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Phosphorus Ligands

P-Stereogenic Secondary Iminophosphorane Ligands and Their Rhodium(I) Complexes: Taking Advantage of NH/PH Tautomerism**

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Phosphane ligands play a key role in metal catalysis. Among these species, bulky electron-rich P-stereogenic phosphanes show high efficiency in asymmetric hydrogenation and other industrially relevant applications.[1,2] An important drawback for this class of compounds is that they are sensitive to oxidation, and therefore must be handled under a strict inert atmosphere. Protection of the phosphorus lone pair with BH_3 is extremely useful in the synthesis of P-stereogenic compounds; however, a final deprotection/isolation of the oxygen-sensitive free phosphane is required before complexation with a metal.[3] Such a procedure is not ideal for routine screening and scale-up. Secondary phosphane oxides (SPOs) do not have this limitation, because they are resistant to oxidation and inert to water.[4] Their potential as ligands arises from the tautomeric equilibrium of these species, as shown in Figure 1. The pentavalent phosphane oxides are in equilibrium with the trivalent phosphinous acids. The equilibrium is usually shifted towards the P^V form, but it can be shifted to the phosphinous acid form by coordination of phosphorus to a metal. Furthermore, P-stereogenic SPOs are configurationally stable and thus chiral information is preserved through the PH/OH equilibrium.

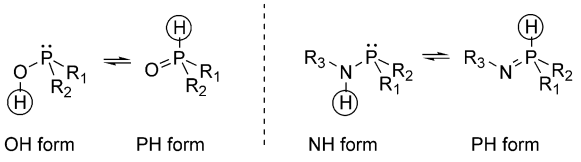

Figure 1. Phosphinous acid/SPO tautomerism (left) and aminophosphane/SIP tautomerism (right).

The analogous equilibrium between aminophosphanes and secondary iminophosphoranes (SIPs) has not been exploited in catalysis.[5] Very recently, Reek and co-workers described the use of phosphinosulfonamide ligands **1** and **2** in rhodium-catalyzed asymmetric hydrogenation reactions (Figure 2).[6] In solution, **1** was found as 1:1.2 mixture of the corresponding aminophosphane/SIP tautomers showing a low exchange rate on the NMR timescale (RT, $CDCl_3$). Under the same conditions, ligand **2** was present only in its NH form. The authors showed that ligands **1** and **2** exhibit rich coordination chemistry and that, depending on the reaction conditions, these ligands could lead to either mono- or dinuclear Rh species, as confirmed by NMR and DFT studies.

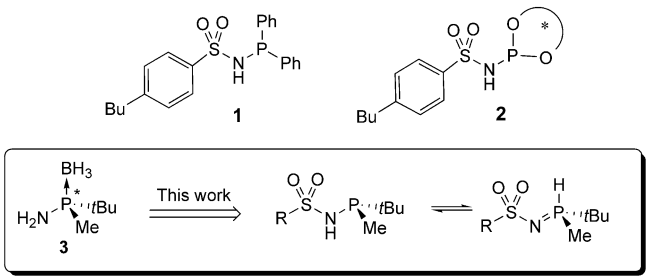

Figure 2. Secondary iminophosphoranes as potential ligands.

We recently reported the synthesis of P-stereogenic aminophosphane **3** (Figure 2) and showed its potential in the synthesis of the ligand maxphos, which forms an efficient PnP* hydrogenation catalyst in conjunction with rhodium.[7] We considered **3** to be highly suitable for the synthesis of electron-rich P*–sulfonyl iminophosphorane ligands and felt that we could benefit from NH/PH tautomerism to render these ligands stable to oxidation. Thus, herein we report on the synthesis of bulky P-stereogenic iminophosphoranes derived from **3**, and show how these compounds can serve as convenient preligands in asymmetric catalysis. The X-ray structure of the resulting monomeric rhodium complexes and their application in the asymmetric [2+2+2] cycloaddition of endiynes are also described.

