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Zwitterionic Relatives to the Classic $[(\text{P–P})\text{Rh(solv)}_2]^+$ Ions: Neutral Catalysts Active for H–E Bond Additions to Olefins (E = C, Si, B)**

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Since their introduction by Osborne and Schrock three decades ago, cationic rhodium $[(\text{P–P})\text{Rh(solv)}_2]^+$ complexes have been used as precatalysts for a wide range of E–H (E = C, Si, B) bond-forming processes.[1–4] Herein, we introduce a new and complementary class of neutral, formally zwitterionic rhodium complexes supported by bis(phosphanyl)- and bis(amino)borate ligands that provide an alternative

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approach to the chemistry of the $[(P–P)Rh(solv)_2]^+$ complexes.[5] The rhodium(I) zwitterions introduced herein (Figure 1) feature a borate counteranion that is fastened within the ligand backbone and partially insulated from the coordinated metal center by tertiary phosphanes and amines.[6,7] These complexes are distinct from previously prepared bis(pyrazolyl)borate rhodium complexes,[8] where resonance delocalization of the borate charge is likely to be more prevalent.

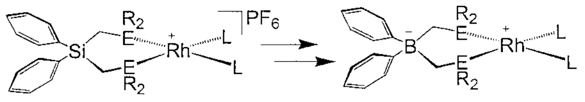


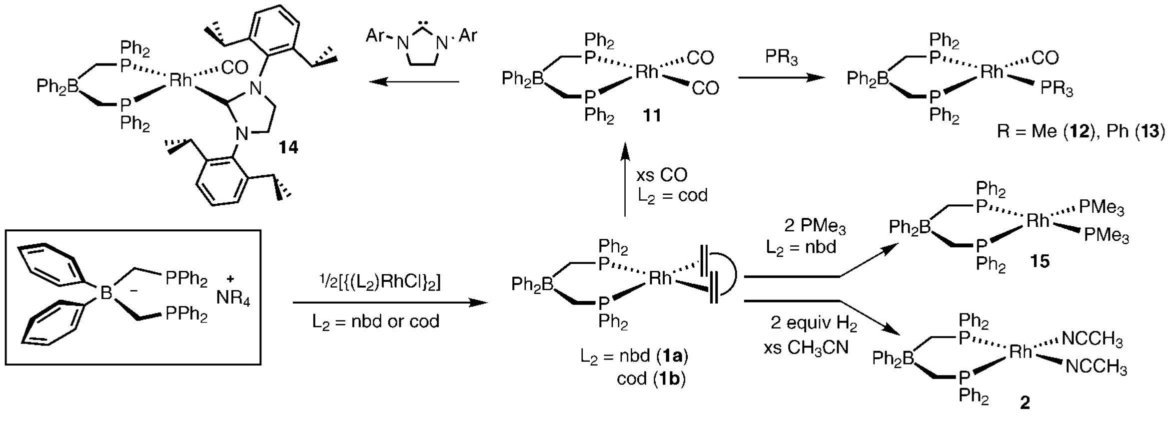
Figure 1. Catalyst systems featured herein. E = P, R = phenyl; E = N, R = methyl.

The key findings described in this report pertain to the catalytic activity and electrophilicity of the structurally similar zwitterionic and cationic complexes that are depicted in Figure 1. This comparative study shows that the phosphane-supported zwitterions are not only catalytically competent, but that they maintain their catalytic activity in both polar and nonpolar solvents, in contrast to their isostructural but cationic phosphane relatives. It is also shown that amine-chelated zwitterions are promising candidates for further catalytic development. The activity exhibited by these zwitterionic P- and N-chelated systems appears to be distinct from that of their corresponding N-donor bis(pyrazolyl)borate rhodium relatives, which seem to be relatively unsuitable for the reactions described herein.[8]

