,100; ^{31}P-{^{1}H} NMR: δ +65.6 and +39.5 (br, t's, $|J_{AX} + J_{AX'}|$ 70 Hz).

[RuCl(dppe)$_2$]BF$_4$ 3d. To a solution of complex *trans*-**1d** (0.26 g, 0.27 mmol) in CH$_2$Cl$_2$ (50 cm^3) was added AgBF$_4$ (0.057 g, 0.29 mmol). The mixture was then heated at reflux for 40 min, and allowed to cool to room temperature. The AgCl was filtered from the dark red solution, and the volume reduced to 20 cm^3 *in vacuo*. The product was precipitated with hexanes, filtered off and dried *in vacuo*. Yield 0.14 g, 56%. Analytical and spectroscopic data were as previously published.[24]

***cis*-[RuCl(CH$_3$CN)(dppen)$_2$]CF$_3$SO$_3$ *cis*-4a.** Complex *trans*-**1a** (0.22 g, 0.23 mmol) in DCE (50 cm^3) was treated with AgOTf (0.0643 g, 0.25 mmol), and the solution refluxed for 40 min, becoming dark red. Upon addition of CH$_3$CN (10 cm^3), the colour changed to pale yellow, and AgCl precipitated. The reaction mixture was refluxed for 10 min and then cooled and filtered. It was evaporated to dryness, and the residue examined by ^{31}P-{^{1}H} NMR spectroscopy (see Results). It was then recrystallised from CH_2Cl_2–hexanes. Yield 0.17 g, 70%. Found: C, 58.14; H, 4.21; N, 1.19%. $C_{55}H_{47}ClF_3NO_3P_4RuS{\cdot}0.5CH_2Cl_2$ requires C, 58.83; H, 4.27; N, 1.24%. FAB-MS data: *m*/*z* 970 (54), M^+; 929 (100), $[M - CH_3CN]^+$; and 893 (80%), $[M - CH_3CN - HCl]^+$. ^{31}P-{^{1}H} NMR: δ +0.8 (1P, m, P_A, J_{AB} 328, J_{AM} 25, J_{AX} 12), −1.5 (1P, m, P_B, J_{BM} 8, J_{BX} 21 Hz), +12.6 (1P, m, P_X) and +19.3 (1P, m, P_M).

***cis*-[RuCl(CH$_3$CN)(dppm)$_2$]BF$_4$ *cis*-4b.** Prepared from complex *trans*-**1b** as for *cis*-**4a**. Yield 87%. Found: C, 59.09; H, 4.50; N, 1.22%. $C_{52}H_{47}BClF_4NP_4Ru{\cdot}0.5CH_2Cl_2$ requires C, 58.62; H, 4.50; N, 1.30%. FAB-MS data: *m*/*z* 946 (44), M^+; 905 (100), $[M - CH_3CN]^+$, and 869 (59%), $[M - CH_3CN - HCl]^+$. ^{31}P-{^{1}H} NMR: δ +0.1 (1P, m, P_M), −6.1 (1P, m, P_X), −19.6 (1P, m, P_A, J_{AB} 322, J_{AM} 43, J_{AX} 24), and −25.2 (1P, m, P_B, J_{BM} 32, J_{BX} 44 Hz).

***cis*-[RuCl(CH$_3$CN)(dppa)$_2$]BF$_4$ *cis*-4c.** Prepared from complex *trans*-**1c** as for *cis*-**4a**. Yield 80%. Found: C, 56.18; H, 4.22; N, 3.50%. $C_{50}H_{45}BClF_4N_3P_4Ru{\cdot}0.5CH_2Cl_2$ requires C, 56.29; H, 4.30; N, 3.90%. FAB-MS data: *m*/*z* 948 (34), M^+; 907 (100), $[M - CH_3CN]^+$, 871 (45), $[M - CH_3CN - HCl]^+$. ^{31}P-{^{1}H} NMR: δ +59.5 (2P, overlapping m, P_X, P_M), +43.0 (1P, m, P_A, J_{AB} 324, J_{AM} 43, J_{AX} 24) and +36.2 (1P, m, P_B, J_{BM} 32, J_{BX} 44 Hz).

***trans*-[RuCl(CH$_3$CN)(dppen)$_2$]PF$_6$ *trans*-4a.** Complex *trans*-**1a** (0.30 g, 0.31 mmol) was dissolved in DCE (60 cm^3) and the solution brought to reflux. To this was added $[Cu(CH_3CN)_4]PF_6$ (0.12 g, 0.32 mmol), and reflux continued for 30 min. The mixture was cooled to room temperature, the CuCl filtered off and the yellow solution evaporated to dryness. Although the product was pure by ^{31}P-{^{1}H} NMR spectroscopy, it was recrystallised from CH_2Cl_2–hexane. Yield 0.271 g, 78%. Found: C, 56.44; H, 4.22; N, 1.20%. $C_{54}H_{47}ClF_6NP_5Ru{\cdot}0.5CH_2Cl_2$ requires C, 56.54; H, 4.18; N, 1.21%. FAB-MS data: *m*/*z* 970 (81), M^+; 929 (100), $[M - CH_3CN]^+$; and 893 (96%), $[M - CH_3CN - HCl]^+$. ^{31}P-{^{1}H} NMR: δ +13.92 (s). Selected ^{1}H NMR: δ 6.28 (‘virtual’ quintet, C=CH$_2$, app. J_{PH} 6 Hz) and 1.25 (s, 3H, CH$_3$CN).

***trans*-[RuCl(CH$_3$CN)(dppm)$_2$]BF$_4$ *trans*-4b.** Complex *trans*-**1b** (0.22 g, 0.23 mmol) was dissolved in 5 : 1 DCE–CH$_3$CN (60 cm^3) at reflux. AgBF$_4$ (0.048 g, 0.25 mmol) was added, and the solution refluxed for 30 min. After cooling to room temperature the AgCl precipitate was filtered off and the solution evaporated to dryness. The pale yellow residue was recrystallised from CH_2Cl_2–hexanes. Yield 0.174 g, 72%. Found: C, 59.00; H, 4.37; N, 1.31%. $C_{52}H_{47}BClF_4NP_4Ru{\cdot}0.5CH_2Cl_2$ requires C, 58.62; H, 4.50; N, 1.30%. FAB-MS data: *m*/*z* 946 (54), M^+; 905 (100), $[M - CH_3CN]^+$; and 869 (59%), $[M - CH_3CN - HCl]^+$. ^{31}P-{^{1}H} NMR: δ −10.2 (s). Selected ^{1}H NMR: δ 5.14 (br t, 4H, PCH$_2$P) and 1.04 (s, 3H, CH$_3$CN).

***trans*-[RuCl(CH$_3$CN)(dppa)$_2$]BF$_4$ *trans*-4c.** Made from complex *trans*-**1c** as for *trans*-**4b**. Yield 89%. Found: C, 55.37; H, 4.23; N, 3.70%. $C_{50}H_{45}BClF_4N_3P_4Ru{\cdot}CH_2Cl_2$ requires C, 54.69; H, 4.23; N, 3.75%. FAB-MS data: *m*/*z* 948 (32), M^+; 907 (100), $[M - CH_3CN]^+$; and 871 (51%), $[M - CH_3CN - HCl]^+$. ^{31}P-{^{1}H} NMR: δ +58.73 (s). Selected ^{1}H NMR: δ 3.71 (s, broad, 2H, PNHP) and 1.31 (s, 3H, CH$_3$CN).

