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Silica Anchored Bis(trialkylphosphine) Platinum Oxalate A Photogenerated Catalyst for Olefin Hydrosilation

Short Communication

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Ultraviolet irradiation of the silica attached complex $Pt(C_2O_4)L_2$, $[L = (H_3CO)_3Si(CH_2)_2PEt_2]$, yields a $[SiO_2]$-L_2Pt species that catalyzes olefin hydrosilation or adds 2 CO to yield a surface dicarbonyl complex.

(Keywords: Catalysis; Photochemistry; Supported platinum complex)

Siliziumverankerte Bis(trialkylphosphin)platinoxalate.
Ein photogenerierter Katalysator für die Hydrosilierung von Olefinen
(Kurze Mitteilung)

Die Ultraviolettbetrahlung des siliziumverknüpften Komplexes $Pt(C_2O_4)L_2$ $[L = (H_3CO)_3Si(CH_2)_2PEt_2]$ ergab eine $[SiO_2]$-L_2Pt-Spezies, die die Hydrosilierung von Olefinen katalysiert oder unter Bildung eines Oberflächen-Dicarbonylkomplexes 2 CO addiert.

The selectivity of homogeneous catalysts and ease of product separation with heterogeneous catalysts are both found in surface anchored homogeneous catalysts. Arylphosphine ligands have been attached to silica or polymer supports to bind transition metal ions for this purpose[1]. Phosphine dissociation and catalyst leaching from the support often plagues these catalyst systems. In this paper we describe the synthesis of a platinum(II) oxalate complex covalently linked to silica with a sterically unhindered and highly basic alkylphosphine ligand. Photolysis yields CO_2 and a surface bound zero-valent platinum complex that catalyzes

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* Dedicated to Prof. Dr. *Kurt L. Komarek* on the occasion of his 60th birthday.

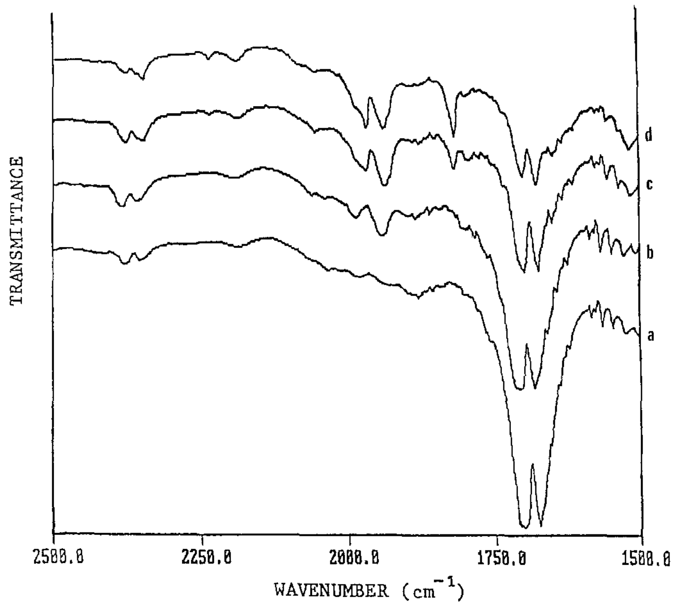
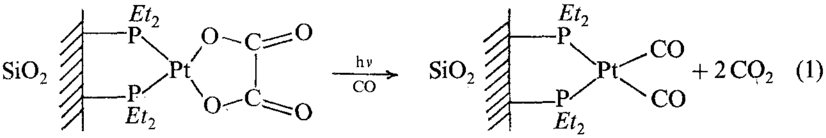


Fig. 1. Formation of supported platinum carbonyl complexes. Figures not on the same scale since mull thickness varies. Spectra a) 2 h irradiation; b) 4 h irradiation; c) 6 h irradiation; and d) 9.5 h irradiation with unfiltered light from a 200 W Hg-Xe arc lamp

hydrosilation of olefins. Platinum complexes are used commercially as homogeneous catalysts for that reaction.

Photochemical addition of $PH\mathit{Et}_2$ to vinyltrimethoxysilane[2] yields $L = (\mathit{Me}O)_3SiCH_2CHP\mathit{Et}_2$ in better than 90% yield. Treatment of $Pt(C_2O_4)(S\mathit{Me}_2)_2$[3], suspended in benzene, with $2L$ yields a solution of $Pt(C_2O_4)L_2$ from which benzene and $S\mathit{Me}_2$ are removed under vacuum. *Davison* grade 62 silica (4.0 g) refluxed in benzene with 0.83 mmol of $Pt(C_2O_4)L_2$ yields $[SiO_2]\text{-}L_2Pt(C_2O_4)$. These samples are refluxed further with hexamethyldisilazane to cap any unreacted surface hydroxyl groups. The maximum surface coverage obtained is 1 Pt/113 Å^2. Elemental analyses yield Pt : P ratios of 1 : 1.9–2.1, close to the 1 : 2 ratio expected.

An FTIR spectrum of a nujol mull of $[SiO_2]\text{-}L_2Pt(C_2O_4)$ exhibits absorptions for the oxalate group at 1 700 cm^{-1} and 1 765 cm^{-1}, which resemble those of the soluble analogue[3], $Pt(C_2O_4)(P\mathit{Et}_3)_2$. On UV irradiation (200 W Hg-Xe arc) the oxalate absorptions disappear and a signal for CO_2 appears at 2 330 cm^{-1}. If a sample of $[SiO_2]\text{-}L_2Pt(C_2O_4)$ is irradiated as a suspension in CO saturated benzene two terminal carbonyl stretches appear (Fig. 1) at 1 921 cm^{-1} and 1 963 cm^{-1}. These frequencies are within 10 cm^{-1} of those reported[4] for $Pt(CO)_2(PEt_3)_2$. A third absorption appears at 1 810 cm^{-1}, in the bridging CO region[5], at long irradiation times. Thus, surface bound platinum carbonyl clusters may form at high conversions. These data suggest the reaction sequence of Eq. (1) occurs on the surface.



Homogeneous platinum catalysts are used for commercial olefin hydrosilation reactions[6]. Irradiation of $[SiO_2]$-$L_2Pt(C_2O_4)$ suspended in either 1-heptene or $MeCl_2SiH$ yields a species that on addition of either $MeCl_2SiH$ or 1-heptene, respectively, catalyzes formation of $MeCl_2Si(n\text{-}C_7H_{15})$. The product exhibits IR, ^{1}H NMR and ^{29}Si NMR spectra identical to those of an authentic sample. The reaction may be conducted in noncoordinating solvents such as hexane. When the catalyst was removed by filtration we observed that the filtrate exhibited no catalytic activity, but the recovered silica possessed nearly full activity even after washing the catalyst with solvent. This shows the catalyst to be heterogeneous and that there is little loss of active platinum from the support during catalysis. The catalyst is extremely air sensitive and all reactions were conducted under a N_2 atmosphere. As many as 2 500 mol of product/mol Pt have been obtained with the catalyst system and mechanistic work is in progress.

Acknowledgement

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