

A Convenient Molecular Self-assembly Route to Thin Films containing Terminal Donor Ligands and Anchored Organotransition-metal Complexes for Heterogenized Homogeneous Catalysis

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Simple acid–base hydrolytic chemistry on the surfaces of glass, quartz or silicon provides an easy access to thin films containing terminal amine and phosphine donor ligands which covalently bind a variety of organometallic complexes, and such oriented ultrathin films supporting a densely packed nickel(0) organometallic complex on glass, catalyse oligomerization of phenylacetylene.

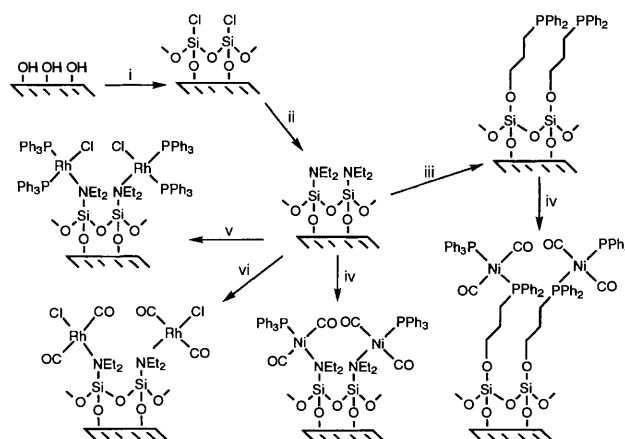
Supported metal complexes offer distinct advantages over their homogeneous counterparts in transition metal catalysed organic transformations. Much of the effort in this area¹ has been directed at tethering organometallic fragments to organic polymers or silica functionalized with donor ligands such as phosphines. Silane condensation reactions using amines or phosphines containing terminal trialkoxy groups have been employed¹ extensively for the surface modification of silica. However, presynthesizing target molecules containing suitable end groups, incomplete surface reactions, side reactions leading to immobilized P^V groups, and controlling unwanted oligomerization of trialkoxysilanes in solution, are significant issues.^{1a,e,2} The flat topological surfaces of glass, quartz and Si offer similar surface chemistry to silica, and yet allow the build-up of robust single layers of densely packed oriented organometallic centres for tailored activity and selectivity of the catalysts. To our knowledge, there are very few reports^{1e,f} of anchored organometallic complexes on the latter surfaces. In this communication, we report (a) a new synthetic approach based on simple acid–base hydrolysis to construct self-assembled monolayers containing terminal amine and phosphine donor ligands, and subsequently their transition metal complexes on silica, glass, quartz and silicon using commercially available reagents; and (b) efficient oligomerization of phenylacetylene using molecularly self-assembled thin films of [Si]–O(CH₂)₃PPh₂Ni(CO)₂(PPh₃) on glass.

Organosilicon halides, e.g. Me₃SiCl, are known³ to react with amines such as NEt₂H yielding Me₃SiNEt₂⁺ and NEt₂H₂Cl. The resulting aminosilane reacts with HO(CH₂)₃PPh₂ and HOC₆H₄PPh₂ almost quantitatively via acid–base hydrolysis to give Me₃SiO(CH₂)₃PPh₂,[†] Me₃SiOC₆H₄PPh₂[†] and NEt₂H. We were intrigued by the possibility of generating anchored amine and phosphine donor ligands on inorganic oxide surfaces by the above acid–base chemistry, and then building covalently immobilized organometallic thin films.

In a typical surface modification process, clean[‡] silica, glass, quartz or silicon substrates were first treated with a toluene solution of SiCl₄ (10% v/v) at room temp. for 14 h, followed by dry NEt₂H in toluene (5% v/v) at 70 °C for 14 h yielding

covalently anchored NEt₂ species. The latter were then treated with HO(CH₂)₃PPh₂ or HOC₆H₄PPh₂ in toluene to give self-assembled monolayers containing terminal phosphine ligands with the elimination of NEt₂H. The introduction of metals was achieved by reacting surface amine and phosphine donor ligands with metal complexes in toluene at 70–100 °C for 24 h (Scheme 1). The monolayer structures in these thin films were characterized by contact angle measurements, solid-state NMR, FTIR, UV–VIS absorption and X-ray photoelectron spectroscopies. The contact angles[‡] of thin films on flat surfaces were in accord^{4,5} with surface wettabilities: clean glass surface, 18° (H₂O) and 87° (hexadecane); monolayers containing terminal phosphines, 95° (H₂O) and 8° (hexadecane).

Solid-state ³¹P NMR spectroscopy is an extremely useful technique to characterize^{1a,e} supports containing phosphorus donors and their transition metal complexes. The single solid-state ³¹P resonance at δ –16.01 in the cross-polarized^{1e} ³¹P



Scheme 1 Reagents and conditions: i, SiCl₄, toluene, room temp., 18 h; ii, NEt₂H, toluene, 70 °C, 14 h; iii, RH, [RH = HO(CH₂)₃PPh₂, HOC₆H₄PPh₂], toluene, 70 °C, 18 h; iv, Ni(CO)₂(PPh₃)₂; v, RhCl(PPh₃)₃; vi, [RhCl(CO)₂]₂, toluene, 70 °C, 24 h.