***cis*-[RuCl(CO)(dppen)$_2$]CF$_3$SO$_3$ *cis*-5a.** Complex *trans*-**1a** (0.26 g, 0.27 mmol) in DCE (50 cm^3) was treated with AgOTf (0.072 g, 0.28 mmol), and the solution refluxed for 30 min, becoming dark red. Upon exposure to CO gas the solution became colourless, and AgCl precipitated. The reaction mixture was then cooled and filtered. It was evaporated to dryness, and the residue examined by ^{31}P-{^{1}H} NMR spectroscopy (see Results). It was then recrystallised from CH_2Cl_2–hexanes. Yield 0.256 g, 85%. Found: C, 56.49; H, 3.90%. $C_{54}H_{44}ClF_3O_4P_4RuS{\cdot}0.5CH_2Cl_2$ requires C, 56.98; H, 3.95%. FAB-MS data: *m*/*z* 957 (100), M^+, 929 (32), $[M - CO]^+$; and 893 (47%), $[M - CO - HCl]^+$. IR (ν_{CO}, cm^{-1}) 1997. ^{31}P-{^{1}H} NMR: δ +9.7 (1P, m, P_C), +4.9 (1P, m, P_A, J_{AB} 277, J_{AM} 25, J_{AX} 18), −1.5 (1P, m, P_B, J_{BM} 18, J_{BX} 28 Hz) and −9.0 (1P, m, P_X).

***cis*-[RuCl(CO)(dppm)$_2$]CF$_3$SO$_3$ *cis*-5b.** Synthesized from complex *trans*-**1b** as for *trans*-**5a**. Yield 79%. Found: C, 56.06; H, 4.06%. $C_{52}H_{44}ClF_3O_4P_4RuS$ requires C, 56.06; H, 4.03%. FAB-MS data: *m*/*z* 933 (100), M^+; 905 (19), $[M - CO]^+$; and 869 (27%), $[M - CO - HCl]^+$. IR (ν_{CO}, cm^{-1}) 2001. ^{31}P-{^{1}H} NMR: δ −9.3 (1P, m, P_C), −13.5 (1P, m, P_A, J_{AB} 278, J_{AM} 43, J_{AX} 19), −30.0 (1P, m, P_B, J_{BM} 31, J_{BX} 43 Hz) and −31.5 (1P, m, P_X).

***trans*-[RuCl(CO)(dppen)$_2$]CF$_3$SO$_3$ *trans*-5a.** Complex *trans*-**1a** (0.34 g, 0.35 mmol) in DCE (50 cm^3) was heated to reflux. Then CO was passed through the solution, and AgOTf (0.090 g, 0.35 mmol) added. On addition of the silver salt the solution rapidly became colourless and AgCl precipitated. The solution was refluxed for 30 min, then allowed to cool to room temperature. It was filtered and then evaporated to dryness. The residue was examined by ^{31}P-{^{1}H} NMR spectroscopy, then recrystallised from CH_2Cl_2–hexanes. Yield 0.27 g, 82%. Found: C, 55.61; H, 3.83%. $C_{54}H_{44}ClF_3O_4P_4RuS{\cdot}CH_2Cl_2$ requires C, 55.45; H, 3.89%. FAB-MS data: *m*/*z* 957 (100), M^+; 929 (5), $[M - CO]^+$; and 893 (16%), $[M - CO - HCl]^+$. IR (ν_{CO}, cm^{-1}) 1972. ^{31}P-{^{1}H} NMR: δ +9.4 (s). Selected ^{1}H NMR: δ 6.53 (m, 4H, C=CH$_2$).

***trans*-[RuCl(CO)(dppm)$_2$]CF$_3$SO$_3$ *trans*-5b.** Synthesized from complex *trans*-**1b** as for *trans*-**5a**. Yield 78%. Found: C, 54.99; H, 3.85%. $C_{52}H_{44}ClF_3O_4P_4RuS{\cdot}CH_2Cl_2$ requires C, 54.53; H, 3.97%. FAB-MS data: *m*/*z* 933 (100), M^+; 905 (7), $[M - CO]^+$; and 869 (17%), $[M - CO - HCl]^+$. IR (ν_{CO}, cm^{-1}) 1974. ^{31}P-{^{1}H} NMR: δ −13.7 (s). Selected ^{1}H NMR: δ 5.20 (br t, 4H, PCH$_2$P).

Results

Reactions of *trans*-[RuCl$_2$(diphos)$_2$] (diphos = dppen, dppm or dppa) to form Ag$^+$ adducts

Solutions of *trans*-[RuCl$_2$(diphos)$_2$] (diphos = dppen, *trans*-**1a**; dppm, *trans*-**1b**; or dppa, *trans*-**1c**) in DCE were treated with 1 equivalent of fresh AgBF$_4$ at room temperature and the progress of the reactions was monitored by ^{31}P-{^{1}H} NMR spectroscopy. Initially, the singlet due to *trans*-**1a**–**1c** (at δ 14.9, −7.2 and 60.7 respectively) was replaced by another singlet (at δ 9.5, −14.9 and 54.6 respectively). These are assigned to chloride-bridged adducts, *trans*-[Cl(diphos)$_2$Ru(μ-Cl)Ag(μ-F–BF$_3$)] *trans*-**2a**–**2c**). The preference of Ag^{I} for linear coordination suggests the latter, at least in the solid state. Moreover, solids with approximately the correct microanalyses for this formulation were obtained by precipitation with hexane for *trans*-**2a** and *trans*-**2b**, and the IR spectrum of these showed distinct splitting of the B–F stretching bands. Use of AgOTf gave identical results. The ^{31}P chemical shifts of the *trans*-**2a**–**2c** complexes in DCE solution were identical for both anions, which may suggest that the Ag^{I}–BF$_4$ or Ag^{I}–OTf interactions evident in the solid state are weak in solution and may be replaced by solvent coordination; there is precedent for coordination of α,ω–dichloroalkanes to Ag^{I}.[25]

On warming a solution of complex *trans*-**1a** and AgBF$_4$ to 50 °C for 5 minutes there was initially no precipitation of AgCl, but several new peaks appeared in the ^{31}P-{^{1}H} NMR

