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Diaminophosphine Oxide Ligand Enabled Asymmetric Nickel-Catalyzed Hydrocarbamoylations of Alkenes

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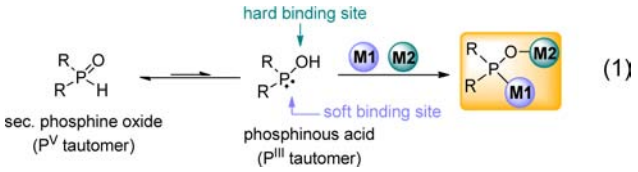
Supporting Information

ABSTRACT: Chiral trivalent phosphorus species are the dominant class of ligands and the key controlling element in asymmetric homogeneous transition-metal catalysis. Here, novel chiral diaminophosphine oxide ligands are described. The arising catalyst system with nickel(0) and trimethylaluminum efficiently activates formamide C−H bonds under mild conditions providing pyrrolidones via intramolecular hydrocarbamoylation in a highly enantioselective manner with as little as 0.25% mol catalyst loading. Mechanistically, the secondary phosphine oxides behave as bridging ligands for the nickel center and the Lewis acidic organoaluminum center to give a heterobimetallic catalyst with superior reactivity.

Chiral ligands are the key controlling element in asymmetric catalysis with transition metals. Trivalent phosphorus species are arguably the most dominant class of ligands for homogeneous transition-metal catalysis.[1] Whereas the vast majority belongs to the class of triaryl- or alkylphosphines, secondary phosphine oxides (SPOs) have only recently attracted more attention as air-stable and robust preligands for transition-metal catalysis.[2] This stability largely stems from its unique tautomerism between the pentavalent and the trivalent tautomer (eq 1).[3] By and large, the P^V form dominates. In the presence of

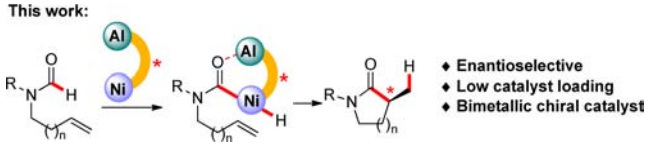


(1)

bases or transition metals, the equilibrium can be shifted toward to the trivalent phosphinous acid form.[4] Whereas its phosphorus atom coordinates well to late-transition metals (M1), the oxygen atom represents a good ligand for early transition metals (M2). The coordination of two different metals on the same secondary phosphineoxide for defined early/late heterobimetallic catalysis is largely unexplored.[5−7]

Despite the tremendous progress of carbon−hydrogen (C−H) bond functionalizations over the past decade,[8] intrinsic reactivity boundaries of substrates often prevent the desired transformation. For instance, formamide C−H bonds are largely less reactive toward transition-metal insertions[9] compared to aldehydes commonly used for hydroacylations.[10] Only two sets of conditions have been developed to effect hydrocarbamoylations with formamides. The first one, involves a ligand-free ruthenium−carbonyl complex and requires a CO atmosphere.[9a−c] Carreira demonstrated its utility for *endo*-cyclizations of allyl formamides to access α-unsubstituted pyrrolidinones.[9c] Alternatively, Nakao and Hiyama developed a nickel/Lewis acid-catalyzed process. With the exception of two examples, this method is largely limited to alkyne substrates[9c] and provides simple alkene linear products.[9d] With either catalyst system, asymmetric reactions are completely elusive. Furthermore, both processes suffer from low catalyst efficiencies and/or harsh reaction conditions. Driven by our interest in the asymmetric functionalization of C−H bonds,[11] we report a novel class of chiral diaminophosphineoxides ligands enabling asymmetric hydrocarbamoylations of homoallylic formamides by a heterobimetallic activation mode (Scheme 1).

