

Reactions of phosphinites with oxide surfaces: a new method for anchoring organic and organometallic complexes†

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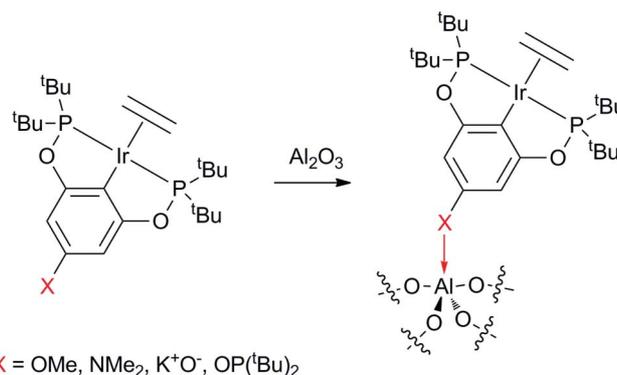
When a pincer-ligated iridium complex with a phosphinite substituent in the *para*-position of the aromatic backbone is immobilized on γ -alumina, it becomes a highly effective supported catalyst for the transfer-dehydrogenation of alkanes. The nature of the interaction between the organometallic complex and the support was investigated using solid-state ^{31}P MAS NMR spectroscopy, solution-state ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, IR and GC/MS analysis of extracted reaction products. The phosphinite substituent is cleaved from the pincer ligand by its reaction with hydroxyl groups on the γ -alumina surface, resulting in covalent anchoring of the complex *via* the aryl ring. A similar reaction occurs on silica, allowing for ready grafting onto this support as well. A strategy for anchoring homogeneous catalysts on hydroxyl-terminated oxide supports through the selective cleavage of [POR]-containing ligand substituents is suggested.

Introduction

Pincer complexes of iridium catalyze the dehydrogenation of alkanes in solution under mild conditions (50–200 °C), and show high selectivity for the formation of α -olefins from *n*-alkanes.¹ This reactivity has been used to achieve alkane metathesis *via* a tandem catalytic sequence involving dehydrogenation of alkanes, metathesis of the olefinic products, and rehydrogenation. In the tandem reactions, short-chain linear alkanes yield longer-chain alkanes,² while cycloalkanes yield ring-expanded cycloalkanes.³ When supported on γ -alumina, these catalysts show good activity and much improved recyclability, *e.g.*, in transfer-dehydrogenation reactions, relative to their homogeneous analogues.⁴ The interactions between the complexes and the γ -alumina surface, and the effectiveness of the latter in promoting catalyst stability, were therefore investigated.

Our initial attempts to immobilize iridium pincer complexes *via* incorporation of a remote trimethoxysilyl substituent resulted in heterogeneous catalysts with low activity.⁴ Methanol generated as a byproduct of the tethering reaction with surface hydroxyls results in the formation of a carbonyl complex that is inactive for

alkane dehydrogenation.⁴ An alternative immobilization strategy was successfully implemented, in which several pincer complexes were designed with Lewis basic substituents (*i.e.*, $-\text{N}(\text{CH}_3)_2$, $-\text{OCH}_3$, $-\text{O}^-\text{K}^+$, $-\text{OP}(t\text{-Bu})_2$) in the *para*-position of the aromatic backbone of the pincer ligand in order to promote their immobilization onto Lewis acidic γ -alumina.⁴ The nature of the interaction was presumed to be binding of the *para*-substituent to a coordinatively-unsaturated surface Al site, Scheme 1. The organometallic complexes vary in their synthetic accessibility, however, the one bearing a phosphinite substituent in the *para*-position is particularly easy to prepare, starting from 1,3,5-tris(di-*tert*-butylphosphinoxy)benzene. It was found to bind strongly to γ -alumina, and is highly effective as a transfer-dehydrogenation catalyst.⁴



Scheme 1 Proposed immobilization of *para*-substituted pincer complexes at Lewis acid sites on γ -alumina.

Lewis acidity in γ -alumina arises due to the presence of four- and five-coordinate Al sites on the partially dehydrated surface.

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The four-coordinate Lewis acid sites are proposed to be highly distorted from tetrahedral geometry, while the five-coordinate Lewis acid sites are square-pyramidal.⁵ Although frequently invoked in computational studies, very energetic three-coordinate Al sites are probably not present in appreciable amounts.^{6–8} Such sites may be present at surfaces created *in silico* by terminating the bulk structure of γ -alumina, but they are proposed to reconstruct to increase the coordination of highly-unsaturated cations.⁹ Tricoordinate Al sites also undergo strongly exothermic reactions with atmospheric water, and are not restored unless the γ -alumina is dehydrated at temperatures higher than 550 °C.⁵

Recently, we reported that the solid-state ³¹P magic-angle spinning (MAS) NMR spectrum of $\{p-[(t\text{-Bu})_2\text{PO}]\text{-C}_6\text{H}_2\text{-2,6-}[\text{OP}(t\text{-Bu})_2]_2\}\text{Ir}(\text{C}_2\text{H}_4)$ supported on γ -alumina contains a signal far upfield from the position expected for a phosphinite interacting with a Lewis acid site, suggesting a more complex chemical interaction with the surface than that shown in Scheme 1.⁴ Similar, unexplained upfield signals were observed for the free pincer ligand, 1,3,5-tris(di-*tert*-butylphosphinoxy)benzene, and the model compound phenyl di-*tert*-butylphosphinite. In this contribution, the nature of the surface reaction is elucidated through studies of the catalyst, the pincer ligand, and model compounds adsorbed onto γ -alumina, and the generality of the immobilization strategy is explored with another commonly-used catalyst support: silica.