Starting from **3**, anion formation with NaH and reaction with commercially available sulfonylchlorides provided the corresponding borane-protected phosphinosulfonamides **4**–**7** (Table 1). Bulky sulfonylchlorides provided the desired products in excellent yields (Table 1, entries 1–3). The synthesis of **7**, bearing a small, electron-withdrawing CF_3SO_2N group, proved troublesome and under the strongly basic conditions used could not be accomplished using TfCl or Tf_2O (Tf = trifluoromethanesulfonyl). However, this compound

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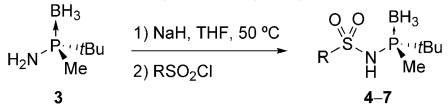
Table 1: Synthesis of borane-protected phosphinosulfonamides.



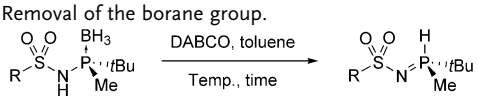
Entry	R	Product	*t* [h]	Yield [%]
1	Mes	**4**	5	85
2	Tripp	**5**	7	85
3	*p*-Tol	**6**	8	78
4[a]	CF_3	**7**	4	95

[a] *N*-phenyl-bis(trifluoromethanesulfonimide) was used instead of the corresponding sulfonylchloride. Mes = 2,4,6-trimethylphenyl, Tripp = 2,4,6-tris(isopropyl)phenyl.

was smoothly prepared in a 95% yield using *N*-phenyl-bis(trifluoromethanesulfonimide) (Table 1, entry 4).[8]

Borane deprotection of compounds **4–7** was conducted under basic conditions in the presence of an excess of 1,4-diazabicyclo[2.2.2]octane (DABCO). Heating was required to attain satisfactory conversions in a reasonable time frame. In this manner, phosphino arylsulfonamides were deprotected readily in excellent yields (Table 2, entries 1–3). Finally, borane removal of the triflamide derivative **7** was not viable

Table 2: Removal of the borane group.



Entry	R	Borane	*T* [°C]	*t* [h]	Product	Yield [%]
1	Mes	**4**	80	2	**8**	89
2	Tripp	**5**	100	2	**9**	92
3	*p*-Tol	**6**	80	5	**10**	78
4[a]	CF_3	**7**	50	6	**11**	38

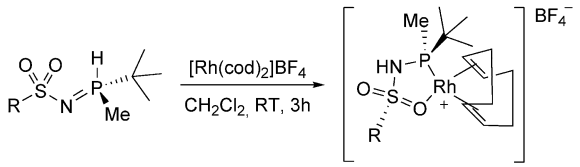
[a] Deprotection was conducted under acidic conditions (HBF_4 in MeOH). DABCO = 1,4-diazabicyclo[2.2.2]octane, Mes = 2,4,6-trimethylphenyl, Tripp = 2,4,6-tris(isopropyl)phenyl.

under basic conditions. We attributed this lack of reactivity to the increased acidity of the NH group. In the presence of DABCO, this group is deprotonated, thereby making the neighboring phosphane even more electron rich. $R_3P{-}BH_3$ complexes of electron-rich phosphanes cannot be deprotected by borane exchange using an amine.[9] Instead, compound **7** was deprotected under acidic conditions (HBF_4, MeOH) to afford the desired compound **11** in 38% yield (Table 2, entry 4).

^{1}H NMR analysis of compounds **8** and **9** in $CDCl_3$ showed a single set of signals and the characteristic resonance of a PH group, with couplings of 452 Hz (J_P) and 4 Hz (J_H). In contrast, compound **10**, which bears a TsN group (Ts = *p*-toluenesulfonyl), showed two sets of signals in a 1:8 ratio in the ^{31}P and ^{1}H NMR spectra ($CDCl_3$, RT), with the PH tautomer being the most abundant in solution. Finally, ligand **11**, which bears an electron-withdrawing TfNH group, was present only as the PH tautomer, as determined by NMR spectroscopy in $CDCl_3$. In contrast with the ligands reported by Reek and co-workers, where the NH form was predominant, the secondary iminophosphorane form was almost exclusively the tautomer found in solution for ligands **8–11**. The relative basicity of the phosphorus lone pair can explain this behavior. Electron-rich groups on the P atom increase the basic character of the lone pair, thus favoring the formation of the PH tautomer. Likewise, electron-withdrawing groups on nitrogen make the NH group more acidic, again favoring the PH form.[10]

