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[(BINAP)Re(O)Cl_3] as an efficient catalyst for olefination of chiral α-substituted aliphatic aldehydes

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ABSTRACT

A convenient one-pot preparation of [(BINAP)Re(O)Cl_3] (**6**) is described. This complex was demonstrated to be an efficient catalyst for the olefination of aldehydes by reaction with α-diazo esters, with essentially quantitative yields and up to 98:2 geometric selectivity. The potential for using enantiopure [(BINAP)Re(O)Cl_3] (**6**) to promote an asymmetric kinetic resolution of racemic α-stereogenic aldehydes was investigated, but no enantiotopic discrimination was observed. Control experiments indicate that this lack of selectivity stems from the in-situ formation of a phosphonium ylide, which accounts for product formation in a non-metal associated reaction pathway.

1. Introduction

The ability to meet an increasing demand for complex molecules in an efficient and sustainable manner relies on the development of new synthetic methods and the strategies that they inspire. Considerable efforts have been invested in the development of asymmetric reactions where new stereogenic units are created, e.g. selective bond formation to one of the enantiotopic faces of a carbonyl or enolate. A different approach, to discriminate between enantiotopic groups or enantiomers, is attractive as in principle any process, also those that do not create new chirogenic units, can be rendered enantioselective this way [1]. An example of such a process is asymmetric olefination, e.g., the asymmetric Horner–Wadsworth–Emmons (HWE) reaction. Chiral phosphonates have been used to differentiate α-stereogenic enantiotopic carbonyls, often with high yields and excellent geometric and diastereoselectivies [2,3]. This strategy has played a key role in several recent total syntheses of complex natural products with anticancer activity [4]. The utility of asymmetric olefination reactions is however currently hampered by the high cost of the most efficient chiral phosphonates as well as by expensive and sensitive additives (i.e. strong bases, crown ethers). A recent report by O'Brien and coworkers recently addressed some of these concerns by presenting a method for Wittig reactions which is catalytic in phosphine [5]. To lower the cost, and ideally improve on operational convenience and scalability, a method relying on readily available materials that recycle the expensive chiral information in a catalytic cycle is desired. Several reports on catalytic asymmetric HWE-type reactions have been published [6], but a general, cheap, convenient and efficient protocol remains elusive. The development of transition metal catalyzed olefination reactions based on metalla-carbenes, formed through catalytic decomposition of diazocompounds, suggests new entries to an asymmetric olefination reaction [7,8]. Seminal work by Herrmann on MTO (methyltrioxorhenium)-catalyzed olefinations serves as a useful starting point in this context. This reaction has been shown to proceed via a metallaoxetane intermediate, arising from cycloaddition of a Re–carbene to an aldehyde (Scheme 1, [9a,b]). The metal is thus associated with the substrate carbonyl in the proposed product-determining step. Attaching chiral ligands to the metal in this process would create a chiral environment at the reaction center that might discriminate between enantiotopic carbonyl groups, either in the same substrate molecule (asymmetric desymmetrization) or in different ones (kinetic resolution), resulting in a catalytic asymmetric olefination reaction. Chen and Zhang subsequently reported a detailed mechanistic study on a cationic Re–bipyridyl catalyst formed from decomposition of [Re_2O_7(bipy)] [9d]. With this catalyst the olefination reaction was shown to proceed via in-situ generation of a Wittig-ylide, which accounts for product formation.

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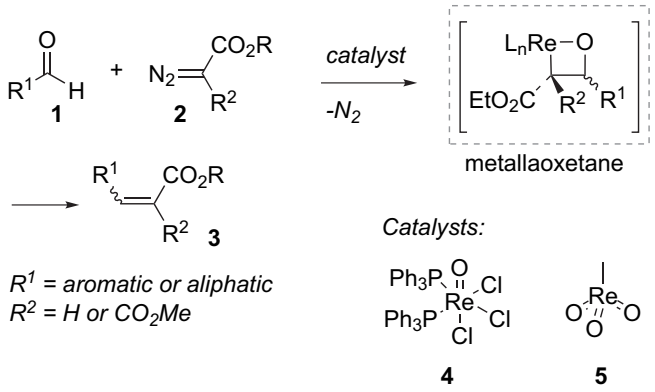


Scheme 1. Rhenium catalyzed olefination of aldehydes.

