Organometallics **2001,** *20,* 2660−2662

Synthesis of Polymer-Supported Rhodium(I)−1,3-Bis(diphenylphosphino)propane Moieties and Their Use in the Heterogeneous Hydrogenation of Quinoline and Benzylideneacetone

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Received December 26, 2000

Summary: A p-styrenyl substituent attached to the ligand framework allows the diphosphine moiety $-(C_6H_4)CH_2OCH_2C(CH_3)(CH_2PPh_2)_2$ *to be introduced as a pendant group in cross-linked styrene/divinylbenzene matrixes via free-radical copolymerization. In conjunction with rhodium(I), the POLYDIPHOS material forms an effective heterogeneous catalyst for the hydrogenation of benzylideneacetone to benzylacetone and of quinoline to a mixture of 1,2,3,4-tetrahydroquinoline, 5,6,7,8-tetrahydroquinoline, and decahydroquinoline. The homogeneous behavior of related 1,3-bis(diphenylphosphino)propane rhodium complexes is different in both activity and selectivity.*

The demand of single-site catalysts combining the advantages of heterogeneous and homogeneous catalysis has recently inspired an extraordinary effort from researchers in both industry and academia.[1−6] One major method of preparation involves the heterogenization of homogeneous catalysts by their immobilization on polymeric hydrocarbon resins, which are attractive for their chemical inertness as well as ease of preparation and functionalization. Cross-linked styrene/divinylbenzene resins amply meet these requirements. A major challenge remains in obtaining sufficiently immobilized catalysts, however. To inhibit metal leaching into the mobile phase during the catalysis, the tethered complex must be thermally and chemically robust. For this reason, the ligand preference is for tertiary phosphines, as they generally form very stable metal complexes. In addition, tertiary phosphines can efficiently control the stereochemical and electronic environment of the metal center. Since chelating diphosphines show superior ligating and control properties to those of monophosphines, the synthesis of chelating diphosphine ligands bound to organic polymers is a research topic of much current interest. To date, only a few examples of chelating diphosphine ligands anchored on cross-linked styrene/divinylbenzene polymers are known, and most of them have been synthesized by reaction of chlorinated resins with metalated ligands.[7−11]

Among chelating diphosphines, 1,3-bis(diphenylphosphino)propane (dppp) plays a central role in homogeneous catalysis due to its superior ligating properties combined with excellent backbone flexibility.[12] Various procedures of heterogenization of dppp have recently been developed, and the supported metal complexes have successfully been employed in heterogeneous reactions.[11,13]

This communication describes the synthesis of a new dppp-like diphosphine anchored to a cross-linked styrene/divinylbenzene polymer and of its complex with the "Rh(cod)$^+$" moiety (cod = cycloocta-1,5-diene). A soluble polystyrene resin containing 1,3-bis(diphenylphosphino)propane moieties has been described previously and used in combination with palladium to catalyze the telomerization of 1,3-butadiene.[11]

It is also shown here that the supported rhodium complex is a versatile, efficient, and easily recyclable hydrogenation catalyst. Quinoline (Q) and benzylideneacetone (BA) have been chosen as model unsaturated substrates for their different electronic and structural properties. Q is a natural contaminant in fossil fuels, from which it is removed by catalytic hydrodenitrogenation (HDN).[14,15] This process is extremely important to allow for effective fuel upgrade as well as to reduce NO_x emission into the atmosphere. BA is an α,β-unsaturated ketone that may undergo the selective hydrogenation of the keto group, the double bond, or both, depending on the metal catalysts.[5]

Our approach in the synthesis of the diphosphine-containing styrene monomer is illustrated in Scheme