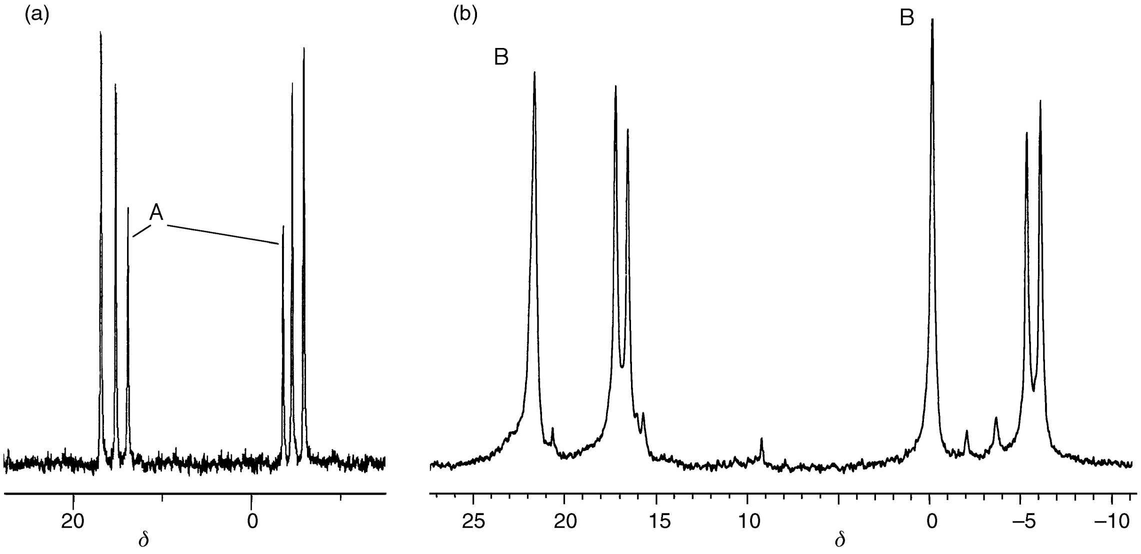

Fig. 1 ^{31}P-{^{1}H} NMR spectra showing the progress of a reaction between *trans*-[$RuCl_2$(dppen)$_2$] *trans*-**1a** and $AgBF_4$ (1 equivalent) in 1,2-dichloroethane. (a) Reaction mixture after addition of $AgBF_4$ at room temperature, and bringing to reflux for ten minutes. (b) Reaction after 40 minutes at reflux. Peaks labeled 'A' are assigned to *cis*-**1a**, 'B' to five-coordinate [RuCl(dppen)$_2$]$^+$ **3a**.

spectrum, the relative intensities of which suggested that they were pairs of related singlets (Fig. 1a). The weakest of these pairs, at δ −3.6 and 13.9, are very close to the resonances previously observed for *cis*-[$RuCl_2$(dppen)$_2$] *cis*-**1a** which we made previously by thermal isomerisation.‡ Two other pairs appeared at δ −6.0 and 16.9 and at −4.7 and 15.2. We ascribe these as due to a mixture of *cis*-**1a** moieties in which the chloride ligands are interacting with Ag^I, and in which the complexes differ only in their coordination at silver. Examples might include 1 : 1 complexes such as [(dppen)$_2$Ru(μ-Cl)$_2$Ag(μ-F)BF_3] and/or [(dppen)$_2$Ru(μ-Cl)$_2$Ag(DCE)]BF_4, and 2 : 1 complexes such as [{Ru(dppen)$_2$(μ-Cl)$_2$}$_2$Ag]BF_4 (Scheme 1). The presence of a mixture of 1 : 1 and 2 : 1 complexes would account for the presence of some free *cis*-**1a** in the mixture. We designate this mixture of products *cis*-**2a**. We have been unable to isolate its individual components. However, precipitation with hexanes gave a yellow-green solid. Microanalyses (C and H) of this gave values which were high for a formulation [$RuCl_2$(dppen)$_2$]·$AgBF_4$, and somewhat variable. Interestingly, the FAB mass spectra of different samples consistently showed a cluster of peaks centred at *m*/*z* 2038, correct for [{Ru(dppen)$_2$(μ-Cl)$_2$}$_2$Ag]$^+$, and at *m*/*z* 1169, almost the correct value (1170) required for a complex [(dppen)$_2$Ru(μ-Cl)$_2$Ag(DCE)]$^+$. We attempted to optimise the synthesis of individual 1 : 1 and 2 : 1 Ru : Ag species by varying the reaction stoichiometry, but an equilibrium mixture was always obtained.

The electronic spectra of *trans*-[RuX_2(diphosphine)$_2$] usually show two d–d bands in the visible region, a lower energy band assigned as $^1A_{1g} \longrightarrow {}^1E_g$ and a higher energy band assigned as $^1A_{1g} \longrightarrow {}^1A_{2g}$, assuming approximate D_{4h} symmetry.[26,27] Complexes *cis*-[RuX_2(diphosphine)$_2$] usually have d–d bands at somewhat higher energy, which accounts for their generally paler colour. Consistent with this, the spectrum of *cis*-**2a** in CH_2Cl_2 showed two shoulders in the visible region, a weak one at 23,300 cm^{-1} and a stronger one at 27,000 cm^{-1}, on the low-energy tail of a charge transfer band. The spectrum was similar in profile to that of *cis*-**1a**, which shows a shoulder at 22,730 and a peak at 27,170 cm^{-1}. In contrast, *trans*-**1a** shows a single, rather broad, peak at 24,150 cm^{-1}.

A DCE solution of complex *trans*-**1b** was refluxed with $AgBF_4$ for 10 min, and the ^{31}P-{^{1}H} NMR spectrum recorded. It showed three pairs of second order triplets. The three downfield triplets of each pair all overlap at δ *ca.* 0.4, and the upfield triplets occur at δ −24.8, −26.0 and −27.5 ($|J_{AX} + J_{AX'}|$ 73 Hz). It is clear that isomerisation to a mixture, *cis*-**2b**, similar to *cis*-**2a**, has occurred. Similarly, on warming solutions of *trans*-**1c** with $AgBF_4$ the singlet at δ 60.7 was replaced by three pairs of second order triplets, the least intense of which (at δ 36.6 and 62.7) are very close to the values found for *cis*-[$RuCl_2$(dppa)$_2$] *cis*-**1c**, which we prepared independently by thermal isomerisation of *trans*-**1c** for comparison. The other signals are due to a mixture of Ag$^+$ adducts, *cis*-**2c**.

The FAB mass spectra of the *cis*-**2b** mixture, isolated as a solid by evaporation of the solvent, showed molecular ion peaks for [{Ru(diphosphine)$_2$(μ-Cl)$_2$}$_2$Ag]$^+$ at *m*/*z* 1990, together with peaks characteristic of the [Ru(dppm)$_2Cl_2$] moiety. There was, however, no sign of a cluster of peaks corresponding to a complex [(dppm)$_2$Ru(μ-Cl)$_2$Ag(DCE)]$^+$. This mixture was further characterised using EXAFS; see below.

Use of AgOTf gave similar results on reaction with all three complexes **1a**–**1c**, with only minor differences in product distribution. Interestingly, we have since found that these reactions can also be performed in more polar solvent systems (thf/EtOH) with no significant change in products.

Formation of [RuCl(diphos)$_2$]$^+$

We next examined the use of catalytic quantities (5–10 mol%) of AgOTf or $AgBF_4$ to effect *trans*–*cis* conversions with complexes **1a**–**1c**, but were unsuccessful because further reactions took place when heating was prolonged, and AgCl precipitated. We therefore investigated these reactions. When *trans*–**1a** was refluxed for 40 mins with one equivalent of $AgBF_4$ in DCE two new, broad singlet resonances in the ^{31}P-{^{1}H} NMR spectrum, at δ 0.5 and 20.9, grew at the expense of the signals due to *cis*-**1a**/**2a** (Fig. 1b). In particular, the signals due to *cis*-**1a** disappeared completely. The solution changed to intense red, and AgCl precipitated. The electronic spectrum of the red solution showed a new band at 14,100 cm^{-1}, consistent with the formation of a five–coordinate complex [RuCl(dppen)$_2$]$^+$ **3a**.[28,29] When the reaction was prolonged the new resonances continued to grow at the expense of those for *cis*-**2a**, but additional resonances due to unidentified decomposition products were also apparent, and it was not possible to isolate **3a** pure.