In addition to Re, several other metals like Mo, Co, Rh, and Fe [10], exhibit catalytic activity in similar reactions. These processes are typically described as proceeding through generation of ylides [9,11].

Getting access to chiral analogs of MTO (**5**) is a synthetically challenging task [12]. An alternative Re complex, also shown by Herrmann to be an efficient catalyst of olefination reactions, is $[(PPh_3)_2Re(O)Cl_3]$ [9b,13] (**4**). A protocol for olefinations catalyzed by $[(PPh_3)_2Re(O)Cl_3]$ (**4**) using $(EtO)_3P$ as the reducing agent instead of PPh_3 was shown to simplify the workup as the solvents and byproducts of this procedure are either volatile or water-soluble [14]. The high stability of **4**, paired with good behavior in catalysis including low catalyst loadings, simple workups, good yields and geometric selectivities makes it an attractive catalyst.

We hypothesized that $[(BINAP)Re(O)Cl_3]$ (**6**) might serve as a chiral homolog of **4** in asymmetric olefination reactions (Fig. 1). This complex is a known, air and shelf stable compound, previously shown to exhibit good catalytic activity in oxidations of sulfides to sulfoxides [15], and more recently in hydrosilylations of aldehydes [16]. The X-ray structure of *rac*-**6** was published by Parr et al. in 2005 [17].

An achiral complex with a bidentate phosphine ligand, $[(DPPE)Re(O)Cl_3]$ (**7**) was previously shown to be inactive in olefination reactions [18], but given that the electronic properties of **6** would resemble those of **4** more closely than those of the bisphenyl-alkyl ligands of **7**, this precedent was not decisive.

2. Experimental

2.1. General methodology

Tetrahydrofuran (THF) was distilled from sodium/benzophenone under a nitrogen atmosphere. Dichloromethane (CH_2Cl_2) was distilled form CaH_2 under a nitrogen atmostphere. All reactions were carried out in oven-dried glassware. Commercially available compounds were used without further purification unless otherwise indicated. TLC analyses were performed on aluminium-backed F_{254} gel plates, using UV and a solution of 5% phosphomolybdic acid in ethanol for visualization. Flash chromatography was performed using silica gel 60 (40–63 μm). Proton ^1H and carbon ^{13}C NMR spectra were recorded on a 400 or 500 MHz instrument using the residual signals from $CHCl_3$ at δ7.26 and δ77.0 as internal references, respectively. ^{31}P NMR was recorded on a 500 MHz instrument using phosphoric acid as external reference. Optical rotations were determined using the sodium-D line (589 nm).

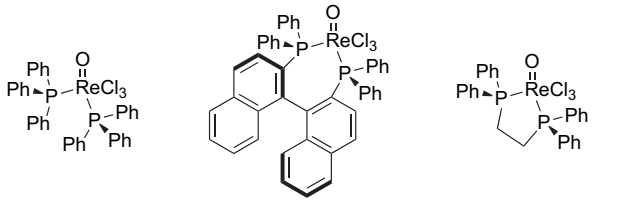


Fig. 1. Re (V) complexes with phosphine ligands.