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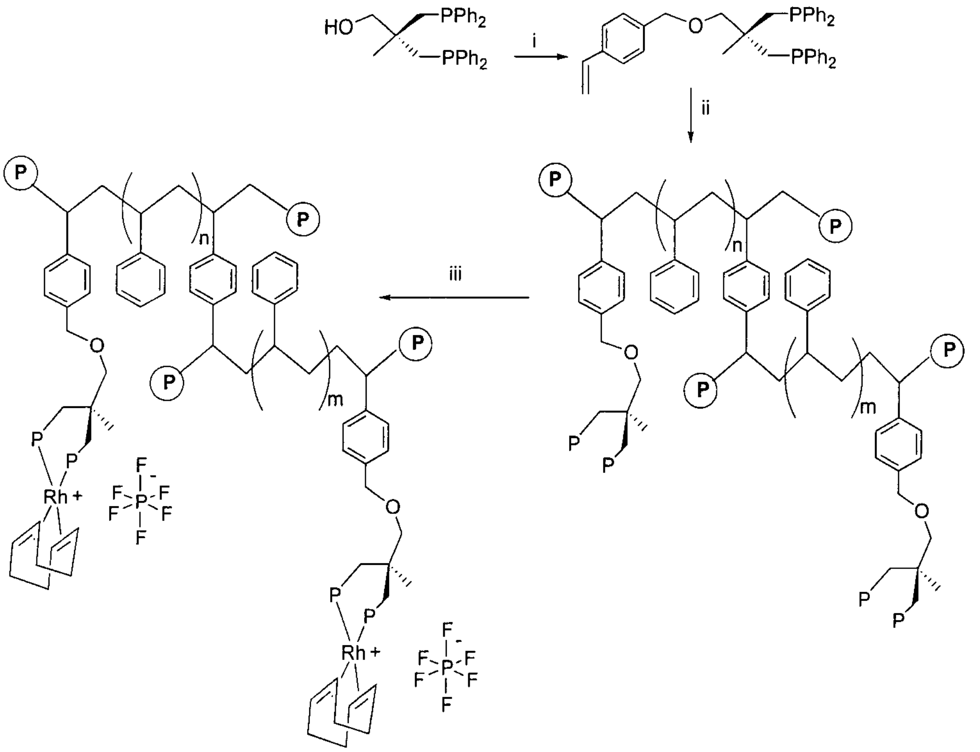
10.1021/om0010868 CCC: $20.00
Publication on Web 05/23/2001

Scheme 1[a]



[a]Reagents and conditions: (i) NaH, 4-vinylbenzyl chloride, DMF (90%); (ii) styrene–divinylbenzene, AIBN, THF/MeOH (1:2, v:v), 85 °C (96%); (iii) $[RhCl(cod)]_2$, Bu_4NPF_6, CH_2Cl_2 (95%).

1. The strategy is to prepare a dppp ligand bearing a *p*-styrenyl group for the copolymerization with styrene/DVB: the reaction of 2,2-bis(diphenylphosphinomethyl)propanol[16] with 4-vinylbenzyl chloride has proven to be a viable method to accomplish the high-yield synthesis of the desired *p*-styrenyl-functionalized diphosphine 2,2-bis(diphenylphosphinomethyl)propyl-4-vinylbenzyl ether (DPPBE).[17]

Copolymerization of DPPBE with styrene-DVB (0.5:1:36) in THF/MeOH using AIBN as the radical initiator generates a cross-linked diphosphine polymer (POLYDIPHOS) which appears as an off-white solid insoluble in organic solvents. Besides elemental analysis (C, H, P), the presence of diphosphine units in the resin was shown by CP MAS ^{31}P NMR spectroscopy. The spectrum of a POLYDIPHOS sample is given in Figure 1a. Noteworthy, the chemical shift (−24.8 ppm) is quite comparable to that of monomeric DPPBE.[18]

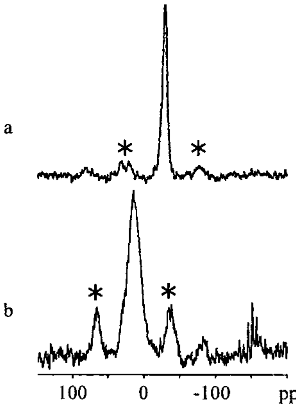


Figure 1. CP MAS ^{31}P NMR (121.50 MHz) spectra of POLYDIPHOS (a) and $[Rh(cod)(POLYDIPHOS)]PF_6$ (b). Spinning sidebands are denoted by asterisks.

Advantages of the present technique over heterogenization procedures involving the reaction of functionalized phosphines with functionalized cross-linked styrene/DVB resins are[7−10] (1) ease of synthesis, as only the phosphine needs to be chemically modified; (2) effective control on the phosphine loading (hence of the metal loading) by simply varying the phosphine/DVB/styrene ratio; and (3) absence of residual functional groups on the resins.