Scheme 1. Asymmetric Hydrocarbamoylations Enabled by a Chiral Heterobimetallic Catalyst



Representing a complementary disconnection strategy for synthetically valuable chiral pyrrolidones and pyrrolidines,[12] we recognized the importance of an efficient enantioselective process. Working toward this goal, a large screen of a broad array of chiral phosphine ligands revealed their global failure for the hydrocarbamoylation of formamide **1a** (Table 1, entries 1−9). Solely methyl phospholane **L9** (entry 9 and 10) seemed to show promising results, although the reproducibility was strongly dependent on the batch of **L9**. We could trace this inconsistency to an impurity (5%) identified as the secondary phosphine oxide **SPO1**. Alone **SPO1** was poorly active, presumably due to kinetically disfavored coordination to the nickel (entry 11). The best reactivity was achieved in conjunction with an additional phosphine helping to displace cyclooctadiene from the nickel center, thus enabling the formation of the catalytically competent species.[13] With added PPh_3, which alone does not catalyze the reaction at all, a very robust catalytic system was found with a 1:1:1 ratio of $[Ni(COD)_2]$, **SPO**, and PPh_3. **SPO1** provided a promising selectivity of 86:14 er (entry 12).[14]

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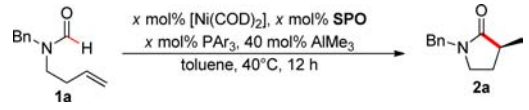
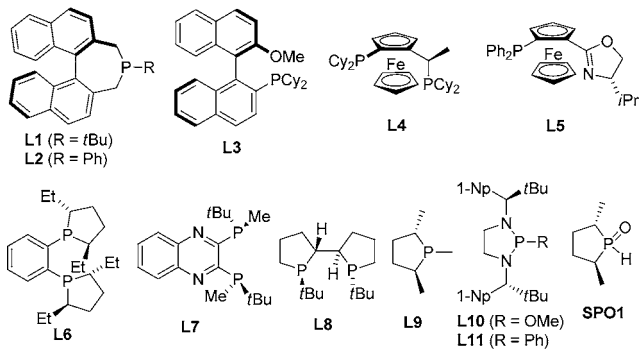
Table 1. Optimization of the Enantioselective Formamide C–H Functionalization[a]



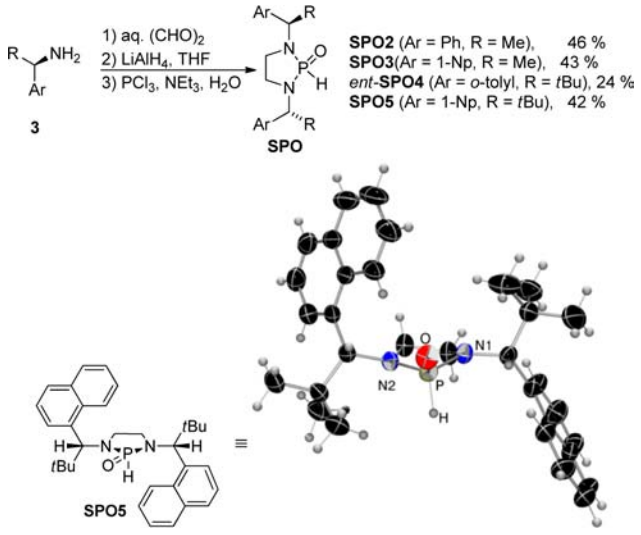
entry	x (mol %)	SPO	PAr_3	yield (%)[b]	er[c]
1	10	**L1** (2 *x*)	–	50	57:43
2	10	**L2** (2 *x*)	–	5	–
3	10	**L3** (2 *x*)	–	2	–
4	10	**L4** (2 *x*)	–	10	51:49
5	10	**L5** (2 *x*)	–	3	–
6	10	**L6** (2 *x*)	–	41	60:40
7	10	**L7** (2 *x*)	–	26	72:28
8	10	**L8** (2 *x*)	–	10	52:48
9	10	**L9** (2 *x*)	–	14	68:32
10	10	**SPO1**	**L9**	83	19:81
11	10	**SPO1**	–	18	61:39
12	10	**SPO1**	PPh_3	87	14:86
13	10	**SPO2**	PPh_3	40	62:38
14	10	**SPO3**	PPh_3	83	84:16
15	10	**SPO4**	PPh_3	82	40:60
16	10	**SPO5**	PPh_3	88	96.5:3.5
17	0.5	**SPO5**	PPh_3	90 (90)	96.5:3.5
18	0.25	**SPO5**	PPh_3	61	96.5:3.5
19	1	**L10**	PPh_3	19	96:4
20	5	**L11**	PPh_3	0	–
21[d]	10	**SPO5**	PPh_3	0	–

