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Synthesis, Crystal Structures and NMR Spectroscopic Studies on Ruthenium Complexes with Phosphanylacetal and Phosphanylthioacetal Ligands

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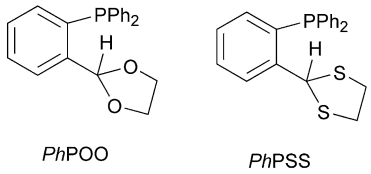
The chemistry of the mixed P,S-donor ligands [2-(1,3-dioxolan-2-yl)phenyl]diphenylphosphane (*Ph*POO, **1**), and [2-(1,3-dithiolan-2-yl)phenyl]diphenylphosphane (*Ph*PSS, **2**) with the Ru^{II} precursors $[RuCl_2(PPh_3)_3]$ and $[RuCl_2(4\text{-cymene})]_2$ has been investigated. The structures of the resulting complexes were analysed by X-ray crystallography and ^1H, ^{13}C and ^{31}P NMR spectroscopy, and their activity as catalysts for hydrosilylation was examined. Reaction of **1** with $[RuCl_2(PPh_3)_3]$ in methanol solution produced $[RuCl_2(PhP(OMe)_2)_2]$ (**3**) {with $[RuCl_2(MeOH)\{PhP(OMe)_2\}(PPh_3)]$ (**3a**) as a side product}, whereas the same reaction with $[RuCl_2(4\text{-cymene})]_2$ produced $[RuCl_2(PhPOO)_2]$ (**4**). The dioxolane complex **4** showed fluxional behaviour by NMR spectroscopy, whereas **3** did not. Reaction of *Ph*PSS with$[RuCl_2(PPh_3)_3]$ in methanol solution produced $[RuCl_2(PhPSS)_2]$ (**5**), and reaction with $[RuCl_2(4\text{-cymene})]_2$ produced the cationic complex $[RuCl(4\text{-cymene})(PhPSS)]^+$ (**6**) by precipitation with $NaBPh_4$. In solution both **5** and **6** exist in two isomeric forms, and neither shows evidence of fluxionality at room temperature. Of the complexes tested only the acetal species **3** showed any significant hydrosilylation activity.

Introduction

There is considerable current interest in mixed-donor ligands combining phosphanyl donor groups with other donor atoms.[1–3] As part of our investigation of mixed P,S-donor ligands[4–6] we have been exploring the chemistry of [2-(1,3-dioxolan-2-yl)phenyl]diphenylphosphane (**1**, *Ph*POO),[7] and [2-(1,3-dithiolan-2-yl)phenyl]diphenylphosphane (**2**, *Ph*PSS) (Scheme 1). As well as possessing an enantiotopic carbon centre, these ligands have several possible binding modes, and have the potential to show hemilabile and fluxional behaviour. In this paper, we describe the chemistry of **1** and **2** with various ruthenium(II) precursors and detail the crystal structures and solution-phase NMR spectroscopy of the complexes formed. The catalytic activity of the complexes in a model hydrosilylation reaction has also been investigated.



*Ph*POO *Ph*PSS

Scheme 1.

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Results and Discussion

Ligand **1** is an intermediate in the preparation of 2-(diphenylphosphanyl)benzaldehyde.[7] Ligand **2** was prepared from the reaction of 2-(diphenylphosphanyl)benzaldehyde, *p*-toluenesulfonic acid monohydrate (TsOH) (5 mol-%) and 1,2-ethanedithiol, in ethanol. This ligand is soluble in many solvents, including methanol, chlorinated solvents, diethyl ether and hexane. Elemental analysis, positive-ion ESMS and ^1H and ^{31}P NMR spectroscopy were all consistent with the proposed formula.

The reaction of $[RuCl_2(PPh_3)_3]$ with *Ph*POO in methanol resulted in the formation of *trans*-$[Ru^{II}Cl_2(PhP(OMe)_2)_2]$ (**3**). This complex is soluble in dichloromethane, sparingly soluble in acetonitrile and insoluble in most other solvents including diethyl ether and dimethyl sulfoxide. Identical products are formed whether the stoichiometry of the reaction is 1:1 or 1:2 for ruthenium precursor/ligand. The yield is maximised with the higher ligand/metal ratio. The reaction is surprising in that the dioxolane has been converted to an acetal by reaction with solvent in the absence of added acid. Complex **3** (Figure 1) is pseudo-octahedral in geometry, with each of the $PhP(OMe)_2$ ligands bound to the metal centre in a bidentate fashion through the phosphorus atom and one of the OMe oxygen atoms, the remaining OMe group is pendant. The Ru–Cl bond lengths are ca. 2.4 Å, Ru–O ca. 2.2 Å and Ru–P ca. 2.3 Å. These are comparable with values for Ru–Cl, Ru–O and Ru–P bond lengths in the literature.[8–11] Bond lengths within the acetal groups are comparable with those of $[ReCl(CO)_3\{2\text{-}CH(OMe)_2C_5H_4N\}]$, which also contains one coordinated

and one pendant OMe group.[12] The molecular unit of **3** is chiral, and both stereogenic carbon centres are in the same configuration. However, the centrosymmetric space group indicates that the crystal is racemic. Proton, carbon and phosphorus NMR spectroscopy of **3** in $CDCl_3$ gave sharp, well-resolved spectra, and show the solution structure to be consistent with that in the solid state.

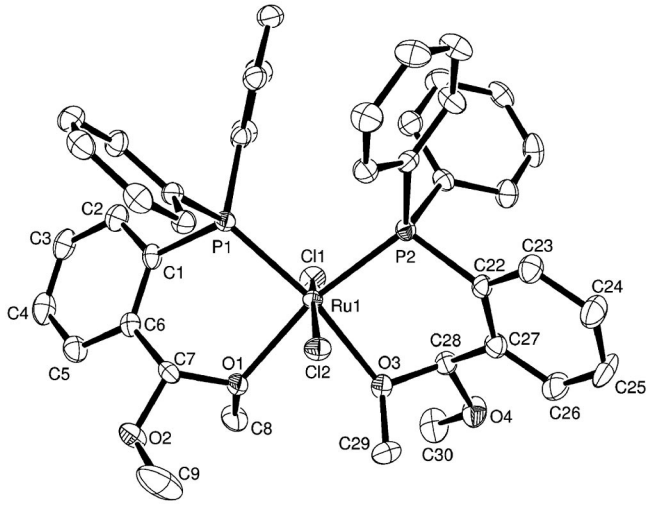


Figure 1. ORTEP representation of **3** (40% thermal ellipsoids, hydrogen atoms omitted for clarity).