Table 1 ³¹P{¹H} NMR and IR data in solution or solid state

Complex ^a	³¹ P{ ¹ H} (C ₆ D ₆) δ ^b	³¹ P{ ¹ H} (Solid state) δ ^b	IR (Nujol) ν _{CO} /cm ⁻¹	IR (KBr disc) ν _{CO} /cm ⁻¹
Me ₃ SiOC ₆ H ₄ PPh ₂	25.5			
[Si]–OC ₆ H ₄ PPh ₂		26.7		
Me ₃ SiO(CH ₂) ₃ PPh ₂	–14.05			
[Si]–O(CH ₂) ₃ PPh ₂		–16.01		
Ni(CO) ₂ (PPh ₃) ₂	35.2		1998, 1935	
[Si]–NEt ₂ Ni(CO) ₂ (PPh ₃)		31.2		1980, 1936
Me ₃ SiO(CH ₂) ₃ PPh ₂ Ni(CO) ₂ (PPh ₃)	36.0, 26.4		1999, 1938	
[Si]–O(CH ₂) ₃ PPh ₂ Ni(CO) ₂ (PPh ₃)		29.5 ^c		1998, 1934
RhCl(PPh ₃) ₃	33.3, 54.6 ^d			
[Si]–NEt ₂ RhCl(PPh ₃) ₂		51.1, 58.3 ^e		
[RhCl(CO) ₂] ₂			2085, 2030	
[Si]–NEt ₂ RhCl(CO) ₂				2081, 2019

^a [Si] = surface of ground glass. ^b Referenced to external H₃PO₄. ^c Broad with overlapping peaks. ^d J_{Rh,P} 146 and 199 Hz. ^e J_{Rh,P} 185 Hz.

NMR spectrum of a monolayer of [Si]–O(CH₂)₃PPh₂ on ground glass[‡] is consistent with the ³¹P NMR solution spectrum of Me₃SiO(CH₂)₃PPh₂ (δ –14.05). It should be noted that preparation of similar monolayers by condensation^{1a,e} of (EtO)₃Si(CH₂)_nPPh₂ (n = 2,3) on silica introduces two chemically distinct phosphorus groups on the support, namely phosphine and phosphine oxide.^{1a,e} This suggests that the surface modification process, reported here, is a simple approach to prepare phosphine oxide-free supports. The solid-state ³¹P spectral resonances for the supported metal complexes, [Si]–O(CH₂)₃PPh₂Ni(CO)₂(PPh₃), [Si]–NEt₂Ni(CO)₂(PPh₃), [Si]–NEt₂Rh(Cl)(PPh₃)₂ (Table 1) are comparable to those in solution for Ni(CO)₂(PPh₃)₂, Me₃SiO(CH₂)₃PPh₂Ni(CO)₂(PPh₃) and RhCl(PPh₃)₃.

IR spectroscopy is a widely used⁶ tool to probe the surface structure of the anchored organometallic species containing bound CO ligands. The FTIR spectrum[‡] of a monolayer of [Si]–O(CH₂)₃PPh₂Ni(CO)₂(PPh₃) on ground glass (KBr disc) shows two peaks at 1998 and 1934 cm^{–1} in the ν_{CO} stretching region which are very similar to those observed for Ni(CO)₂(PPh₃)₂ at 1998 and 1935 cm^{–1} in Nujol. Similarly, the ν_{CO} stretching frequencies (Table 1) for [Si]–NEt₂Ni(CO)₂(PPh₃) and [Si]–NEt₂RhCl(CO)₂ are in accord with those observed for Ni(CO)₂(PPh₃)₂ and [RhCl(CO)₂]₂.

An estimation of the surface density in a monolayer of [Si]–O(CH₂)₃PPh₂Ni(CO)₂(PPh₃) was made based on the solution absorption spectrum[§] of Ni(CO)₂(PPh₃)₂ and Beer Lambert's law.⁷ Using the extinction coefficient of Ni(CO)₂(PPh₃)₂ (λ_{max} = 236, ε = 1.81 × 10⁷ cm² mol^{–1}), surface coverage was calculated to be 3 × 10^{–9} mol cm^{–2} which is indicative⁷ of a densely packed film. An analysis of the X-ray photoelectron spectrum of a monolayer of [Si]–O(CH₂)₃PPh₂Ni(CO)₂(PPh₃) on quartz showed the presence of Si (2p, 102.6 eV), P (2s, 199 eV), C (1s, 284.9 eV), O (1s, 532 eV) and Ni (2s, 1013 eV) peaks. This, together with the data presented above, suggests that the chemistry depicted in Scheme 1 is consistent with the course of the reactions taking place on the surface.

