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Facile Synthesis of a Monosulfonated Triphenylphosphane (TPPMS) Derived Ligand having Strong π-Acceptor Character

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Abstract: Two phenyl rings of triphenylphosphane have been modified by electron-withdrawing trifluoromethyl groups. A methoxy group has been introduced at the *para*-position of the third ring. Due to the activating effect of the methoxy group, the phosphane can be monosulfonated under mild conditions and with complete selectivity. The novel ligand, sodium 5-[bis-(4-trifluoromethylphenyl)-phosphanyl]-2-methoxybenzenesulfonate, has been obtained in quantitative yield, and it has an outstanding π-acceptor capacity among the known sulfonated triarylphosphanes. It is not soluble in water but soluble in light alcohols and ionic liquids. Its solubility properties allow facile catalyst separation without water.

Keywords: π-acceptor character; fluorinated ligands; ligand design; P ligands; phosphanes; sulfonation

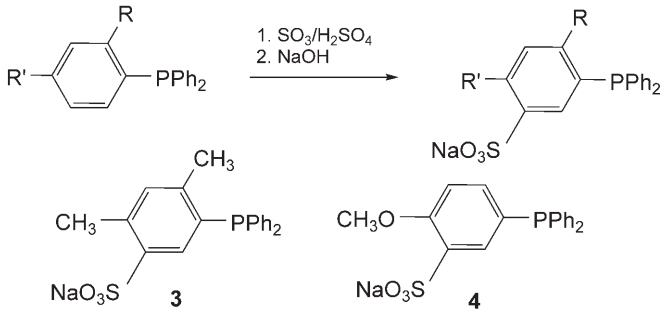
Homogeneous catalysis has been proved to be a powerful tool in a wide range of organic syntheses. Due to an increasing pressure on the chemical society to consider environmental aspects of chemical production, certain areas of homogeneous catalysis have become of increasing interest. Aqueous-organic, organic-organic, fluorous-non-fluorous, ionic liquid-organic two-phase systems, supported aqueous phase catalysis, etc. allow the separation of the catalysts from the products, and can be the base of "greener", sustainable chemical processes.[1]

Complexes modified with hydrophilic phosphanes can be suitable catalysts for most of the above-mentioned techniques, however, concerning applicability, the hydrophilic character of the phosphane is a key feature in some cases.

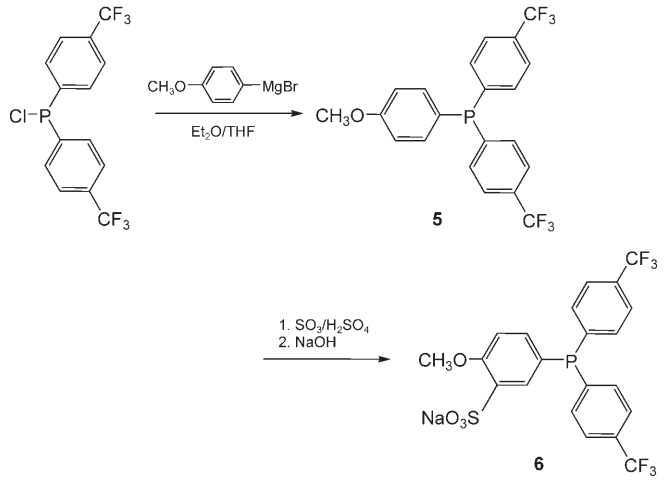
Mono- and trisulfonated derivatives of triphenylphosphane [TPPMS = (3-diphenylphosphanyl)benzenesulfonic acid (**1**); TPPTS = 3,3′,3″-phosphanetriyltribenzensulfonic acid (**2**)] are the most frequently used hydrophilic ligands in both industry and academic research. Conditions of the sulfonation of triphenylphosphane have continuously been developed over the last decades in order to improve selectivity, increase yields and suppress oxidation of the products.[2] Recently we have suggested an alternative approach that provides access to a wide range of sulfonated triarylphosphanes. Upon activating the phenyl rings with electron-donating groups, the syntheses do not suffer from the usual drawbacks of direct sulfonation, and additionally, the electronic, steric, and hydrophilic characteristics of the phosphanes can be controlled.[3] Some of these ligands are already being used in complex-catalyzed reactions with rather promising results [e.g., TXPTS = trisulfonated tris(2,4-xylyl)phosphane,[4a–c] TAPTS = trisulfonated tris(*p*-anisyl)phosphane[4c,d]].