[a]Conditions: 0.10 mmol **1a**, *x* mol % catalyst (**L**/PAr_3/[$Ni(COD)_2$] = 1:1:1), 40 mol % $AlMe_3$, 0.25 m in toluene at 40 °C for 24 h. [b]NMR yields (isolated yields). [c]Determined by HPLC with a chiral stationary phase. [d]with 40 mol % of BPh_3 instead of $AlMe_3$.



However, the phospholane scaffold is not very user-friendly in terms of simple and modular ligand modifications. In contrast, heteroatom-substituted secondary phosphine oxides are easily accessible and offer this synthetic advantage.[15] Surprisingly, with the exception of reports from Hamada,[16] diaminophosphine oxides have been largely neglected for asymmetric catalysis. Our herein envisioned ligands class is readily prepared from the corresponding widely used chiral alkylbenzylamine precursors **3** (Scheme 2).[17] To the ethylenediamines **4**, PCl_3 is added, and after cyclization proceeded, the remaining P–Cl bond is hydrolyzed giving directly the air and moisture stable ligands **SPO2-SPO5**. The salient structural features of this new ligand class can be visualized by the X-ray crystal structure of **SPO5**.[18] In contrast to **SPO1**, the chirality is shifted outside of the cycle. The large 1-naphthyl and *t*-butyl substituents arrange in a pseudo C_2-symmetric fashion. In analogy to the Kündig carbenes built from the same diimino intermediates,[19] this arrangement minimizes

Scheme 2. Synthesis and X-Ray Crystal Structure of Diaminophosphine Oxide SPO5



severe *syn*-pentane strain and thus fixing conformation and efficiently shielding two quadrants.

To our delight, the diaminophosphine oxide **SPO2-SPO5** is well stable to $AlMe_3$, and bulky **SPO5** turned out to be a particularly reactive and selective catalyst, yielding **2a** in 88% and 96.5:3.5 er (entry 16).[20] Most notably, the catalyst loading could be reduced to 0.5 mol % without affecting the reaction outcome at all (entry 17).[21] Even at 0.25 mol % loading **2a** is obtained, though no full conversion and some double-bond isomerization proceeds (entry 18). To explore the impact of the hetero-bimetallic assembly of the catalyst for the reactivity, structurally similar trivalent P-ligand **L10** which is not able to form a covalent adduct with the aluminum Lewis acid was tested.[22] Compared to **SPO5**, it exhibits even at double catalyst loading a drastically reduced activity, albeit comparable enantioselectivity (entry 19). Ligand **L11**, not able to coordinate at all to $AlMe_3$, did not give even trace amounts of product (entry 20). Additionally, BPh_3, a Lewis acid which is unable to form a bridging complex with the SPO failed as well completely (entry 21).

With the optimized reaction conditions in hand, the scope of the activation/cyclization was evaluated (Table 2). As expected, deuterated formamide **2b** led to a complete deuterium transfer to the terminal carbon atom of substrate **1b**. The selectivity of the reaction is largely independent of the substitution of the nitrogen atom, allowing for alkyl, aryl, and benzyl groups as well as esters. *Bis*-allylated formamides are competent substrates giving lactams **2h–2n** in high yields and enantioselectivities. The observed diastereoselectivity ranges from 4:1 to >20:1, evidencing a good enantiotopic allyl group selection. Such bicyclic pyrrolidone framework is a ubiquitous structural feature in important pyrrolizidine and indolizidine alkaloids.[12] Besides cyclization to γ-lactams,[23] the reaction concept is suitable for larger ring sizes (**2o**), though competing *endo*-cyclization to **4** becomes a side reaction.