2.2. Representative procedure for Re-catalyzed olefinations

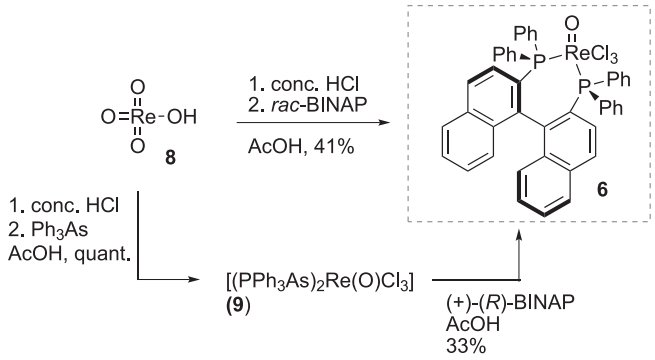
To a stirred solution of acrolein dimer **10** (54 μl, 0.53 mmol), triphenylphosphine (46 mg, 0.18 mmol) and (+)-$[(BINAP)Re(O)Cl_3]$ (**6**) (9 mg, 0.009 mmol) in refluxing CH_2Cl_2 (2 mL) was added ethyldiazoacetate (EDA) (22 μl, 0.21 mmol) dissolved in CH_2Cl_2 (1 mL) over 4 hours using a syringe pump, during which time the reaction slowly turned brown. The reaction was refluxed a further 20 minutes and then cooled to room temperature. The volatiles were removed under reduced pressure and the crude residues were purified by flash chromatography (eluting with 3.13–6.25% EtOAc/pentane) to give alkene **11** as a separable mixture of (*E*)- and (*Z*) isomers, as a clear oil (27.5 mg, 84%).

(2*E*)-Ethyl 3-(3,4-Dihydro-2*H*-pyran-2-yl)acrylate (**11**) [19]. IR (film) 2942 (m), 1720 (s), 1303 (m), 1180 (m), 1033 (m); ^1H NMR (500 MHz, $CDCl_3$) 6.94 (dd, $J = 15.7$, 4.3 Hz, 1H major isomer), 6.41 (td, $J = 6.6$, 1.9 Hz, 1H), 6.08 (dd, $J = 15.7$, 1.8, Hz, 1H), 4.77–4.70 (m, 1H), 4.55–4.49 (tdd, $J = 8.7$, 4.3, 2.3 Hz, 1H), 4.22 (q, $J = 7.1$ Hz, 2H), 2.17–2.06 (m, 1H), 2.05–1.95 (m, 2H), 1.77–1.66 (m, 1H), 1.31 (t, $J = 7.2$ Hz, 3H), ^{13}C NMR (125 MHz, $CDCl_3$), 166.8, 146.7, 143.7, 121.3, 101.1, 73.6, 60.9, 27.7, 19.5, 14.6; HPLC e.r. = 50:50, Chiracel OD-RH column, 60–25% MeCN/H_2O over 30 min., 0.5 mL/min; $t_{R1} = 14.38$ min, $t_{R2} = 14.90$ min; MS (ESI, $M + H^+$) = calcd' for $C_{10}H_{15}O_3$ 183.1, found 183.

(2*E*)-Ethyl 3-(1-Tosylpiperidin-2-yl)acrylate (**13**). IR (film) 2942 (m), 1720 (s), 1446 (m), 1263 (m), 1155 (s); ^1H NMR (500 MHz, $CDCl_3$) 7.72–7.66 (m, 2H), 7.32–7.27 (m, 2H), 6.77 (dd, $J = 15.8$, 5.3 Hz, 1H), 5.90 (dd, $J = 15.8$, 1.9 Hz, 1H major isomer), 4.79–4.29 (m, 1H), 4.19 (q, $J = 7.1$, 2H), 3.80–3.75 (d, $J = 13.4$ Hz, 1H), 3.06–2.96 (m, 1H), 2.43 (s, 3H), 1.80–1.68 (m, 2H), 1.64–1.40 (m, 4H) (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 145.3, 143.3, 137.4, 129.6, 127.2, 123.3, 60.5, 53.9, 41.8, 29.6, 24.7, 21.5, 19.3, 14.2; HPLC e.r. = 50:50, Chiracel, OD-J column, 3% *i*PrOH/Hexanes, 0.9 mL/min; $t_{R1} = 29.46$ min, $t_{R2} = 35.76$ min; MS (ESI, $M + H^+$) calcd' for $C_{17}H_{24}NO_4S$ 338.1, found 338.