Initial catalytic studies with monosulfonated triarylphosphanes have drawn our attention to an old demand that our original approach could not satisfy. Sulfonation of triarylphosphanes having one ring activated by electron-donating groups results in more basic derivatives of the monosulfonated triphenylphosphane (**3** and **4**, Scheme 1).[3] However, several catalytic reactions would require ligands having weaker σ-donor, but stronger π-acceptor capacities.

Triphenylphosphane derivatives modified by electron-withdrawing groups on the phenyl rings possess these desirable features, but their further functionalization by direct sulfonation is troublesome. To the best of our knowledge only one attempt has been made at the sulfonation of a pronounced π-acceptor



Scheme 1. Recently developed derivatives of TPPMS.



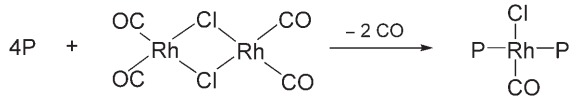
Scheme 2. Synthesis of **6**, a π-acceptor TPPMS derivative.

type triarylphosphane. Fell and Papadogianakis tried to trisulfonate the tris(*p*-fluorophenyl)phosphane in 25% oleum, however, after 410 h of reaction time, the isolated product contained mainly the disulfonated derivative. Besides a lack of selectivity, the researchers also observed the usual side reaction of direct sulfonation: oxidation of the phosphane.[5]

Since sulfonation of triarylphosphanes having one *activated* and two *non-activated* rings (phenyl) resulted in monosulfonated phosphanes with complete selectivity (Scheme 1),[3] we reasoned that (*i*) parent ligands having one *activated* and two *deactivated* rings could certainly be monosulfonated selectively, (*ii*) despite activation of one of the rings, the phosphane could be supplied with an overall π-acceptor character by careful design of its structure.

Based on this concept, (*p*-anisyl)bis(*p*-trifluoromethylphenyl)phosphane (**5**) has been prepared by the reaction of $ClP(p\text{-}C_6H_4CF_3)_2$ and $p\text{-}CH_3OC_6H_4MgBr$ (Scheme 2). Hammett substituent constants suggest that the *para*-positioned methoxy group ($\sigma_{para-OCH_3} = -0.27$) should support the *meta*-sulfonation of the anisylphosphane **5**, but its effect on the basicity of the ligand should be overcompensated by the CF_3 groups ($\sigma_{para-CF_3} = 0.54$).

Table 1. Carbonyl stretching frequencies of *trans*-$RhP_2(CO)Cl$ complexes.[a]



P = phosphane

Phosphane	ν_{CO} [cm^{-1}]	Ref.
PPh_3[b]	1966 (1965)[d]	This work, [6]
$PPh_2(p\text{-}C_6H_4OCH_3)$[c]	1964	This work
5	1983	This work
$P(p\text{-}C_6H_4CF_3)_3$	(1990)[d,e]	[7]

[a] Recorded in KBr pellets. The frequencies given in the Table are the average values of several experiments. For further details see the Supporting Information.
[b] Parent ligand of **1**.
[c] Parent ligand of **4**.
[d] Literature values are in parentheses.
[e] Recorded in CH_2Cl_2.

In order to obtain experimental evidence for the overall electronic nature of the new phosphane, carbonyl-rhodium complexes have been prepared and studied by IR spectroscopy (Table 1). The triarylphosphanes compared in Table 1 have similar steric properties, since they have been modified with *para*-substituents only. Thus, the differences in carbonyl stretching frequencies of their *trans*-$RhP_2(CO)Cl$ complexes can exclusively be attributed to the electronic nature of the ligands. In accordance with the Hammett parameters of the substituents, the ν_{CO} frequency of the *trans*-$Rh(\mathbf{5})_2(CO)Cl$ complex (Table 1) indicates the considerable π-acceptor character of the new phosphane.