It is well known⁸ that phenylacetylene can be trimerized using Ni(CO)₂(PPh₃)₂ as a catalyst in solution to give cyclic, 1,3,5-triphenylbenzene (ca. 1%), 1,2,4-triphenylbenzene (30%) and linear, 1,3,6-triphenylhex-1-yne-3,5-diene (70%) products. We have attempted catalytic oligomerization of phenylacetylene by a similar Ni⁰ complex surface immobilized on a 1 × 1 inch (1 inch = 2.54 cm) glass slide, [Si]–O(CH₂)₃PPh₂Ni(CO)₂(PPh₃). Our preliminary results[¶] indicate that the latter organometallic thin films are very efficient for catalysing the above reaction, affording a product mixture containing the dimer (7%), trimer (81%), tetramer (3%), pentamer (7%) and hexamer (1%). The formation of the trimer products is similar to the homogeneous reaction,⁸ however, with the supported metal catalysts, dimer and higher oligomers are also obtained. In addition, an analysis of the product distribution in the trimer fraction indicated that (a) the symmetric 1,3,5-triphenylbenzene predominates over the unsymmetrical isomer; and (b) the linear trimeric product is 1,4,6-triphenylhex-1-yne-3,5-diene. Similar linear derivative has also been reported recently by Werner *et al.*⁹ from the reaction of phenylacetylene with an acetatorhodium(I) complex. The above results suggest different selectivity of the surface immobilized Ni⁰ complex.

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Footnotes

† These complexes were characterized by NMR and MS: *Selected data* for Me₃SiNEt₂: ¹H NMR (270 MHz, C₆D₆) δ 0.25 (s, Me₃Si), 1.55 (3 H, t, J 7 Hz, Me), 3.27 (2 H, q, J 7 Hz, CH₂). For Me₃SiO(CH₂)₃PPh₂: ¹H NMR (200 MHz, C₆D₆) δ 0.09 (9 H, s, Me₃Si), 1.72 (2 H, m, J 6 Hz, CH₂), 2.09 (2 H, m, J 6 Hz, CH₂), 3.52 (2 H, t, J 6 Hz, CH₂), 7.10, 7.46 (10 H, m, PPh₂); EI-MS *m/z* 316. For Me₃SiOC₆H₄PPh₂: ¹H NMR (200 MHz, C₆D₆) δ 0.06 (9 H, s, Me₃Si), 6.70, 7.05, 7.88 (14 H, m, C₆H₄PPh₂); EI-MS *m/z* 351.

‡ The substrates were cleaned by (a) soaking in soap solution and sonicating for 30 min; (b) washing with deionized water; (c) treating with piranha solution (70% H₂SO₄, 30% H₂O₂) at 100 °C for 1 h.

CAUTION: The piranha solution is highly potent and explosive. Care should be taken while using this mixture; (d) washing copiously with deionized water; (e) soaking in ammonia solution; and (f) drying with a stream of nitrogen before placing them in a dry box. The static contact angles on the substrates were measured with a Rame-Hart NRL 100 goniometer. ³¹P{¹H} NMR solution spectra were measured at 109.4 MHz and the ³¹P cross-polarization spectra were obtained at 121.279 MHz. The IR spectra were measured on a Bruker IFS-48 FT-IR spectrometer.

§ UV-VIS (CH₂Cl₂): λ_{max} = 236 nm (A = 2.55); monolayer (quartz) λ_{max} = 208 (A = 0.20). The spectra were collected from a quartz slide functionalized on both sides. For calculating surface coverage, absorbance was divided by 2 to obtain the value for each individual monolayer.

¶ A functionalized glass slide was placed in a benzene solution of phenylacetylene and the mixture was heated to 90 °C for 4 h. The product analysis was carried out by melting point determination, MS, UV-VIS, IR and NMR. The percentages of the oligomers are based on the EI-MS results: 204 (dimer), 306 (trimer), 408 (tetramer), 510 (pentamer), 612 (hexamer). Mixed melting points: 99.9 °C (1,2,4-triphenylbenzene, I); 107 °C (1,4,6-triphenylhex-1-yne-3,5-diene, II), 174 °C (1,3,5-triphenylbenzene, III). UV-VIS (C₆H₁₂) λ_{max} = 252 nm, other peaks at 236, 275 (sh), 328 nm. ¹H NMR (270 MHz, C₆D₆), for I δ: 7.15 (s), 7.24 (m); for II δ: 8.09 (d, J_{H,H} 16 Hz), 6.82 (d, J_{H,H} 16 Hz), 5.89 (s), 7.24 (m); for III δ: 7.77 (s), 7.69, 7.51 (m). IR (CH₂Cl₂) ν/cm^{–1} 2974, 1602, 1096, 996, 860.

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