Most interestingly, the SIPs **8–11** are stable to oxidation and can be stored for months under air without noticeable decomposition. They are also configurationally stable, as confirmed by $[\alpha]_D$ analysis in chloroform.[11] From a practical point of view, SIPs **8–11** are of interest because they can be considered a new class of P-stereogenic preligands, like the SPOs. As such, they are unique in the sense that they bear a *tert*-butylmethylphosphino fragment that is crucial in the construction of highly effective ligands such as quinoxP*,[12] tcfp,[13] and maxphos.[7a]

We next studied the capacity of SIP ligands for coordination to rhodium (Scheme 1). Ligands **8**, **9**, and **10**, which were conveniently scaled up and easily purified, were chosen for



R = Mes, **8**
Tripp, **9**
p-Tol, **10**

R = Mes, **12** (90% yield)
Tripp, **13** (87% yield)
p-Tol, **14**

Scheme 1. Synthesis of cationic Rh^I complexes with SIP ligands. Cod = 1,5-cyclooctadiene, Mes = 2,4,6-trimethylphenyl, Tripp = 2,4,6-tris(isopropyl)phenyl.

this purpose.[14] The reaction of bulky iminophosphoranes with $[Rh(cod)_2]BF_4$ resulted in the exchange of a single 1,5-cyclooctadiene (cod) unit, as determined by ^{1}H NMR spectroscopy. The addition of an excess of the SIP ligand did not lead to a dimeric species; we propose that the steric bulk of the ligand is responsible for this behavior. Complexes **12** and **13** were isolated as air-stable yellow solids.[15] In contrast, **14** resulted in an oil that slowly decomposed to an unidentified mixture of complexes and, in our hands, could not be purified.

Upon coordination to rhodium, the tautomeric equilibrium is effectively displaced towards the phosphinosulfonamide form. This leaves a relatively acidic NH group in place that shows a resonance around 8 ppm in the ^{1}H NMR spectrum ($CDCl_3$). Accordingly, we attempted to prepare the analogous neutral complexes in the presence of a base. These were expected to be similar from a structural point of view, but very different electronically. The reaction of SIP ligands **8** and **9** with $[Rh(cod)_2]BF_4$ in the presence of triethylamine provided the neutral, highly apolar complexes **15** and **16**, which were then purified by either extraction with hexanes or filtration through alumina to separate them from the salt byproduct (Scheme 2).

Scheme 2. Preparation of neutral Rh^{I} complexes with SIP ligands. Cod = 1,5-cyclooctadiene, Mes = 2,4,6-trimethylphenyl, Tripp = 2,4,6-tris(isopropyl)phenyl.

Given their novelty and the lack of structural studies for this class of ligands, we sought a definitive structural elucidation for the corresponding rhodium complexes. In this regard, we succeeded in growing crystals suitable for X-ray analysis of cationic complex **12** (Figure 3).[16] The structure of **12** showed that the ligand coordinates to the

