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Silylated organometals: a family of recyclable homogeneous catalysts†

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A general strategy has been developed to synthesize a family of silylated organometals (M-PPh_2-T_S and DPEN-Ru-PPh_2-Ts, M = Pd^{2+}, Rh^+, Pt^{2+}, Ir^+, or Ru^{2+}, PPh_2-Ts = $PPh_2CH_2CH_2Si(OEt)_3$), DPEN = (1R,2R)-1,2-diphenylethylenediamine). They can act as homogeneous catalysts with high efficiencies in various organic reactions using THF, CH_2Cl_2 or toluene as the reaction medium. After reaction, they could be thoroughly settled down by adding pentane and then used repeatedly owing to the complete catalyst recovery and good preservation of the catalyst structure. This is particularly important due to the increasing concerns regarding the cost, toxicity and limited availability of these nonrenewable transition metals.

Green chemistry requires chemical reactions to be conducted with low cost, clean reactants, products and processes, recyclable and environmentally friendly catalysts, and high activity and selectivity (*i.e.*, economic reactions). Homogeneous organometal catalysts have been widely used in organic synthesis and have enjoyed great success as a result of their high activity, selectivity and stereoselectivity.[1] However, they are difficult to be recycled and reused, leading to enhanced costs and even environmental pollution from heavy metallic ions.[2] Immobilized homogeneous catalysts on solid supports are easily recycled and reused, but they usually display remarkably decreased catalytic efficiencies due to the enhanced diffusion limit, reduced dispersion degree and unmatchable chemical microenvironment of the active sites.[3] There is always a dream of designing recyclable homogeneous catalysts combining the merits of both homogeneous and heterogeneous catalysts. Such catalysts could be used homogeneously during reactions and then easily recycled after reactions for subsequent reuse. To date, only a few recyclable homogeneous catalysts have been reported, which can be settled down and recycled by interphase,[4] clathrate-enabled,[5] ionic-[6] and fluorous-tagged,[7] redox-,[8] photo-[9] and phase-switchable[10] technologies. However, their discovery and design are quite rare, which greatly limits the number of catalysts and their practical applications. Obviously, a universal method for preparing recyclable homogeneous catalysts is strongly desired.

Herein, we reported a general way to synthesize a family of silylated organometals using *in situ* coordinating metallic ions with the PPh_2-ligand in $PPh_2CH_2CH_2Si(OEt)_3$, denoted as M-PPh_2-Ts, where M refers to Pd^{2+}, Rh^+, Pt^{2+}, Ir^+, or Ru^{2+}, while PPh_2-Ts corresponds to $PPh_2CH_2CH_2Si(OEt)_3$. They behaved as homogeneous catalysts with high activities and selectivities in various organic reactions using common solvents including THF, CH_2Cl_2 or toluene as the reaction media. After reaction, they could be completely precipitated by adding pentane and then used repeatedly without a significant decrease in the catalytic efficiencies. Moreover, we could further synthesize the chiral catalyst DPEN-Ru-PPh_2-Ts by further coordinating Ru-PPh_2-Ts with DPEN-ligand, where DPEN refers to (1*R*,2*R*)-1,2-diphenylethylenediamine. DPEN-Ru-PPh_2-Ts could act as a homogeneous chiral catalyst in CH_2Cl_2-medium organic reactions with high efficiencies and ee values. After each round of reactions, it could also be totally recovered by adding pentane and then used repeatedly many times. Obviously, these homogeneous silylated catalysts combine the advantages of both the typical homogeneous and heterogeneous catalysts.