A possible mechanism for the conversion of **1** to the acetal in the complex is that nucleophilic attack of the dioxolane carbon atom by the solvent is promoted by coordination of the adjacent oxygen atom to the ruthenium centre. The metal atom could thus be acting as a Lewis acid catalyst for the hydrolysis. There are very few reported acetal complexes of ruthenium.[13] However, several diacetal–rhenium and –platinum complexes reported in the literature have a similar structure, with only one oxygen atom of each diacetal ligand coordinated to the metal centre and the second alkoxy group pendant. NMR spectroscopy studies in solution have shown these complexes to be fluxional, with coordination switching between the two oxygen atoms of a single acetal group.[12] If this occurs in **3** at room temperature it must be slower than the NMR spectroscopic timescale, since both the ^1H and ^{13}C NMR spectra show two distinct methoxy signals. After recrystallisation of crude **3**, the filtrate was allowed to stand in air, and a further species crystallised. This was found to be $[Ru^{II}Cl_2(MeOH)\{PhP(OMe)_2\}(PPh_3)]$ (**3a**) by X-ray crystal structure determination (Figure 2). In this case one $PhP(OMe)_2$ ligand is bound to the metal centre in the bidentate mode, and the remainder of the pseudo-octahedral coordination sphere is made up of two chlorido ligands, a triphenylphosphane ligand (from the Ru precursor) and a methanol molecule. The bond lengths and angles of **3a** are very similar to those of **3**. The Ru–O bonds of the coordinated $PhP(OMe)_2$ and MeOH ligands differ, however [these are 2.274(2) Å and 2.209(2) Å, respectively]. Complex **3a** crystallised in a non-centrosymmetric space group, but is twinned by inversion as shown by the Flack parameter of 0.43(2). In principle, therefore, it may be possible to separate the two enantiomers of this complex by crystallisation.

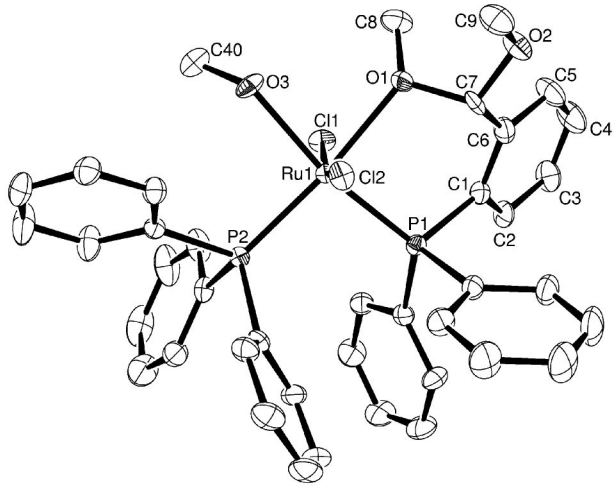


Figure 2. ORTEP representation of **3a** (40% thermal ellipsoids, hydrogen atoms omitted for clarity).

Reaction of $[RuCl_2(4\text{-cymene})]_2$ with *Ph*POO under reflux in methanol resulted in the formation of a single isomer, *trans*-$[Ru^{II}Cl_2(PhPOO)_2]$ (**4**). This complex is soluble in chlorinated solvents but insoluble in hexane and diethyl ether. The structure of the complex was determined by single-crystal X-ray diffraction analysis (Figure 3). The molecular unit is chiral, and both stereogenic carbon centres are in the same configuration. However, the centrosymmetric space group indicates that the crystal is racemic. The structure shows the two phosphorus atoms and the two oxygen atoms to be *cis* to one another, and the two chlorido ligands to be approximately *trans*, as in the structure of **3**. The bond angles are also very similar. For example, the Cl(1)–Ru(1)–Cl(2) angle is 165.53(4)°. The Ru–Cl, Ru–O and Ru–P bond lengths measure ca. 2.4 Å, ca. 2.2 Å and ca. 2.3 Å, respectively. Interestingly, the use of $[RuCl_2(4\text{-cymene})]_2$ as the ruthenium precursor in this reaction results in the dioxolane ligand remaining intact. Lindner and co-workers have studied a series of ruthenium complexes with phosphane–dioxolane ligands and demonstrated their potential as ring-opening metathesis polymerisation catalysts.[14–16] In some examples the dioxolane showed fluxional behaviour though, to be dependent on the strength of the Ru–O bond as dictated by the co-ligands present at the ruthenium centre. At ambient temperature in $CDCl_3$ both the proton and carbon NMR spectra of **4** show several broad peaks. The ^1H NMR spectrum contains two broad singlets at δ = 4.22 and 4.75 ppm attributed to the CH_2 groups and a third at δ = 6.43 ppm corresponding to the CH groups. Sharp multiplets due to the phenyl protons are observed in the range 6.65–7.81 ppm. In the ^{13}C NMR spectrum a broad singlet is present at δ = 65.5 ppm due to the overlapping CH_2 group signals, a single peak at δ = 101.8 ppm for the equivalent CH groups and the phenyl carbon resonances are ob-

served in the range δ = 125.7–139.6 ppm. At this temperature the ^{31}P NMR spectrum shows a single peak at δ = 54.36 ppm. The observed spectral broadening is presumably the result of a fluxional process. Two types of fluxional behaviour are possible. Firstly, two or more of the five possible geometrical isomers could be present in solution with interconversion taking place between them on the NMR spectroscopic timescale. The second possibility is that the Ru–O bond in the complex is sufficiently labile, such that rotation about the C–C bond between the phenyl ring and the two oxygen atoms brings first one oxygen atom of each ligand into contact with the metal centre and then the other (Scheme 2).