Results and discussion

Adsorption of phosphinites onto γ -alumina

When a red solution of the pincer complex $\{p-[(t\text{-Bu})_2\text{PO}]\text{-C}_6\text{H}_2\text{-2,6-}[\text{OP}(t\text{-Bu})_2]_2\}\text{Ir}(\text{C}_2\text{H}_4)$, **1**, in hexanes is stirred over γ -alumina, the support turns red while the solution becomes colorless, indicating that **1** is adsorbed onto the support, as previously reported.⁴ The solid-state ³¹P MAS NMR spectrum of **1** supported in this way on γ -alumina is shown in Fig. 1a. The most intense signal, at 176 ppm, is assigned to the two phosphinite groups coordinated to iridium, and is shifted slightly upfield compared to the chemical shift of the phosphinite donors in the molecular complex (181.1 ppm in C_6D_6). However, the solid-state ³¹P signal of the uncoordinated *para*-phosphinite substituent at 155 ppm (150.8 ppm in C_6D_6) is much weaker than expected. It appears that much of its ³¹P signal has undergone a dramatic upfield shift, resulting in a broad feature at 75 ppm. By integration of the peaks at 176 and 75 ppm, the ratio of phosphorus coordinated to iridium to the new phosphorus environment represented by the isotropic signal at 75 ppm is 2.1, which corresponds closely to the expected ratio of Ir-coordinated and non-Ir-coordinated phosphinite groups.

Adsorption of the free ligand, 1,3,5-tris(di-*tert*-butylphosphinoxy)benzene, onto γ -alumina gave the ³¹P MAS NMR spectrum shown in Fig. 1c. The signal at 155 ppm is assigned to non-interacting or weakly-interacting phosphinite groups by analogy to their solution-state chemical shift (151.2 ppm in CDCl_3).⁴ The spectrum of the supported triphosphinite ligand also contains a signal at 75 ppm, with the same upfield shift as that observed for adsorbed **1**. The intensity ratio of the two major signals, including the isotropic peaks at 155 and 75 ppm and their incompletely-resolved spinning side-bands, is *ca.* 1.5, suggesting that either one

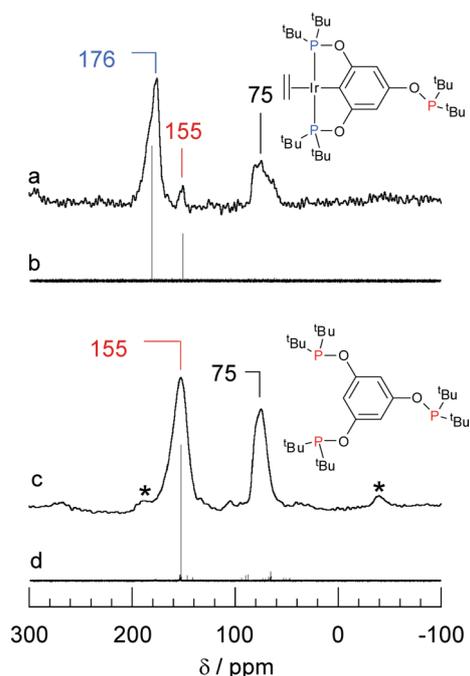


Fig. 1 Comparison of ³¹P NMR spectra of $\{p-[(t\text{-Bu})_2\text{PO}]\text{-C}_6\text{H}_2\text{-2,6-}[\text{OP}(t\text{-Bu})_2]_2\}\text{Ir}(\text{C}_2\text{H}_4)$, **1**: (a) solid-state MAS spectrum, for **1** supported on γ -alumina, and (b) solution-state spectrum, for **1** dissolved in C_6D_6 ; and ³¹P NMR spectra of 1,3,5-((*t*-Bu)₂PO)₃-C₆H₃: (c) solid-state MAS spectrum, for the triphosphinite supported on γ -alumina, and (d) solution-state spectrum, for the triphosphinite dissolved in CDCl_3 . Solid-state spectra were recorded with 14 kHz MAS; asterisks denote spinning sidebands.^{4,10}

or two of the three phosphinite groups for each molecule have reacted. We infer that the free ligand and the iridium complex **1** undergo closely-related reactions with γ -alumina surfaces.