Similar conclusions could be drawn by measuring the $^1J_{P-Se}$ coupling constants of the selenides prepared from the triarylphosphanes of Table 1.[8] The $^1J_{P-Se} = 747$ Hz coupling constant of $Se{=}P(p\text{-}C_6H_4CF_3)_2(p\text{-}C_6H_4OCH_3)$ is considerably higher than those of $Se{=}PPh_2(p\text{-}C_6H_4OCH_3)$ (723 Hz) and $Se{=}PPh_3$ (729 Hz), further confirming the increased π-acceptor capacity (Table 2).

Sulfonation of **5** has been carried out at room temperature, in 20% oleum (Scheme 2). The corresponding monosulfonated derivative (**6**) can be isolated practically in quantitative yield after one hour of reaction time. The sulfonation is completely ring selective, and only traces of the corresponding phosphane oxide have been observed (*ca.* 2–3%, $^{31}P\{^1H\}$-NMR).

The new monosulfonated triarylphosphane is not soluble in either water or apolar organic solvents, but readily soluble in light alcohols, in water-alcohol mixtures and in ionic liquids.[10] This degree of hydrophilic character allows special catalytic applications. For example, in a methanol-hexane mixture rhodium complexes of **6** are localized in the methanol phase,

Table 2. $^{31}P\{^1H\}$-NMR data of phosphane selenides.[a]

Phosphane	$\delta(^{31}P\{^1H\})$ [ppm]	Se=PAr(Ar′)$_2$ $^1J_{P-Se}$ [Hz]	Ref.
PPh_3	37.3	729	This work
$PPh_2(p\text{-}C_6H_4OCH_3)$	36.1	723	This work
5	35.4	747	This work
$P(p\text{-}C_6H_4CF_3)_3$	34.9	765	[9]

[a] Recorded in $CDCl_3$.

which is well-separated from the hexane. On heating the mixture above 40 °C, it forms one single phase. On cooling, the orange alcohol phase separates from the colorless hydrocarbon phase again. A similar system has been described by Bianchini and is based on the monosulfonated tridentate ligand sulphos (p-NaO_3S-C_6H_4)$CH_2C(CH_2PPh_2)_3$.[11] This type of solvent systems allows facile catalyst separation without water, thus, it can be an alternative to the fluorous biphasic systems.[12]

It is worth mentioning that the sulfonate group also considerably influences the electronic nature of the phosphane. The $^1J_{P-Se} = 754$ Hz coupling constant observed for the selenide of **6** indicates that the sulfonation further increases the π-acceptor capacity.[13]

The beneficial effect of the pronounced π-acceptor character of **6** has already been observed in several catalytic reactions. For example, an interesting electronic effect has been found in the course of a study on the rhodium-catalyzed hydrogenation of cinnamic aldehyde. An *in situ* formed **1**/$Rh(NBD)_2BF_4$ catalyst provided only 12% conversion under the applied conditions (methanol, 20 atm of H_2, room temperature, 1:200 Rh to substrate ratio, 40 min). The corresponding rhodium complex modified by the sterically similar but more basic sulfonated phosphane **4** proved to be even less active (4% conversion). However, the rhodium complex of **6** hydrogenated 76% of the cinnamic aldehyde to phenylpropanal, practically with complete selectivity (>99%).

The catalytic application mentioned above might confirm that updating this synthetic approach can provide access to useful ligands. Currently, following the presented approach, we are compiling a pool of hydrophilic phosphanes of a fine scale of electronic nature. This set of ligands should support our efforts to develop efficient and environmentally benign catalytic systems.

