Titanium Dioxide Nanoparticles Functionalized with Pd and W Complexes of a Catecholphosphane Ligand

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Palladium and tungsten complexes containing the bifunctional ligand 4-diphenylphosphanylcatechol (L^1) have been synthesized. The catecholate functionality strongly binds to titanium dioxide nanoparticles, effectively anchoring the complexes to the TiO_2 surface. Solid-state ^{31}P NMR spectroscopy was used to probe the surface-bound compounds. Diffuse reflectance infrared spectroscopy also provided data on surface-bound tungsten carbonyl complexes. Preliminary experiments show that the palladium phosphane complex $[PdBr_2(L^1)_2]$ supported on TiO_2 catalyzes the Sonogashira coupling of phenylacetylene with 4-iodonitrobenzene.

Introduction

Immobilizing materials on metal oxide supports is attracting sustained interest with applications in areas such as catalysis, electrocatalysis, electrochromic display, photodegradation of organic compounds, and photovoltaic power generation.[1−4] Titanium dioxide is a useful support because it is inexpensive, inert, and nontoxic, as well as having an electronic band structure suitable for the aforementioned applications.

Our aim was to use a bifunctional catechol (1,2-dihydroxybenzene)−phosphane compound to anchor transition metal complexes ligated via the P atom to TiO_2 bound by the catecholate group. We envisaged that the soft phosphane donor should preferentially coordinate to soft metal centers,[5−8] and the catechol group, which is a source of the hard catecholate dianion, should preferentially bind to hard Ti^{IV} metal centers.[9−18] Anchoring groups such as carboxylate and phosphonate are regularly used to immobilize molecules on TiO_2 and other metal oxide surfaces. Although it is known that catechol forms a strongly immobilized complex with TiO_2 surfaces,[13,14] the use of catechol as an anchoring substituent for metal complexes has been scarcely documented.[15] The catecholate binding group is "non-innocent" in the sense that it is redox active, able to bind metal centers as catecholate, semiquinone and quinonoid forms.[16−18] Attractively, use of a catechol anchor could potentially increase communication between a surface-immobilized transition metal species and the titania surface.[19] We chose phosphanes as the metal-binding groups because phosphanes are amongst the most common ligands in transition metal chemistry and phosphane complexes of transition metals exhibit a diverse range of desirable photophysical and redox properties in addition to being the largest class of molecular catalysts.[5,6]

Scheme 1 outlines two approaches toward our goal of phosphane-substituted metal complexes on titania. We anticipated that either TiO_2 particles could be functionalized with a phosphanyl-catechol and then treated with transition metal sources or that metal phosphane complexes bearing the free catechol group could be prepared which would directly attach to the TiO_2 surface. Phosphanes bearing phosphonite or alkoxysilane-substituted tethers have been previously employed to immobilize metal complexes on SiO_2,[20−32] but to the best of our knowledge not to titania, and never before has the "non-innocent" catecholate group been employed to anchor a transition metal phosphane complex to a metal oxide surface. Raymond et al.[12] recently reported a catecholphosphane (L^1, see below) that suited our purposes. In this paper, we present the results of investigations on L^1 and transition metal complexes of L^1 immobilized on nanocrystalline TiO_2 particles.

Results and Discussion

Syntheses

The precursor 4-(diphenylphosphanyl)veratrole (L^2) was prepared using an adaptation of the method of Schmid et

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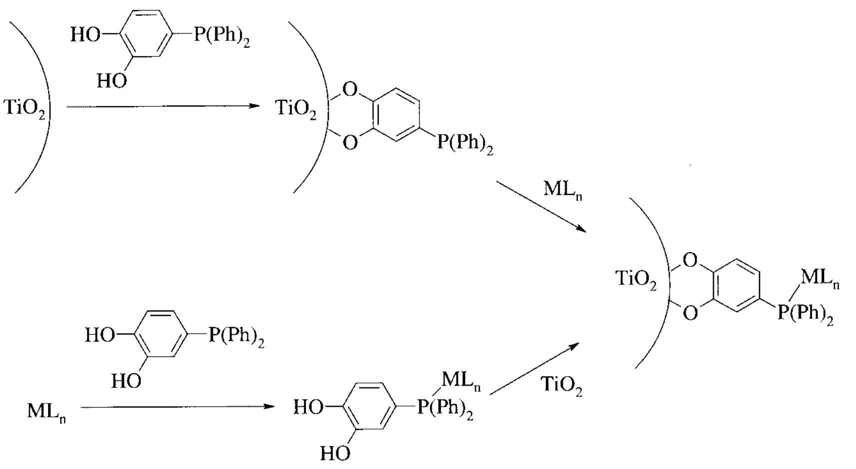
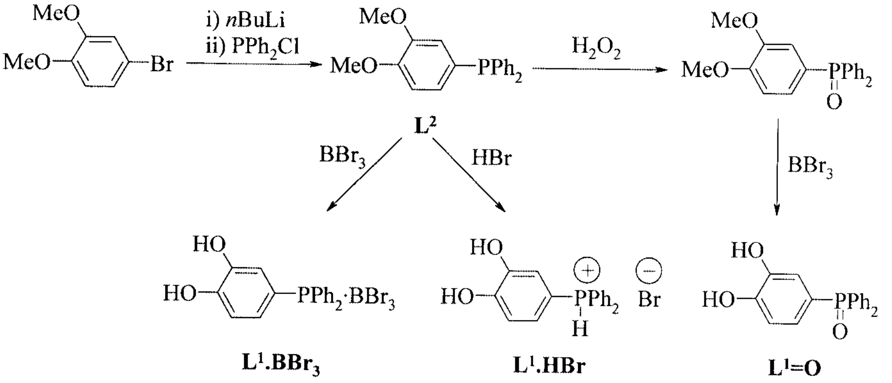


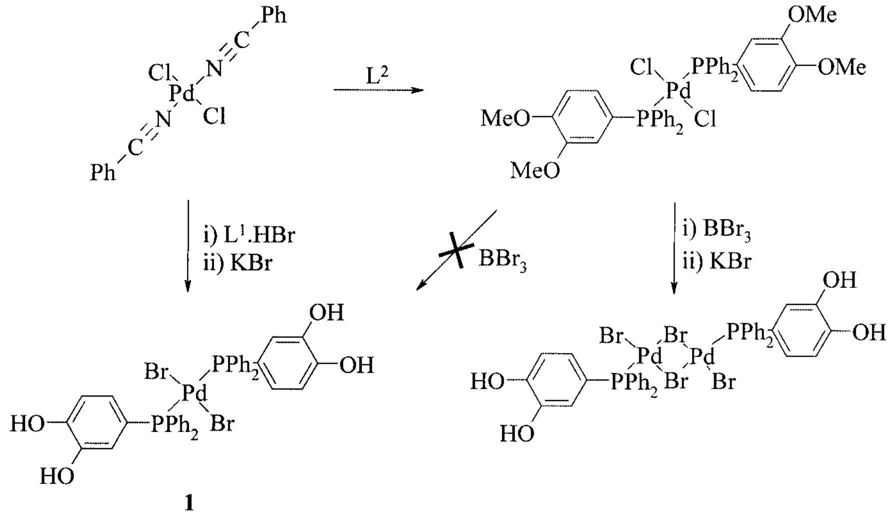
Scheme 1. Approaches to using a bifunctional catecholphosphane compound to anchor transition metals complexes to TiO_2 surfaces