A general approach to prepare silylated organometals (M-PPh_2-Ts and DPEN-Ru-PPh_2-Ts) is illustrated in Scheme 1 (see ESI† for experimental details). It is noteworthy that when the resulting complex was treated with pentane, it was precipitated out and a pure product was obtained after washing with pentane without using chromatography. This implies that the silylated complex can indeed be easily purified and potentially recycled. To determine the catalyst compositions, the metal

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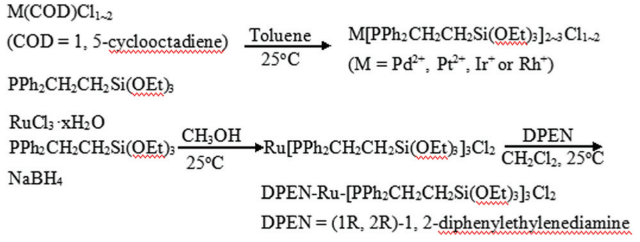
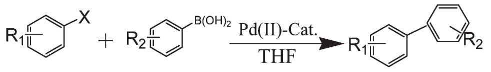


Scheme 1 Illustration of the catalyst preparation.

contents were determined by inductively coupled plasma spectrometer (ICP, Varian VISTAMPX), while the C, N, and H contents were detected by elemental analysis (Elementar Vario ELIII, Germany). Some results are listed as follows (see the structural formula of catalysts in Scheme S1†): (1) Pd-PPh_2-Ts = Pd(II)[$PPh_2CH_2CH_2Si(OEt)_3]_2Cl_2$: calculation values, C (51.64) and H (6.28), experimental results, C (51.59) and H (6.22). (2) Rh-PPh_2-Ts = Rh(I)[$PPh_2CH_2CH_2Si(OEt)_3]_3Cl$: calculation values, C (56.84) and H (6.92), experimental results, C (56.64), H (6.85). (3) Ru-PPh_2-Ts = Ru(II)[$PPh_2CH_2CH_2Si(OEt)_3]_3Cl_2$: calculation values, C (55.37), H (6.74), experimental results, C (55.55) and H (6.74). (4) DPEN-Ru-PPh_2-Ts = Ru(II)[(DPEN)/$PPh_2CH_2CH_2Si(OEt)_3]_3Cl_2$: calculation value, C (55.37), N (1.85) and H (6.74), experimental results, C (55.31), N (1.81) and H (6.75). The sample compositions and structures could be further determined by NMR spectra (Fig. S1†). The ^1H NMR ($CDCl_3$) spectra displayed characteristic peaks at 7.2–7.5, 7.6–7.7 (2 m, ArH), 3.71 (q, CH_2CH_2), 2.47 (m, CH_2P), 1.13 (t, CH_3CH_2), and 0.79 (m, $SiCH_2$). The DPEN-Ru-PPh_2-Ts displayed two new peaks around 4.1 and 5.2 ppm, indicative of the H–N group.[11] Meanwhile, the ^{13}C NMR spectra exhibited two peaks at 18 and 30 ppm, corresponding to two C atoms in the ethyl group connecting with the PPh_2 terminal. The peak at 58 ppm was attributed to the C^b atom in the $C^aH_3C^bH_2O$–Si group. An intense peak at 133 ppm was assigned to the C atoms in the benzene ring.[12] The DPEN-Ru-PPh_2-Ts displayed two additional peaks around 29 and 62 ppm, characteristic of two C atoms in the ethyl group connecting with the NH_2 terminal.[13] The ^{29}Si NMR spectra (Fig. S8†) of the PPh_2-Ts, and Pd-PPh_2-Ts catalyst displayed an intense signal at −47.1 ppm, which demonstrated that only one Si chemical environment existed in the two samples. No obvious Q^n peaks were observed, where $Q^n = Si(OSi)_n\text{-}(OH)_{4-n}$, $n = 2$–4, indicating that the Pd-PPh_2-Ts catalyst did not undergo hydrolysis and condensation reactions under the present conditions. There is a very small wide peak at about −110 ppm (Q^4), which was attributed to the hydrolysis and condensation of very few $Si(OEt)_3$ groups, as it is very