When complex *trans*-**1b** was refluxed for 30 min with $AgBF_4$

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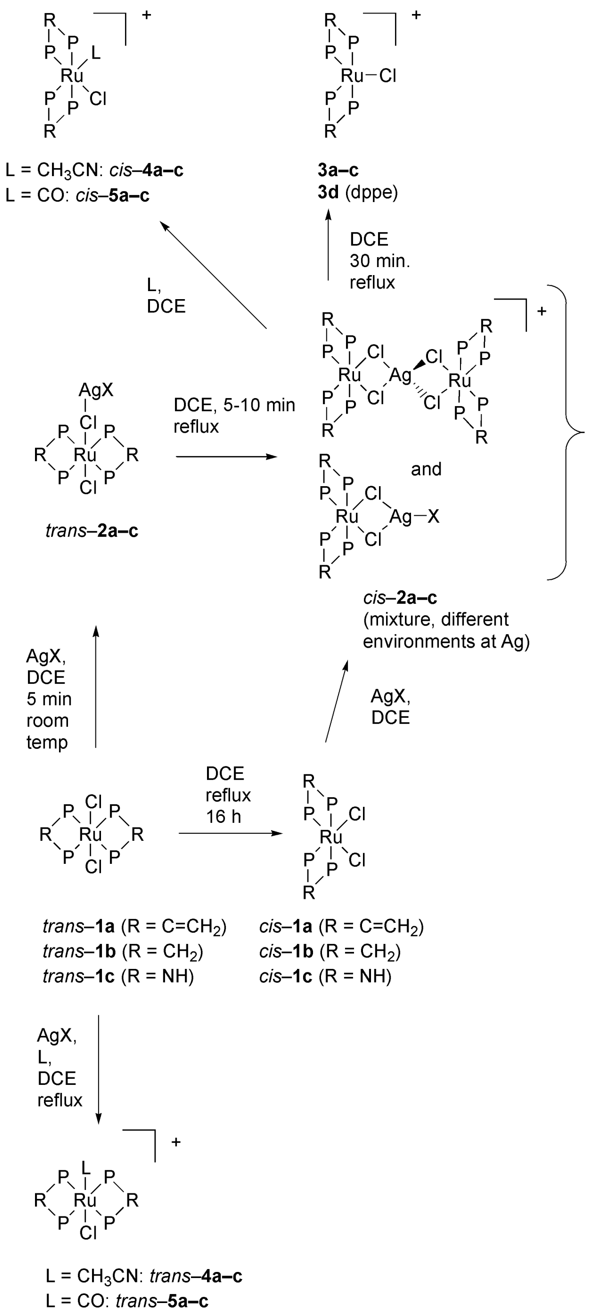
‡ The reason why these complexes show two apparent singlets in their ^{31}P-{^{1}H} NMR spectra, instead of the more usual second-order triplets, has been discussed in an earlier paper.[10]



Scheme 1

in DCE, AgCl precipitated, the colour became intense red, and an additional pair of rather broad second order triplets, assigned as due to $[RuCl(dppm)_2]^+$ **3b**, appeared in the ^{31}P-$\{^1H\}$ NMR spectrum at δ −20.6 and 6.2 (Fig. 2). At the same time the weakest pair of triplets present in the spectrum of the *cis*-**1b**/*cis*-**2b** mixture had disappeared (some small additional resonances due to unidentified impurities are also present, *e.g.* the multiplet at δ *ca.* −6). The electronic spectrum showed a new band at 19,600 cm^{-1}. Similarly, treatment of *trans*-**1c** with $AgBF_4$ in refluxing DCE for 40 min resulted in the growth of two new second order triplets, at δ 39.5 and 65.6, in the ^{31}P-$\{^1H\}$ NMR spectrum, and the appearance of a new band at 14,500 cm^{-1} in the electronic spectrum, due to **3c**. Although treatment of *cis*-**1a**–**1c** with silver salts in DCE resulted in the formation of somewhat larger proportions of **3a**–**3c** (^{31}P-$\{^1H\}$ NMR evidence) this route also failed to yield pure samples.

Treatment of *trans*-$[RuCl_2(dppe)_2]$ *trans*-**1d** with AgOTf in DCE resulted only in halide abstraction to give dark red $[RuCl(dppe)_2]$OTf, previously isolated (as a PF_6^- salt) by treatment of a CH_2Cl_2 solution of *cis*-**1d** with $NaPF_6$ suspension.[24]

Table 1 Comparison of EXAFS and crystallography parameters for *cis*-$[RuCl_2(dppm)_2]$ *cis*-**1b**

		Crystallography		EXAFS		
Shell type		C.N.	r_{cr}/Å (av.)	r_{ex}/Å	$2\sigma^2$/Å^2	Residual
1	P	4	2.324	2.32	0.010	
2	Cl	2	2.447	2.42	0.013	
3	C	2	3.122	3.11	0.016	
4	C	8	3.655	3.70	0.029	26.3

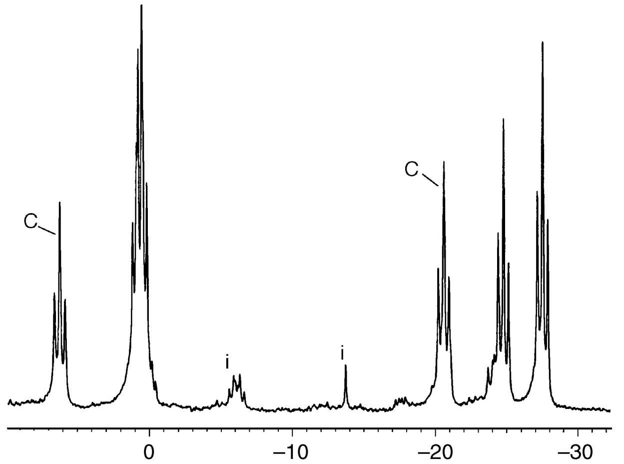


Fig. 2 ^{31}P-$\{^1H\}$ NMR spectrum of the species obtained upon reaction of *trans*-$[RuCl_2(dppm)_2]$ *trans*-**1b** and $AgBF_4$ (1 equivalent) in 1,2-dichloroethane at reflux for 40 min. Peaks labeled 'C' are assigned to $[RuCl(dppm)_2]^+$ **3b**, those labelled 'i' to unidentified impurities.

Complex *cis*-**1d**, or adduct(s) of *cis*-**1d** with Ag^I, could not be detected in the reaction mixture under any conditions, although the reaction was slow enough to follow by ^{31}P-$\{^1H\}$ NMR spectroscopy.