Scheme 2. Preparation of derivatives of catecholphosphane L^1

al.[33] Lithiation of 4-bromoveratrole in tetrahydrofuran using *n*-butyllithium and subsequent reaction with chlorodiphenylphosphane gave L^2 in 95% yield (Scheme 2). Attempted demethylation of L^2 to afford L^1 using boron tribromide yielded instead the boron tribromide adduct $L^1{\cdot}BBr_3$. The ^{31}P NMR spectrum of $L^1{\cdot}BBr_3$ has four peaks of equal intensity because of ^{31}P-^{11}B scalar coupling (^{11}B: $I = {}^3/_2$, 80.4% abundance). The chemical shift, $\delta = -2.4$ ppm, is consistent with other $P(Ar)_3BBr_3$ adducts.[34] The P−B bond was found to be quite stable and we were unable to cleanly displace the boron tribromide by reaction with strong Lewis bases such as di- and triethylamine, or by hydrolysis with aqueous hydroxide. Demethylation of L^2 was achieved by the procedure of Raymond et al.[12] to yield the catecholphosphane hydrobromide, $L^1{\cdot}HBr$. Oxidation of L^2 with hydrogen peroxide followed by demethylation with boron tribromide afforded the catecholphosphane oxide $L^1{=}O$ in 81% overall yield.

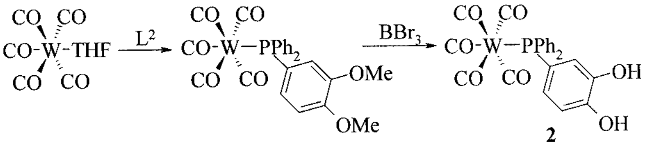
The reaction of $[PdCl_2(PhCN)_2]$ with L^2 gave $[PdCl_2(L^2)_2]$ in 80% yield (Scheme 3). Treatment of this complex with boron tribromide did not yield the desired catecholphosphane complex, $[PdBr_2(L^1)_2]$ (**1**), but the bromide-bridged bi-metallic complex $[Pd_2Br_4(L^1)_2]$, which was isolated in 70% yield. The ^1H and ^{31}P NMR spectra, ESI-MS, and elemental microanalysis are all consistent with the dimeric structure for $[Pd_2Br_4(L^1)_2]$. The presence of the adduct $L^1{\cdot}BBr_3$ in the crude reaction mixture (about 1:1 by ^1H NMR spectroscopy) suggests that one of the phosphane groups is captured by boron tribromide resulting in a coordinatively unsaturated palladium species. Combination of two such species would give the stable bromide-bridged dimer. A similar reaction has been previously reported by Sembiring et al.[35] Complex **1** was eventually and conveniently obtained in 70% yield from the reaction of $[PdCl_2(PhCN)_2]$ with $L^1{\cdot}HBr$ followed by treatment with excess KBr. During this reaction, bromide for chloride li-



Scheme 3. Preparation of catecholphosphane palladium(II) complexes

gand metathesis occurs and stirring the crude reaction mixture with excess potassium bromide ensures that the amount of chloride-containing complex in the product is negligibly small.

The tungsten(0) carbonyl complex [W(CO)$_5$(L^2)] was prepared by the in situ reaction of L^2 with freshly prepared [W(CO)$_5$(THF)] (THF = tetrahydrofuran) (Scheme 4). Boron tribromide effected cleavage of the methyl groups in [W(CO)$_5$(L^2)], without significant decomplexation of the phosphane from the tungsten, to afford the tungsten(0) carbonyl derivative [W(CO)$_5$(L^1)] (**2**) in 72% yield.



Scheme 4. Preparation of catecholphosphane tungsten(0) complexes

Preparation of TiO$_2$-Bound Catecholphosphane Compounds

The TiO$_2$-bound compounds were prepared by stirring a solution of the compound with TiO$_2$ nanoparticles (Degussa P-25). The particles were then filtered and rinsed successively with a number of solvents to ensure that no free compound remained before drying in vacuo at room temperature.

Solid-State ^{31}P NMR Studies of TiO$_2$-Bound Catecholphosphane Compounds

Solid state ^{31}P{^{1}H} NMR spectra have been acquired of the catecholphosphane L^1, its oxide L^1=O, and its metal complexes, **1** and **2**, adsorbed onto titanium dioxide nanoparticles as well as in their pure form. Spectra were obtained using cross-polarization to enhance the NMR sensitivity of the dilute species bound to titania.

The CP/MAS ^{31}P NMR spectrum of L^1·HBr (Figure 1, a) shows an isotropic signal at $\delta_P = -3.6$ ppm, (linewidth, $\nu_{1/2} = 450$ Hz, chemical shift anisotropy, $\Delta\sigma = 100$ ppm) little shifted from the solution value, $\delta_P = -6.73$ ppm ([D$_7$]dimethylformamide).[12] In contrast, the CP/MAS ^{31}P NMR spectrum of the phosphane oxide L^1=O (Figure 1, e) yields two values for the isotropic chemical shift, δ_P =