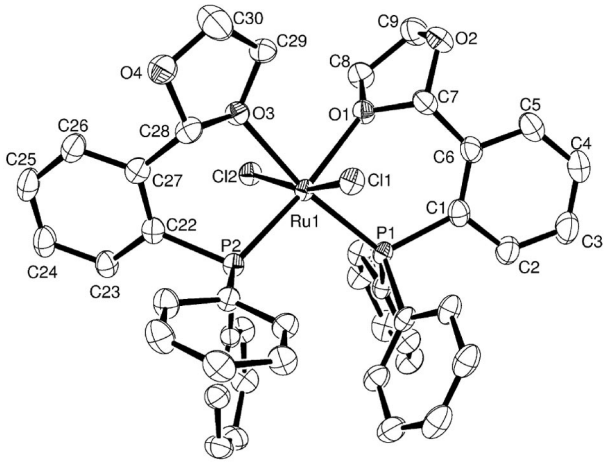
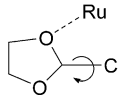


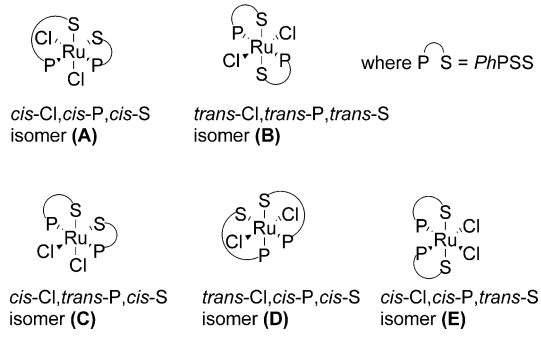
Figure 3. ORTEP representation of **4** (40% thermal ellipsoids, hydrogen atoms omitted for clarity).



Scheme 2. Possible rotation around the C–C bond of *Ph*POO.

Variable-temperature ^1H and ^{31}P NMR spectroscopy experiments were carried out. Upon increasing the temperature to 50 °C the proton spectrum became sharper, especially in the CH_2 and CH regions. Presumably, the increase in temperature causes the isomers to interconvert more rapidly and/or speeds up rotation about the C–C bond of the ligand. Upon decreasing the temperature to –20 °C and then to –30 °C, these same peaks also became much sharper, and several multiplets were observed in both the CH_2 and CH regions. At –30 °C the broad signal at δ = 65.5 ppm in the room-temperature ^{13}C NMR spectrum is separated into several sharp singlets, and the ^{31}P NMR spectrum displays a whole range of singlet and doublet peaks. The multiplets seen in the ^{31}P NMR spectrum suggest that several isomers are present at low temperature, with both *cis* and *trans* phosphane ligands. The appearance of isomers at low temperature is analogous to the room-temperature behaviour of the more rigid PSS ligands discussed below. The lability of the O-donor atom of the dioxolane permits reorganisation of the coordination sphere to occur. Upon warming to room temperature the original spectra were observed again. This dynamic process is similar to that observed for acetal–rhenium and –platinum complexes.[12] It is interesting that complex **4** shows fluxional behaviour in the NMR spectrum (between –30 and 50 °C), with evidence for both rotation of the acetal group and geometric reorganisation, whereas complex **3** appears rigid at room temperature. Possibly the orientation of the methyl groups in the latter offers more steric resistance to rotation than the dioxolane group of the former.

Reaction of $[RuCl_2(PPh_3)_3]$ with *Ph*PSS in refluxing methanol produced $[RuCl_2(PhPSS)_2]$ (**5**) in good yield. To the best of our knowledge this is the first reported ruthenium complex of a phosphanyl–dithiolane ligand. The ^{31}P NMR ($CDCl_3$) spectrum shows two doublets and a singlet [δ = 30.1 ($J_{P\text{-}P}$ = 27 Hz), 32.6 ($J_{P\text{-}P}$ = 27 Hz), 46.1 ppm], which indicates the presence of two species. The species appear to be stable over time in $CDCl_3$ and are likely to be two of the five possible geometrical isomers of **5** (Scheme 3). Peak integration shows an approximately 1:1 ratio. Of the possible isomers, only **A** possesses inequivalent phosphorus atoms, and hence the observed pair of doublets at δ = 30.1 and 32.6 ppm are assigned to this isomer. The dithiolane CH_2 and CH groups in this isomer are also inequivalent. The diastereotopic CH_2 protons give rise to eight individual signals between δ = 2.58 and 4.80 ppm in the ^1H NMR spectrum, whereas the CH protons give values of δ = 5.54 and 6.04 ppm, respectively. The second isomer could not be identified by NMR spectroscopy alone, but must be more symmetrical since it shows only four signals due to CH_2 protons (δ = 3.12–3.48 ppm) and one signal for the CH proton (δ = 6.52 ppm).



Scheme 3. Geometrical isomers of $[RuCl_2(PhPSS)_2]$ (**5**).

The structure of complex **5** was determined by single-crystal X-ray diffraction analysis (Figure 4), and shows the two phosphorus atoms, both chlorido ligands and both sulfur atoms to be *trans* to one another, corresponding to isomer **B**. This is in contrast to the structure obtained of **4** in which the chlorido ligands are *trans* to one another but both phosphorus and oxygen atoms are *cis*. Similar bond angles occur in both structures, however. For example, in **5** the P(1)–Ru(1)–S(1) angle is 88.81(4)° and the analogous angle in **4** [P(1)–Ru(1)–O(1)] is 86.6(1)°. Interestingly, the Ru–P bond of 2.3836(12) and 2.3976(12) Å are substantially longer than the corresponding Ru–P bonds of **4**

[2.2649(12) and 2.2562(13) Å]. Ru–Cl bond lengths are similar in both structures (Table 1). The structure of **5** is chiral, and both stereogenic carbon centres are in the same configuration. However, as before, the centrosymmetric space group indicates that the crystal is racemic.

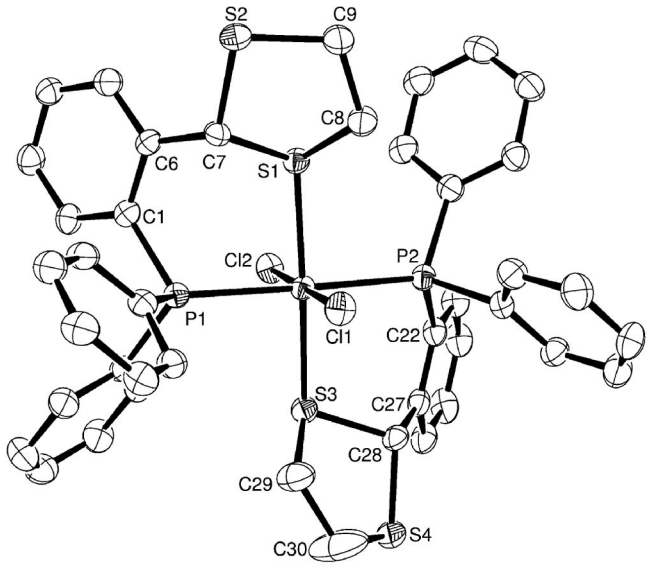


Figure 4. ORTEP representation of **5** (40% thermal ellipsoids, hydrogen atoms omitted for clarity).