The supported complex $[Rh(cod)(POLYDIPHOS)]PF_6$ has been prepared by stirring a CH_2Cl_2 solution of $[RhCl(cod)]_2$ and Bu_4NPF_6 in the presence of POLYDIPHOS at room temperature for 24 h. The filtered yellow solid was washed with CH_2Cl_2 at reflux temperature with a Soxhlet apparatus and then dried. The rhodium loading in the heterogeneous catalyst was determined as 0.74 wt % by inductively coupled plasma

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[17] Selected NMR data in $CDCl_3$: ^1H NMR δ_H 1.24 (s, 3H, CH_3), 2.48 (second-order multiplet, 4H, CH_2P), 3.35 (s, 2H, CH_2C), 4.09 (s, 2H, OCH_2), 5.26 (dd, H_{cis}, CH_2=CH, J_{cis} = 10.86 Hz, J_{gem} = 0.87 Hz), 5.76 (dd, H_{trans}, CH_2=CH, J_{trans} = 17.62 Hz), 6.74 (dd, 1H C*H*=CH_2); $^{13}C\{^1H\}$ NMR δ_C 26.1 (t, CH_3, *J*(CP) = 9.4 Hz), 39.5(t, *C*(CH_2P), *J*(CP) = 13.5 Hz), 40.5 (dd, CH_2P *J*(CP) =16.8 Hz, *J*(CP) = 8.0 Hz), 73.1 (s, $PhCH_2O$), 78.1 (t, CH_2OC, *J*(CP) = 8.52 Hz), 114.03 (s, CH_2=CH), 126.7−140.6 (m, Ph), 133.9 (s, *C*H=CH_2); $^{31}P\{^1H\}$ NMR δ_P −24.6 (s).

[18] Solid-state ^{31}P NMR spectra were recorded at room temperature on a Bruker AMX 300 WB spectrometer equipped with a 4 mm BB-CP MAS probe at a working frequency of 121.50 MHz. The spectra were acquired using the cross-polarization pulse sequence under magic angle spinning at a spinning rate of 10 kHz. The 90° pulse was 3.3 μs, and the contact pulse was 1 ms. The spectra of the supported diphosphine were collected after 400 scans with a recycle delay of 1 s and a line broadening of 30 Hz, while the spectra of the supported rhodium complex were acquired with 700 scans, a recycle delay of 1 s, and a line broadening of 50 Hz. H_3PO_4 (85%) was used as the external standard.

Scheme 2. Hydrogenation of Q to ^{1}THQ, ^{5}THQ, and DHQ

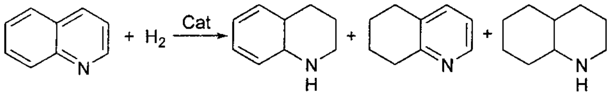

Table 1. Hydrogenation of Q with [Rh(cod)(POLYDIPHOS)]PF_6 (0.74 wt %)[a]

entry	t (h)	^{1}THQ %	^{5}THQ %	DHQ %	conv %
1	1	31.7	6.7	4.2	42.6
2[b]	1	31.3	5.2	3.6	40.1
3[c]	15	65.5	8.2	23.8	97.5
4[d]	1	30.2			30.2

[a] Experimental conditions: 100 mL Parr reactor, 30 mL of n-octane, Rh 1.1 × 10^{-3} mmol, Q 2.2 mmol, 80 °C, 30 bar H_2, 1500 rpm; product composition determined by GC/MS. [b] First recyling in the same conditions of entry 1. [c] Second recycling in the same conditions except for the reaction time. [d] Homogeneous reaction in THF catalyzed by [Rh(cod)(dppp)]PF_6.

atomic emission (ICP-AES). The coordination of rhodium(I) to the tethered phosphine was readily shown by the low-field shift to 24.8 ppm of the phosphorus resonance as well as the presence of the PF_6^- sextuplet at −144.5 ppm (Figure 1b).[18]

As an example of the great potential of POLYDIPHOS metal complexes in heterogeneous catalysis, [Rh(cod)-(POLYDIPHOS)]PF_6 has been employed to hydrogenate Q in n-octane (Scheme 2).