difficult to completely exclude air when conducting the NMR experiments. The ^{31}P NMR spectra further showed the intense signals around 21.2, 39.2 and 38.7 ppm indicative of the Pd-PPh_2, Rh-PPh_2 and Ru-PPh_2 coordination bonds in the Pd-PPh_2-Ts, Rh-PPh_2-Ts, and Ru-PPh_2-Ts samples,[14] respectively. The different peak positions could be attributed to the different chemical environments of the P atoms due to the change of metallic ions. The DPEN-Ru-PPh_2-Ts displayed three signals at around 20, 35, and 47 ppm, corresponding to three kinds of P-Ru coordination models.[15] Meanwhile, according to the FTIR spectra (Fig. S2†), all the M-PPh_2-Ts samples displayed absorbance bands at around 695, 2897, 2973, 1439, and 1083 cm^{-1} due to the asymmetric and symmetric stretching vibrations of C–H, P–CH_2, Si–O bonds, and the -H out-of-plane deformation of the monosubstituted benzene ring.[16] The DPEN-Ru-PPh_2-Ts exhibited a new absorption band at 1641 cm^{-1} owing to the N–H stretching vibration.[17] Furthermore, the TG curves (Fig. S3†) revealed a total weight loss of around 60.2% at around 250 °C for all the M-PPh_2-Ts samples, which could be attributed to the subsequent combustion of the PPh_2-CH_2-CH_2- and the C_2H_5-groups, in good accordance with theoretical values. The DPEN-Ru-PPh_2-Ts showed 10% more weight loss resulting from the removal of the additional DPEN ligand. In addition, the XPS spectra (Fig. S4†) revealed that all the Pd and Ru species were present in the +2 oxidation state while the Rh species were present in the +1 oxidation state, corresponding to binding energies (BE) of 338.0, 280.6 and 307.7 eV in the $Pd_{3d5/2}$, $Ru_{3d5/2}$ and $Rh_{3d5/2}$ levels, respectively.[18] One could see that the metallic ions in either M-PPh_2-Ts or M$(PPh_3)_xCl_y$ (M = Pd^{2+} and Rh^+) displayed slightly lower BE than the corresponding ones in M$(COD)Cl_2$, which confirmed the coordination between metallic ions with the PPh_2 or the PPh_3 ligand instead of the COD ligand, making metallic ions more electron-enriched owing to the stronger electron-donating ability of PPh_2 or PPh_3 than that of COD. Moreover, the metallic ions in the M-PPh_2-Ts (M = Pd^{2+}, Rh^+, and Ru^{2+}) exhibited slightly lower BE than the corresponding ones in M$(PPh_3)_xCl_y$, implying the weaker electron-donation ability of the PPh_3-ligand than PPh_2-CH_2-CH_2-ligand. This could be easily understood by considering the conjugated system between one P atom with three Ph groups. The PPh_2-CH_2-CH_2-ligand contains a conjugated system between one P atom and two Ph rings, while the PPh_3-ligand contains a bigger conjugated system between one P atom and three Ph rings, which might dilute the electron density on the P atom, leading to the lower electron-donating ability.[19] In comparison with the Ru-PPh_2-Ts, no significant BE shift was observed in the DPEN-Ru-PPh_2-Ts, suggesting the similar electron-donating ability of the DPEN-ligand to that of the PPh_2-CH_2-CH_2-ligand.