Table 1. Selected bond lengths and angles for complexes **3**–**6**.

3	Ru(1)–Cl(1)	2.3958(8)	Cl(1)–Ru(1)–Cl(2)	167.87(3)
	Ru(1)–P(1)	2.2668(9)	Cl(1)–Ru(1)–P(1)	87.86(3)
	Ru(1)–O(1)	2.221(2)	Cl(2)–Ru(1)–P(1)	101.68
			Cl(1)–Ru(1)–O(1)	89.97(6)
			P(1)–Ru(1)–O(1)	90.63(6)
			P(1)–Ru(1)–P(2)	100.49(3)
3a	Ru(1)–Cl(1)	2.3722(7)	Cl(1)–Ru(1)–Cl(2)	164.12(3)
	Ru(1)–P(1)	2.2688(8)	Cl(1)–Ru(1)–P(1)	89.41(3)
	Ru(1)–O(1)	2.274(2)	Cl(1)–Ru(1)–O(1)	89.41(3)
			P(1)–Ru(1)–O(1)	89.63(6)
			P(1)–Ru(1)–P(2)	89.63(6)
			Cl(1)–Ru(1)–O(3)	85.45(6)
4	Ru(1)–Cl(1)	2.3923(11)	Cl(1)–Ru(1)–Cl(2)	165.53(4)
	Ru(1)–P(1)	2.2649(12)	Cl(1)–Ru(1)–P(1)	90.69(4)
	Ru(1)–O(1)	2.202(3)	Cl(2)–Ru(1)–P(1)	102.36(4)
			Cl(1)–Ru(1)–O(1)	88.2(1)
			P(1)–Ru(1)–O(1)	86.6(1)
			P(1)–Ru(1)–P(2)	99.26(5)
			O(1)–Ru(1)–P(2)	173.9(1)
5	Ru(1)–Cl(1)	2.4046(11)	Cl(1)–Ru(1)–Cl(2)	179.42(4)
	Ru(1)–P(1)	2.4046(11)	Cl(1)–Ru(1)–P(1)	90.82(4)
	Ru(1)–S(1)	2.3421(11)	Cl(1)–Ru(1)–S(1)	93.06(4)
			P(1)–Ru(1)–S(1)	88.81(4)
			S(1)–Ru(1)–P(2)	90.12(4)
			P(1)–Ru(1)–P(2)	175.96(4)
6	Ru(1)–Cl(1)	2.3969(6)	Ru(1)–C(22)	2.290(2)
	Ru(1)–P(1)	2.3246(7)	Cl(1)–Ru(1)–P(1)	86.29(2)
	Ru(1)–S(1)	2.3388(6)	Cl(1)–Ru(1)–S(1)	89.66(2)
			P(1)–Ru(1)–S(1)	85.23(2)

The [RuCl(4-cymene)(*Ph*PSS)]BPh_4 complex **6** was synthesised by the reaction of $[RuCl_2(4\text{-cymene})]_2$ with **2** in methanol, followed by precipitation with $NaBPh_4$ This complex is soluble in dimethyl sulfoxide, sparingly soluble in chloroform and insoluble in hexane, methanol and diethyl ether. Unlike the previous complexes **3**, **4** and **5**, there is no evidence for the formation of the disubstituted species. This is possibly because the cymene ring stabilises the heteroleptic complex against further ligand substitution. The ^{31}P NMR spectrum in [D_6]DMSO shows two singlets at δ = 29.2 and 36.2 ppm, consistent with the presence of two isomers in approximately equal proportions. Four dithiolane CH_2 signals are observed at δ = 3.62, 3.73, 3.89 and 4.32 ppm in the ^1H NMR spectrum and two dithiolane CH resonances at δ = 4.48 and 5.92 ppm. In the ^{13}C NMR spectrum only two dithiolane CH_2 group signals are observed at δ = 32.2 and 35.4 ppm, which is presumably due to the two CH_2 groups in each isomer having coincident chemical shifts. The dithiolane CH groups have resonances at δ = 51.4 and 56.1 ppm. Further investigation is required to correlate each set of signals to a specific isomer. The structure of complex **6** was determined by single-crystal X-ray diffraction analysis (Figure 5). The centrosymmetric space group indicates that the crystal is racemic. In this structure the ruthenium atom lies 1.75 Å from the plane of the C6 ring. The ring is coordinated symmetrically, and the ring centroid–ruthenium vector lies only 0.3° from the normal to the plane of best fit. Interesting bond angles include Cl(1)–Ru(1)–S(1) and P(1)–Ru(1)–S(1) [89.66(2) and 85.23(2)°, respectively], both of which are close to 90°. The *Ph*PSS ligand is bound almost symmetrically with respect to the coordinated cymene. The Ru–C (ca. 2.2–2.3 Å), Ru–Cl (ca. 2.4 Å), Ru–P (ca. 2.3 Å) and Ru–S (ca. 2.3 Å) bond lengths are similar to those of **5** and are consistent with those of other reported ruthenium(II) complexes.[9,17,18]

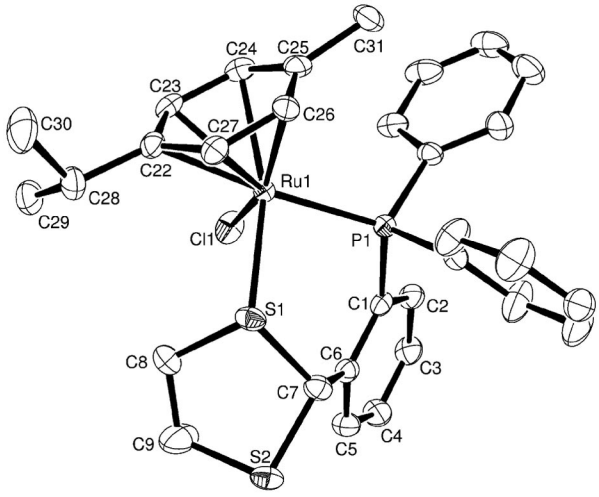


Figure 5. ORTEP representation of $[\mathbf{6}]^+$ (40% thermal ellipsoids, hydrogen atoms omitted for clarity).