EXAFS studies on *cis*-1b/*cis*-2b mixture

Since we were unable to obtain crystals of any of the Ru–Cl–Ag complexes we have employed EXAFS in an effort to obtain some structural information. A sample of the *cis*-**1b**/*cis*-**2b** mixture was prepared using AgOTf in DCE. *cis*-**1b** was used as a model compound since its crystal structure has been determined.[30] The analysis of the ruthenium K-edge EXAFS spectrum of *cis*-**1b** is compared in Table 1 with the crystal structure data. The final model included four P atoms at 2.32 Å and two Cl atoms at 2.42 Å (the major contribution to the fit), and eight C atoms at 3.70 Å. Two more C atoms at 3.11 Å improved the fit only marginally. The data agree well with those from the crystal structure, as expected.

The Fourier transform of the silver K-edge EXAFS spectrum of the *cis*-**1b**/*cis*-**2b** mixture shows two clear peaks (Fig. 3). The best fit for the first shell was with one O atom at 2.43 Å, and two Cl atoms at 2.79 Å (Table 2). The second shell was fitted with one, or two, Ru atoms at 3.94 Å, with the latter giving slightly the better fit. The ruthenium K-edge spectrum (Fig. 3) did not show a clear outer shell in the Fourier transform. The inner sphere was fitted with four P atoms at 2.33 Å and two Cl atoms at 2.41 Å, although the contribution of the Cl atoms made less of an improvement to the fit than for *cis*-**1b**. This may indicate a change in coordination about Ru, the most likely cause being an asymmetry in the two Ru–Cl distances. A shell of eight C atoms at 3.69 Å improved the fit significantly. The addition of a contribution from a silver atom at 4.05 Å did result in further improvement of the fit, but not sufficiently to demonstrate conclusively the presence of this shell with the ruthenium data alone.

Table 2 Comparison of various fits to EXAFS spectra for the *cis*-**1b**/*cis*-**2b** mixture (triflate). The final fits are in bold characters

Edge	Fit no.	Shell	Atom	No.	r_{ex}/Å	$2\sigma^2$/Å^2	Residual
Ag K-edge	1	1	O	4	2.60	0.025	56.3
Ag K-edge	2	1	Cl	4	2.72	0.033	44.0
Ag K-edge	3	1	O	1	2.42	0.005	
		2	Cl	2	2.77	0.017	42.6
Ag K-edge	4	1	O	1	2.43	0.001	
		2	Cl	2	2.78	0.017	
		3	Ru	1	3.94	0.008	39.4
Ag K-edge	**5**	**1**	**O**	**1**	**2.43**	**0.001**	
		2	**Cl**	**2**	**2.79**	**0.016**	
		3	**Ru**	**2**	**3.94**	**0.014**	**38.8**
Ru K-edge	1	1	P	4	2.35	0.011	22.3
Ru K-edge	2	1	P	4	2.34	0.012	
		2	Cl	2	2.42	0.035	21.8
Ru K-edge	3	1	P	4	2.34	0.012	
		2	Cl	2	2.41	0.037	
		3	C	8	3.69	0.022	20.5
Ru K-edge	**4**	**1**	**P**	**4**	**2.33**	**0.012**	
		2	**Cl**	**2**	**2.41**	**0.032**	
		3	**C**	**8**	**3.69**	**0.022**	
		4	**Ag**	**1**	**4.05**	**0.022**	**20.1**

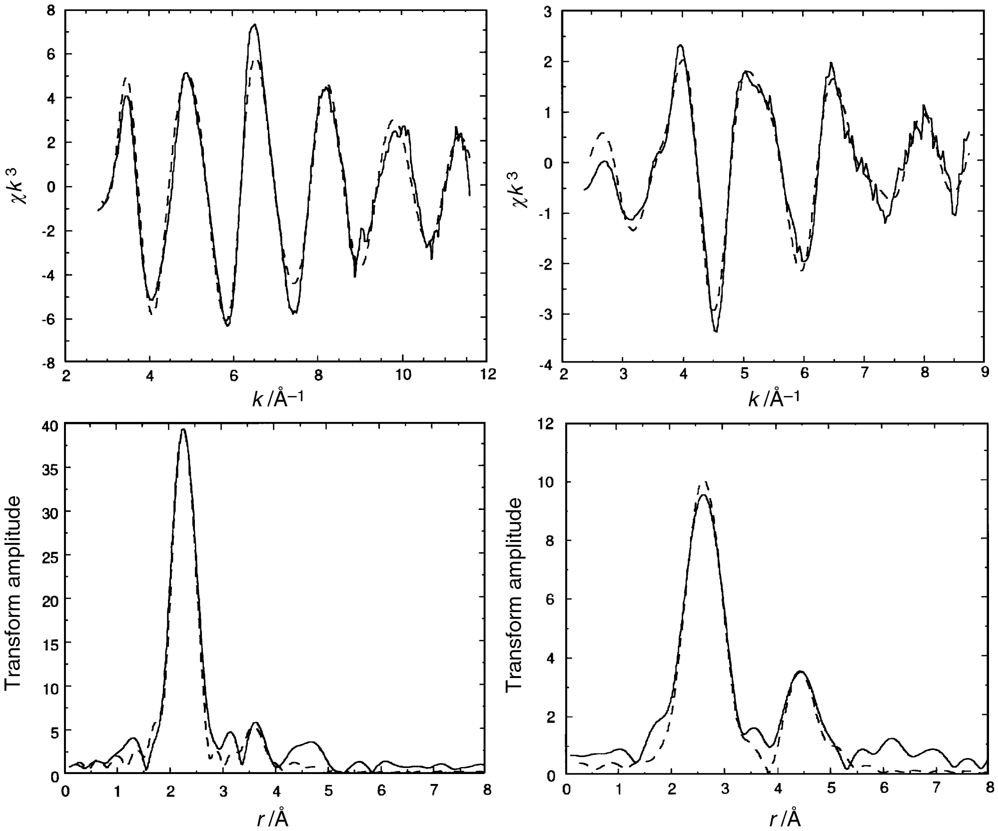


Fig. 3 Ruthenium (left) and silver (right) K-edge EXAFS spectra (top) and Fourier transforms (bottom) for the *cis*-**1b**/*cis*-**2b** mixture (triflate salt). The solid lines are experimental data and the dotted lines are for the best fits (those shown in bold in Table 2).

Treatment of complexes *trans*-1a–1c with other Lewis acids

It was of interest to see whether the isomerisation of *trans*-**1a**–**1c** could be effected by other Lewis acid catalysts. Recently, Zhu *et al.* reported that the isomerisation of *trans*-**1b** to *cis*-**1b** was catalysed by CuCl.[16] On treatment of *trans*-**1a** with an excess of CuCl in CH_2Cl_2 or DCE at room temperature its ^{31}P-{^1H} resonance broadened, and shifted slightly to δ +15.9. On heating at reflux *partial* conversion into a mixture of *cis* species occurred. These are probably analogous to [{Ru(dppm)$_2$-(μ-Cl)$_2$}$_2$Cu][CuCl$_2$], characterised crystallographically, and related species differing in their coordination at Cu^{I}.[16] However, CuCl did not catalyse the conversion of *trans*-**1a** into *cis*-**1a** under conditions used successfully for conversion of *trans*-**1b** into *cis*-**1b**.[16]

On treatment of complex *trans*-**1a** with the more powerful Lewis acid [Cu(CH$_3$CN)$_4$]BF$_4$ in DCE, *trans*-[RuCl(CH$_3$CN)-(dppen)$_2$]BF$_4$ **4a** and a precipitate of CuCl were the only products (see below).