The synthetic and characterization data for each of the phosphane-chelated zwitterions is provided in the Supporting Information. The synthetic details for the amine-chelated complexes were recently communicated elsewhere.[7] Briefly, zwitterionic phosphane precatalysts were prepared in high yield by reaction of the diene–rhodium precursors $[\{(nbd)RhCl\}_2]$ and $[\{(cod)RhCl\}_2]$ with $[Ph_2B(CH_2PPh_2)_2]^-$ (nbd = norbornadiene; cod = cyclooctadiene; Figure 1). Hydrogenative removal of the norbornadiene ligand of $[\{Ph_2B(CH_2PPh_2)_2\}Rh(nbd)]$ (**1a**) occurred in the presence of acetonitrile to afford the complex $[\{Ph_2B(CH_2PPh_2)_2\}Rh(CH_3CN)_2]$ (**2**) (Scheme 1). The related amine-chelated complexes $[\{Ph_2B(CH_2NMe_2)_2\}Rh(nbd)]$ (**3**) and $[\{Ph_2B(CH_2NMe_2)_2\}Rh(CH_3CN)_2]$ (**4**) were similarly prepared.[7] The isostructural but cationic systems $[\{Ph_2Si(CH_2PPh_2)_2\}Rh(nbd)][PF_6]$ (**5**), $[\{Ph_2Si(CH_2PPh_2)_2\}Rh(CH_3CN)_2][PF_6]$ (**6**), $[\{Ph_2Si(CH_2NMe_2)_2\}Rh(nbd)][PF_6]$ (**7**), and $[\{Ph_2Si(CH_2NMe_2)_2\}Rh([D_6]acetone)_2][PF_6]$ (**8**) were independently prepared to allow comparisons of the reactivity.[9,10] The acetonitrile adducts for the cationic systems supported by $Ph_2PCH_2CH_2PPh_2$ (dppe) and $Ph_2PCH_2CH_2CH_2PPh_2$ (dppp), $[(dppe)Rh(CH_3CN)_2][PF_6]$ (**9**) and $[(dppp)Rh(CH_3CN)_2][PF_6]$ (**10**), were derived in a similar fashion from norbornadiene precursors that were previously reported.[11,4a]

Owing to their novelty, it was of interest to briefly canvass the structural characteristics and substitution chemistry of the phosphane-based zwitterions $[\{Ph_2B(CH_2PPh_2)_2\}RhL_2]$ (Scheme 1). Treatment of the cyclooctadiene analogue of **1a**, $[\{Ph_2B(CH_2PPh_2)_2\}Rh(cod)]$ (**1b**), with CO gas produced the dicarbonyl complex $[\{Ph_2B(CH_2PPh_2)_2\}Rh(CO)_2]$ (**11**) quantitatively. Dicarbonyl **11** underwent single substitution by PMe_3, PPh_3, and an N-heterocyclic carbene to produce the monocarbonyl adduct complexes $[\{Ph_2B(CH_2PPh_2)_2\}Rh(CO)(PMe_3)]$ (**12**), $[\{Ph_2B(CH_2PPh_2)_2\}Rh(CO)(PPh_3)]$ (**13**), and $[\{Ph_2B(CH_2PPh_2)_2\}Rh(CO)(carbene)]$ (**14**), respectively. The tetrakis(phosphane) complex $[\{Ph_2B(CH_2PPh_2)_2\}Rh(PMe_3)_2]$ (**15**) was available directly from **1a** by treatment with excess PMe_3.

The solid-state structures of complexes **1a**, **2**, **11**, and **14** were determined by X-ray diffraction studies.[12] The structures of **2** and **11** are displayed in Figure 2, and those of **1a** and **14** are available in the Supporting Information. In each case, the borate unit is locked rigidly in the backbone of the $[Ph_2B(CH_2PPh_2)_2]^-$ ligand at a distance of approximately 4 Å from the coordinated rhodium center. No inter- or intramolecular ion-pairing interactions are observed, consistent with the amine-chelated zwitterion that was characterized previously.[7] The $[Ph_2B(CH_2PPh_2)_2]^-$ ligand conformation for dicarbonyl **11** is distinct from its conformation in the other three structures and places the borate unit slightly closer (≈0.1 Å) to the bound rhodium center (Rh–B 3.908(3) Å in **11**). One possible explanation for this ligand distortion is that the borate unit is drawn closer to the metal center to



Scheme 1. Synthesis of zwitterionic $[\{Ph_2B(CH_2PPh_2)_2\}RhL_2]$ complexes.