Adsorption of phosphine oxides onto γ -alumina

The chemical shift of the unexpected signal at 75 ppm in the solid-state ³¹P MAS NMR spectra of both the free triphosphinite ligand and its iridium complex supported on γ -alumina (Fig. 1) resembles that of an aryl(di-*tert*-butyl)phosphine oxide.¹¹ We considered the possibility that arylphosphinites undergo γ -alumina-induced rearrangement to the corresponding arylphosphine oxides, which can then interact with γ -alumina *via* the P=O moiety through either adsorption onto Lewis acidic Al sites or hydrogen bonding to surface hydroxyl groups.

In order to test this hypothesis, authentic samples of (*t*-Bu)₂(PhO)P and (*t*-Bu)₂(Ph)P=O were adsorbed from toluene onto γ -alumina. The solid-state ³¹P MAS NMR spectrum of adsorbed (*t*-Bu)₂(PhO)P, Fig. 2a, exhibits a broad signal with a large upfield shift, to 71 ppm, relative to its solution value (153 ppm in CDCl_3),⁴ similar to that observed for some of the phosphinite groups of the triphosphinite ligand supported on γ -alumina (Fig. 1c). The ³¹P signals of adsorbed (*t*-Bu)₂(Ph)P=O appear at similar positions: 69 (major) and 64 ppm (minor), Fig. 2b. Both are shifted downfield relative to the solution-state chemical shift of (*t*-Bu)₂(Ph)P=O (52 ppm),¹² due to its interactions with the γ -alumina surface.

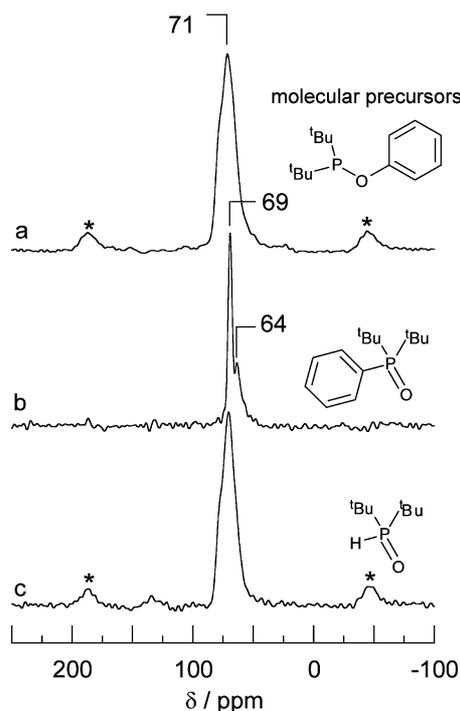


Fig. 2 Solid-state ^{31}P MAS NMR spectra of three molecular model compounds, following their adsorption on γ -alumina: (a) phenyl di-*tert*-butylphosphinite;^{4,10} (b) di(*tert*-butyl)phenylphosphine oxide; and (c) di-*tert*-butylphosphine oxide. All spectra were recorded with 14 kHz MAS; asterisks denote spinning sidebands.

Although the locations of the isotropic ^{31}P signals for (*t*-Bu) $_2$ (Ph)P=O and (*t*-Bu) $_2$ (PhO)P adsorbed on γ -alumina are similar, Fig. 2 shows that their linewidths are quite different. In addition, the spectrum of (*t*-Bu) $_2$ (Ph)P=O on γ -alumina lacks the prominent spinning-sidebands observed in the spectrum of (*t*-Bu) $_2$ (PhO)P on γ -alumina, indicating that adsorbed (*t*-Bu) $_2$ (Ph)P=O is considerably more mobile (consistent with its principal interaction with Brønsted acid sites *via* H-bonding rather than with Lewis acid sites). Thus, supporting (*t*-Bu) $_2$ (PhO)P on γ -alumina yields a species with a solid-state ^{31}P MAS NMR spectrum similar, but not identical, to that of adsorbed (*t*-Bu) $_2$ (Ph)P=O.

Identification of reaction products

When a portion of the γ -alumina modified with (*t*-Bu) $_2$ (PhO)P was washed with dry THF, no ^{31}P MAS NMR signals were detected in the washed solid, confirming that all phosphorus-containing compounds had been removed from the support. The solution-state $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the soluble material, recovered from the washing solvent and redissolved in THF-*d* $_8$, contains a major signal at 61.9 ppm, Fig. S1 (see ESI †). The ^{31}P and ^1H NMR chemical shifts, as well as the J_{PH} coupling constant (419 Hz) of the extracted species, match precisely those reported for (*t*-Bu) $_2$ (H)P=O.¹³ For direct comparison, an authentic sample of (*t*-Bu) $_2$ (H)P=O was supported on γ -alumina. Both the appearance and the chemical shift of the signal in the ^{31}P MAS NMR spectrum at 71 ppm, Fig. 2c, closely resemble those of the spectrum of (*t*-Bu) $_2$ (PhO)P on γ -alumina.