rac-$[BINAP]Re(O)Cl_3$ (*rac*-**6**). Perrhenic acid (224 mg, 53% in H_2O, 0.537 mmol) was dissolved in HCl (200 μL, conc.), and the resulting solution was added dropwise to a stirred suspension of BINAP (318 mg, 0.426 mmol) in AcOH (6 mL). The resulting mixture immediately turned green and a dark green precipitate was formed. After 1 h, the reaction mixture was filtered and the filtrate washed repeatedly with Et_2O (3x) and cold CH_2Cl_2 (2x) to give **6**, as dark green microcrystals (205 mg, 41%): IR (KBr) 3054 (m), 2954 (m), 2856 (m), 1722 (m), 1434 (s); ^1H NMR (500 MHz, $CDCl_3$) 7.80–7.73 (m, 3H), 7.71–7.59 (m, 5H), 7.56–7.39 (m, 11H), 7.36 (ddd, $J = 8.2$, 6.8, 1.2 Hz, 1H), 7.30–7.18 (m, 4H), 7.09–7.03 (m, 1H), 6.90 (d, $J = 8.7$ Hz, 1H), 6.87–6.76 (m, 4H), 6.59 (dt, $J = 8.1$, 2.4 Hz, 2H); ^{31}P NMR (202 MHz, $CDCl_3$), −17.8, −21.0.

(+)-$[BINAP]Re(O)Cl_3$ (**6**) [20]. To a stirred solution of $[(AsPh_3)_2Re(O)Cl_3]$ (**9**) (590 mg, 0.643 mmol) in CH_2Cl_2 (5 mL) was added (+)-(*R*)-BINAP (405 mg, 0.650 mmol). The resulting bright green solution was stirred for 3 h after which it was concentrated to 0.5 mL. Addition of hexanes (7 mL) resulted in precipitation of **6**, which was collected by filtration. The solid was washed repeatedly



Scheme 2. One-pot synthesis of *rac*-**6** and preparation of (+)-**6**.

(5x) with Et_2O to give *rac*-**6** as a light green powder (200 mg, 33%), readily soluble in CH_2Cl_2, and indistinguishable from *rac*-**6** by NMR. $[\alpha]_D^{20} = +178.5$ ($c = 0.4$, CH_2Cl_2).

3. Results and discussion

3.1. Synthesis of Re-catalysts

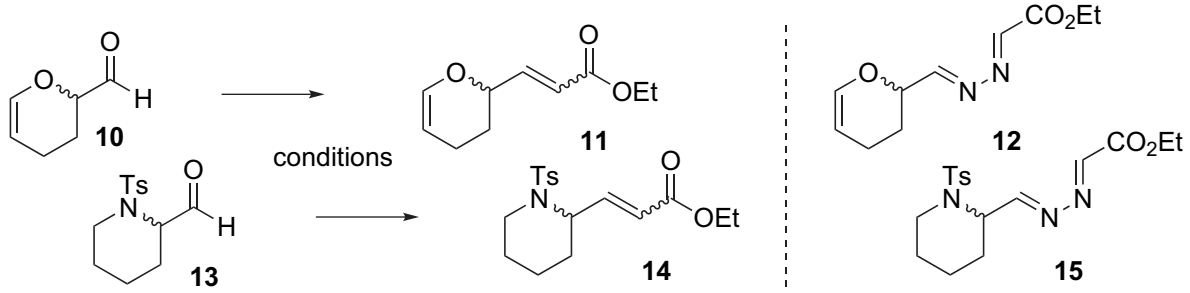
Previous syntheses of *rac*-**6** and similar compounds relied on ligand exchange of the toxic triaryl arsine ligands of $[(AsPh_3)_2Re(O)Cl_3]$ (**9**) [16]. To avoid the use of arsines we developed a convenient single pot preparation of *rac*-**6** that should be amenable to other complexes of this type as well (Scheme 2). Addition of a mixture of HCl and perrhenic acid (aq) to a suspension of *rac*-BINAP in glacial acetic acid gave *rac*-[(BINAP)Re(O)Cl_3] *rac*-(**6**) as dark green microcrystals. Filtration and washing with a small amount of cold CH_2Cl_2 gave *rac*-**6**, homogenous as judged by ^1H and ^{31}P NMR in moderate yield (41%).