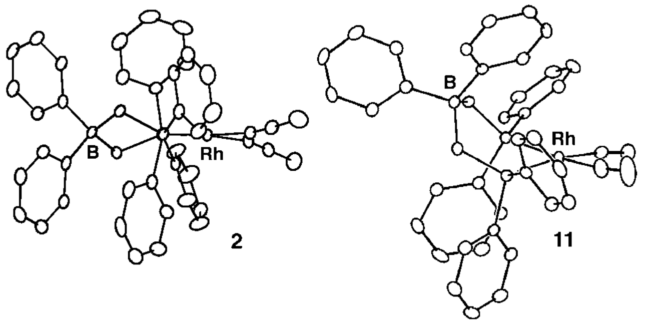


Figure 2. Molecular structures of **2** and **11** (ellipsoid representations, 50%; hydrogen atoms and residual solvent molecules are omitted for clarity).

compensate for the increased electrophilicity at the rhodium center because of the strongly π-acidic carbonyl ligands.

Complexes **1**–**4** are most simply described as zwitterions in which some of the borate unit's charge is dissipated through space and/or through the σ-bond framework of the ligand arms to the coordinated rhodium center. This situation might be anticipated to result in an appreciably more electron-rich metal center by comparison to an isostructural but cationic complex. This view is supported by the comparative IR data obtained for the carbonyl complexes **11** and $[\{Ph_2Si(CH_2PPh_2)_2\}Rh(CO)_2][PF_6]$ (**16**). The symmetric and antisymmetric vibrations for the zwitterion **11** in dichloromethane (2080 and 2029 cm^{-1}, respectively) are much lower in frequency than those for the cation **16** (2099 and 2056 cm^{-1}, respectively). Cationic **16** is electronically similar to the dppe- and dppp-supported dicarbonyl complexes, where both of the latter species exhibit vibrations at 2100 and 2056 cm^{-1}, respectively.[13] A similar trend has been observed for the amine-based systems.[7] The increased electron-richness of the zwitterions in comparison to their corresponding cations might be expected to attenuate or shut down their ability to mediate catalytic transformations, especially those reactions typical of electrophilic $[(P–P)Rh(solv)_2]^+$ complexes. Our data, however, suggests otherwise.

Comparative Catalytic Studies: Four model reactions were probed as exemplary of the $[(P–P)RhL_2]^+$ ions. These include the hydrogenation, hydroboration, and hydrosilation of styrene,[1–3] in addition to the hydroacylation of 4-methyl-4-pentenal, a transformation popularized by Bosnich and co-workers.[4] For each model study, we compared the catalytic activity of the isolated zwitterions to their cationic but structurally analogous cousins that incorporate a diphenylsilane unit in the phosphane backbone. To ensure that these Ph_2Si-based cationic systems give rise to activities similar to more conventional phosphane systems with all-carbon backbones, we also canvassed the reactivity of cationic congeners supported by dppe and dppp.

As a first catalytic screen, the norbornadiene adduct complexes **1a**, **3**, **5**, and **7** were assessed for their ability to mediate the hydrogenation of styrene to ethylbenzene in $[D_6]$acetone (monitored by ^1H NMR spectroscopy). For the neutral and cationic phosphane systems **1a** and **5**, hydrogenative removal of the norbornadiene ligands occurred rapidly, whereas the conversion of styrene to ethylbenzene proceeded more slowly (Table 1). The cationic systems $[(P–P)Rh(nbd)]^+$ ((P–P) = dppe, dppp) gave similar results. A possible mode of catalyst deactivation for the zwitterion **1a** is the formation of an arene-bridged Rh–Rh dimer. Unlike the cationic dimers that are broken up by coordinating solvents to provide catalytically active species,[4a–c] the zwitterionic dimer is very robust and requires forcing conditions to reform a monomeric species.[14]

Table 1: Styrene hydrogenation results.[a]