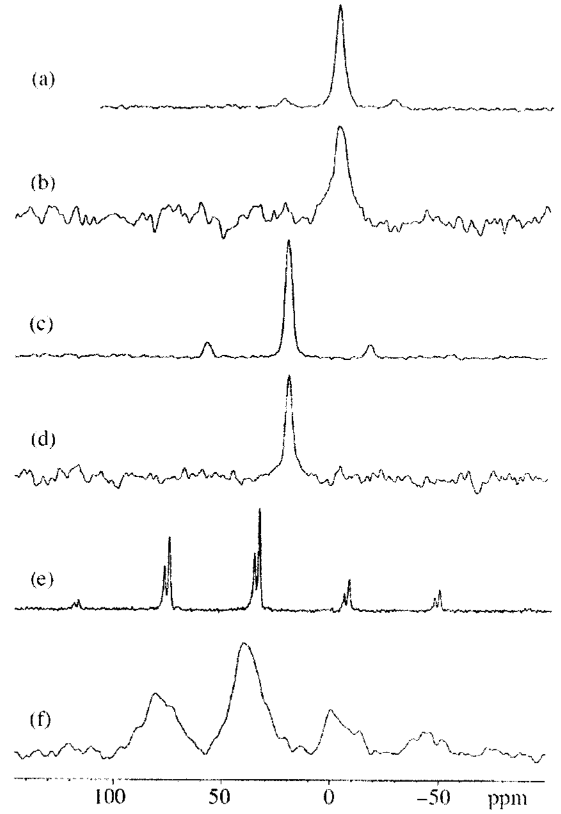


Figure 1. ^{31}P CP/MAS solid-state NMR spectra of (a) pure L^1·HBr; (b) TiO$_2$-bound L^1; (c) pure **2**; (d) TiO$_2$-bound **2**; (e) pure L^1=O; (f) TiO$_2$-bound L^1=O; for all spectra, the temperature was 303 K and the spin rate was 5 kHz, except for (e): 3 kHz

36.0 and 33.9 ppm, suggestive of two chemically distinct phosphorus environments either within the crystal lattice or in two crystal polymorphs. The chemical shift anisotropy, $\Delta\sigma = 200$ ppm, is indicative of a less isotropic electronic distribution about the phosphorus(V) atom in L^1=O than about the phosphorus(III) atom in L^1·HBr. The magnitude of the chemical shift anisotropy for L^1=O is identical to the literature value for $OPPh_3$.[20] Interestingly, the linewidths for L^1=O, $\nu_{1/2} = 145$ Hz, are appreciably narrower than those for L^1·HBr, perhaps reflecting increased crystallinity for the L^1=O sample.

It was anticipated that immobilization of L^1 on the TiO_2 surface would provide titania particles functionalized with phosphane groups. The spectra of L^1·HBr adsorbed to TiO_2 (Figure 1, b) yielded an isotropic chemical shift, $\delta_P = -2.8$ ppm, similar to that for unbound L^1·HBr. The spectra show no peaks for the phosphane oxide L^1=O (see below). Clearly, the catechol group effectively immobilizes L^1 on the TiO_2 surface without significant oxidation of the phosphane functionality. The linewidth of L^1 on TiO_2, $\nu_{1/2} = 750$ Hz, is of a comparable order of magnitude to that for pure L^1·HBr, $\nu_{1/2} = 400$ Hz. Likewise, the CP/MAS ^{31}P NMR spectrum of pure **2** shows an isotropic signal at $\delta_P = 20.1$ ppm (Figure 1, c), while that of TiO_2-bound **2** (Figure 1, d) is at $\delta_P = 19.9$ ppm. Again the linewidths of **2**, $\nu_{1/2} = 370$ Hz, and TiO_2-bound **2**, $\nu_{1/2} = 260$ Hz, are comparable. The relatively invariant chemical shift dispersion upon immobilization of ligand L^1 or complex **2** is indicative of the surface-bound species, in each case, occupying near identical environments on the TiO_2 surface. In each case, the surface sites occupied by the immobilized species appear remarkably the same.

The CP/MAS ^{31}P NMR spectrum of phosphane oxide L^1=O adsorbed to TiO_2 (Figure 1, f) yields an isotropic chemical shift, $\delta_P = 39.7$ ppm, and chemical shift anisotropy, $\Delta\sigma = 200$ ppm, suggesting the local environment of the phosphorus atom does not appreciably change upon binding to TiO_2. The linewidth for TiO_2-bound L^1=O, $\nu_{1/2} = 1.5$ kHz, however, is substantially broader than anticipated. Phosphane oxides are known to bind to TiO_2 surfaces,[36–38] and it is possible that, for TiO_2-bound L^1=O, the phosphane oxide oxygen atom also binds to the surface, which leads to disordered surface environments and consequently to substantial chemical shift dispersion. This is in agreement with the trend observed for solid PPh_3 and $OPPh_3$ bound to silica surfaces.[20–23,25–30,32,36–38]

Infrared Experiments on TiO_2-Bound Tungsten Complexes

The strong infrared-active carbonyl absorption bands of the tungsten(0) carbonyl **2** make it an appropriate probe for the binding of the catechol group of L^1 to titania. Figure 2 shows solution and diffuse reflectance infrared spectra of **2**. The solution spectrum of **2** (Figure 2, a) is characteristic of complexes of the type $[W(CO)_5(PAr_3)]$. The bands at approximately 2070 and 1935 cm^{-1} are assigned to the A_1^{eq} and E vibrational modes,[39] respectively, and are associated with the four equivalent carbonyl ligands.

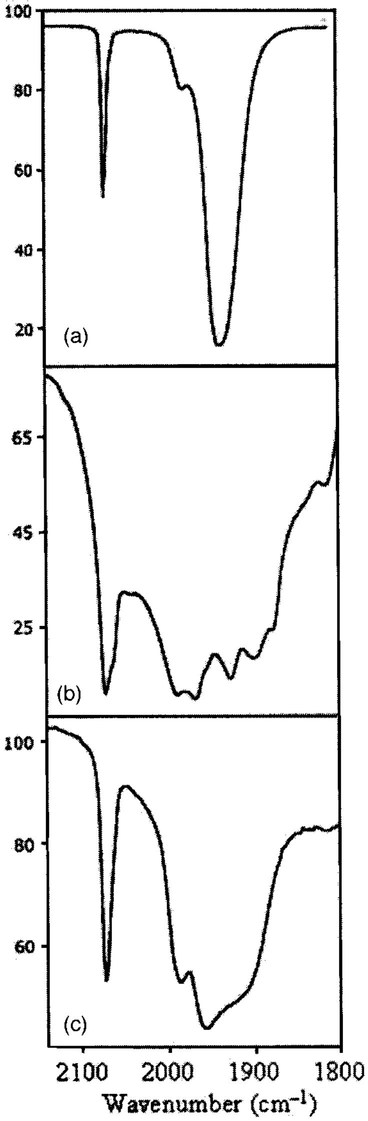


Figure 2. (a) FTIR spectrum of **2** in dichloromethane solution; (b) diffuse reflectance FTIR spectrum of solid **2**; (c) diffuse reflectance FTIR spectrum of TiO_2-supported **2**

The diffuse reflectance infrared spectrum of a solid sample of **2** is shown in Figure 2, b. The A_1^{eq} band appears at 2071 cm^{-1}, a value similar to that observed in the solution spectrum. Most noticeable is the splitting of the E infrared modes, with peaks at 1967, 1926, and 1900 cm^{-1}, due to different carbonyl environments created by packing in the solid state.