The catalytic performances of the as-prepared organometals were examined in various organic reactions including Pd-catalyzed Suzuki coupling reactions (Table 1),[20] Rh-catalyzed aldehyde methylenation reactions (Table 2),[21] Ru-catalyzed homoallylic alcohol isomerization reactions (Table 3),[22] DPEN/Ru-catalyzed asymmetric hydrogenations of acetophenone (Table 4),[23] Pt-catalyzed carboselenation of alkynes by selenoesters (Table S1†), and Ir-catalyzed transfer hydrogenation reactions (Table S2†). In these reactions, all the M-PPh_2-Ts catalysts and the DPEN-Ru-PPh_2-Ts chiral catalyst could be completely dissolved in the THF, CH_2Cl_2 or toluene used as the reaction media and precipitated at the end of organic reactions by adding fresh pentane. The catalytic performance of the Pd-PPh_2-Ts was examined for the Suzuki coupling reactions in

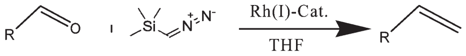
Table 1 Pd-catalyzed Suzuki coupling reactions[a]



Entry	R^1	R^2	X	Yield (%)
1	H	H	Cl	41 (36)
2	H	H	Br	89 (84)
3	H	H	I	92 (89)
4	4-NO$_2$	H	I	96 (98) 86^c
5	2-NO$_2$	H	Br	88 (92)
6	2-NO$_2$	H	I	90 (93)
7	4-Me	H	I	80 (84)
8	2-Me	H	I	78 (75)
9	4-OMe	H	I	82 (85)
10	H	4-F	Cl	30 (24)
11	H	4-F	Br	60 (62)
12	H	4-F	I	72 (68)
13	H	4-OMe	Cl	34 (27)
14	4-NO$_2$	4-OMe	I	91 (95) 93^b 80^c
15	4-NO$_2$	F	I	61 (63)
16	H	4-OMe	I	78 (77)
17	H	4-OMe	Br	75 (72) 65^c
18	4-CONH$_2$	4-OMe	Br	Trace
19	4-NH$_2$	4-OMe	I	29 (31) 33^b
20	4-CO$_2$C$_2$H$_5$	4-OMe	I	75 (76) 66^c
21	4-CN	4-OMe	I	93 (96) 82^c

[a] Reaction conditions: 0.50 mmol arylhalide, 0.60 mmol organoboronic acid, 1.0 mmol K$_2$CO$_3$, 5.0 ml of THF and a catalyst containing 0.021 mmol Pd(II), 25 °C, 24 h. The data in brackets were obtained from the Pd(PPh$_3$)$_2$Cl$_2$ catalyst. [b] The Pd(PPh$_3$)$_4$ catalyst used. [c] The Pd-PPh$_2$-PMO(Ph) catalyst used from. ref. 12.

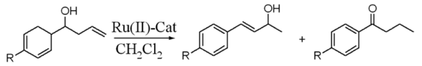
Table 2 Rh-catalyzed aldehyde methylenation reactions[a]



Entry	R	Time (h)	Conversion (%)	Selectivity (%)	Yield (%)
1	Ph	1	96 (95)	90 (94)	86 (89)
2	4-Cl–Ph	4	97 (94)	90 (88)	87 (83)
3	2-Cl–Ph	4	89 (89)	87 (90)	77 (80)
4	Ph–C═C	1	94 (92)	96 (96)	90 (88)
5	4-CH$_3$–Ph	2	72 (78)	93 (94)	67 (73)
6	4-CH$_3$O–Ph	2	76 (79)	91 (92)	69 (73)
7	C–C	6	93 (90)	96 (97)	89 (87)
8	2-OH–Ph	8	68 (60)	89 (88)	61 (53)
9	4-OH–Ph	8	88 (94)	85 (83)	75 (78)
10	4-NO$_2$–Ph	12	84 (86)	84 (87)	71 (75)

[a] Reaction conditions: 1.0 mmol aldehydes, 1.4 mmol trimethylsilyldiazomethane, 1.1 mmol iPrOH, 1.1 mmol PPh$_3$, 5.0 ml of THF and a catalyst with 0.030 mmol Rh(I), 25 °C. The data in brackets were obtained from the Rh(PPh$_3$)Cl catalyst.

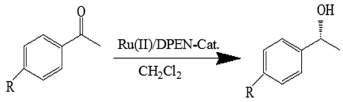
Table 3 Ru-catalyzed isomerization reactions[a]



Catalyst	R	Time (h)	Conversion (%)	Selectivity (%)	Yield (%)
Ru-PPh$_2$-Ts	H	10	91	77	70
Ru(PPh$_3$)$_3$Cl$_2$			90	77	69
Ru-PPh$_2$-PMO(Ph)^b			79	73	58
Ru-PPh$_2$-Ts	CH$_3$	12	94	75	71
Ru(PPh$_3$)$_3$Cl$_2$			94	76	71

[a] Reaction conditions: a catalyst with 0.032 mmol Ru(II), 25 µl of homoallylic alcohol, 5.0 ml of CH$_2$Cl$_2$, 40 °C, 10 h. [b] Ru–PPh$_2$–PMO-(Ph) catalyst used from ref. 12.