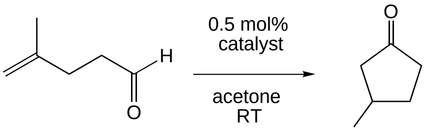
Entry	Catalyst		T [h][b]	TOF [h^{-1}][c]
1	$[\{Ph_2B(CH_2PPh_2)_2\}Rh(nbd)]$	**1a**	26	19
2	$[\{Ph_2Si(CH_2PPh_2)_2\}Rh(nbd)][PF_6]$	**5**	34	15
3	$[(dppe)Rh(nbd)][PF_6]$	–	44	11.4
4	$[(dppp)Rh(nbd)][PF_6]$	–	28	18
5	$[\{Ph_2B(CH_2NMe_2)_2\}Rh(nbd)]$	**3**	2.5	200
6	$[\{Ph_2Si(CH_2NMe_2)_2\}Rh(nbd)][PF_6]$	**7**	5	100

[a] Conditions: Rh catalyst (0.1 mol%) in $[D_6]$acetone (0.65 mL); H_2 (1 mL) at 1 atm added by syringe at 25 °C. [b] Time T to consume 50% of styrene as determined by ^1H NMR spectroscopy. [c] Turnover frequency (TOF) values expressed as mol of product per mol of catalyst per h.

Perhaps more intriguing was that the zwitterionic amine complex **3** exhibited activity far superior to both the neutral and cationic phosphane systems, and was twice as active as its cationic amine counterpart **7** (Table 1). Zwitterion **3** also proved tolerant to repeated addition of fresh styrene substrate. For further comparison, the related bis(pyrazolyl)borate complex $[\{Ph_2B(Pz)_2\}Rh(nbd)]$ was found to be completely inactive for the hydrogenation of styrene under similar conditions.[8] In fact, attempts to hydrogenatively remove the norbornadiene ligand from $[\{Ph_2B(Pz)_2\}Rh(nbd)]$ under the mild conditions used were unsuccessful.

The catalytic activity of the zwitterionic systems was more pronounced in the hydroacylation of the model substrate 4-methyl-4-pentenal ([Eq. (1)]; Table 2). The precatalysts used to canvass the hydroacylation of this substrate to racemic 3-methylcyclopentanone were the acetonitrile adduct complexes **2**, **4**, **6**, **9**, **10**, and the acetone adduct derivative **8**, which required in situ generation.[10] The turnover frequency (TOF) for hydroacylation of 4-methyl-4-pentenal by **2** was 40 times greater than its cationic phosphane counterparts **6**, **9**, and **10**. The data collected for the conventional phosphane systems **9** and **10** compares well with that for the diphenylsilane system **6**. This comparison suggests that the $[Ph_2Si(CH_2PPh_2)_2]$ ligand provides a good structural model for the anionic $[Ph_2B(CH_2PPh_2)_2]^-$ ligand, and also a good benchmark for comparing the activity of the zwitterionic systems to more familiar bis(phosphane)-supported catalysts. The activity of **2** also compares well with the BINAP catalyst systems of Bosnich and co-workers.[4] Their studies were typically performed in acetone, and more strongly coordinating solvents such as CH_3CN were strictly excluded as they act as catalyst poisons. The presence of CH_3CN likely attenuated the activity observed for the cationic species in entries 3–5 of Table 2. The disparity in hydroacylation activity between zwitterionic **2** and the cationic, phosphane catalysts could be

Table 2: Hydroacylation results.[a]



(1)

Entry	Catalyst		Yield [%][b]	T[c]	TOF [h^{-1}]
1	$[\{Ph_2B(CH_2PPh_2)_2\}Rh(CH_3CN)_2]$	**2**	99	5 min	2400
2	$[Ph_2B(CH_2NMe_2)_2]Rh(CH_3CN)_2$	**4**	95	30 min	380
3	$[\{Ph_2Si(CH_2PPh_2)_2\}Rh(CH_3CN)_2][PF_6]$	**6**	78	3 h	52
4	$[(dppe)Rh(CH_3CN)_2][PF_6]$	**9**	84	3 h	56
5	$[(dppp)Rh(CH_3CN)_2][PF_6]$	**10**	70	3 h	47
6	$[\{Ph_2Si(CH_2NMe_2)_2\}Rh(solv)_2][PF_6]$	**8**[d]	0	3 h	0