Experimental Section

General Remarks

All manipulations were carried out under argon using Schlenk techniques. Solvents were purified, dried and deoxygenated by standard methods. Triphenylphosphane and styrene were purchased from Sigma–Aldrich and used as received. $[Rh(CO)_2Cl]_2$,[14] $[Rh(NBD)_2]BF_4$,[15] (p-anisyl)diphenylphosphane,[3b] and the phosphane selenides[16] were prepared according to the literature. Sulfonation of (p-anisyl)diphenylphosphane was published earlier.[2g] Monosulfonated triphenylphosphane was prepared by a slightly modified literature method (see below).[1 g] $^{31}P\{^1H\}$-, ^1H NMR and $^{13}C\{^1H\}$- spectra were recorded on either a Varian Unity 300 spectrometer operating at 121.42 MHz, 300.15 MHz and 75.43 MHz, respectively, or on a Bruker DRX-500 spectrometer operating at 202.45 MHz, 500.13 MHz and 125.76 MHz, respectively. Infrared spectra were recorded on Nicolet AVATAR 330, Bio-Rad (Digilab) FTS-185 and Bio-Rad (Digilab) FTS-60 FT-IR spectrometers. Gas chromatographic analyses were run on a Hewlet-Packard 5830 A gas chromatograph (30 m SPB-1 column, film thickness 0.1 μm, N_2 carrier gas 2 mL min^{-1}).

(4-Methoxyphenyl){bis[4-(trifluoromethyl)phenyl]}-phosphane (5)

4-Anisylmagnesium bromide (24 mmol, dissolved in 25 mL THF) was slowly added to chlorbis(trifluormethylphenyl)-phosphane (7.69 g, 21.6 mmol, dissolved in 75 mL Et_2O) at −5 to +3 °C internal temperature (ice/salt bath). The reaction mixture was stirred for 3 h while the temperature reached 15 °C. The bath was removed. The reaction mixture was stirred further and allowed to warm to room temperature (30 min, 23 °C). The reaction mixture was cooled again (ice/salt bath, −5 °C internal temperature) and carefully quenched with NH_4Cl solution (50 g, 10%). The aqueous phase was removed using a cannula. The organic phase was washed with $NaHCO_3$ solution (2×25 g, 10%), then water (2×25 mL). The organic phase was dried over $MgSO_4$. The solvent was removed under vacuum. The crude product (dense yellow oil) was crystallized from methanol. (Crystallization was initiated in a refrigerator.) At this stage the phosphane contained *ca.* 3% of phosphane oxide and ~3% of $H(O)P(p\text{-}C_6H_4CF_3)_2$ ($^{31}P\{^1H\}$-NMR). It was recrystallized from hot MeOH/water (V/V = 45/4) to give 2.77 g of pure product. The mother liquors were combined, the solvent was removed, then the residue was recrystallized similarly ($V_{MeOH}/V_{water} = 15$) to give further 1.62 g of pure product. Total yield: 4.39 g (48%); white microcrystalline solid; mp 52–55 °C; ^1H NMR ($CDCl_3$): $\delta = 3.75$ (s, 3H, OCH_3), 6.86 (dd, $^3J_{HH} \approx 8.8$ Hz, $^4J_{PH} \approx 0.8$ Hz, 2H, C3{p-$C_6H_4OCH_3$}-H), 7.21 (pseudo t, $^3J_{PH} \approx 8.8$ Hz, $^3J_{HH} \approx 8.8$ Hz, 2H, C2{p-$C_6H_4OCH_3$}-H), 7.30 (broad pseudo t, $^3J_{PH} \approx 8$ Hz, $^3J_{HH} \approx 8$ Hz, 4H, C2{p-$C_6H_4CF_3$}-H), 7.51 (broad pseudo d, $^3J_{HH} \approx 8$ Hz, 4H, C3{p-$C_6H_4CF_3$}-H); $^{13}C\{^1H\}$-NMR ($CDCl_3$): $\delta =$ 55.31 (s, OCH_3), 114.61 (d, $^3J_{PC} = 9.7$ Hz, C3{p-$C_6H_4OCH_3$}), 123.84 (q, $^1J_{FC} = 271.3$ Hz, CF_3), ~125.05 (d, C1{p-$C_6H_4OCH_3$}), 125.11 (m, C3{p-$C_6H_4CF_3$}), 130.64 (q, $^2J_{FC} =$ 31.5 Hz, C4{p-$C_6H_4CF_3$}), 133.27 (d, $^2J_{PC} = 19.4$ Hz, C2{p-$C_6H_4CF_3$}), 135.84 (d, $^2J_{PC} = 24.2$ Hz, C2{p-$C_6H_4OCH_3$}), 142.11 (d, $^1J_{PC} = 14.5$ Hz, C1{p-$C_6H_4CF_3$}), 160.86 (s, C4{p-$C_6H_4OCH_3$}); $^{31}P\{^1H\}$-NMR ($CDCl_3$): $\delta = -6.9$ (s); anal. calcd. for $C_{21}H_{15}F_6OP$ ($M_r = 428.31$): C 58.89, H 3.53; found: C 58.71, H, 3.17.