Table 4 Ru-catalyzed asymmetric ketone hydrogenations[a]



Catalyst	R	Conversion (%)	ee (%)
Ru(PPh$_3$)$_3$Cl$_2$+DPEN	H	99	68
DPEN-Ru-PPh$_2$-Ts		97	70
Ru(PPh$_3$)$_3$Cl$_2$+DPEN	CH$_3$	98	71
DPEN-Ru-PPh$_2$-Ts		98	72
Ru(PPh$_3$)$_3$Cl$_2$+DPEN	CH$_3$O	99	72
DPEN-Ru-PPh$_2$-Ts		98	73

[a] Reaction conditions: a catalyst with 5.0 µmol Ru(II), 0.50 mmol ketone, 1.0 ml of propanol, 0.10 mmol potassium *tert*-butoxide, 5.0 ml of CH$_2$Cl$_2$, 50 °C, 36 h.

THF solution (Table 1). Non-silylated Pd(PPh$_3$)$_2$Cl$_2$ and Pd(PPh$_3$)$_4$ (entries 14 and 19, Table 1) and the Pd-PPh$_2$-PMO (Ph) catalyst[12] (entries 4, 14, 17, 20 and 21, Table 1) were used in parallel for comparison under the same reaction conditions and the yields are provided in brackets. All these reactions were absolutely selective for the target products under the present conditions since no significant side products were identified by GC-MS. As homogeneous catalysts, the Pd-PPh$_2$-Ts exhibited comparable catalytic activities owing to the similar coordination model and chemical micro-environment of the Pd(II) active sites. The Suzuki reactions with chlorobenzene exhibited much lower product yields than either those with bromobenzene or iodobenzene since the activation of the C–Cl bond was much more difficult than that of either the C–Br or the C–I bond. The electron withdrawing groups on the aryl halides promoted the reactions while the electron donating groups disfavored the reactions. Similarly, the electron contributing groups on the arylboronic acids were also detrimental to the reaction.

As shown in Tables 2 and 3, both the Rh-PPh$_2$-Ts and the Ru-PPh$_2$-Ts catalysts displayed almost identical activities and selectivities with their corresponding Rh(PPh$_3$)Cl and Ru-(PPh$_3$)$_3$Cl$_2$ homogeneous catalysts in THF-medium aldehyde methylenation reactions and CH$_2$Cl$_2$-medium homoallylic alcohol isomerization reactions, respectively, which further confirms the similar coordination models and chemical micro-environment of the metal active sites. In the aldehyde methylenation reactions, both the benzaldehyde and the cinnamaldehyde displayed much higher activities than the propaldehyde, possibly owing to the conjugated system, which favored the formation of the carbon cation connecting with the O atom and thus facilitated the attack by the trimethylsilyldiazomethane molecule. The presence of either the electron-withdrawing or the electron-donating groups on the Ph ring connecting with the C=O greatly decreased the activity, obviously due to the steric hindrance for the attack of the trimethylsilyldiazomethane molecule with very large size. Similarly, the Pt-PPh_2-Ts catalyst also exhibited equivalent efficiencies with the traditional $Pt(PPh_3)_2Cl_2$ homogeneous catalyst in the toluene-medium cyclization of propargylic esters (see Table S1†), while the Ir-PPh_2-Ts displayed nearly the same efficiencies as the $[Ir(COD)Cl]_2$ and phosphine homogeneous catalyst system in the toluene-medium transfer hydrogenation reactions of ketones (see Table S2†). Moreover, Table 4 further indicates that, during the CH_2Cl_2-medium asymmetric hydrogenation of ketones, the DPEN-Ru-PPh_2-Ts chiral catalyst also displayed comparable conversion and ee value to the traditional homogeneous system comprised of soluble $RuCl_2(PPh_3)_3$ and DPEN chiral reagent. These results clearly demonstrated the general properties of the as-prepared homogeneous catalysts.