The IR spectra of both (*t*-Bu) $_2$ (H)P=O and (*t*-Bu) $_2$ (PhO)P on γ -alumina show a broad band at *ca.* 2350 cm^{-1} , Fig. 3a,b. This feature occurs in the P–H stretching region,^{14,15} and further confirms that (*t*-Bu) $_2$ (PhO)P is transformed into (*t*-Bu) $_2$ (H)P=O when it is adsorbed onto γ -alumina. The bands appear to be comprised of at least two components, at 2360 and 2340 cm^{-1} .¹⁵ These are tentatively assigned to (*t*-Bu) $_2$ (H)P=O interacting with two different types of Lewis acid sites, *e.g.*, four- and five-coordinate Al. For each type of adsorption site, the heterogeneity of acidities is likely to be responsible for the width of the peaks observed in Fig. 3a,b.

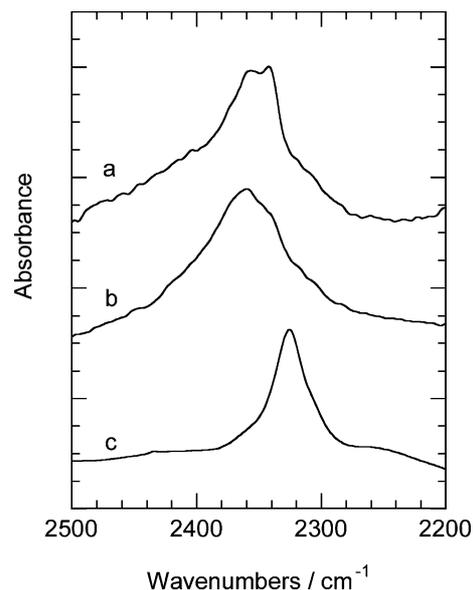
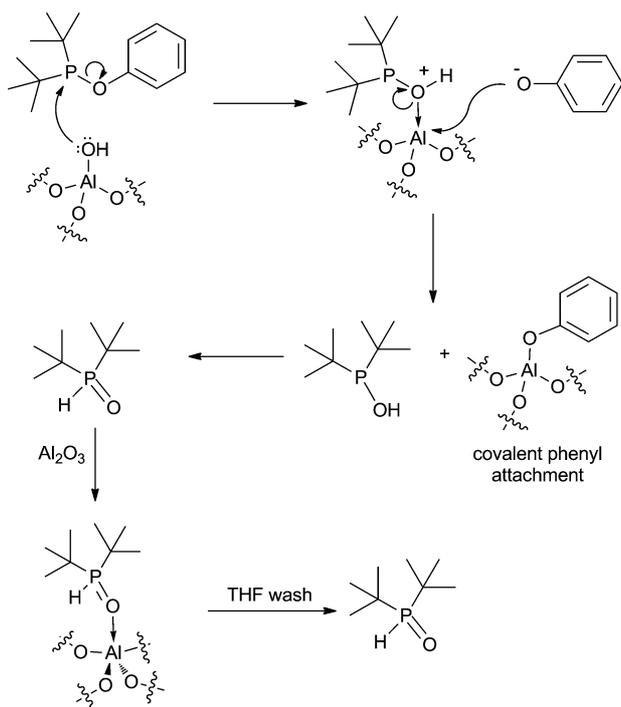


Fig. 3 Transmission FT-IR spectra of (a) (*t*-Bu) $_2$ (H)P=O supported on γ -alumina; (b) (*t*-Bu) $_2$ (PhO)P supported on γ -alumina; and (c) 1,3,5-((*t*-Bu) $_2$ PO) $_3$ -C $_6$ H $_3$ supported on silica.

A plausible route for the transformation of (*t*-Bu) $_2$ (PhO)P to (*t*-Bu) $_2$ (H)P=O is shown in Scheme 2. Since phenoxide is an effective leaving group, the attack of a surface hydroxyl group on the aryl phosphinite could result in phenoxide displacement, creating the coordinated phosphinous acid shown in the first step. The surface of γ -alumina bears several types of hydroxyls (acidic, basic and neutral) differing in the coordination number of the Al and the disposition of the hydroxyl group (terminal, doubly- or triply-bridging).^{5,16} The most nucleophilic hydroxyls are the terminal [O_nAlOH] sites, as represented in Scheme 2.

Subsequent phenoxide displacement of di(*tert*-butyl)phosphinous acid from the coordination sphere of aluminium will yield a phenoxide group covalently attached to the surface. Phosphinous acids tautomerize readily to phosphine oxides,^{17,18} and the favorable isomerization provides an additional driving force for phenoxide attachment. In related chemistry, hydrolysis of (*t*-Bu) $_2$ (PhO)P in solution was reported to give (*t*-Bu) $_2$ (H)P=O; the presumed phosphinous acid intermediate was not observed.¹⁹

Di-(*tert*-butyl)phosphine oxide, but not phenoxide, was extracted from the alumina support by washing with dry THF, as shown by solution-state ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy of the filtrate, Fig. S2 (see ESI †). This experiment demonstrates that the phenoxide is covalently attached to γ -alumina, since physisorbed



Scheme 2 Proposed mechanism for the reaction of phenyl di(*tert*-butyl)phosphinite with a basic surface hydroxyl group on γ -alumina to give a phosphinous acid which rearranges to the corresponding phosphine oxide, and its eventual displacement by THF.