The diffuse reflectance infrared spectrum of TiO_2-bound **2** is shown in Figure 2, c. The A_1^{eq} band is seen at 2073 cm^{-1}, almost unchanged from the previous two spectra. A broad E band with a transmittance minimum at approximately 1956 cm^{-1} is observed with a much less symmetrical shape than that in the solution spectrum. This may also be attributed to packing-induced anisotropy and indicates the TiO_2-bound **2** also experiences different carbonyl environments, created by packing and orientation on the surface.

To explore if TiO_2 particles treated with $L^1 \cdot HBr$ react with a metal center, we treated $[W(CO)_5(THF)]$ with TiO_2 particles bearing surface-bound ligands. The diffuse reflectance infrared spectrum was recorded. Bands at 2072, 1984 and a broad strong band at approximately 1955 cm^{-1} may be attributed to successful reaction between $[W(CO)_5(THF)]$ and L^1-derivatized TiO_2 to afford TiO_2-bound **2**. We also found that stirring $[W(CO)_5(THF)]$ with untreated TiO_2 particles followed by washing resulted in a surface-bound tungsten carbonyl species. The diffuse reflectance infrared spectrum of this species exhibits characteristic carbonyl stretching bands. Comparison with solution infrared spectra of $[W(CO)_5OH]^-$ [40,41] gives some indication of the nature of the bound tungsten carbonyl species.

These spectra are similar to the surface-bound tungsten carbonyl species formed upon reaction of $[W(CO)_5(THF)]$ with TiO_2. It appears that the species formed involves a Ti−O−W bond such as that illustrated in Figure 3.

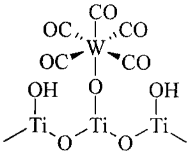
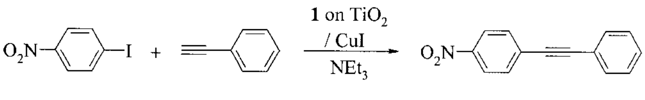


Figure 3. A possible surface-bound tungsten carbonyl species resulting from the reaction of $[W(CO)_5(THF)]$ and TiO_2

Coupling of Phenylacetylene with 4-Iodonitrobenzene Catalyzed by $[PdBr_2(L^1)_2]$ Supported on TiO_2

Palladium complexes are effective catalysts in the coupling reaction between aryl halides and terminal alkynes (Sonogashira coupling).[42−43,44,45] In order to establish the potential of surface-immobilized catecholphosphane metal complexes in catalysis, a preliminary study of the coupling between 4-iodonitrobenzene and phenylacetylene in the presence of the palladium complex **1** supported on TiO_2 (Scheme 5) was undertaken.



Scheme 5. Coupling reaction between 4-iodonitrobenzene and phenylacetylene catalyzed by CuI and TiO_2-supported **1**

The supported catalyst was prepared by stirring a dichloromethane solution of **1** with TiO_2 at room temperature for 24 h (no special treatment was undertaken to remove any TiO_2 surface-bound water). The suspension was filtered and rinsed successively with dichloromethane, acetone, methanol and diethyl ether to ensure that no unbound material remained. The estimated loading of **4** on titania was 1−2% w/w. The TiO_2-supported **1** was added to a triethylamine solution of 4-iodonitrobenzene and phenylacetylene, together with a cocatalyst, copper(I) iodide. The reaction proceeded to completion after stirring at room temperature for 24 h (^1H NMR spectroscopy showed quantitative conversion of 4-iodonitrobenzene to (4-nitrophenyl)phenylethyne). The reaction mixture was decanted from the settled catalyst, and fresh solvent, reactants, and copper(I) iodide were added. After the same reaction time and conditions as the first batch, the reaction had again proceeded to completion (as evidenced by ^1H NMR spectroscopy). The process was repeated a third time whereupon the reaction reached about 75% completion after the same reaction time, because of the deactivation of the palladium catalyst. A control reaction was also performed where unmodified TiO_2 was added to a triethylamine solution of 4-iodonitrobenzene and phenylacetylene, together with a cocatalyst, copper(I) iodide. After 24 h, no coupling was detected using ^1H NMR spectroscopy.

These preliminary results suggest that palladium complexes anchored to TiO_2 by catecholphosphane ligands do function as catalysts, although with limited turnover cycles. A full study is required to establish the cause of deactivation of the palladium catalyst as well as comparative studies with existing catalysts. Overall, the amount of palladium employed is no larger than that used in conventional homogeneous catalysis (typically 1−5 mol %). Because of the ease of catalyst separation (simple filtering from the reaction mixture) this TiO_2-confined catalyst may be useful in situations where product and catalyst are difficult to separate such as where the reagents and products have highly polar groups and are difficult to purify by the usual chromatographic procedures.

Conclusion

Our results reveal that TiO_2-immobilized transition metal−phosphane complexes are readily accessible starting from catecholphosphanes. Infrared experiments indicate binding of a pre-formed catecholphosphane complex to TiO_2 to give a more precisely defined material than does sequential surface derivatization with the catecholphosphane ligand and subsequent reaction with a metal precursor. Further investigations of applications, such as those summarized in the Introduction, are clearly warranted.

Experimental Section

General Remarks: Reactions were carried out under nitrogen by using Schlenk techniques. All solvents were analytical grade (AR). The following reaction solvents were dried and distilled under nitrogen using standard methods: dichloromethane over calcium hydride; tetrahydrofuran over sodium or potassium benzophenone ketyl. Acetone, diethyl ether, absolute ethanol and triethylamine were used without drying but were purged with nitrogen prior to use. Column chromatography was performed using Merck silica gel 60 of particle size 0.040−0.063 mm (230−400 mesh ASTM). Analytical TLC was carried out on Merck aluminum sheets coated with 0.25 mm silica gel 50 PF_{254}.

The reagents 4-bromoveratrole, *n*-butyllithium, boron tribromide, tungsten hexacarbonyl, phenylacetylene (Aldrich), hydrogen peroxide (20%), MnO_2, KBr, 4-nitroiodobenzene and CuI were purchased commercially and used as received. Chlorodiphenylphosphane (Aldrich) was distilled before use. The titanium dioxide (TiO_2) was Degussa P25 (ca. 25-nm particles). Literature procedures were used to prepare 4-(diphenylphosphanyl)catechol hydrobromide (L^1·HBr),[12] and $[PdCl_2(NCPh)_2]$.[46]

^1H and ^{31}P NMR solution spectra were recorded in $CDCl_3$ (Cambridge Isotope Laboratories or Aldrich) or [D_6]acetone (Aldrich) using a Bruker Avance 300 spectrometer (at 300 MHz for ^1H, 121 MHz for ^{31}P). The ^1H NMR spectra were referenced internally to residual protic solvent, and ^{31}P to external 85% H_3PO_4.