Thallium(I) salts are sometimes used as non–oxidising alternatives to silver(I) salts in halide abstraction reactions. Interestingly, when *trans*-**1a** was treated with TlOTf in DCE at room temperature the singlet at δ +14.9 was replaced by two resonances in the ^{31}P-{^1H} NMR spectrum of the reaction mixture, a broad singlet at δ +13.5 and a sharp singlet at δ +9.5, the latter similar to that of *trans*-[RuCl(dppen)$_2$(μ-Cl)Ag]$^+$. Similarly, when *trans*-**1b** was treated with TlOTf in DCE, the singlet at δ −7.2 was replaced by a broad singlet at δ −8.1 and a sharp singlet at δ −13.9, the latter similar to that of *trans*-$[RuCl(dppm)_2(\mu\text{-}Cl)Ag]^+$. FAB mass spectrometry of the solids precipitated upon addition of hexanes to these reaction mixtures revealed a cluster of peaks centred at near the correct values (*m*/*z* 1167 and 1145 respectively) for *trans*-$[RuCl(diphos)_2(\mu\text{-}Cl)Ag]^+$. However, when these reaction mixtures were brought to reflux no further changes were observed, In particular, no evidence for *trans* into *cis* conversion was seen, and no halide abstraction occurred.

Reactions of $[OsCl_2(diphos)_2]$ with silver(I) salts

In an attempt to obtain Os–Cl–Ag adducts we investigated the reaction of *trans*-$[OsCl_2(dppm)_2]$ with silver(I) salts in DCE. However, we obtained only silver metal, and $[OsCl_2(dppm)_2]^+$; it is known that M^{II}–M^{III} redox potentials for such osmium(II) complexes are significantly less positive than for analogous ruthenium complexes.[20,31,32] Since the potentials are also considerably more positive for *cis* complexes than *trans*,[20] we also investigated the reaction of *cis*-$[OsCl_2(dppm)_2]$ with silver(I) salts in DCE. Interestingly, this appeared to result in halide abstraction initially, with the formation of a red solution and a AgCl precipitate. However, even in the absence of oxygen, the red solution rapidly turned green and the isolated product was paramagnetic.

Syntheses of $[RuCl(diphosphine)_2(L)]^+$ from $[RuCl_2(diphosphine)_2]$ by halide abstraction

A preliminary investigation of the use of Ag^I-mediated isomerisation of complexes *trans*-**1a**–**1c** in ligand substitution reactions was undertaken. Treatment of *trans*-**1a** with $AgBF_4$ in DCE at 50 °C for 40 min, *followed* by treatment with CH_3CN, gave a precipitate of AgCl. Treatment of the remaining yellow solution with hexanes gave, exclusively, *cis*-$[RuCl(CH_3CN)(dppen)_2]BF_4$ *cis*-**4a**. This was identified by the fact that its $^{31}P\text{-}\{^1H\}$ NMR spectrum was almost identical with *cis*-$[RuCl(CH_3CN)(dppen)_2]Cl$, which forms when *cis*-**1a** is dissolved in CH_3CN,[10] and by its FAB mass spectrum, which showed a cluster of peaks at *m*/*z* 970 due to M^+, and at 929 due to $[M - CH_3CN]^+$. Alternatively, *cis*-**4a** could be made (as the PF_6^- salt) by treatment of *cis*-**1a** with one equivalent of $[Cu(CH_3CN)_4]PF_6$ in DCE; CuCl precipitated from the reaction mixture in this case.

Interestingly, in contrast, when complex *trans*-**1a** was brought to reflux in 5 : 1 CH_3CN : DCE in the presence of 1 mol of $AgBF_4$, AgCl precipitated immediately. Pale yellow *trans*-$[RuCl(CH_3CN)(dppen)_2]BF_4$ *trans*-**4a** was the main product ($^{31}P\text{-}\{^1H\}$ NMR evidence), but was difficult to separate from an unidentified impurity (δ +23.3). A better method was treatment of *trans*-**1a** with one equivalent of $[Cu(CH_3CN)_4]PF_6$ in DCE, which afforded exclusively *trans*-**4a** (as the PF_6^- salt) and CuCl. The *trans*-**4a** had a very similar FAB mass spectrum to that of *cis*-**4a**, but its $^{31}P\text{-}\{^1H\}$ NMR spectrum showed a singlet at δ +13.9.

Treatment of complex *trans*-**1a** with $AgBF_4$ in DCE at 50 °C for 40 min, *followed* by bubbling CO through the solution, gave > 95% *cis*-$[RuCl(CO)(dppen)_2]BF_4$ *cis*-**5a** ($^{31}P\text{-}\{^1H\}$ NMR spectroscopic evidence), from which pure *cis*-**5a** was isolated on recrystallisation. This had $\nu(CO)$ at 1997 cm^{-1} in its IR spectrum, and its $^{31}P\text{-}\{^1H\}$ NMR spectrum showed an ABMX spin system (Fig. 4). When *trans*-**1a** was treated with CO in DCE, and one equivalent of $AgBF_4$ was then added, *trans*-$[RuCl(CO)(dppen)_2]BF_4$ *trans*-**5a** was obtained. This had a similar FAB mass spectrum to that of *cis*-**5a**, but $\nu(CO)$ at 1972 cm^{-1} in its IR spectrum and a singlet at δ +9.3 in its $^{31}P\text{-}\{^1H\}$ NMR spectrum.

Therefore, the stereochemical outcome of the reactions of complex *trans*-**1a** with silver salts and CH_3CN, or CO, is dependent upon whether or not Ag^+-mediated isomerisation is allowed to occur before introduction of the neutral ligand.

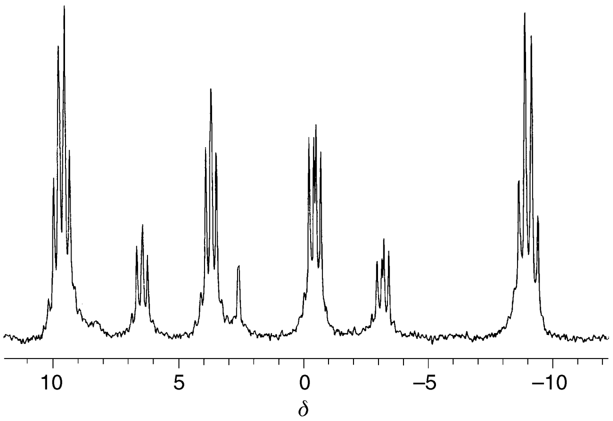


Fig. 4 $^{31}P\text{-}\{^1H\}$ NMR spectrum of the crude product from treatment of complex *trans*-**1a** with $AgBF_4$ in DCE at 50 °C for 40 min, *followed* by bubbling CO through the solution. It can be seen that the major product, with an ABMX spin system, is *cis*-$[RuCl(CO)(dppen)_2]BF_4$ *cis*-**5a**.