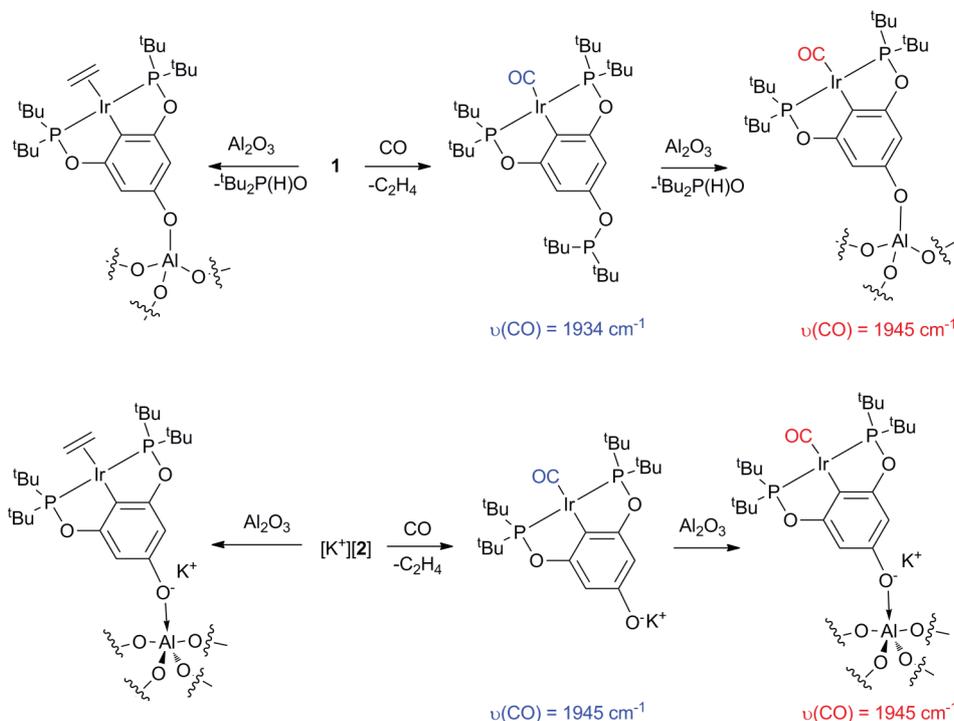
phenol would be expected to desorb even in the absence of a proton source. As expected, phenoxide was displaced by protonolysis when $(t\text{-Bu})_2(\text{PhO})\text{P}=\text{O}$ -treated γ -alumina was washed with slightly

acidic water: in this experiment, both phenol and $(t\text{-Bu})_2(\text{H})\text{P}=\text{O}$ were detected in the aqueous phase by GC/MS, Fig. S3 (see ESI†).

The solid-state ^{31}P MAS NMR spectrum of **1**/ γ -alumina (Fig. 1a) suggests that the *para*-phosphinite substituent of the coordinated pincer ligand reacts with terminal hydroxyl groups of γ -alumina in a manner analogous to that observed for $(t\text{-Bu})_2(\text{PhO})\text{P}$ and 1,3,5- $(t\text{-Bu}_2\text{PO})_3\text{-C}_6\text{H}_3$, resulting in detachment of the uncoordinated phosphinite group. The resulting supported Ir complex closely resembles the presumed product of direct grafting of $[\{p\text{-O-C}_6\text{H}_4\text{-2,6-[OP}(t\text{-Bu})_2]_2\}\text{Ir}(\text{C}_2\text{H}_4)]^-$, **2**, onto Lewis acidic sites on the γ -alumina surface. The grafting reactions are compared in Scheme 3. The solid-state ^{31}P MAS NMR chemical shift of the phosphinite arms that remain coordinated to iridium in supported **1** (176 ppm, Fig. 1a) is very similar to that of an authentic sample of $[\text{K}^+][\mathbf{2}]$ supported on γ -alumina (177 ppm).⁴ In addition, the supported monocarbonyl complexes generated by the reactions of **1** and $[\text{K}^+][\mathbf{2}]$ with $\text{CO}_{(g)}$ followed by their adsorption onto γ -alumina have the same $\nu(\text{IrC}\equiv\text{O})$ frequency, at 1945 cm^{-1} . Since the synthesis of **1** is considerably more convenient than that of $[\text{K}^+][\mathbf{2}]$, *in situ* generation of the phenoxide-substituted pincer complex provides a much simpler route to this highly-active supported dehydrogenation catalyst.