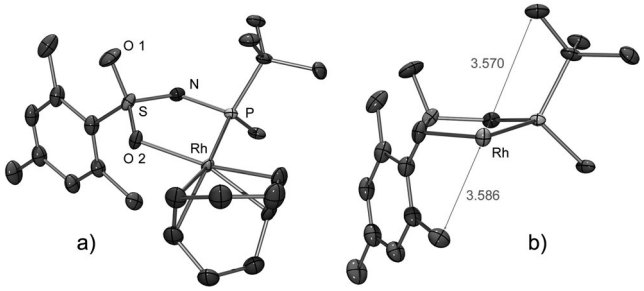


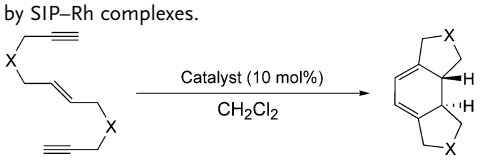
Figure 3. a) Ortep plot for the X-ray structure of **12** with thermal ellipsoids shown at 50% probability; anion is omitted for clarity. b) Metal and ligand assembly showing the *pseudo*-C_2 disposition of bulky groups around the metal. Selected bond distances (Å): O(1)–S 1.419(7), O(2)–S 1.456(6), S–N 1.603(7).

metal center through the phosphorus atom and the O2 of the sulfone group. The steric repulsions between the bulky *tert*-butyl group attached to phosphorus and the aromatic group of the sulfone force them to adopt a *trans* orientation and so direct the coordination of the sulfone. In this scenario, the sulfur atom of the sulfone group becomes stereogenic and adopts an *R* configuration. Interestingly, the bulky *trans* groups are in similar proximity to the metal center (3.57 and 3.58 Å), thereby creating a *pseudo*-C_2 symmetry.

We have recently reported the use of *N*-phosphinosulfinamide ligands (PNSO) in the [2+2+2] intramolecular cycloaddition of enediynes with terminal alkynes.[17] Enediynes with terminal alkynes are challenging substrates to cyclize.[18] For instance, Tanaka reported the Rh-catalyzed cyclization of **17** with 78% yield and 48% *ee* using the tolbinap/[Rh(cod)$_2$]BF_4 system (tolbinap = 2,2′-bis[di(*p*-methylphenyl)-phosphino]-1,1′-binaphthyl).[19] The PNSO ligands showed an acceptable reactivity profile, but afforded low selectivity (up to 32% *ee*). The low selectivity was attributed to the fact that the chiral information in these ligands is located at the hemilabile sulfinyl group. At this point, we thought that the rhodium–SIP complexes **12**–**16**, with the chiral *tert*-butylmethylphosphino moiety strongly attached to the rhodium center and the hemilabile sulfonyl group, could provide good results in the cyclization of this type of substrates.

Thus, we started studying the use of cationic complexes **12** and **13** as catalysts in the cyclization of the oxygen-tethered enediyne **17** in refluxing CH_2Cl_2 (Table 3, entries 1 and 2). Under these conditions, the reaction took place cleanly and with complete conversion to afford diene **20** as the sole product with up to 63% enantiomeric excess. Catalyst **13**, which contains the bulky Tripp group, was more selective than the mesityl complex **12**. Using **13**, the selectivity was improved to 69% *ee* when the reaction was run at room temperature (Table 3, entry 3). In contrast, the neutral complexes **15** and **16**, with a more electron-rich metal center, did not provide any cyclization product and were inactive in the [2+2+2] cyclization of enediynes (Table 3, entries 4 and 5). The N-tethered substrate **18** was cyclized with similar levels of selectivity (67% *ee*) at both room temperature and at reflux (Table 3, entries 6 and 7). However, after some experimentation, we found that the addition of a catalytic amount of acid enhanced the selectivity with this substrate. The addition of HBF_4 (10 mol%) allowed an

Table 3: [2+2+2] Intramolecular cycloaddition of terminal enediynes catalyzed by SIP–Rh complexes.