Treatment of complex *trans*-**1b** with $AgBF_4$ in DCE at 50 °C, followed by removal of the solvent and treatment of the residue with CH_3CN, gave mainly *cis*-$[RuCl(CH_3CN)(dppm)_2]BF_4$ *cis*-**4b**, although two minor species were also detected in the crude product by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy. A pair of 'virtual' triplets at δ −18.0 and −3.1 was due to *cis*-$[Ru(CH_3CN)_2(dppm\text{-}P,P')_2]^{2+}$, and a singlet at δ −10.15 to *trans*-$[RuCl(CH_3CN)(dppm)_2]^+$ *trans*-**4b**. Pure *cis*-**4b** was isolated upon recrystallisation. Complex *trans*-**4b** was the only product when *trans*-**1b** was refluxed in 5 : 1 CH_3CN–DCE with one equivalent of $AgBF_4$. It too was isolated and fully characterised. Treatment of *trans*-**1b** with $AgBF_4$ in DCE at 50 °C, *followed* by bubbling with CO, gave *cis*-$[RuCl(CO)(dppm)_2]BF_4$ *cis*-**5b** in high yield after recrystallisation, whereas treatment of *trans*-**1b** with CO, then $AgBF_4$, in DCE, gave exclusively *trans*-$[RuCl(CO)(dppm)_2]BF_4$ *trans*-**5b**. The carbonyl complexes were isolated and fully characterised. Both carbonyl cations have been described previously.[33]

With the ligand dppa, treatment of complex *trans*-**1c** with one equivalent of $AgBF_4$ in 5 : 1 CH_3CN–DCE did not give exclusively *trans*-$[RuCl(CH_3CN)(dppa)_2]BF_4$ *trans*-**4c**, but 70% *trans*-**4c**, 25% *cis*-**4c** and 5% of an unidentified complex ($^{31}P\text{-}\{^1H\}$ NMR spectroscopy). Treatment of *trans*-**1c** with $AgBF_4$ in DCE for 40 min, *followed* by treatment with CH_3CN, gave exclusively *cis*-**4c**, as did treatment of *cis*-**1c** with $AgBF_4$ in CH_3CN, or with $[Cu(CH_3CN)_4]PF_6$ in DCE (PF_6^- salt).

Interestingly, treatment of *trans*-$[RuCl_2(dppe)_2]$ *trans*-**1d** with one equivalent of $[Cu(CH_3CN)_4]PF_6$ in DCE gave, after recrystallisation, *trans*-$[RuCl(CH_3CN)(dppe)_2]PF_6$ *trans*-**4d**. Treatment of *trans*-**1d** with $AgBF_4$ or AgOTf in the presence of CO, however, gave a mixture of *cis*- and *trans*-$[RuCl(CO)(dppe)_2]^+$ **5d**. The formation of **3d** *in situ* in DCE, *followed* by the addition of CH_3CN or CO, was stereoselective, giving *cis*-**4d** or *cis*-$[RuCl(CO)(dppm)_2]^+$ *cis*-**5d** respectively, in agreement with an earlier publication.[24]

The complexes *cis*-**5a** and -**5b** were not stable in CH_2Cl_2 solution, and slowly isomerised to *trans*-**5a** and -**5b**. It is likely that the CO ligand prefers to be *trans* to the π-donor Cl^- rather than the rival π-acceptor phosphine ligand.

Discussion

Ag^+–mediated isomerisations

The first products formed when complexes *trans*-**1a**–**1c** were treated with $AgBF_4$ were the adducts *trans*-**2a**–**2c**. There is plenty of precedent for interactions of this type between substitutionally inert metal halide complexes and Ag^I. For example, reaction of $[Ru_2Cl_4(PEtPh_2)_5]$, $[Ru_2Cl_3(PEtPh_2)_6]Cl$ or $[RuCl_2(PEtPh_2)_3]$ with AgCl resulted in phosphine migration from Ru to Ag, and the formation of $[Ru_2Cl_2(\mu\text{-}Cl)_3(PEtPh_2)_4Ag(PEtPh_2)]$, in which the $Ag(PEtPh_2)$ unit is coordinated to one of the terminal and two of the three bridging chloride ligands.[34] Reaction of $[M(C_5H_5)_2(NO)I]$ (M = Mo or W) with $AgBF_4$ or $AgSbF_6$ in CH_2Cl_2 gave precipitates of the corresponding adducts, $[M(C_5H_5)_2(NO)I\cdot AgY]$.[35] Moreover, when *trans*-**1b** was treated with CuCl its $^{31}P\text{-}\{^1H\}$ NMR resonance broadened and shifted slightly; this was attributed to the formation of *trans*-$[Cl(dppm)_2Ru(\mu\text{-}Cl)CuCl]$.[16]

Subsequently, and more rapidly (20–30 minutes) on warming, complexes *trans*-**2a**–**2c** isomerise cleanly to mixtures, *cis*-**1a**–**1c**/*cis*-**2a**–**2c**. In the absence of Ag^+, refluxing *trans*-**1a** in chlorobenzene for 16 h is necessary to effect 90% conversion into *cis*-**1a**.[10] Similarly, refluxing *trans*-**1b** in DCE for 16 h is necessary to effect conversion into *cis*-**1b**.[20] Recently, other workers reported that the isomerisation of *trans*-**1b** to *cis*-**1b** was catalysed by CuCl and CuI, and they were able to isolate, and characterise crystallographically, the heterotrimetallic chloride–bridged complex $[\{Ru(dppm)_2(\mu\text{-}Cl)_2\}_2Cu][CuCl_2]$.[16] On dissolution in CD_2Cl_2 the $^{31}P\text{-}\{^1H\}$ NMR spectrum showed that this complex was in equilibrium with a species with similar chemical shifts and coupling constants, assigned as $[(dppm)_2Ru(\mu\text{-}Cl)_2CuCl]$ in which Cu^I has trigonal planar coordination to all three chlorines, and another species with broad resonances for which the formulation *cis*-$[RuCl(dppm)_2(\mu\text{-}Cl)\}CuCl]$ was suggested, the broadening being ascribed to exchange of CuCl between the two chloride ligands.[16] Our observation of a cluster of peaks in the FAB mass spectra of *cis*-**2a**–**2c** corresponding to $[\{Ru(dppen)_2(\mu\text{-}Cl)_2\}_2Ag]^+$, the $^{31}P\text{-}\{^1H\}$ NMR data, and the EXAFS data all suggest that *cis*-**2a**–**2c** consist of a similar mixture of species differing only in their coordination at silver. In particular, although the ruthenium K-edge EXAFS spectrum of *cis*-**2b** showed only one distinct shell, and inclusion of a silver atom only resulted in a marginal fit improvement, the silver K-edge data did show two distinct shells. The fact that the inner shell could best be fitted with two Cl atoms at 2.77 Å (a reasonable distance for a Ru–Cl–Ag-bridge species[34]) and one O atom (for this triflate salt) suggests the possibility that a 1 : 1 species such as $[(dppen)_2Ru(\mu\text{-}Cl)_2Ag(\eta^1\text{-}OTf)]$ may be present, while the fact that the outer shell could be fitted well by between one and two ruthenium atoms lends support to the formulation of the mixture as a combination of *cis*-$Ru(\mu\text{-}Cl)_2Ag$ and *cis*-$\{Ru(\mu\text{-}Cl)_2\}_2Ag$ species.