Solid state ^{31}P NMR spectra were obtained using a Varian Inova 300 NMR spectrometer at 121.395 MHz using Chemagnetics cross-polarization magic-angle spinning (CP/MAS) probes. The samples were packed into 4 mm or 7.5 mm o.d. zirconia rotors and spun at between 3 and 5 kHz. Spectra were recorded at 303 K and referenced to the CP/MAS spectrum of external solid ammonium dihydrogen phosphate, $\delta_P = 1.0$ ppm.[47] Cross-polarized spectra were obtained after optimizing by using the following parameters: recycle time, 20−120 s; contact time, 4−5 ms; ^1H 90° pulse width, 5−6 μs.

Infrared spectra were recorded on a Nicolet Avatar 320 FT-IR spectrometer in a solution cell or using a diffuse reflectance infrared FT (DRIFTS) attachment. The background for DRIFTS samples was air (for neat samples) or oven-dried TiO_2 (for supported samples). Electrospray ionization mass spectra (ESI-MS) were acquired on a VG Quattro mass spectrometer with a capillary voltage of 4 kV and a cone voltage of 30 V. Elemental microanalyses were carried out by the Microanalytical Service Unit at the Research School of Chemistry, Australian National University.

Synthesis of 4-(Diphenylphosphanyl)veratrole (L^2): A solution of 4-bromoveratrole (4.00 mL, 27.8 mmol) in freshly distilled tetrahydrofuran (110 mL) was cooled to −78 °C and *n*-butyllithium solution (1.55 M) was added dropwise over 3 min. After stirring for 15 min, chlorodiphenylphosphane was added dropwise to the cooled solution. The stirred solution was allowed to warm to room temperature over 17 h after which all volatile materials were removed in vacuo. The white residue was extracted several times with dichloromethane and the washings taken to dryness in a rotary evaporator. The crude material was loaded onto a 15 × 3 cm silica column and eluted with petroleum spirit/dichloromethane (up to 1:1) with the collection of fractions. Fractions containing the product (as identified by analytical TLC, $R_f = 0.55$, petroleum ether/dichloromethane, 1:1) were combined and taken to dryness using a rotary evaporator to afford white−pale green crystals identified as 4-(diphenylphosphanyl)veratrole (L^2) (8.50 g, 26.4 mmol, 95%).[5,11] ^1H NMR ($CDCl_3$): δ = 3.76 (s, 3 H, Me), 3.92 (s, 3 H, Me), 6.92−6.86 (m, 3 H, C_6H_3), 7.37−7.28 (m, 10 H, Ph) ppm. ^{31}P NMR ($CDCl_3$): $\delta = -3.2$ ppm.

Attempted Synthesis of 4-(Diphenylphosphanyl)catechol (L^1): A solution of 4-(diphenylphosphanyl)veratrole (982 mg, 3.0 mmol) in dichloromethane (20 mL) was cooled to −78 °C and BBr_3 (1.05 mL, 11.1 mmol) was added dropwise with stirring. The mixture was stirred for a further 10 min before the cooling bath was removed and the mixture allowed to warm to room temperature over 3 h. Methanol (1 mL) was carefully added to quench the excess BBr_3, followed by water (5 mL), and the mixture was transferred to a separating funnel. The aqueous phase was neutralized and the dichloromethane phase collected, dried with $MgSO_4$, filtered, and taken to dryness on a rotary evaporator. A fluffy white solid was isolated and identified as the adduct, 4-(diphenylphosphanyl)catechol−boron tribromide (L^1·BBr_3) (1.38 g, 83%). ^1H NMR ([D_6]acetone): δ = 7.04 (dd, $^1J_{H,H} = 8$, $^2J_{PH} = 3$ Hz, 1 H, 6-C_6H_3), 7.14 (ddd, $^1J_{PH} = 11$, $^1J_{H,H} = 8$, $^2J_{H,H} = 2$ Hz, 1 H, 5-C_6H_3), 7.38 (dd, $^1J_{PH} = 12$, $^2J_{H,H} = 2$ Hz, 1 H, 3-C_6H_3), 8.70 (br. s, 1 H, OH), 7.95−7.57 (m, 10 H, Ph), 8.92 (br. s, 1 H, OH) ppm. ^{31}P NMR ($CDCl_3$): $\delta = -2.4$ (1:1:1:1 q, $J_{BP} = 149$ Hz).

Synthesis of L^2=O: A solution of L^2 (1.02 g, 3.2 mmol) in acetone (50 mL) was cooled to 0 °C and hydrogen peroxide solution (3.5 mL) was added dropwise with stirring. The mixture was stirred at 0 °C for 2 h at which point TLC indicated that the reaction was complete. MnO_2 was added in batches until no effervescence was observed, then the suspension was stirred for a further 1 h. The brown residue was removed by paper filtration, the filtrate tested for peroxides before being taken to dryness in a rotary evaporator to yield a cream colored solid identified as L^2=O (0.90 g, 84%).10,11 ^1H NMR ($CDCl_3$): δ = 3.83 (s, 3 H, Me), 3.90 (s, 3 H, Me), 6.87 (dd, $^1J_{H,H} = 8$, $^2J_{PH} = 3$ Hz, 1 H, 6-C_6H_3), 7.01 (ddd, $^1J_{PH} = 12$, $^1J_{H,H} = 8$, $^2J_{H,H} = 2$ Hz, 1 H, 5-C_6H_3), 7.28 (dd, $^1J_{PH} = 12$, $^2J_{H,H} = 2$ Hz, 1 H, 3-C_6H_3), 7.39−7.54 (m, 6 H, Ph), 7.59−7.67 (m, 4 H, Ph) ppm. ^{31}P NMR ($CDCl_3$): $\delta = 32.0$ ppm.

Synthesis of L^1=O: A solution of L^2=O (900 mg, 2.7 mmol) in dichloromethane (80 mL) was cooled to −78 °C and BBr_3 (0.80 mL, 8.4 mmol) was added dropwise with stirring. The mixture was allowed to warm to room temperature over 18 h. Dilute NaOH solution was carefully added to destroy excess BBr_3, then the reaction mixture was transferred to a separating funnel, acidified with HCl (5 M), and the dichloromethane layer was collected. The aqueous phase was extracted again with dichloromethane (2 × 25 mL). The dichloromethane washings were combined and washed with dilute acid (ca. 0.1 M HCl, 20 mL), dried with $MgSO_4$, filtered, and taken to dryness in a rotary evaporator. A cream-colored powder was isolated and identified as the hydrate of the product, L^1=O·H_2O (800 mg, 96%). ^1H NMR ($CDCl_3$): δ = 6.61 (ddd, $^1J_{PH} = 12$, $^1J_{H,H} = 8$, $^2J_{H,H} = 2$ Hz, 1 H, 5-C_6H_3), 6.85 (dd, $^1J_{H,H} = 8$, $^2J_{PH} = 4$ Hz, 1 H, 6-C_6H_3), 7.40−7.65 (m, 10 H, Ph), 8.00 (br. m, 2 H, OH), 7.81 (dd, $^1J_{PH} = 13$, $^2J_{H,H} = 2$ Hz, 1 H, 3-C_6H_3) ppm. ^{31}P NMR ($CDCl_3$): $\delta = 35.3$ ppm. ^{31}P CP/MAS NMR: δ = 33.9, 36.1 (about 3:1). $C_{18}H_{15}O_3P$·H_2O (328.30): calcd. C 65.85, H 5.22; found C 66.82, H 4.87.