The most important advantage of the present family of silylated organometals (M-PPh_2-Ts and DPEN-Ru-PPh_2-Ts) is that they could be used as homogeneous catalysts with high efficiencies in various organic reactions using THF, CH_2Cl_2 or toluene solvent as the reaction medium. After reaction, they could be totally settled down by adding fresh pentane for reuse in subsequent runs of the reactions. Fig. 1 clearly demonstrated that the Pd-PPh_2-Ts, Rh-PPh_2-Ts, Ru-PPh_2-Ts, and DPEN-Ru-PPh_2-Ts catalysts could be absolutely dissolved in THF or CH_2Cl_2 and could then be completely precipitated by adding fresh pentane. Similarly, we also found that both the Pt-PPh_2-Ts and the Ir-PPh_2-Ts catalysts could be totally dissolved in toluene and could then be completely settled down by adding fresh pentane. From Table 5, one could see the high catalyst separation efficiencies of the as-prepared silylated organometals from the THF, CH_2Cl_2 or toluene solutions with the neglected metal leaching by adding fresh pentane, showing excellent catalyst recycling efficiencies. An increase in the solvent quantity or decrease in the temperature could further decrease the metal leaching.

As shown in Fig. 2, the Pd-PPh_2-Ts, Rh-PPh_2-Ts and Ru-PPh_2-Ts catalysts could be used repeatedly more than 6 times without significant deactivation. Similarly, the Pt-PPh_2-Ts, Ir-PPh_2-Ts as well as the DPEN-Ru-PPh_2-Ts chiral catalyst could also be reused (see Table S3†). Besides the high recycling efficiency of the catalysts with negligible loss of metal active sites (see Table 5), the identical XPS spectra (Fig. S5†), ^1H NMR spectra (Fig. S6†), FTIR spectra (Fig. S7†), ^{29}Si NMR and ^{31}P NMR spectra (Fig. S8†) clearly demonstrated the preservation of the catalyst structure and the chemical microenvironment of metal active sites after being reused, which could sufficiently account for the excellent durability of the catalysts upon recycling.

Table 5 Catalyst recycling efficiencies by adding pentane[a]

Catalyst	Solvent	Separation efficiency (%)	Metal leaching (ppm)
Pd-PPh_2-Ts	THF	99.4	2.5
Rh-PPh_2-Ts	THF	99.6	2.4
Pt-PPh_2-Ts	Toluene	99.1	2.0
Ir-PPh_2-Ts	Toluene	98.7	2.6
Ru-PPh_2-Ts	CH_2Cl_2	98.4	2.8
DPEN-Ru-PPh_2-Ts	CH_2Cl_2	99.0	1.4

[a] Reaction conditions: see Tables 1–4, and Tables S1, S2 respectively.

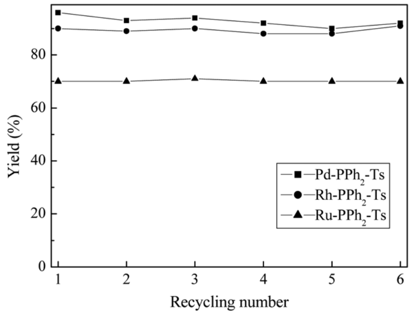


Fig. 2 Recycling test of catalysts in Suzuki reaction of 4-nitroiodobenzene with phenylboronic acid, methylenation reaction of cinnamaldehyde with trimethylsilyldiazomethane, and isomerization reaction of 1-phenyl-3-buten-1-ol.

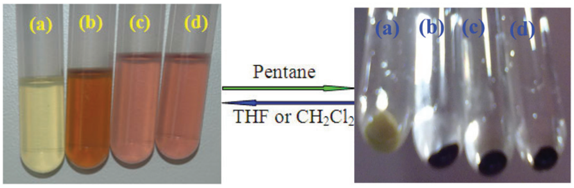


Fig. 1 Representative pictures indicating the alternative dissolving and precipitating of (a) Pd-PPh_2-Ts, (b) Rh-PPh_2-Ts, (c) Ru-PPh_2-Ts, and (d) DPEN-Ru-PPh_2-Ts in THF or CH_2Cl_2 solvent and pentane.