Hydrosilyation Catalysis

The newly synthesised complexes were screened for their activity towards the hydrosilylation of acetophenone to 1-phenylethanol by using diphenylsilane. Hydrosilylation is a generally accepted indicator of catalytic activity. Four

known complexes were used as a standard: $[Ru_2Cl_4(4\text{-cymene})_2]$, $[RuCl_2(PPh_3)_3]$,[19] $[RuCl_2(dppe)_2]$[20] and $[RuCl_2(PhPOMe)_2]$.[21,22] The method used was adapted from the procedure described by Uemura, Hidai et al.[23] The results are shown in Table 2. Of the four new complexes tested only the acetal complex $[RuCl_2\{PhP(OMe)_2\}_2]$ (**3**) showed catalytic activity, with the dioxolane and dithiolane complexes giving sub-stoichiometric conversion.

Table 2. Results of catalytic hydrosilylation by using PXX′ complexes compared to known catalysts.

Catalyst	Conversion [%][a]
$[RuCl_2(PPh_3)_3]$	19
$[RuCl_2(4\text{-cymene})]_2$	1
$[RuCl_2(dppe)_2]$	0.2
$[RuCl_2\{PhP(OMe)_2\}_2]$ (**3**)	3
$[RuCl_2(PhPOO)_2]$ (**4**)	0.4
$[RuCl_2(PhPSS)_2]$ (**5**)	0.2
$[RuCl(cymene)(PhPSS)]BPh_4$ (**6**)	0
$[RuCl_2(PhPOMe)_2]$	16
$[RuCl(PhPNO\text{-}\eta^6\text{-}C_6H_5)Cl]BPh_4$	0.5

[a] Under the experimental conditions conversion [%] = TON = TOF [h^{-1}].

Conclusions

Reaction of ruthenium(II) precursors with **1** and **2** generally produced complexes in which the mixed-donor ligands bind in a bis(bidentate) fashion. Reaction of **1** with $[RuCl_2(PPh_3)_3]$ led to the conversion of the dioxolane to the dimethyl acetal by reaction with the solvent, whereas in the reaction with $[RuCl_2(4\text{-cymene})]_2$ the dioxolane remained intact. Dioxolane complex **4** showed fluxional behaviour at room temperature in $CDCl_3$ solution with several isomers visible in the ^1H, ^{13}C and ^{31}P NMR spectra. In contrast, in the solution phase, **3** appears (at room temperature) to exist as a single isomer, corresponding to its solid-state structure. Both dithiolane complexes **5** and **6** exist as mixtures of geometric isomers in $CDCl_3$ solution, but there is no evidence of interconversion at room temperature. The kinetic stability provided by the strength of the Ru–S bonds is also likely to be the reason why these complexes do not show any catalytic activity. In comparison, the Ru–O bonding in **3** and **4** is presumably weaker and leads to the fluxional behaviour of **4**, and although the acetal donor groups in **3** did not appear to be labile, it was only this species which showed any activity in hydrosilylation catalysis.

Experimental Section

General: Unless otherwise stated, all manipulations were carried out under dinitrogen with dry solvents and using Schlenk line techniques. Solvents were pre-dried with sodium wire or calcium chloride prior to heating at reflux over the appropriate drying agent/indicator: methanol (magnesium methoxide), tetrahydrofuran (sodium/benzophenone), toluene (sodium). All solvents were degassed prior to use. $[RuCl_2(PPh_3)_3]$[19] and 2-(diphenylphosphanyl)benzaldehyde[7] were prepared according to literature procedures. All other reagents and solvents were purchased from commercial sources and were used as received. ^1H, ^{13}C and ^{31}P NMR spectra of the redissolved isolated solids were recorded with a Varian Mercury-Vx 300 spectrometer at 300.0, 75.4 and 121.4 MHz, respectively, or a Varian Unit 500 MHz spectrometer at 499.9 MHz, 125.7 MHz and 202.4 MHz, respectively, at ambient temperature unless otherwise stated. ^1H and ^{13}C NMR spectra were referenced internally to residual solvent resonances or tetramethylsilane at δ = 0 ppm (for ^1H NMR), and ^{31}P NMR spectra were externally referenced to 85% H_3PO_4 at δ = 0 ppm. Electrospray mass spectrometry was performed with a Micromass LCT time of flight mass spectrometer. Electron impact mass spectrometry was performed with a Micromass GCT time of flight mass spectrometer, with a heated solid probe. FAB mass spectrometry was performed with a Fisons Autospec instrument, using dithiothreitol and dithioerythritol or *m*-nitrobenzyl alcohol as the matrix. HPLC was carried out with a GILSON analytical/preparative instrument and a UV/Vis detector (λ = 250 nm). A reverse-phase HAMILTON PRP-1 analytical column (4.1 × 150 mm, 10 μm) was used with an isocratic mobile phase of acetonitrile/water (95%:5%) and a flow rate of 1.5 mL/min. Gas chromatography was carried out with a Unicam ProGC gas chromatogram system using helium as the carrier gas and a Flame Ionisation Detector (FID) with a hydrogen/air flame. A 2 m Carbowax 20M packed column was used. Elemental analyses were carried out by the elemental analysis service of the Inorganic Chemistry Laboratory, University of Oxford. X-ray crystallography was performed with a Bruker-Nonius KappaCCD diffractometer, using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Single crystals were mounted on a glass fibre using perfluoropolyether oil and cooled rapidly to 150 K in a stream of cold nitrogen using an Oxford Cryosystems CRYOSTREAM unit. Intensity data were processed using the DENZO-SMN package.[24] Structures were solved using the direct-methods programme SIR92,[25] which located all non-hydrogen atoms. Subsequent full-matrix least-squares refinement was carried out using the CRYSTALS programme suite.[26] Coordinates and anisotropic thermal parameters of all non-hydrogen atoms were refined. Hydrogen atoms were positioned geometrically after each cycle of refinement. A 3-term Chebychev polynomial weighting scheme was applied. Crystallographic data is shown in Table 3. CCDC-666148 (**3**), -666149 (**3a**), -666150 (**4**), -666151 (**5**), -666152 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