Synthesis of $[PdCl_2(L^2)_2]$: A solution of $[PdCl_2(NCPh)_2]$ (500 mg, 1.30 mmol) in dichloromethane (15 mL) was added to a solution of L^2 (890 mg, 2.76 mmol) in dichloromethane (15 mL) at room temperature. The resulting clear yellow solution was stirred for 30 min, the volume was reduced to about 10 mL, and methanol was added dropwise to give a yellow precipitate. The mixture was cooled in ice, and the precipitate was collected on a sintered glass funnel, washed with methanol and dried at the pump. Slow diffusion of diethyl ether into an acetone solution of the crude material yielded yellow-orange prisms of $[PdCl_2(L^2)_2]$ (862 mg, 80%). ^1H NMR ($CDCl_3$): δ = 6.86 (br. d, 2 H, C_6H_3), 3.89 (s, 6 H, Me), 3.75 (s, 6 H, Me), 7.11−7.18 (m, 2 H, C_6H_3), 7.33−7.45 (m, 12 H, Ph), 7.54−7.59 (m, 2 H, C_6H_3), 7.71−7.63 (m, 8 H, Ph) ppm. ^{31}P NMR ($CDCl_3$): $\delta = 25.3$ ppm. $C_{40}H_{38}Cl_2O_4P_2Pd$ (822.01): calcd. C 58.45, H 4.66; found C 57.55, H 4.72.

Synthesis of $[PdBr_2(L^1)_2]$ (1): A solution of $[PdCl_2(NCPh)_2]$ (240 mg, 0.63 mmol) in acetone (20 mL) was added to a stirred suspension of L^1·HBr (496 mg, 1.32 mmol) in acetone (30 mL) at room temperature. The resulting clear orange solution was stirred for a further 1 h, then KBr (6.30 g, 53 mmol) was added and the suspension stirred vigorously for 16 h. The mixture was filtered and taken to dryness to yield $[PdBr_2(L^1)_2]$ (**1**) (375 mg, 70%) as a yellow solid. ^1H NMR ([D_6]acetone): δ = 6.92 (br. d, 2 H, C_6H_3), 7.16−7.28 (m, 4 H, C_6H_3), 7.37−7.45 (m, 12 H, Ph), 7.64−7.72

(m, 8 H, Ph) ppm. ^{31}P NMR ([D$_6$]acetone): $\delta = 23.7$ ppm. Negative ion ESI-MS (methanol): 935 ([M + Br]$^-$, 100), 854 ([M − H]$^-$, 55). Positive ion ESI-MS (methanol): 775 ([M − Br]$^+$, 100). $C_{36}H_{30}Br_2O_4P_2Pd$ (854.81): calcd. C 50.59, H 3.54; found C 49.64, H 4.07.

Reaction of [PdCl$_2$(L^2)$_2$] with BBr$_3$: A solution of [PdCl$_2$(L^2)$_2$] (1.00 g, 1.2 mmol) in dichloromethane (30 mL) was cooled to −80 °C, and BBr$_3$ (0.56 mL, 5.9 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature overnight, the excess BBr$_3$ quenched with water, and the mixture was transferred to a separating funnel. Diethyl ether was added, and the organic phase was washed with brine (acidified with HCl), dried, filtered and taken to dryness. The crude material was dissolved in acetone (30 mL), KBr (5.8 g, 4.9 mmol) was added, and the suspension was stirred vigorously for 16 h. The mixture was transferred to a separating funnel, diethyl ether (30 mL) was added, and the resulting organic layer was washed twice and then dried over MgSO$_4$. The mixture was filtered and taken to dryness to give an orange solid identified as [Pd$_2$Br$_4$(L^1)$_2$] (375 mg, 70%). ^{1}H NMR ([D$_6$]acetone): $\delta = 6.95$ (dd, $^1J_{H,H} = 8$, $^2J_{PH} = 3$ Hz, 2 H, 5-C$_6$H$_3$), 7.08−7.17 (m, 2 H, 6-C$_6$H$_3$), 7.28 (dd, $^1J_{PH} = 13$, $^2J_{H,H} = 2$ Hz, 2 H, 3-C$_6$H$_3$), 7.43−7.59 (m, 12 H, Ph), 7.67−7.77 (m, 8 H, Ph), 8.67 (s, 4 H, OH) ppm. ^{31}P NMR (CDCl$_3$): $\delta = 36.8$ ppm. Negative ion ESI-MS (methanol): 1121 ([M]$^-$, 100). Positive ion ESI-MS (methanol): 775 ([M/2]$^+$, 45). $C_{36}H_{30}Br_4O_4P_2Pd_2$ (1121.04): calcd. C 38.57, H 2.70; found C 38.39, H 2.68.

Synthesis of [W(CO)$_5$(L^2)]: L^2 (1.38 g, 4.3 mmol) was added to a rapidly stirred yellow solution of [W(CO)$_5$(THF)], obtained by irradiating [W(CO)$_6$] (1.50 g, 4.3 mmol) in tetrahydrofuran (60 mL) with a mercury lamp for 3 h (with N$_2$ purge). The mixture was stirred at room temperature for 2 h after which all the volatile materials were removed in vacuo. The pale yellow residue was purified on a silica column by eluting with petroleum spirit/dichloromethane mixtures (up to 1:1). Fractions were collected and compared by using analytical thin-layer chromatography; the major band (pale yellow) was evaporated to dryness to give a pale yellow solid, identified as [W(CO)$_5$(L^2)] (1.69 mg, 61%). ^{1}H NMR (CDCl$_3$): $\delta = 3.79$ (s, 3 H, Me), 3.91 (s, 3 H, Me), 6.87−6.98 (m, 2 H, 5,6-C$_6$H$_3$), 7.07 (br. d, $^1J_{PH} = 13$ Hz, 1 H, 3-C$_6$H$_3$), 7.41−7.47 (m, 10 H, Ph); ([D$_6$]acetone): $\delta = 3.74$ (s, 3 H, Me), 3.88 (s, 3 H, Me), 6.98−7.15 (m, 3 H, C$_6$H$_3$), 7.48−7.57 (m, 10 H, Ph) ppm. ^{31}P NMR (CDCl$_3$): $\delta = 23.0$ ($J_{WP} = 242$ Hz) ppm; ([D$_6$]acetone): $\delta = 21.9$ ($J_{WP} = 242$ Hz) ppm. $C_{25}H_{19}O_7PW$ (646.25): calcd. C 46.46, H 2.96; found C 46.82, H 2.93.