The synthesis of enantiopure **6** is challenging due to its high solubility compared to the racemate. When formed from (+)-BINAP (**6**) is a non-crystalline light green amorphous powder that rapidly dissolves even in cold CH_2Cl_2 which precludes purification by repeated washing or recrystallization. Since our one-pot procedure gave slightly impure material we instead opted to prepare (+)-**6** using the two-step protocol via $[(AsPh_3)_2Re(O)Cl_3]$ (**9**) developed by Grubbs [20].

3.2. Optimization of the olefination reaction

With convenient access to both enantiopure (+)-**6** and the cheaper *rac*-**6** we turned to developing a protocol for their use in olefination of aldehydes (Table 1). As aldehyde substrates, we chose acrolein dimer **10** and sulfonamide aldehyde **13** [21]. Both of these are sterically congested, aliphatic aldehydes. Aliphatic substrates are challenging compared to electron poor aromatic aldehydes in metal catalyzed olefinations, due to their propensity to form azines, with reduced yields as a consequence. Aldehydes **10** and **13** also display a series of functional groups such as enolizable carbonyls, an electron-rich vinyl ether, and a sulfonamide functionality. These structural motifs are useful in further synthetic elaborations of the products, and also serve to probe the functional group tolerance of the reaction. Both aldehydes **10** and **13** carry a heteroatom substituted stereogenic center in the alpha position, a feature

Table 1
Optimization of the olefination of aldehydes **10**, and **13**.



Entry	Aldehyde (equiv.)	Catalyst (mol%)	Reducing agent	Solvent	Temp.	(*E*):(*Z*)[a]	e.r.[b]	Alkene (NMR yield %)[c,d]	Azine (NMR yield %)[c,d]
1	**10** (1.0)	**6** (1)	$P(OEt)_3$	THF	rt	–	–	<5%	–
2	**10** (1.0)	**4** (1)	PPh_3	CH_2Cl_2/THF (1:2)	rt	85:15	–	**11** (~20)[e]	–[f]
3	**10** (1.0)	**6** (1)	PPh_3	CH_2Cl_2/THF (1:2)	rt	83:17	–	**11** (13)	**12** (63)
4[g]	**10** (3.0)	**6** (1)	PPh_3	THF	rt	82:18	–	**11** (13)	**12** (40)
5[h]	**10** (3.0)	**6** (5)	PPh_3	CH_2Cl_2/THF (1:2)	rt	82:18	–	**11** (57)	**12** (41)
6[h]	**10** (3.0)	**6** (5)	PPh_3	THF	rt	82:18	–	**11** (39)	**12** (35)
7[h]	**10** (3.0)	**6** (5)	PPh_3	CH_2Cl_2	rt	75:25	–	**11** (51)	**12** (45)
8[h]	**10** (3.0)	**6** (5)	PPh_3	CH_2Cl_2	0 °C	67:33	–	**11** (15)	**12** (52)
9[h]	**10** (3.0)	(+)-**6** (5)	PPh_3	CH_2Cl_2	40 °C	82:18	50:50	**11** (100), 84[i]	**12** (<5)
10[h]	**10** (3.0)	(+)-**6** (5)	$P(OEt)_3$	CH_2Cl_2	40 °C	58:42	50:50	**11** (29)	–
11[h]	**13** (3.0)	(+)-**6** (5)	PPh_3	CH_2Cl_2	40 °C	98:2	50:50	**14** (100), 72[i]	**15** (<5)
12[h]	**13** (3.0)	(+)-**6** (5)	$P(OEt)_3$	CH_2Cl_2	40 °C	98:2	50:50	**14** (33)	–

General Conditions: To a stirred solution of aldehyde, reductant (1 equiv) and catalyst in the solvent indicated was added EDA dropwise at the temperature indicated.
[a] Determined by ^1H NMR of the crude reaction mixture.
[b] Determined by chiral HPLC.
[c] Based on the limiting component.
[d] Determined by ^1H NMR of the crude reaction mixture using 1-methoxynaphthalene added upon reaction completion as internal standard.
[e] Estimated from crude ^1H NMR.
[f] Not measured.
[g] EDA was added as a CH_2Cl_2 solution over 1 h.
[h] EDA was added as a CH_2Cl_2 solution over 4 h.
[i] Isolated yield.

designed to serve as a handle to facilitate enantiotopic discrimination when carrying out the reaction with an enantioenriched catalyst.