Decomposition of γ -alumina-supported iridium pincer complexes

The observed cleavage of uncoordinated phosphinite substituents on γ -alumina suggests a general decomposition pathway for this family of supported pincer iridium complexes. The coordinated phosphinite arms may also react with the surface hydroxyl groups, albeit more slowly due to the need for initial de-coordination from Ir. This hypothesis was explored using complex **2**, since



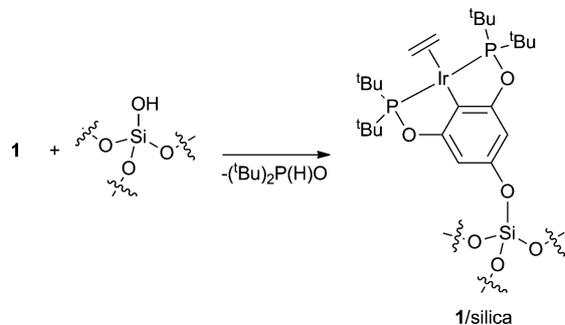
Scheme 3 Proposed structures of the immobilized ethylene complexes $\{p\text{-}[(t\text{-Bu})_2\text{PO}]\text{-C}_6\text{H}_4\text{-2,6-[OP}(t\text{-Bu})_2]_2\}\text{Ir}(\text{C}_2\text{H}_4)$, **1**, and $[\text{K}^+][\{p\text{-O-C}_6\text{H}_4\text{-2,6-[OP}(t\text{-Bu})_2]_2\}\text{Ir}(\text{C}_2\text{H}_4)]^-$, $[\text{K}^+][\mathbf{2}]$, on γ -alumina, as well as the corresponding adsorbed carbonyl complexes.

it does not generate phosphine oxide upon initial adsorption. The ^{31}P MAS NMR spectrum of fresh $[\text{K}^+][\{p\text{-O-C}_6\text{H}_2\text{-2,6-}[\text{OP}(t\text{-Bu})_2\text{]}_2\}\text{Ir}(\text{C}_2\text{H}_4)\text{-}], [\text{K}^+][\mathbf{2}]$, supported on γ -alumina showed only the expected isotropic signal at 177 ppm,⁴ confirming that both phosphinite arms of the pincer ligand are intact and coordinated to Ir. After being used as a transfer hydrogenation catalyst,^{4,20} the ^{31}P MAS NMR spectrum of $[\text{K}^+][\mathbf{2}]/\gamma$ -alumina shows a second isotropic signal at *ca.* 66 ppm.⁴ Its chemical shift is similar to the signal observed at 71 ppm in the spectrum of $\mathbf{1}/\gamma$ -alumina, and assigned to adsorbed $(t\text{-Bu})_2(\text{H})\text{P}=\text{O}$ (see above).

Another possible decomposition pathway for the supported pincer complexes is the direct oxidation of an Ir-coordinated phosphinite to give the corresponding phosphinate, $(t\text{-Bu})_2(\text{ArO})\text{P}=\text{O}$. A sample of 1,3,5- $((t\text{-Bu})_2\text{PO})_3\text{-C}_6\text{H}_3$ that had been exposed to air was supported on γ -alumina. In addition to the expected signals at 155 ppm and 71 ppm (in common with an intact sample), a new peak at 59 ppm was present for the air-exposed sample, Fig. S4 (see ESI[†]). It is assigned to (di-*tert*-butyl)phenylphosphinate, $(t\text{-Bu})_2(\text{PhO})\text{P}=\text{O}$ (see ESI[†]). The similarity in chemical shifts for the products of phosphinite oxidation and hydrolysis/isomerization makes precise assessment of the decomposition pathway difficult for the supported complex, and it is possible that both occur.

Adsorption onto silica

Other oxide supports whose surfaces are terminated by nucleophilic hydroxyl groups are expected to induce similar phosphinite transformations, leading to anchored organic and organometallic compounds. We therefore investigated the reaction of phosphinites with silica. In terms of anchoring pincer catalysts, we envisage the formation of a covalent linkage between the phenoxide and the support, as illustrated in Scheme 4.



Scheme 4 Proposed grafting of $\{p\text{-}[(t\text{-Bu})_2\text{PO}]\text{-C}_6\text{H}_2\text{-2,6-}[\text{OP}(t\text{-Bu})_2\text{]}_2\}\text{-Ir}(\text{C}_2\text{H}_4)$, $\mathbf{1}$, onto silica.

The ^{31}P MAS NMR spectrum of 1,3,5- $((t\text{-Bu})_2\text{PO})_3\text{-C}_6\text{H}_3$ supported on silica is shown in Fig. 4a. The signal at 160 ppm is assigned to intact phosphinite groups, while the signal at 71 ppm is attributed to the phosphine oxide formed by surface-mediated hydrolysis/isomerization. The appearance of a P–H stretch at 2326 cm^{-1} in the IR spectrum of 1,3,5- $((t\text{-Bu})_2\text{PO})_3\text{-C}_6\text{H}_3$ supported on silica, Fig. 3c, confirms the generation of $(t\text{-Bu})_2(\text{H})\text{P}=\text{O}$, which is presumably attached to unreacted surface hydroxyl groups *via* hydrogen bonding (since silica lacks Lewis acidity). Other phosphine oxides have been shown to interact with silica in this way.²¹ A similar reaction of $\text{P}(\text{OMe})_3$ with silica was reported to generate $\equiv\text{SiOMe}$ and $(\text{MeO})_2(\text{H})\text{P}=\text{O}$, where the