Synthesis of [W(CO)$_5$(L^1)]: A solution of [W(CO)$_5$(L^2)] (615 mg, 0.95 mmol) in dichloromethane (10 mL) was cooled to −80 °C, and BBr$_3$ (0.30 mL, 3.2 mmol) was added dropwise. The mixture was allowed to warm to about −10 °C over 1.5 h, before it was cooled again to −80 °C, and NEt$_3$ (1 mL) and methanol (1 mL) were added to quench the excess BBr$_3$. After warming to room temperature, water (1 mL) was carefully added, and the mixture was transferred to a separating funnel and washed with dilute HCl solution (3 × 20 mL). The organic phase was dried over MgSO$_4$, filtered and taken to dryness to yield [W(CO)$_5$(L^1)] (**2**) (425 mg, 72%) as a cream-colored powder. ^{1}H NMR ([D$_6$]acetone): $\delta = 6.91−7.03$ (m, 3 H, C$_6$H$_3$), 7.47−7.55 (m, 10 H, Ph), 8.41 (s, 1 H, OH), 8.53 (s, 1 H, OH) ppm. ^{31}P NMR ([D$_6$]acetone): $\delta = 20.8$ ($J_{WP} = 241$ Hz). ^{31}P CP/MAS NMR: $\delta = 20.1$ ppm. Negative ion ESI-MS (methanol): 1236 ([2M]$^-$ dimer, 100). $C_{23}H_{15}O_7PW$ (618.19): calcd. C 44.69, H 2.45; found C 44.98, H 2.45.

Adsorption of Phosphanylcatechol-Containing Compounds onto TiO$_2$

L^1 on TiO$_2$: L^1·HBr (320 mg, 0.85 mmol) was added to a rapidly stirred suspension of TiO$_2$ (3.4 g) in methanol (150 mL). The color of the particles changed rapidly from white to pale orange. After stirring at room temperature for 1 h, triethylamine (0.5 mL, 3.6 mmol) was added, and the stirring was continued for a further 3 h. The suspension was then allowed to settle, and the colorless solution was removed using a cannula. The material was washed with methanol (150 mL), then filtered and rinsed successively with methanol (150 mL), acetone (2 × 50 mL), tetrahydrofuran (2 × 50 mL), dichloromethane (2 × 50 mL), and diethyl ether (2 × 15 mL), and then dried in vacuo at room temperature for 8 h. ^{31}P CP/MAS NMR: $\delta = -2.8$ ppm.

L^1=O on TiO$_2$: TiO$_2$ (1.50 g) was added to a colorless solution of L^1=O (203 mg, 0.65 mmol) in methanol (30 mL), and the suspension was stirred at room temperature for 18 h. The pale orange suspension was filtered and rinsed successively with methanol (3 × 15 mL) and diethyl ether (10 mL), and then dried in vacuo at room temperature for 6 h. ^{31}P CP/MAS NMR: $\delta = 40.1$ ppm.

[W(CO)$_5$(L^1)] on TiO$_2$: TiO$_2$ (1.0 g) was added to a solution of [W(CO)$_5$(L^1)] (100 mg, 0.16 mmol) in dichloromethane (100 mL), and the suspension was stirred at room temperature for 24 h. The pale orange suspension was then filtered and rinsed successively with dichloromethane (5 × 20 mL), acetone (2 × 20 mL), and diethyl ether (2 × 20 mL), then dried in vacuo at room temperature for 3 h. ^{31}P CP/MAS NMR: $\delta = 19.91$ ppm.

[W(CO)$_5$(THF)] on TiO$_2$: Photolytically generated [W(CO)$_5$(THF)] (10 mL, 28.4 mM in tetrahydrofuran, 0.284 mmol) was added to TiO$_2$ (1.0 g) and the suspension was stirred at room temperature for 24 h. The white-gray suspension was then filtered and rinsed successively with tetrahydrofuran (3 × 40 mL), acetone (2 × 40 mL), and diethyl ether (2 × 40 mL), then dried in vacuo at room temperature for 3 h.

[PdBr$_2$(L^1)$_2$] on TiO$_2$: TiO$_2$ (1.50 g) was added to an orange-yellow solution of [PdBr$_2$(L^1)$_2$] (150 mg, 0.18 mmol) in dichloromethane (100 mL), and the suspension was stirred at room temperature for 24 h. The suspension was then filtered and rinsed successively with dichloromethane (2 × 20 mL), acetone (2 × 15 mL), methanol (2 × 15 mL), and diethyl ether (2 × 15 mL), then dried in vacuo at room temperature for 8 h.

Catalytic Studies

Coupling of Phenylacetylene with 4-Iodonitrobenzene Catalyzed by [PdBr$_2$(L^1)$_2$] Supported on TiO$_2$: Phenylacetylene (0.15 mL, 1.3 mmol), CuI (10 mg, 0.05 mmol) and [PdBr$_2$(L^1)$_2$]-TiO$_2$ (800 mg, ca. 1% w/w) was added to a solution of 4-iodonitrobenzene (80 mg, 0.32 mmol) in triethylamine (30 mL, N$_2$-purged), and the suspension was stirred at room temperature for 24 h. The particles were allowed to settle, and the solution was transferred to a second flask using a cannula. The solid residue was washed with triethylamine (20 mL). The combined reaction solution and washing was taken to dryness, and the crude residue was passed through a short silica plug by using CH$_2$Cl$_2$/hexane (3:7) eluent. The ^{1}H NMR spectrum of the resulting pale yellow solid indicated quantitative conversion of 4-iodonitrobenzene to the product (4-nitrophenyl)phenylethyne[48] (<1% of the homo-coupled tolane product was also observed). A second batch of reactants and CuI catalyst (same scale) was added to a triethylamine (30 mL) suspension of the same Pd catalyst from above. Again, quantitative conversion into (4-nitrophenyl)phenylethyne was observed. The cycle was repeated a third time using the same Pd catalyst with a reduction of conversion to 75%.