Under relatively mild experimental conditions (80 °C, 30 bar H_2), the heteroaromatic substrate was mainly converted to 1,2,3,4-tetrahydroquinoline (^{1}THQ), but appreciable formation of both 5,6,7,8-tetrahydroquinoline (^{5}THQ) and decahydroquinoline (DHQ) occurred. Table 1 reports catalytic data obtained for runs at 1 h (entry 1). An effective catalyst recycling with no loss of catalytic activity was accomplished by removing the liquid phase via the liquid sampling valve and recharging the autoclave with a solution containing the substrate (entries 2 and 3). In all cases, no rhodium leaching was observed by ICP-AES (<1 ppm). The homogeneous behavior of the 1,3-bis(diphenylphosphino)propane complex [Rh(cod)(dppp)]PF_6 in THF is different in both activity and selectivity (entry 4).

The data reported in Table 1 are of great relevance in the field of model studies of heterogeneous hydrodenitrogenation, as they show, for the first time, that a single metal site belonging to the class of HDS/HDN promoters[15] can hydrogenate both the heterocyclic and carbocyclic rings of Q, although at different rates. Independent reactions with isolated samples of ^{1}THQ and ^{5}THQ showed that both compounds are further reduced to DHQ. Fish has shown that "$RhCl(PPh_3)_2$" moieties tethered to a cross-linked phosphinated styrene/DVB resin catalyze the selective hydrogenation of Q to ^{1}THQ in heterogeneous phase.[19] Notably, it was found that the heterogeneous hydrogenations of various N-heterocycles were initially much faster than in the homogeneous phase by 10−20 times. This remarkable effect was attributed to steric requirements surrounding the active metal center, which would favor the coordination of the heterocycle and disfavor that of PPh_3.[19]

Scheme 3. Hydrogenation of Benzylideneacetone to Benzylacetone

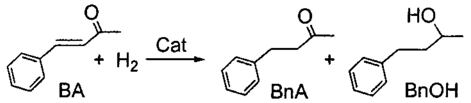

Table 2. Hydrogenation of BA with [Rh(cod)(POLYDIPHOS)]PF_6 (0.74 wt %)[a]

entry	t (h)	BnA %	BnOH %	selectivity %	conv %
1	2	>99	<1	>99	87
2[b]	2	>99	<1	>99	86
3[c]	2	98.0	2.0	98	86
4	4	94.1	5.9	94	100
5	2	86.9	13.1	87	100

[a] Experimental conditions: 100 mL Parr reactor, 30 mL of n-octane, Rh 1.1 × 10^{-3} mmol, BA 2.2 mmol, 100 °C, 30 bar H_2, 1500 rpm; product composition determined by GC/MS. [b] First recyling. [c] Second recycling. [d] Homogeneous reaction in THF catalyzed by [Rh(cod)(dppp)]PF_6.

In the presence of [Rh(cod)(POLYDIPHOS)]PF_6 suspended in n-octane, BA was selectively converted to benzylacetone (BnA) (Scheme 3).

Besides being selective to the saturated ketone, the catalyst system is very robust and was recycled three times with no appreciable decay of catalytic activity (Table 2, entries 1−3). Only for long reaction times was observed the further hydrogenation of BnA to 4-phenylbutan-2-ol (BnOH) (entry 4). Like in the case of Q hydrogenation, the homogeneous complex [Rh(cod)-(dppp)]PF_6 behaves as a much less selective catalyst in THF (entry 5).

It is worth stressing that the chemoselective hydrogenation of α,β-unsaturated ketones is a difficult task for traditional heterogeneous catalysts, which generally are much more efficient for the reduction of α,β-unsaturated aldehydes.[20] Two examples of selective hydrogenation of α,β-unsaturated ketones by molecular catalysts anchored on silica have recently been described, but the reported catalytic activity is much lower than that obtained with [Rh(cod)(POLYDIPHOS)]-PF_6.[5,21]

Acknowledgment. We are grateful to Claudia Forte (IQCEM-CNR of Italy) for assistance in recording the CP MAS ^{31}P NMR spectra and to MURST (Italy) for financial support (legge 95/95).

Supporting Information Available: Details of the synthetic procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0010868

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