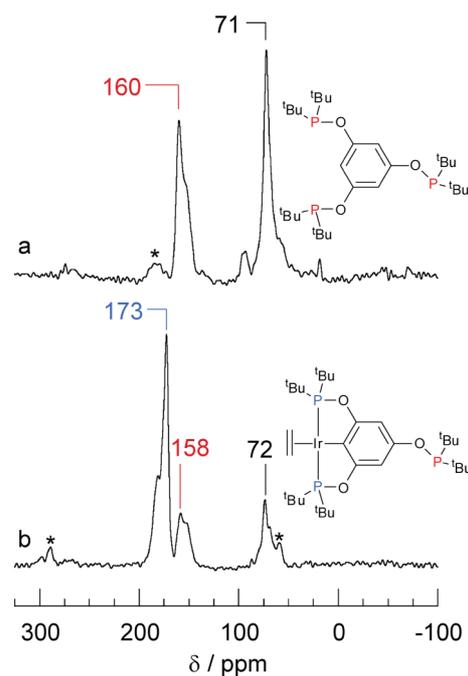


Fig. 4 Solid-state ^{31}P MAS NMR spectra of (a) 1,3,5- $((t\text{-Bu})_2\text{PO})_3\text{-C}_6\text{H}_3$ supported on Aerosil-380 silica (previously dehydrated at $500\text{ }^\circ\text{C}$); and (b) $\mathbf{1}$ supported on the same silica. Spectra were recorded with 14 kHz MAS; asterisks denote spinning sidebands.

latter was observed to be hydrogen bonded to residual hydroxyl groups.¹⁵

When a red solution of $\mathbf{1}$ in hexanes was stirred with an excess of silica (*i.e.*, containing more surface hydroxyl groups than $\mathbf{1}$), the support acquired the color of the Ir pincer complex while the solvent became completely decolorized. The ^{31}P MAS NMR spectrum of $\mathbf{1}$ supported on silica, Fig. 4b, shows a major signal at 173 ppm with a shoulder at 183 ppm, assigned to the Ir-coordinated phosphinites of the pincer complex. The minor signal at 72 ppm corresponds to adsorbed $(t\text{-Bu})_2(\text{H})\text{P}=\text{O}$. These results confirm that a grafting reaction similar to that observed on γ -alumina also occurs on silica.

The ^{31}P MAS NMR spectrum of $\mathbf{1}/\text{silica}$ also contains a broad peak at 158 ppm, assigned to uncoordinated phosphinite groups on the basis of its chemical shift. It appears that, in addition to covalent anchoring *via* phosphinite cleavage, $\mathbf{1}$ can also adsorb on the silica surface *via* hydrogen bonding, so that the uncoordinated phosphinite at the *para*-position remains intact. We were unable to remove this species by washing the silica-supported pincer complex with hexanes. The ratio of the signals at 72 and 158 ppm, representing reacted and unreacted *para*-phosphinite groups, respectively, is *ca.* 1.1. Thus the two adsorbed species are present in roughly equal amounts. The ratio of the area of the signal at 173 ppm to the sum of the areas of the signals at 72 and 158 ppm is 2.1, close to the original ratio of 2.0 for Ir-coordinated and non-Ir-coordinated phosphinite groups of intact $\mathbf{1}$.

Finally, we tested $\mathbf{1}/\text{silica}$ in the transfer dehydrogenation of cyclooctane and *tert*-butylethylene (TBE) to cyclooctene and 2,2-dimethylbutane at $200\text{ }^\circ\text{C}$. In order to rule out leaching of $\mathbf{1}$ into solution during reaction, the catalyst was washed repeatedly with hexanes prior to use. After 1 h, a turnover number of 612 was

achieved. No TBE isomerization products (2,3-dimethyl-2-butene or 2,3-dimethyl-1-butene) were detected by GC/MS, consistent with the low Brønsted acidity of silica relative to γ -alumina.

Conclusions

The uncoordinated phosphinite substituents of pincer ligands react with surface hydroxyl groups on γ -alumina as well as silica, resulting in covalent anchoring of the ligands to the oxide surface by elimination of $(t\text{-Bu})_2(\text{H})\text{P}=\text{O}$. The latter interacts with oxide surfaces at Lewis acid sites and/or hydroxyl sites, but it can be displaced by other Lewis bases. The surface-mediated phosphinite rearrangement allows for the *in situ* generation of a supported analogue of $[p\text{-O-C}_6\text{H}_4\text{-2,6-}[\text{OP}(t\text{-Bu})_2]_2]\text{Ir}(\text{C}_2\text{H}_4)^-$, using the more synthetically accessible complex $\{p\text{-}[(t\text{-Bu})_2\text{PO}]\text{-C}_6\text{H}_4\text{-2,6-}[\text{OP}(t\text{-Bu})_2]_2\}\text{Ir}(\text{C}_2\text{H}_4)$. A similar transformation of the Ir-coordinated phosphinite arms represents a possible decomposition pathway for these supported pincer complexes.