Sodium 5-[Bis(4-trifluoromethylphenyl)phosphanyl]-2-methoxybenzenesulfonate (6)

Fuming sulfuric acid (2.5 mL, 20% of free SO_3) was transferred in a round-bottom flask under argon. The flask was placed in a salt/ice bath, and (4-anisyl)bis(4-trifluoromethylphenyl)phosphane (**5**, 1 g, 2.33 mmol) was added to the fuming sulfuric acid in small portions. The bath was removed and the reaction mixture was stirred for one hour. The flask was placed in an ice/salt bath again and crushed ice (~10 g) was added over a 30 min period. In the course of the procedure the phosphonium salt precipitated as a sticky material. Sufficient blending was maintained by shaking the flask gently. The acidic reaction mixture was carefully neutralized with aqueous NaOH solution (3.95 g NaOH in 30 mL water). The pH of the suspension was set to ~7. (Controlled by special pH paper.) The aqueous suspension was transferred in a 500 mL flask under argon, and the water was removed under vacuum. (Due to intensive foam formation, the use of a smaller flask is not advisable.) The white residue was extracted with methanol (2×50 mL). Water (10 mL) was added to the methanol solution, then the solvent was removed. The product is a white solid. Yield: 1.20 g (94%); ^{1}H NMR (CD_3OD): $\delta = 3.94$ (s, 3H, OCH_3), 7.17 (dd, $^3J_{HH} = 8.4$ Hz, $^4J_{PH} = 0.7$ Hz, 1H, C5{sulfonated}-H), 7.41–7.51 (m, 5H, C2{*p*-$C_6H_4CF_3$}-H, C6{sulfonated}-H), 7.66 (broad pseudo d, $^3J_{HH} \approx 8$ Hz, 4H, C3{*p*-$C_6H_4CF_3$}-H), 7.96 (dd, $^3J_{PH} = 7.7$ Hz, $^4J_{HH} = 2.4$ Hz, 1H, C2{sulfonated}-H); ^{13}C{^{1}H}-NMR (CD_3OD): $\delta = 56.49$ (s, OCH_3), 113.77 (d, $^3J_{PC} = 9.7$ Hz, C3{*p*-$C_6H_4OCH_3$}), 125.32 (q, $^1J_{FC} = 271.3$ Hz, CF_3), 125.91 (d, $J_{PC} = 9.7$ Hz, sulfonated), 126.28 (m, $^3J_{FC} = 3.6$ Hz, C3{*p*-$C_6H_4CF_3$}), 131.70 (q, $^2J_{FC} = 32.7$ Hz, C4{*p*-$C_6H_4CF_3$}), 133.67 (d, $J_{PC} = 10.9$ Hz, sulfonated), 134.60 (d, $^2J_{PC} = 19.4$ Hz, C2{*p*-$C_6H_4CF_3$}), 135.61 (d, $^2J_{PC} = 23.0$ Hz, C2{sulfonated}), 139.54 (d, $^2J_{PC} = 24.2$ Hz, C2{sulfonated}), 143.68 (broad d, $^1J_{PC} = 14.5$ Hz, C1{*p*-$C_6H_4CF_3$}), 159.53 (s, C4{sulfonated}); ^{31}P{^{1}H}-NMR (CD_3OD): $\delta = -2.4$ (s) ppm; MS (ESI^-): $m/z = 507.1$ [$M-Na^+$]; MS (ESI^+): $m/z = 508.9$ [$M-Na^+ + 2H^+$]$^+$; anal. calcd. for $C_{21}H_{14}F_6NaO_4P \cdot H_2O$ ($M_r = 548.37$): P 5.64, S 5.84, Na 4.19; found: P 5.58, S 5.81, Na 3.89. Degree of sulfonation: S/P = 1.01.