Initial experiments with **6** as catalyst and $(EtO)_3P$ as the stoichiometric reductant gave no detected product formation in the reaction with acrolein dimer **10** (entry 1, Table 1) [22]. One reason could be that complex **6** has a very low solubility in THF. Exchanging $(EtO)_3P$ for PPh_3 and using a mixture of THF and CH_2Cl_2 as the reaction medium, we obtained the desired alpha-beta unsaturated ester in fair yield, using either **4** or **6** as catalyst, along with substantial amounts of azine side-products (entries 2 and 3). This result prompted us to optimize the process aiming to increase the yield and suppress azine formation.

We found that slow addition of EDA over 4 h with 5 mol% catalyst in refluxing CH_2Cl_2 gave an essentially quantitative yield, determined by crude NMR using an internal standard as reference, and pushed the formation of azines below detectable levels. The geometric selectivity for reaction with **10** under these conditions was $(E):(Z) = 82:18$ (Table 1, entry 9). Under the same conditions, the reaction with amino-aldehyde **13** also gave complete conversion into the desired product with an excellent geometric selectivity $(E):(Z) = 98:2$ (Table 1, entry 11). In most reactions, an excess of aldehyde was used with applications in kinetic resolutions in mind [23]. The isolated yields of **11** and **14** (entries 9 and 11, Table 1) were somewhat diminished by difficult separation from excess starting material.

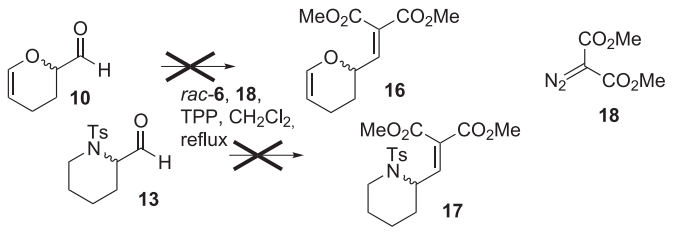
When re-attempting the reaction under the optimized conditions using triethyl phosphite instead of triphenylphosphine as reducing agent (entries 10 and 12), we were able to obtain the desired products **11** and **14** in fair yields albeit with considerably diminished geometric selectivity for **11**.

The catalytic performance in terms of yield using (+)-[(BINAP)Re(O)Cl_3] (**6**) paralleled that of [$(PPh_3)_2$Re(O)Cl_3] (**4**) with essentially quantitative yields under the optimized conditions (e.g. conditions used in entry 9). We note however that **4** is slightly more active, resulting in less azine formation, under suboptimal conditions (entries 2 and 3).

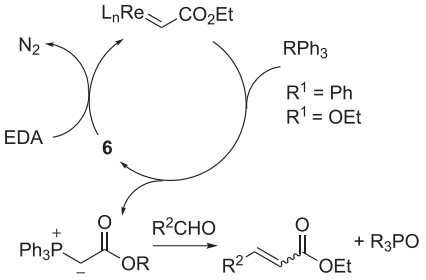
With an efficient olefination protocol at hand, we investigated the possibility of using this reaction in a kinetic resolution of racemic aldehydes **10** and **13** (entries 9–12). To this end, we were not able to achieve any discrimination between the enantiomers of either aldehyde, and all reactions using (+)-[(BINAP)Re(O)Cl_3] (**6**) as catalyst gave racemic products regardless of aldehyde or reductant. This result indicates that either the catalyst is not associated with the reaction center in the stereo-discriminating step, or that BINAP is replaced by achiral ligands on the metal center.

3.3. Mechanistic discussion

The mechanism of the olefination catalyzed by [$(PPh_3)_2$Re(O)Cl_3] (**4**) has not been discussed in detail previously. In the original paper by Herrmann, it was assumed to proceed through a manifold similar to that of the reaction catalyzed by MTO (**5**) through a metallaoxedane (Scheme 1), via replacement of one of the



Scheme 3. Unsuccessful olefination with **18** as the carbene precursor.