We envisage that reactions of phosphinite-, phosphonite- or phosphite-containing ligands ($\text{P}(\text{OR}^1)_n\text{R}^2_{3-n}$, where $n = 1, 2, 3$) with surface hydroxyls to be a new, general method for the non-hydrolytic immobilization of homogeneous catalysts onto silica, alumina, or other oxide supports bearing surface hydroxyl groups. The formation of a phosphine oxide provides a driving force for the attachment reaction. The use of [POR]-containing substituents remote from the active center of the catalyst may produce immobilized metal catalysts with activities similar to their homogeneous analogues, but with longer lifetimes due to the suppression of bimolecular decomposition pathways. Catalyst loadings can be controlled by adjusting the hydroxyl density of the support, which also minimizes decomposition induced by reactions with residual hydroxyl groups.

Experimental methods

Materials

γ -Alumina (Strem, $185\text{ m}^2\text{ g}^{-1}$) was calcined overnight in flowing O_2 at $550\text{ }^\circ\text{C}$. Silica Aerosil-380 (Evonik Industries, $363\text{ m}^2\text{ g}^{-1}$) was dried under dynamic vacuum (10^{-4} Torr) at $500\text{ }^\circ\text{C}$ overnight. After thermal pretreatment, the supports were handled under strictly air-free conditions to prevent re-adsorption of atmospheric moisture and CO_2 . Solvents were rigorously dried and standard glovebox and Schlenk techniques were used to keep samples air-free. Chloroform-*d* (99.8% D) and THF-*d*₈ (99.5% D) were purchased from Cambridge Isotopes Laboratories, Inc. (Andover, MA).

The syntheses of phosphinite compounds and the iridium-pincer complexes were reported previously.⁴ Bis(*tert*-butyl)phenylphosphine oxide was prepared from di-*tert*-butylchlorophosphine (Strem, 96%), as described by Gray *et al.*¹¹ A solution-state $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum in CDCl_3 confirmed its identity ($\delta = 51.7\text{ ppm, s}$). Di-*tert*-butylphosphine oxide was purchased from Strem, and used as received. To prepare the supported phosphorus compounds, the phosphinite or phosphine oxide (approx. 20 mg) dissolved in toluene (3 mL) was stirred under N_2 over the appropriate oxide (γ -alumina or silica, 400 mg) for 2 h, filtered, washed with excess toluene, and dried in vacuum. To prepare γ -alumina- or silica-supported iridium-pincer complexes, the appropriate complex was

dissolved in dry hexanes, stirred over γ -alumina or silica under N_2 , filtered, and washed with excess hexanes. Residual hexanes were allowed to evaporate without application of vacuum, under air- and moisture-free conditions.

NMR characterization

Solid samples (approx. 120 mg) were packed under N_2 into 4 mm zirconia rotors, then closed with tight-fitting rotor caps equipped with O-ring seals (Wilmad). Solid-state MAS NMR spectra were recorded at room temperature on a Bruker Avance DSX300 spectrometer equipped with a 4-mm broadband MAS probehead operating at 121.49 MHz for ^{31}P , and using 14 kHz MAS. ^{31}P MAS NMR experiments were performed with a 90° pulse length of 3 μs , an acquisition time of 0.25 ms, and a recycle delay of 3 s. Between 5000 and 12 800 scans were acquired to achieve an adequate signal-to-noise ratio. Solution-state NMR spectra were recorded on a Bruker Avance DMX500 spectrometer operating at 202.45 MHz and 500.13 MHz for ^{31}P and ^1H , respectively. ^{31}P NMR chemical shifts are referenced to aqueous 85% H_3PO_4 .

Infrared characterization

Self-supporting pellets of silica or γ -alumina, pretreated thermally to removed adsorbed water and with the appropriate phosphine oxide or phosphinite adsorbed, were pressed under N_2 . Spectra were recorded in transmission mode on a Bruker ALPHA-T spectrophotometer under N_2 . Background and sample spectra were recorded by co-addition of 64 scans at a resolution of 4 cm^{-1} .

Identification of reaction products by GC/MS

Analyses were performed on a Shimadzu GCMS-QP2010 fitted with an Agilent DB-1 column (100% dimethylpolysiloxane, $30\text{ m} \times 0.25\text{ mm i.d.}, 0.25\text{ }\mu\text{m}$ film thickness). A typical temperature program involved 5 min isothermal operation at $40\text{ }^\circ\text{C}$ followed by a $25\text{ }^\circ\text{C min}^{-1}$ ramp to $220\text{ }^\circ\text{C}$. The inlet and ion source temperatures were $250\text{ }^\circ\text{C}$ and $260\text{ }^\circ\text{C}$, respectively.

Transfer dehydrogenation

A glass reactor was loaded with 50 mg of 1/silica (1 wt% Ir), 0.40 mL cyclooctane, and 0.30 mL *tert*-butylethylene (TBE). The reactor was tightly sealed under N_2 with a Teflon plug equipped with a Viton O-ring. The suspension was stirred in an oil bath at $200\text{ }^\circ\text{C}$ for 1 h, then cooled to room temperature. The liquid in the reactor was analyzed by GC/MS, and the turnover number was calculated as the molar ratio of 2,2-dimethylbutane formed to Ir present.

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