Sodium (Diphenylphosphanyl)benzenesulfonate (1)

Triphenylphosphane (20.0 g, 76.3 mmol) was slowly added to fuming sulfuric acid (50 mL, 20% of free SO_3). When the phosphane had completely dissolved, the homogenous reaction mixture was heated at 97–98 °C for 75 min. The reaction mixture was allowed to cool to room temperature, and then it was poured on crushed ice (400 g). The pH of the milky reaction mixture was set to ~4 using 50% NaOH solution. The precipitate was filtered and recrystallized twice from water [1) 550 mL of warm water, then refrigerator overnight. 2) 60 mL of hot water.] The second recrystallization yielded 7.0 g analytically pure TPPMS monohydrate. In a refrigerator further 3.5 g of pure product crystallized from the mother liquor in two days. Total yield: 10.5 g (36%); ^{1}H NMR (CD_3OD): $\delta = 7.24$–7.36 (m, 11H, Ph and 1H sulfonated), 7.40 (broad pseudo t, $J \approx 7$–8 Hz, 1H, sulfonated), 7.84 (broad d, $J \approx 7.6$ Hz, 1H, sulfonated), 7.87 (broad d, $J \approx 7.5$ Hz, 1H, sulfonated) ppm; ^{13}C{^{1}H}-NMR (CD_3OD): $\delta = 127.45$ (s, C4{sulfonated}), 129.57 (d, $J_{PC} = 6.1$ Hz, sulfonated), 129.74 (d, $^3J_{PC} = 7.2$ Hz, *meta*-phenyl), 130.12 (s, *para*-phenyl), 131.97 (d, $J_{PC} = 22.9$ Hz, sulfonated), 134.80 (d, $^2J_{PC} = 19.1$ Hz, *ortho*-phenyl), 136.27 (d, $J_{PC} = 18.2$ Hz, sulfonated), 137.99 (d, $^1J_{PC} = 10.8$ Hz, *ipso*-phenyl), 139.68 (d, $J_{PC} = 14.6$ Hz, sulfonated), 146.59 (d, $J_{PC} = 6.2$ Hz, sulfonated); ^{31}P{^{1}H}-NMR (CD_3OD): $\delta = -5.0$ (s) ppm; anal. calcd. for $C_{18}H_{14}NaO_4PS \cdot H_2O$ ($M_r = 382.28$): P 8.10, S 8.37, Na 6.01; found: P 8.07, S 8.64, Na 5.94. Degree of sulfonation: S/P = 1.03.

Rh(phosphane)$_2$(CO)Cl Complexes [Phosphane = PPh_3, PPh_2(*p*-$C_6H_4OCH_3$), P(*p*-$C_6H_4CF_3$)$_2$(*p*-$C_6H_4OCH_3$)]