***Ph*PSS (2):** 2-(Diphenylphosphanyl)benzaldehyde (669 mg, 2.31 mmol) and *p*-toluenesulfonic acid monohydrate (13 mg, 0.07 mmol) were suspended in non pre-dried ethanol (50 mL), and the reaction mixture was heated gently to give a yellow solution. 1,2-Ethanedithiol (0.19 mL, 2.31 mmol) was added, and the reaction mixture was heated at just below reflux temperature overnight. The now colourless solution was cooled to room temperature, and the volume of solvent was reduced in vacuo to produce a white precipitate. This was collected by filtration in air, washed with ethanol and dried in vacuo. *Ph*PSS was obtained as a white powdery solid (565 mg, 67%). $C_{21}H_{19}PS_2$ (366.48): calcd. C 68.8, H 5.2; found C 68.6, H 5.0. FTIR (nujol mull): $\tilde{\nu}$ = 1000–1500 cm^{-1}; no S=O stretch. MS (ES^+): *m*/*z* = 367 $[M]^+$, 339 $[M - CH_2CH_2]^+$. HPLC: t_r = 5.48 min. ^1H NMR ($CDCl_3$): δ = 3.25 (m, 2 H, H^1 or H^2), 3.42 (m, 2 H, H^1 or H^2), 6.48 (d, $J_{H\text{-}P}$ = 9 Hz, 1 H, H^3), 6.82 (m, $J_{H5\text{-}H6}$ = 8, $J_{H5\text{-}H7}$ = 4 Hz, 1 H, H^5), 7.11 (m, $J_{H6\text{-}H5}$ = 8, $J_{H6\text{-}H7}$ = 8, $J_{H6\text{-}H8}$ = 1 Hz, 1 H, H^6), 7.22–7.37 (m, 10 H, Ph), 7.31 (m, $J_{H7\text{-}H5}$ = 4, $J_{H7\text{-}H6}$ = 8, $J_{H7\text{-}H8}$ = 7 Hz, 1 H, H^7), 7.93 (m, $J_{H\text{-}P}$ = 5, $J_{H8\text{-}H6}$ = 1, $J_{H8\text{-}H7}$ = 7 Hz. 1 H. H^8) ppm. ^{31}P NMR ($CDCl_3$): δ = –16.4 ppm. ^{13}C NMR ($CDCl_3$): δ = 40.4 (s, C^1, C^2), 53.5 (d,

Table 3. Crystallographic data for complexes **3**–**6**.

	3	**3a**	**4**	**5**	**6**
Empirical formula	$C_{42}H_{42}Cl_2O_4P_2Ru$	$C_{41}H_{44}Cl_2O_4P_2Ru$	$C_{45}H_{41}Cl_{11}O_4P_2Ru$	$C_{42}H_{41}Cl_{11}P_2RuS_4$	$C_{55}H_{53}BClPRuS_2 \cdot xC_2H_3N \cdot yH_2O$ ($x \approx 0.69$, $y \approx 0.21$)
Formula mass	844.72	834.72	1198.82	1263.06	988.58
T [K]	150	150	150	150	150
λ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	orthorhombic	monoclinic	triclinic	triclinic	monoclinic
Space group	*Pbcn*	*Pn*	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a [Å]	29.8017(3)	11.1725(2)	11.4441(3)	10.0250(2)	9.8503(2)
b [Å]	11.3137(2)	11.7916(2)	15.0416(3)	12.1110(2)	19.3006(2)
c [Å]	22.3869(2)	14.8140(3)	16.4074(4)	22.3615(3)	25.7455(2)
α [°]	90	90	113.2293(11)	104.4111(5)	90
β [°]	90	94.0849(9)	102.6241(11)	98.8140(5)	98.6551(5)
γ [°]	90	90	95.5941(12)	95.5039(7)	90
V [Å^3]	7584.14(17)	1946.7	2487.9	2572.9	4838.9
Z	8	2	2	2	4
D [Mg/m^3]	1.487	1.424	1.606	1.630	1.344
μ [mm^{-1}]	0.684	0.662	1.016	1.134	0.536
F(000)	3467.79	858.196	1208.600	1273.423	2049.565
Crystal size [mm]	$0.08 \times 0.08 \times 0.14$	$0.18 \times 0.24 \times 0.24$	$0.20 \times 0.20 \times 0.24$	$0.06 \times 0.12 \times 0.12$	$0.18 \times 0.22 \times 0.22$
Reflections measured	61345	18668	35503	41689	60370
Unique reflections	9394	8244	11296	11672	11012
R_{int}	0.054	0.036	0.047	0.066	0.058
Parameters refined	460	460	568	568	568
Goodness of fit	1.0681	1.0962	0.9879	1.0351	1.0382
R	0.0306	0.0285	0.0739	0.0527	0.0367
wR	0.0298	0.0281	0.0802	0.0593	0.0436

$J_{C\text{-}P}$ = 33 Hz, C^3), 127.9 (s, C^6), 128.5 (d, $J_{C\text{-}P}$ = 7 Hz, Ph), 128.7 (d, $J_{C\text{-}P}$ = 5 Hz, C^8), 128.8 (s, Ph), 129.6 (s, C^7), 133.4 (s, C^5), 133.8 (d, $J_{C\text{-}P}$ = 20 Hz, Ph), 135.6 (d, $J_{C\text{-}P}$ = 13 Hz C^4), 136.2 (d, $J_{C\text{-}P}$ = 10 Hz, Ph), 145.1 (d, $J_{C\text{-}P}$ = 23 Hz, C^9) ppm.