Scheme 4. Proposed pathway for the olefination of aldehydes catalyzed by **6**.

phosphine ligands. The lack of enantiodiscrimination in the reactions catalyzed by (+)-[(BINAP)Re(O)Cl_3] (**6**) suggested to us that the reaction proceeds through formation of an ylide, thus paralleling the mechanism proposed by Chen for [Re_2O_7(bipy)] catalysis (Scheme 4). To gain further insight, a set of control experiments were performed:

(i) A reaction in the absence of aldehyde resulted in formation of a phosphonium ylide, $Ph_3P{=}CHCO_2Et$, as detected by crude ^1H NMR and ESI-MS.
(ii) Refluxing a mixture of **6** with a 100-fold excess of PPh_3 in CD_2Cl_2 for 4 h did not give detectable amounts of **4** (^{31}P NMR).
(iii) A reaction in the absence of PPh_3 using stochiometric amounts of **6** or **4** gave no detected product formation.
(iv) Replicating the reactions in entries 9 and 11, Table 1, with regards to solvent, concentration and temperature but using Ph_3PCHCO_2Et instead of EDA/TPP gave, within limits of detection, similar levels of geometric selectivity compared to the metal catalyzed reactions.

It can be argued that trace amounts of **4**, formed by ligand exchange of BINAP with PPh_3, can be the active catalyst in the reaction. The combined observations that the catalytic performance of **4** and **6** is within an order of magnitude (vide infra), and the absence of significant formation of **4** upon prolonged heating of **6** with a 100-fold excess of PPh_3, however supports **6** as an active catalyst.

In addition, MTO (**5**) is known to olefinate aldehydes with dimethyldiazomalonate as the carbene precursor [9a]. Reaction of dimethyldiazomalonate (**18**) with **10** or **13** did not give any olefinated product with **6** as the catalyst (Scheme 3). This result is in agreement with what would be expected in a reaction that generates an ylide, as $(PPh_3){=}C(CO_2Me)_2$ is known to be unreactive towards aldehydes [9a].

Furthermore, the significant influence of the reductant ($P(OEt)_3$ or PPh_3) on the geometric selectivity in reactions with aldehyde **10** suggests that different reactive species (i.e., different ylides) are involved in the two reactions [24].

Together, the results of these experiments are consistent with a reaction proceeding through a metal catalyzed decomposition of EDA and insertion into the phosphine (or phosphite) to generate an ylide (Scheme 4). This is in contrast to the mechanism proposed for the MTO-catalyzed reaction, but is in line with observations for reactions catalyzed by many other metal complexes.

4. Conclusions

A convenient protocol for preparation of [(BINAP)Re(O)Cl_3] (**6**) was developed. This complex was found to be an efficient catalyst for metal catalyzed olefination of aldehydes and constitute the first example of a catalyst containing bis-phoshine ligands in this type of

transformation. Under optimized conditions, essentially quantitative conversion into product in reactions with electron-rich alpha substituted enolizable aliphatic aldehydes **10** and **13** was observed. The described procedure using refluxing CH_2Cl_2 as reaction medium with slow addition of EDA should be of value in similar reactions where azine formation is a problem. The efficient product formation in reactions with sensitive and reactive moieties such as electron-rich vinyl ethers and sulphonamides suggests a wide functional group tolerance. While the substrate scope was not exhaustively studied, based on the proposed mechanism, we expect the scope to parallel that of similar processes for less challenging substrates than **10** and **13**.

The mechanistic investigation does not support using the title reaction in kinetic resolutions of racemic aldehydes or desymmetrizations of prochiral dialdehydes. However, the possibility of using a chiral catalyst like (+)-[(BINAP)Re(O)Cl_3] (**6**) to deliver a carbene to phosphines suggests opportunities in kinetic resolutions of chiral (or prochiral) phosphines to form enantioenriched ylides for use in e.g. asymmetric olefination reactions.

Acknowledgement

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