Conclusions

In summary, this work developed a general way to design Pd-, Rh-, Ru-, Pt-, and Ir-based silylated organometals as a new family of recyclable homogeneous catalysts, since they could be used as homogeneous catalysts in THF-, CH_2Cl_2- or toluene-medium organic reactions and could be easily recycled by adding pentane after the reactions. The catalysts could be used repeatedly without significant deactivation. Other silylated organometals could also be synthesized, which may enlarge the catalyst family and thus offer more opportunities for industrial applications.

Experimental section

General

The following general procedures were applied for all experiments in this work. Unless specifically stated, all organic reactions were performed under water-free atmosphere with absolute exclusion of moisture from all reagents, solvents and glassware. The reproducibility was checked by repeating each experiment at least three times and was found to be within acceptable limits (±5%).

Catalyst preparation

In a typical synthesis run, 2.7 g of $PPh_2CH_2CH_2Si(OEt)_3$ was added dropwise into a suspension comprised of 1.0 g of Pd(COD)Cl_2 (COD = 1,5-cyclooctadiene) and 25 ml of toluene. The mixture was kept stirring until it reached a clear orange solution. After being concentrated to 5.0 ml, 25 ml of pentane was added, leading to the Pd-PPh_2-Ts catalyst in yellow solid, which was washed thoroughly with pentane more than three times. The remaining yellow solid was dried at 60 °C and 0.10 Torr to remove residual solvents, leading to the Pd-PPh_2-Ts catalyst. The preparation of M-PPh_2-Ts (M = Rh^+, Pt^{2+}, Ir^+ and Ru^{2+}) and the chiral catalyst DPEN-Ru-PPh_2-Ts followed similar procedures. Detailed preparation procedures are described in the ESI.†

Characterization

The carbon and hydrogen contents in the samples were determined by elemental analysis on a CHN analyzer (Elementar Vario ELIII, Germany). Contents of palladium, ruthenium, rhodium, silica, nitrogen, and phosphor were determined by inductively coupled plasma spectrometer (ICP, Varian VISTAMPX). The catalyst structure was characterized by FTIR spectra (Nicolet Magna 550), NMR spectra (Bruker AV-400) and thermogravimetry (TG, Shimadzu DT-60). The surface electronic states were analyzed by X-ray photoelectron spectroscopy (XPS, PerkinElmer PHI 5000C). All the binding energy (BE) values were calibrated using the standard BE value of contaminant carbon (C1S = 284.8 eV) as a reference.

Activity test

Generally, the catalytic performances were examined in various organic reactions including Pd-catalyzed Suzuki coupling reactions (Table 1), Rh-catalyzed aldehyde methylenation reactions (Table 2), Ru-catalyzed homoallylic alcohol isomerization reactions (Table 3), Pt-catalyzed carboselenations of alkynes by selenoesters (Table S1†), Ir-catalyzed transfer hydrogenation reactions (Table S2†), and DPEN/Ru-catalyzed asymmetric hydrogenations of acetophenone (Table 4). Unless specially stated, all organic reactions were performed under a water-free atmosphere with absolute exclusion of moisture from all reagents, solvents and glassware. The reaction conditions are listed in the corresponding tables and the reaction products were analyzed by GC, GC-MS and HPLC-MS. The reproducibility was checked by repeating each experiment at least three times and was found to be within acceptable limits (<±5%).

Determination of catalyst leaching and durability

All reactions were carried out under dry, oxygen-free argon using Schlenk techniques unless otherwise stated. Solvents used were of spectrophotometric purity, dried over a molecular sieve, degassed, and stored under argon. In order to determine the catalyst durability, any solids in the reaction system were first filtered after each reaction run and the solids were washed more than two times with dry solvent. After being concentrated to about 2.0 ml, 2 times volume of dry pentane (about 4.0 ml) was added and then the silylated organometallic catalyst in the solution was precipitated, typically at 25 °C, using 4.0 ml of pentane for about 2 min (if at 5 °C, 2.0 ml of pentane for about 30 s), followed by decanting the solvents, washing with fresh pentane and vacuum drying at 60 °C overnight. Then, the catalyst was re-used with fresh THF, CH_2Cl_2 or toluene and reactants for subsequent runs of reactions under identical conditions.

Acknowledgements

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