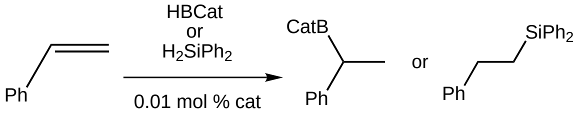
[a] Conditions: Rh catalyst (0.5 mol%) in [D$_6$]acetone (1.0 mL) at 25 °C. [b] Determined by ^{1}H NMR spectroscopy. [c] Time T to consume starting material. [d] Hydrogenated in [D$_6$]acetone prior to substrate introduction; two equivalents of CD_3CN added to reaction mixture.

further amplified as a function of the solvent medium. For example, the activity of cationic **6** fell precipitously when solvents of varying polarities such as benzene, THF, and acetonitrile were employed (TOF for **6** = 15, 8, and 0 in these solvents, respectively). The decreasing activity is likely due to strong coordination of the donor solvent (CH_3CN), inability of THF or the substrate to break up intermediate Rh–Rh dimers, and poor solubility of the cation in benzene. In sharp contrast, zwitterionic **2** maintained TOF values near 2400 in all three solvent systems. Furthermore, the amine zwitterion **4** was also a relatively active catalyst for the hydroacylation reaction, superior to all cationic systems examined. Like zwitterionic **2**, **4** maintained its catalytic activity in benzene and in CH_3CN. While the in-situ-generated catalyst system $[\{Ph_2Si(CH_2NMe_2)_2\}Rh(acetone)_2]^+$ did afford racemic 3-methylcyclopentanone, the reaction was only 90% complete after 2 h and was completely inhibited when two equivalents of CH_3CN were added with substrate to the solution.

The precatalysts **2**, **4**, **6**, **9**, and **10** were next examined for the hydroboration and hydrosilation of styrene ([Eq. (2)]; Table 3). The cationic precatalyst **8** was also examined, though the data obtained for this system were highly irreproducible due to a propensity for the complex to precipitate Rh^0 upon reaction with the borane and silane reagents. For the hydroboration system, monitored in situ by ^{11}B NMR spectroscopy, only the branched product was obtained for all cases as determined by ^{1}H NMR spectroscopy.[15] The hydrosilation reactions, monitored by GC/MS and ^{1}H NMR spectroscopy, in all cases afforded a single anti-Markovnikov product, even when excess styrene was used. The cationic phosphane complexes **6, 9,** and **10** exhibited very similar activities that compared favorably with data that has been previously reported.[16] These cationic phosphane complexes were in general three to four times more active than the zwitterionic phosphane and amine complexes. However, the catalytic activity for all the cationic phosphane systems was completely shut down when an appreciable quantity of acetonitrile was present. Remarkably, the (phosphanyl)- and (amino)borate zwitterions were extremely tolerant to both acetonitrile and THF. For example, virtually no loss of activity was observed in 50/50 solvent mixtures of CH_3CN/THF and CH_3CN/acetone.

In summary, this study shows that zwitterionic phosphane and amine rhodium systems are promising catalysts for H–E addition reactions to olefins. The reactivity that the zwitterionic systems display parallels that of the cationic $[(P\text{–}P)RhL_2]^+$ systems with two important distinctions: The zwitterions are active in the presence of large quantities of a strongly coordinating donor solvent such as acetonitrile, which may reflect their attenuated electrophilicity in comparison to the cationic systems. Moreover, because the neutral systems are appreciably soluble in nonpolar hydrocarbons such as ben-

Table 3: Hydroboration and hydrosilation results.[a]



(2)

Catalyst	Reagent	Solvent	Yield [%][b]	T [h][c]	TOF [h^{-1}]
2	HBCat	THF	95	1.25	7600
2	HBCat	THF/CH_3CN	96	1.5	6400
4	HBCat	THF	93	1.5	6200
4	HBCat	THF/CH_3CN	94	1.65	5700
6	HBCat	THF	>99	0.5	20000
6	HBCat	THF/CH_3CN	0	24	0
9	HBCat	THF	92	1	9200
9	HBCat	THF/CH_3CN	0	24	0
10	HBCat	THF	98	0.75	13000
10	HBCat	THF/CH_3CN	0	24	0
2	H_2SiPh_2	acetone	98	1.5	6500
2	H_2SiPh_2	acetone/CH_3CN	96	1.5	6400
4	H_2SiPh_2	acetone	91	2	4600
4	H_2SiPh_2	acetone/CH_3CN	88	2	4400
6	H_2SiPh_2	acetone	>99	0.5	20000
6	H_2SiPh_2	acetone/CH_3CN	0	24	0
9	H_2SiPh_2	acetone	96	0.5	19200
9	H_2SiPh_2	acetone/CH_3CN	0	24	0
10	H_2SiPh_2	acetone	>99	0.5	20000
10	H_2SiPh_2	acetone/CH_3CN	0	24	0