[RuCl$_2${*Ph*P(OMe)$_2$}$_2$] (3): [RuCl$_2$(PPh$_3$)$_3$] (247 mg, 0.26 mmol) and *Ph*POO (172 mg, 0.51 mmol) were suspended in methanol (15 mL) and heated at reflux overnight. The reaction mixture became orange in colour, and an orange precipitate formed. This was collected by filtration in air, washed with methanol and dried in vacuo. [RuCl$_2${*Ph*P(OMe)$_2$}$_2$] was obtained as an orange solid (217 mg, 58%). $C_{42}H_{42}Cl_2O_4P_2Ru$ (844.70): calcd. C 59.7, H 5.0; found C 60.1, H 5.1. MS (ES$^+$): *m*/*z* = 844 [M]$^+$, 809 [M – Cl]$^+$, 776 [M – 2 Cl]$^+$, 712 [M – (2 Cl + 2 OMe)]$^+$. HPLC: t_r = 4.98 min. ^{1}H NMR (CDCl$_3$): δ = 3.39 (s, 6 H, OMe^1), 3.55 (s, 6 H, OMe^2), 6.70 (s, 2 H, CH), 6.89–7.80 (m, 20 H, Ph), 7.28 (m, $J_{H\text{-}H}$ = 8, 1 Hz, 2 H, H^3), 7.39 (m, $J_{H\text{-}H}$ = 8, 1 Hz, 2 H, H^4), 7.46 (m, $J_{H\text{-}P}$ = 3, $J_{H\text{-}H}$ = 8, 1 Hz, 2 H, H^5), 7.76 (m, $J_{H\text{-}H}$ = 8 Hz, 2 H, H^6) ppm. ^{31}P NMR (CDCl$_3$): δ = 48.2 ppm. ^{13}C NMR (CDCl$_3$): δ = 48.3 (s, OMe), 56.2 (s, OMe), 103.0 (s, CH), 126.7 (s, Ph), 127.0 (s, C^6), 128.5 (d, $J_{C\text{-}P}$ = 12 Hz, Ph), 128.8 (s, C^4), 129.3 (d, $J_{C\text{-}P}$ = 24 Hz, Ph), 131.1 (s, C^3), 131.9 (d, $J_{C\text{-}P}$ = 3 Hz, Ph), 132.1 (d, $J_{C\text{-}P}$ = 10 Hz, C^5), 134.9 (s, Ph), 138.3 (s, Ph) ppm.

[RuCl$_2$(*Ph*POO)$_2$] (4): Tetrachlorobis(4-cymene)diruthenium (98 mg, 0.16 mmol) and *Ph*POO (214 mg, 0.64 mmol) were dissolved in methanol (15 mL) and were heated under reflux overnight. The reaction mixture became orange in colour, and an orange precipitate formed. This was collected by filtration in air, washed with methanol and dried in vacuo. [RuCl$_2$(*Ph*POO)$_2$] was obtained as a pink/orange powder (188 mg, 70%). $C_{42}H_{38}Cl_2O_4P_2Ru$ (840.67): calcd. C 60.0, H 4.6; found C 60.3, H 4.6. MS (ES$^+$): *m*/*z* = 805 [M – Cl]$^+$, 770 [M – 2 Cl]$^+$. HPLC: t_r = 3.50 min. ^{1}H NMR (CDCl$_3$): δ = 4.22 (br. s, 4 H, CH$_2$), 4.75 (br. s, 4 H, CH$_2'$), 6.43 (br. s, 2 H, CH), 6.65–7.81 (m, 28 H, Ph) ppm. ^{31}P NMR: (CDCl$_3$): δ = 54.4 ppm. ^{13}C NMR (CDCl$_3$): δ = 65.5 (br. s, CH$_2$, CH$_2'$), 101.8 (s, CH), 125.7–139.6 (Ph) ppm.

[RuCl$_2$(*Ph*PSS)$_2$] (5): [RuCl$_2$(PPh$_3$)$_3$] (184 mg, 0.19 mmol) and *Ph*PSS (141 mg, 0.39 mmol) were suspended in methanol (15 mL) and the reaction mixture was heated under reflux for 6 h. The colour changed from brown to yellow, and a yellow precipitate formed. After cooling to room temperature, the precipitate was collected by filtration in air, washed with methanol and dried in vacuo. [RuCl$_2$(*Ph*PSS)$_2$] was obtained as a yellow powder (131 mg, 75%). $C_{42}H_{38}Cl_2P_2RuS_4$ (904.93): calcd. C 55.8, H 4.2; found C 56.1, H 3.9. MS (FAB$^+$): *m*/*z* = 906.0 [M]$^+$, 869.0 [M – Cl]$^+$, 834.0 [M – 2 Cl]$^+$, 467.0 [M – (2 Cl + PSS)]$^+$. ^{1}H NMR (CDCl$_3$): isomer 1: δ = 2.58 (m, $J_{H\text{-}H}$ = 7 Hz, 1 H, CH$_2$H^1), 3.27 (m, 1 H, CH$_2$H^2), 3.45 (m, $J_{H\text{-}H}$ = 7, 2 Hz, 1 H, CH$_2$H^3), 3.55 (m, $J_{H\text{-}H}$ = 11, 7, 4 Hz, 1 H, CH$_2$H^4), 3.67 (m, $J_{H\text{-}H}$ = 7 Hz, 1 H, CH$_2$H^5), 4.05 (m, $J_{H\text{-}H}$ = 11, 7, 4 Hz, 1 H, CH$_2$H^6), 4.74 (m, $J_{H\text{-}H}$ = 2 Hz, 1 H, CH$_2$H^7), 4.80 (m, $J_{H\text{-}H}$ = 9, 2 Hz, 1 H, CH$_2$H^8), 5.54 (d, $J_{H\text{-}P}$ = 2 Hz, 1 H, CH H^9), 6.04 (s, 1 H, CH H^{10}) ppm; isomer 2: δ = 3.12 (m, 2 H, CH$_2$H^{11}), 3.30 (m, 2 H, CH$_2$H^{12}), 3.33 (m, 2 H, CH$_2$H^{13}), 3.48 (m, 2 H, CH$_2$H^{14}), 6.52 (s, 2 H, CH H^{15}) ppm; isomers 1 + 2: δ = 6.42–8.06 (m, 56 H, Ph) ppm. ^{31}P NMR (CDCl$_3$): isomer 1: δ = 30.1 (d, $J_{P\text{–}P}$ = 27 Hz), 32.6 (d, $J_{P\text{–}P}$ = 27 Hz) ppm; isomer 2: δ = 46.1 ppm. ^{13}C NMR (CDCl$_3$): isomer 1: δ = 35.8 (s, CH$_2$ C^2, C^4), 39.1 (s, CH$_2$ C^5, C^7), 39.8 (s, CH$_2$ C^1, C^6), 41.4 (s, CH$_2$ C^3, C^8), 56.6 (d, $J_{C\text{-}P}$ = 11 Hz, CH C^9), 62.0 (d, $J_{C\text{-}P}$ = 10 Hz, CH C^{10}) ppm; isomer 2: δ = 34.8 (s, CH$_2$ C^{11}, C^{12}), 36.2 (s, CH$_2$ C^{13}, C^{14}), 61.5 (d, $J_{C\text{-}P}$ = 11 Hz, CH^{15}) ppm; isomers 1 + 2: δ = 127.1–138.2 (Ph) ppm.