The described reaction can be used as well to override intrinsic substrate control of a preexisting stereogenic center (Scheme 3). Exposing enantiopure formamide (*S*)-**1p** to the reaction conditions with Cy_2POH as prototypical achiral ligand, lactam **2p** is formed in moderate yield and 4:1 diastereomeric ratio in favor of the *cis*-isomer *cis*-**2p**. Whereas *cis*-**2p** was produced in high diastereoselectivity (16:1) using (*R*)-**SPO5** in the matched

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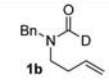
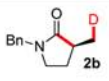
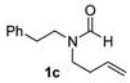
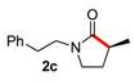
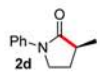
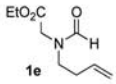
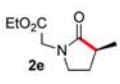
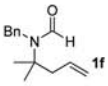
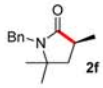
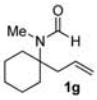
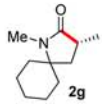
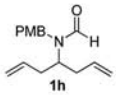
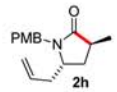
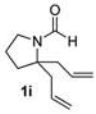
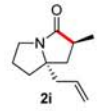
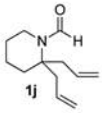
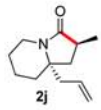
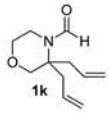
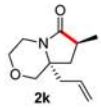
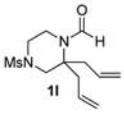
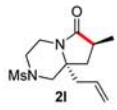
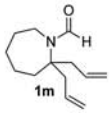
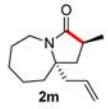
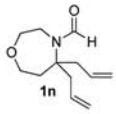
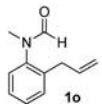
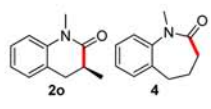
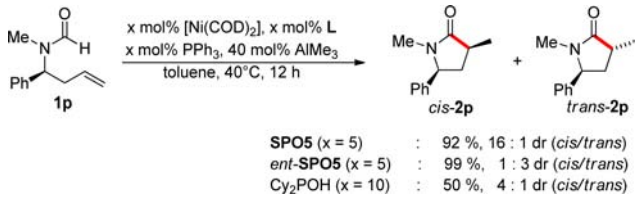
Table 2. Substrate Scope of the Enantioselective Hydrocarbamoylation[a]

entry	substrate **1**	product **2**	yield[b]	er[c]
1	 **1b**	 **2b**	89 % >95 % D	94:6
2	 **1c**	 **2c**	79 %	97:3
3	 **1d**	 **2d**	91 %	96.5:3.5
4	 **1e**	 **2e**	75 %	96:4
5	 **1f**	 **2f**	95 %	89.5:10.5
6[d]	 **1g**	 **2g**	82 %	92:8
7[e]	 **1h**	 **2h**	81 % 5:1 dr	97.5:2.5
8[e]	 **1i**	 **2i**	98 % 4:1 dr	94.5:5.5
9[e]	 **1j**	 **2j**	83 % >20:1 dr	94:6
10[e,f]	 **1k**	 **2k**	90 % 9:1 dr	96:4
11[e]	 **1l**	 **2l**	94 % 5:1 dr	96:4
12[e]	 **1m**	 **2m**	77 % >20:1 dr	93:7
13[e]	 **1n**	 **2n**	81 % >20:1 dr	96:4
14	 **1o**	 **2o** **4**	46 % 40 % **4**	94:6

[a]0.10 mmol **1**, 5 mol % $[Ni(COD)_2]$, 5 mol % **SPO5**, 5 mol % PPh_3, 40.0 μmol $AlMe_3$, 0.25 m in toluene at 40 °C for 12 h. [b]Isolated yields. [c]Determined by HPLC with a chiral stationary phase.[19] [d]With 10 mol % **SPO1**, 10 mol % $[Ni(COD)_2]$, 10 mol % PPh_3. [e]At 60 °C. [f]0.5 mmol scale with 1 mol % catalyst loading.