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[1] D. W. Goodman, *J. Catal.* **2003**, *216*, 213−222.
[2] A. Fujishima, T. N. Rao, D. A. Tryk, *J. Photochem. Photobiol. C: Photochem. Rev.* **2000**, *1*, 1−21.
[3] M. Grätzel, *Prog. Photovoltaics: Res. Appl.* **2000**, *8*, 171−185.
[4] D. J. Cole-Hamilton, *Science* **2003**, *299*, 1702−1706.
[5] E. W. Abel, F. G. A. Stone, G. Wilkinson, J. A. Labinger, M. J. Winter (Eds.), *Comprehensive Organometallic Chemistry II*, Pergamon Press, Oxford, **1995**.
[6] B. Cornils, W. A. Herrman, *Applied Homogeneous Catalysis with Organometallic Compounds*, VCH, Weinheim (Germany), **1996**.
[7] S. E. Watkins, D. C. Craig, S. B. Colbran, *J. Chem. Soc., Dalton Trans.* **2002**, 2423−2436.
[8] S. E. Watkins, D. C. Craig, X.-H. Yang, S. B. Colbran, *J. Chem. Soc., Dalton Trans.* **1999**, 1539−1540.
[9] M. Albrecht, R. J. Frohlich, *J. Am. Chem. Soc.* **1997**, *119*, 1656−1661.
[10] M. Albrecht, *Chem. Eur. J.* **1997**, *3*, 1466−1471.
[11] M. Albrecht, M. Napp, M. Schneider, P. Weis, R. Fröhlich, *Chem. Eur. J.* **2001**, *7*, 3966−3975.
[12] X. Sun, D. W. Johnson, D. L. Caulder, K. N. Raymond, E. H. Wong, *J. Am. Chem. Soc.* **2001**, *123*, 2752−2763.
[13] R. Rodríguez, M. A. Blesa, A. E. Regazzoni, *J. Colloid Interface Sci.* **1996**, *177*, 122−131.
[14] P. A. Connor, K. D. Dobson, A. J. McQuillan, *Langmuir* **1995**, *11*, 4193−4195.
[15] C. R. Rice, M. D. Ward, M. K. Nazeeruddin, M. Grätzel, *New J. Chem.* **2000**, *24*, 651−652.
[16] C. G. Pierpont, *Coord. Chem. Rev.* **2001**, *216-217*, 99−125.
[17] C. G. Pierpont, C. W. Lange, *Prog. Inorg. Chem.* **1994**, *41*, 331−442.
[18] C. G. Pierpont, R. M. Buchanan, *Coord. Chem. Rev.* **1981**, *38*, 45−87.
[19] M. Grätzel, *Pure Appl. Chem.* **2001**, *73*, 459−467.
[20] L. Bemi, H. C. Clark, J. A. Davies, C. A. Fyfe, R. E. Wasylishen, *J. Am. Chem. Soc.* **1982**, *104*, 438−445.
[21] R. A. Komoroski, A. J. Magistro, P. P. Nicholas, *Inorg. Chem.* **1986**, *25*, 3917−3925.
[22] L. Reven, *J. Mol. Catal.* **1994**, *86*, 447−477.
[23] J. Blumel, *Inorg. Chem.* **1994**, *33*, 5050−5056.
[24] K. D. Behringer, J. Blumel, *Chem. Commun.* **1996**, 653−654.
[25] O. Krocher, R. A. Koppel, M. Froba, A. Baiker, *J. Catal.* **1998**, *178*, 284−298.
[26] P. Braunstein, H. P. Kormann, W. Meyer-Zaika, R. Pugin, G. Schmid, *Chem. Eur. J.* **2000**, *6*, 4637−4646.
[27] C. M. Crudden, D. Allen, M. D. Mikoluk, J. Sun, *Chem. Commun.* **2001**, 1154.
[28] A. J. Sandee, J. N. H. Reek, P. C. J. Kamer, P. W. N. M. van Leeuwen, *J. Am. Chem. Soc.* **2001**, *123*, 8468−8476.
[29] H. H. Wagner, H. Hausmann, W. F. Holderich, *J. Catal.* **2001**, *203*, 150−156.
[30] C. Merckle, J. Blumel, *Chem. Mater.* **2001**, *13*, 3617−3623.
[31] P. W. N. M. van Leeuwen, A. J. Sandee, J. N. H. Reek, P. C. J. Kamer, *J. Mol. Catal. A-Chem.* **2002**, *182*, 107−123.
[32] Z. L. Lu, E. Lindner, H. A. Mayer, *Chem. Rev.* **2002**, *102*, 3543−3578.
[33] R. Schmid, J. Foricher, M. Cereghetti, P. Schönholzer, *Helv. Chim. Acta* **1991**, *74*, 370−389.
[34] E. Muylle, G. P. Van Der Kelen, *Spectrochim. Acta A: Mol. Biomol. Spectr.* **1976**, *32*, 599−603.
[35] S. B. Sembiring, S. B. Colbran, D. C. Craig, M. L. Scudder, *J. Chem. Soc., Dalton Trans.* **1995**, *22*, 3731−3741.
[36] G. Guerrero, P. H. Mutin, A. Vioux, *Chem. Mater.* **2001**, *13*, 4367−4373.
[37] B. Hu, I. D. Gay, *Langmuir* **1995**, *11*, 3845−3847.
[38] L. Baltusis, J. S. Frye, G. E. Maciel, *J. Am. Chem. Soc.* **1986**, *108*, 7119−7120.
[39] R. J. Angelici, M. D. Malone, *Inorg. Chem.* **1967**, *9*, 1731−1736.
[40] D. J. Darensbourg, M. L. Meckfessel Jones, J. H. Reibenspies, *Inorg. Chem.* **1993**, *32*, 4675−4676.
[41] J. L. Cihonski, R. A. Levenson, *Inorg. Chem.* **1975**, *14*, 1717−1720.
[42] S. Takahashi, Y. Kuroyama, K. Sonogashira, N. Hagihara, *Synthesis* **1980**, 627−630.
[43] F. Quignard, S. Larbot, S. Goutodier, A. Choplin, *J. Chem. Soc., Dalton Trans.* **2002**, 1147−1152.
[44] C. C. Tzschucke, C. Markert, H. Glatz, W. Bannwarth, *Angew. Chem. Int. Ed.* **2002**, *41*, 4500−4503.
[45] E. Gonthier, R. Breinbauer, *Synlett* **2003**, 1049−1051.
[46] P. Braunstein, R. Bender, J. Jud, *Inorg. Synth.* **1989**, *26*, 341−350.
[47] S. Hayashi, K. Hayamizu, *Bull. Chem. Soc., Jpn.* **1989**, *62*, 2429−2430.
[48] K. Okuro, M. Furuune, M. Enna, M. Miura, M. Nomura, *J. Org. Chem.* **1993**, *58*, 4716−4721.

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