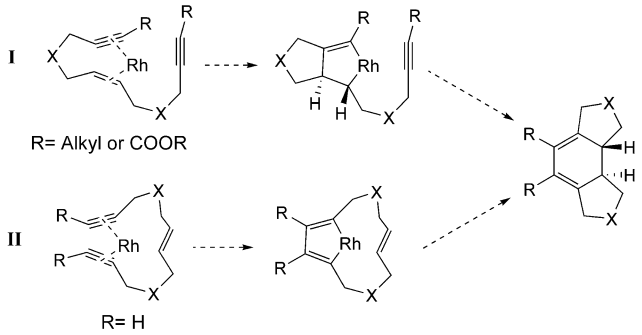


Entry	X	Catalyst	Conditions	Conv. [%][a]	*ee* [%][b]
1	O	**12**	reflux, 6 h	99	59
2	O	**13**	reflux, 6 h	99	63
3	O	**13**	RT, 26 h	98[c]	69
4	O	**15**	reflux, 7 h	0	–
5	O	**16**	reflux, 7 h	0	–
6	NTs	**13**	reflux, 8 h	99	67
7	NTs	**13**	RT, 15 h	99	67
8	NTs	**13**	reflux, 3 h, 10 mol% HBF_4	95[c]	85
9	NTs	**13**	RT, 24 h, 10 mol%, HBF_4	99	90
10	NTs	**13**	RT, 24 h, 100 mol% HBF_4	99	81
11	NSO_2Mes	**13**	reflux, 24 h	99	68
12	NSO_2Mes	**13**	reflux, 24 h 10 mol% HBF_4	91[c]	83
13	NSO_2Mes	**13**	reflux, 24 h 10 mol% TFA	99	94
14	NSO_2Mes	binap[d]	reflux, 24 h	45[c]	54
15	NSO_2Mes	binap[d]	reflux, 24 h 10 mol% TFA	29[c]	52

[a] Selectivity was 100% when using catalysts **12** and **13**. Conversion was determined by ^{1}H NMR spectroscopy. [b] In all cases the major product was the levorotatory one. [c] Yield of isolated product. [d] A mixture of [Rh(cod)$_2$]BF_4/(*R*)-binap (1:1) was used as catalyst. Binap = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl, Mes = 2,4,6-trimethylphenyl, TFA = trifluoroacetic acid, Ts = *p*-toluenesulfonyl.

increase to 90% *ee* (Table 3, entries 8 and 9). This behavior was also observed for substrate **19**, which, upon addition of trifluoroacetic acid (TFA; 10 mol%), provided the corresponding diene **22** in 94% *ee* (Table 3, entry 13). Finally, for comparison, enediyne **19** was submitted to cyclization using the standard binap/$[Rh(cod)_2]BF_4$ catalytic system (binap = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl) to afford **22** in only 45% yield and 54% *ee* (Table 3, entries 14 and 15).[20]

Cyclization of enediynes **17**–**19** can occur through pathways I or II (Scheme 3). It has been postulated that pathway I, which includes an early-stage stereodetermining step, provides a high level of stereocontrol, while pathway II leads to



Scheme 3. Possible reaction pathways for the [2+2+2] cycloaddition of enediynes.

a lower enantiomeric bias.[18a] On the other hand, DFT calculations indicated that enediynes with terminal alkynes cyclize preferentially through initial alkyne–alkyne coupling (pathway II), usually leading to low enantiomeric excess.[21] Most remarkably, the selectivities found in this study of new SIP ligands are the highest reported for substrates that cyclize through pathway II, and thus highlight the utility of ligands with PH/NH tautomerism in catalysis.

In summary, herein we disclose P-stereogenic *N*-sulfonyl secondary iminophosphorane ligands as a novel class of preligands in metal catalysis. These compounds are configurationally stable and, thanks to NH/PH tautomerism, they do not undergo oxidation in air. We have shown that the tautomeric equilibrium is displaced towards the NH form in the presence of a rhodium source, thus allowing efficient P,O coordination with the metal center. Upon complexation, the bulky groups on the sulfone and the phosphane are placed *trans* to each other, thereby creating a *pseudo*-C_2 symmetry around the metal center. Finally, we have demonstrated that these complexes are efficient and selective catalysts for the [2+2+2] cycloaddition of enediynes with terminal alkynes. In this regard, our system provides satisfactory results where other methods fall short.

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