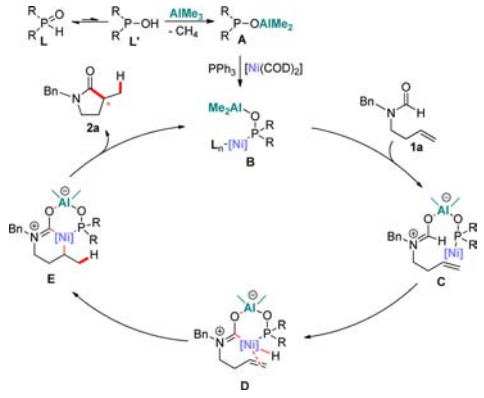
chirality scenario, *trans*-**2p** could be selectively obtained in a moderate inverse dr of 3:1 with (*S*)-**SPO5**.

Scheme 3. Matched/Mismatched Stereocontrol of Chiral Substrate 1p



Taking the unique reactivity of secondary phosphine oxides for this type of transformation into account, the following mechanism is suggested: The secondary phosphine oxide **L** tautomerizes to its phosphinous acid form **L′** (Scheme 4). The

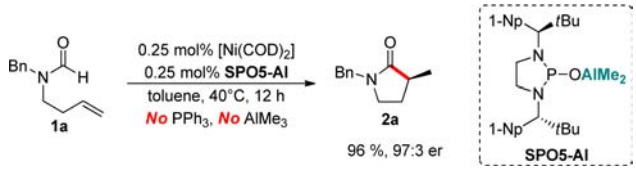
Scheme 4. Mechanistic Proposal of the Bimetallic Activation with SPO Ligands



acidic hydroxyl group of **L′** reacts with $AlMe_3$ liberating methane and gives adduct **A**,[24] while retaining the Lewis acidic character of the aluminum center. $[Ni(COD)_2]$ coordinates to the phosphorus atom to deliver **B**. The Lewis acidic aluminum center activates the carbonyl group of **1a** giving **C**. Subsequently, the nickel center could oxidatively insert into the now activated C−H bond in a favorable intramolecular fashion forming the six-membered bimetallic heterocycle **D**. Migratory insertion leads to metallocycle **E**, which in turn reductively eliminates releasing lactam **2a** and regenerates the bimetallic catalyst **B**.

To support our hypothesis of the linked bimetallic species, we independently prepared putative intermediate **SPO5-Al** by stoichiometric deprotonation with butyllithium, followed by salt metathesis with $ClAlMe_2$. Though **SPO5-Al** THF adduct is sensitive and only moderately stable, it is able to catalyze the process with slightly superior results (96% yield and 97:3 er) at 0.25 mol % catalyst loading without any added additional $AlMe_3$ and PPh_3 (Scheme 5). These findings clearly indicate that neither free $AlMe_3$ nor PPh_3 are active participants in the catalytic cycle. Their requirements in the instant protocol point toward their importance in entering the catalytic cycle.

Scheme 5. Catalytic Performance of the Preformed Lewis Acid/Ligand SPO5-Al



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In conclusion, we report a new class of air and moisture stable and readily accessible chiral bulky diaminophosphine oxide preligands. We demonstrate their potential for asymmetric early/late heterobimetallic catalysis with nickel(0)/Lewis acid catalyzed C−H activations of formamides providing a complementary access to chiral γ-lactams. The diaminophosphineoxide ligand is believed to simultaneously bond to the nickel center and the aluminum Lewis acid resulting in superior reactivity and performance.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Procedures and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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