[RuCl(cymene)(*Ph*PSS)]BPh$_4$ (6): Tetrachlorobis(4-cymene)diruthenium (56 mg, 0.09 mmol) and *Ph*PSS (134 mg, 0.37 mmol) were suspended in methanol (15 mL), and the reaction mixture was heated at reflux for 6 h. An orange solution formed, and, after cooling to room temperature, a methanolic solution of sodium tetraphenylborate (310 mg, 0.91 mmol, in 5 mL of non pre-dried

methanol) was added. A yellow/orange precipitate formed and was collected by filtration in air, washed with methanol and diethyl ether and dried in vacuo. [RuCl(cymene)(*Ph*PSS)]BPh_4 was obtained as a yellow powder (156 mg, 90%). $C_{55}H_{53}BClPRuS_2$ (956.45): calcd. C 69.1, H 5.6; found C 69.1, H 5.6. MS (ES^+): *m*/*z* = 637 $[M]^+$, 602 $[M - Cl]^+$. HPLC: t_r = 1.18 min. ^1H NMR ([D_6]-DMSO): isomer 1: δ = 1.05 (d, $J_{H\text{-}H}$ = 7 Hz, 3 H, Me), 1.15 (d, $J_{H\text{-}H}$ = 7 Hz, 3 H, Me′), 2.16 (s, 3 H, Me^{cy}), 2.65 (m, $J_{H\text{-}H}$ = 7 Hz, 1 H, CH), 4.92 (d, $J_{H\text{-}H}$ = 5 Hz, 1 H, H^{3cy}), 5.48 (d, $J_{H\text{-}H}$ = 6 Hz, 1 H, H^{2cy}), 6.03 (d, $J_{H\text{-}H}$ = 5 Hz, 1 H, $H^{2'cy}$), 6.30 (d, 1 H, $H^{3'cy}$) ppm; isomer 2: δ = 0.91 (d, $J_{H\text{-}H}$ = 7 Hz, 3 H, Me), 1.09 (d, $J_{H\text{-}H}$ = 7 Hz, 3 H, Me′), 1.96 (s, 3 H, Me^{cy}), 2.45 (m, $J_{H\text{-}H}$ = 7 Hz, 1 H, CH), 5.91 (s, 1 H, H^{6cy}), 6.11 (d, $J_{H\text{-}H}$ = 6 Hz, 1 H, $H^{6'cy}$), 6.22 (d, $J_{H\text{-}H}$ = 6 Hz, 1 H, H^{7cy}), 6.28 (d, 1 H, $H^{7'cy}$) ppm; isomers 1 + 2: δ = 3.62 (m, $J_{H\text{-}H}$ = 12, 7 Hz, 2 H, CH_2^{PSS}), 3.73 (m, $J_{H\text{-}H}$ = 12, 7 Hz, 2 H, CH_2^{PSS}), 3.89 (m, $J_{H\text{-}H}$ = 13, 7 Hz, 2 H, CH_2^{PSS}), 4.32 (m, 2 H, CH_2^{PSS}), 4.48 (s, 1 H, CH^{PSS}), 5.92 (s, 1 H, CH^{PSS}), 6.72–7.99 (m, 48 H, Ph) ppm. ^{31}P NMR ([D_6]DMSO): δ = 29.2, 36.2 ppm. ^{13}C NMR ([D_6]DMSO): isomer 1: δ = 17.5 (s, Me^{cy}), 20.7 (s, Me), 22.8 (s, Me′), 30.4 (s, CH), 104.4 (s, C^{1cy}), 111.1 (s, C^{4cy}) ppm; isomer 2: δ = 15.2 (s, Me′), 17.3 (s, Me^{cy}), 20.3 (s, Me), 29.4 (s, CH), 107.0 (s, C^{5cy}), 113.3 (s, C^{8cy}) ppm; isomers 1 + 2: δ = 32.2 (s, CH_2^{PSS}), 35.4 (s, CH_2^{PSS}), 51.4 (s, CH^{PSS}), 56.1 (s, CH^{PSS}), 89.3 (s, cy), 89.8 (s, cy), 91.6 (s, cy), 92.2 (s, cy), 92.4 (s, cy), 94.2 (s, cy), 94.5 (s, cy), 97.6 (s, cy), 121.1–138.5 (Ph), 162.4–164.3 (BPh_4^-) ppm.

Catalytic Hydrosilyation of Acetophenone: The method utilised to ascertain the activity of the complexes was derived from that of Nishibayashi et al.[23] The catalyst (0.01 mmol, 1 mol-%) was dissolved in tetrahydrofuran (10 mL), in a Schlenk flask. Acetophenone (117 μL, 1 mmol) was added, and the reaction mixture was heated to 65 °C. An excess of diphenylsilane (371 μL, 2 mmol) was added and the flask sealed. Heating continued for a further 1 h. After cooling to room temperature, the reaction mixture was quenched with non pre-dried methanol (1 mL), to consume the remaining silane. After stirring at room temperature for 30 min, 0.2 M hydrochloric acid (2.5 mL) was added to hydrolyse the silyl ether. The reaction mixture was stirred in air overnight and was then analysed by GC. Percentage conversions were calculated from the ratio of areas of the eluted peaks of acetophenone and 1-phenylethanol. Calibration using standards showed the two substances to elute in a 1:1 ratio when equal amounts of both were injected. No correction factors were therefore applied to the areas. Temperature profile for GC analysis: maintain 60 °C for 2 min, increase 10 °C per min for 14 min, maintain 200 °C for 4 min; injector temperature: 220 °C; detector temperature: 300 °C.

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