Phosphanes (0.168 mmol) dissolved in CH_3CN (2 mL) were added to $[Rh(CO)_2Cl]_2$ (15.6 mg, 0.04 mmol) dissolved in CH_3CN (1 mL). The Schlenk flask of the phosphanes was rinsed with further 1 mL of CH_3CN. The reaction mixtures were stirred for 60–120 min. The solvent was removed under vacuum. The isolated solids were washed with Et_2O and dried under vacuum for 15 min at room temperature. (The last operation should not be carried out in the case of **5**, since the complex is considerably soluble in Et_2O.) Each complex was also prepared in a similar manner using CH_2Cl_2 as solvent instead of CH_3CN. ^{31}P{^{1}H}-NMR ($CDCl_3$) spectra were recorded of the products prepared in CH_3CN. ^{31}P{^{1}H}-NMR data of the complexes are as follows. Rh(PPh_3)$_2$(CO)Cl: $\delta = 31.0$ ppm (d, $^1J_{RhP} = 128$ Hz); Rh[PPh_2(*p*-$C_6H_4OCH_3$)]$_2$(CO)Cl: $\delta = 27.6$ ppm (d, $^1J_{RhP} = 127$ Hz); Rh[P(*p*-$C_6H_4CF_3$)$_2$(*p*-$C_6H_4OCH_3$)]$_2$(CO)Cl: $\delta = 30.5$ ppm (d, $^1J_{RhP} = 128$ Hz). IR (KBr pellets) spectra were recorded of each batch using three different FT-IR spectrometers. 6–10 spectra were recorded of each complex. Depending on the conditions of the syntheses and the measurements, the ν_{CO} values fell in the following ranges: Rh(PPh_3)$_2$(CO)Cl: $\nu = 1964.8$–1966.2 cm^{-1}; Rh[PPh_2(*p*-$C_6H_4OCH_3$)]$_2$(CO)Cl: $\nu = 1963.2$–1965.1 cm^{-1}; Rh[P(*p*-$C_6H_4CF_3$)$_2$(*p*-$C_6H_4OCH_3$)]$_2$(CO)Cl: $\nu = 1982.3$–1984.0 cm^{-1}. The average (rounded) ν_{CO} values are summarized in Table 1.

Phosphane Selenides [Phosphane = PPh_3, PPh_2(*p*-$C_6H_4OCH_3$), 5, 6]

The selenides were prepared by the reaction of the phosphanes and elemental selenium in refluxing $CHCl_3$ (EtOH in the case of **6**) according to a literature method.[16] ^{31}P{^{1}H}-NMR ($CDCl_3$) spectra were recorded in $CDCl_3$. ^{31}P{^{1}H}-NMR data of the complexes are as follows: Se=PPh_3: $\delta = 37.3$ ppm (d, $^1J_{Se-P} = 729$ Hz); Se=PPh_2(*p*-$C_6H_4OCH_3$): $\delta = 36.1$ ppm (d, $^1J_{Se-P} = 723$ Hz); selenide of **5**: $\delta = 35.4$ ppm (d, $^1J_{Se-P} = 747$ Hz); selenide of **6**: $\delta = 35.3$ ppm (d, $^1J_{Se-P} = 754$ Hz).

Catalytic Reactions

$[Rh(NBD)_2]BF_4$ (7.5 mg, 0.02 mmol), sulfonated phosphane (0.1 mmol), MeOH (4 mL), NaOH (10 μl, 2 M) were transferred successively in a Schlenk tube under argon. The mixture was stirred for 30 min. Cinnamic aldehyde (529 mg, 4 mmol) was added, then the reaction mixture was transferred in a stainless steel autoclave (20 mL). The autoclave was pressurized with H_2 to 20 bar, then the reaction mixture was agitated (220 s^{-1}) at room temperature for 40 min. After the run the autoclave was vented carefully. The reaction mixture was poured into a Schlenk tube filled with argon, then analyzed by GC.

Supporting Information

$^{31}P\{^1H\}$-NMR and ^1H NMR spectra of **5**. $^{31}P\{^1H\}$-NMR spectra of two subsequent batches of the isolated **6**. ^1H NMR spectrum of **6**. $^{31}P\{^1H\}$-NMR and ^1H NMR spectra of *trans*-$Rh[PPh_2(p\text{-}C_6H_4OCH_3)]_2(CO)Cl$. Pictures of methanol-hexane mixture in the presence of Rh complexes of **6** at different temperatures.

Acknowledgements

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