[a] Conditions: Rh catalyst (0.01 mol%). [b] For hydroborations: determined by ^{11}B NMR spectroscopy based on borane conversion; for hydrosilations: determined by ^{1}H NMR spectroscopy based on styrene conversion. [c] Time elapsed to convert styrene.

zene, they maintain their activity over a rather broad solvent polarity range. This solvent range is not spanned by more typical cationic catalysts, as illustrated by the cationic model complexes described in this study. We are encouraged to suggest that a zwitterionic approach to catalyst design will provide new systems with the potential for a high degree of functional group and solvent compatibility.

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Keywords: borates · boron · hydrogenation · rhodium · zwitterions

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[9] The Supporting Information contains complete synthetic and characterization data for all new compounds.

[10] The complex $[\{Ph_2Si(CH_2NMe_2)_2\}Rh(CH_3CN)_2][PF_6]$ could not be isolated due to problematic precipitation of Rh^0. $[\{Ph_2Si(CH_2NMe_2)_2\}Rh(acetone)_2][PF_6]$ could be generated, but only in situ as it also proved unstable to a typical workup procedure.

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[12] Summarized crystallographic data: $[\{Ph_2B(CH_2PPh_2)_2\}Rh(CO)_2]$ (**11**): ($C_{40}H_{34}BO_2P_2Rh$), $M_r = 722.33$, yellow plate, collection temperature = 96 K, monoclinic, space group $P2_{1/n}$, $a = 9.8984(9)$, $b = 18.7925(16)$, $c = 18.1113(16)$ Å, $\beta = 98.108(2)$, $V = 3335.3(5)$ Å^3, $Z = 4$, $R_1 = 0.0433$ $[I > 2\sigma(I)]$, GOF = 1.468. $[\{Ph_2B(CH_2PPh_2)_2\}Rh(CH_3CN)_2]\cdot THF$ (**2**): ($C_{42}H_{40}BN_2P_2Rh \cdot C_4H_8O$), $M_r = 820.52$, yellow cube, collection temperature = 98 K, monoclinic, space group $P2_{1/n}$, $a = 11.8228(9)$, $b = 16.4484(13)$, $c = 21.5822(17)$ Å, $\beta = 102.1030(10)$, $V = 4103.7(6)$ Å^3, $Z = 4$, $R_1 = 0.0425$ $[I > 2\sigma(I)]$, GOF = 1.192. CCDC-195381 (**1a**), CCDC-195383 (**2**), CCDC-195382 (**11**), CCDC-195384 (**14**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

[13] $[(dppp)Rh(CO)_2][PF_6]$ was not previously reported and thus prepared in an analogous fashion to **14** and is reported in the Supporting Information. $[(dppe)Rh(CO)_2][PF_6]$ was previously reported in ref [4b].

[14] The neutral "$[\{Ph_2B(CH_2PPh_2)_2\}Rh^I]$" unit can dimerize to a catalytically inactive $[\{[Ph_2B(CH_2PPh_2)_2]Rh\}_2]$ complex presumably stabilized by phosphine aryl-rhodium(I) interactions, a process also common of cationic "$[(P–P)Rh]^+$" systems.[4] The dimer has limited solubility but has been characterized by ^{31}P and ^1H NMR spectroscopy, as well as ES·MS and combustion analysis (see Supporting Information). The presence of the $[\{[Ph_2B(CH_2PPh_2)_2]Rh\}_2]$ dimer has been detected by ^{31}P NMR spectroscopy in situ during hydrogenation reactions with a 2% catalyst loading.

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