The mechanism of the Ag–mediated isomerisation to *cis* stereochemistry is likely to be related to that suggested for the Cu^I-mediated isomerisation of complex *trans*-**1b**, namely that coordination of one of the chlorides to Ag^I weakens the Ru–Cl bond, allowing facile conversion into the thermodynamically preferred *cis* isomer.[16] It is possible that some additional driving force may come from the chelate effect, on formation of the *cis*-$Ru(\mu\text{-}Cl)_2Ag$ bridges. These complexes, from the point of view of silver(I) coordination chemistry, make an interesting comparison with halogenocarbon complexes $[Ag(I\{CH_2\}_nI)_2]PF_6$, described recently.[36]

Formation of $[RuCl(diphos)_2]^+$

Like these silver(I)–iodocarbon complexes, *cis*-**2a**–**2c** slowly react to form silver halide. The colour changes and the appearance of new peaks in the $^{31}P\text{-}\{^1H\}$ NMR spectra both indicate that five-coordinate $[RuCl(diphosphine)_2]^+$ **3a**–**3d** are formed. The tendency for six–coordinate $[RuCl_2(diphosphine)_2]$ to dissociate in polar solvents to $[RuCl(diphosphine)_2]Cl$ increases with increasing chelate ring size and with increasing size of substituents at phosphorus,[24,28,29,37] and no examples of $[RuCl(diphosphine)_2]^+$ have been structurally characterised for four-membered chelate ring ligands. However, such species have been suggested as intermediates in ligand substitution reactions,[13,38] and *trans*-$[RuCl_2(2,2\text{-}dppp)_2]$ (2,2-dppp = 2,2-bis[diphenylphosphino]propane) dissociates to $[RuCl(2,2\text{-}dppp)_2]^+$ in $CHCl_3$.[39] Although, coincidentally, ruthenium(III) complexes $[RuCl_2(diphosphine)_2]BF_4$ have visible spectra similar to those of $[RuCl(diphos)_2]^+$,[31] and silver(I) salts have been used to oxidise other $[RuX_2(diphosphine)_2]$ to Ru^{III},[31] the ruthenium(III) formulation can be excluded since (i) for **3a** we confirmed that the precipitate was AgCl (not Ag) by dissolving it in aqueous ammonia, and (ii) normal $^{31}P\text{-}\{^1H\}$ NMR spectra are observed, which would not be the case for paramagnetic low spin d^5 Ru^{III}.

Although our experience is that the chemistry of complexes *cis*-**1a** and *cis*-**1b** differs in some respects,[10] and other workers have found differences between the behaviour of dppm and dppa as ligands,[40,41] we did not observe any significant difference in the reactions of *trans*-**1a**–**1c** with silver salts.

Other Lewis acids

There are several examples of adducts between ruthenium(II) halide complexes and Tl^I, and their chemistry suggests that the interaction can be remarkably strong. For example, treatment of a CH_2Cl_2 solution of $[Ru(H)Cl(PP_3)]$ ($PP_3 = P[CH_2CH_2PPh_2]_3$) with aqueous $TlPF_6$ resulted in extraction of Tl^+ from the aqueous layer and formation of $[(H)(PP_3)Ru(\mu\text{-}Cl)Tl]PF_6$,[42] and treatment of $[RuCl_2(PPh_3)([9]aneS_3)]$ ($[9]aneS_3$ = 1,4,7-trithiacyclononane) with $TlPF_6$ gave a chloride-bridged Ru_2Tl_2 cluster dication.[43] Both of these complexes were characterised by X-ray crystallography. However, although $^{31}P\text{-}\{^1H\}$ NMR spectroscopy indicates that *trans*-**1c** and -**1b** interact in an as yet undefined way with TlOTf in DCE, this Lewis acid does not induce *trans* to *cis* conversion.

CuCl does not act as a catalyst for conversion of complex *trans*-**1a** into *cis*-**1a**, although it does do so for *trans*-**1b**. We previously observed that the thermal *trans*–*cis* conversion of **1a** was more difficult than for **1b**. Stoichiometric amounts of CuCl do cause the formation of some *cis* Ru–Cl–Cu species from *trans*-**1a**, but the reaction was not quantitative. We therefore tried $[Cu(CH_3CN)_4]PF_6$, which we anticipated might be a more powerful Lewis acid than CuCl, but this simply abstracted halide from *trans*-**1a**–**1c**, giving CuCl and *trans*–$[RuCl(CH_3CN)(dppen)_2]PF_6$. This is, in fact, the most convenient route to these complexes.

$^{31}P\text{-}\{^1H\}$ NMR spectra of *cis*-$[RuCl(diphosphine)(L)]^+$

The $^{31}P\text{-}\{^1H\}$ NMR spectrum of complex *cis*-**5a** (Fig. 4) showed that all four phosphorus atoms are inequivalent. The two mutually *trans* phosphorus resonances, at δ *ca.* +4.9 and −1.5, form an AB system (J_{AB} is 277 Hz, a value typical of P *trans* P coupling in ruthenium(II) complexes[44–46]), with further coupling to the two mutually *cis* phosphorus atoms. The values of $|J_{PP}|$ for the latter are all very similar (24–26 Hz). Although it is unusual for the two mutually *trans* phosphorus atoms in complexes like *cis*-**5a** to show a marked chemical shift difference, there is precedent for this type of spectrum with a complex involving a *cis*-$[Ru(dppm'P,P')_2]$ moiety. Crystallographically characterised $[(dppm\text{-}P,P')_2Ru(\mu\text{-}Cl)(\mu\text{-}H)Rh(cod)]BF_4$ (cod = cycloocta-1,5-diene) showed two resonances for the *trans* phosphorus atoms at δ −2.0 and −18.9 (J_{PP} 294 Hz).[47]

The $^{31}P\text{-}\{^1H\}$ NMR spectrum of complex *cis*-**4a** was then re-recorded with improved signal/noise ratio. The 'multiplet' near δ 0[10] was found to be, in fact, the two inner lines of a closely spaced AB system (δ P_A 1.0; δ P_B −0.4; J_{AB} 320 Hz) with further coupling to the other *cis* phosphorus atoms. Moreover, all four phosphorus atoms in the $^{31}P\text{-}\{^1H\}$ NMR spectrum of *cis*-**4b** are also inequivalent. The two mutually *trans* phosphines of *cis*-**4b** resonate at δ −20.13 and −24.89 (J_{AB} 319 Hz).

In conclusion, we have discovered a silver(I)-mediated isomerisation of *trans*-[RuCl$_2$(diphos)$_2$] (diphos = four-membered chelate diphosphine) to *cis*-oriented Ru–Cl–Ag species, and have shown that, as a consequence, the stereochemistry of complexes [RuCl(L)(diphos)$_2$]$^+$, synthesized from *trans*-[RuCl$_2$(diphos)$_2$] by Ag^I-mediated halide abstraction, can be controlled by the order of addition of the reagents.

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