From transition metals to organocatalysis*

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Several classes of transition metal-catalyzed reactions and the gradual transition to organocatalysis are summarized as the authors' personal account. This includes a brief overview of novel nonsymmetrically substituted 1,1′-binaphthyls and their application in Pd-catalyzed reactions and as chiral phase-transfer catalysts, and new chiral complexes of 2,2′-bipyridine-type ligands with Mo, Cu, and Pd and their catalytic applications. The attention is focused on chiral pyridine-type *N*-oxides as novel Lewis-basic organocatalysts applied in allylation of aromatic aldehydes with allyltrichlorosilane.

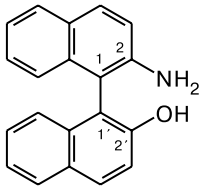
Key words: 1,1′-binaphthyls, chiral complexes, phase transfer catalysis.

This is a personal, noncomprehensive account, which reflects our 15-year affair with asymmetric catalysis.[1] The main purpose is to show the development of various ideas in the historical perspective and to illustrate the diversity and links between transition metal catalysts and organocatalysis, as reflected in the activities of our group.

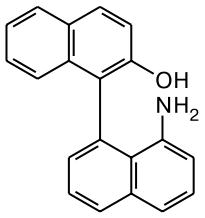
2,2′-Disubstituted 1,1-binaphthyls

For about 15 years we have been interested in binaphthyl chemistry and have developed[2] a series of 1,1′-binaphthyls with different groups in positions 2 and 2′, *i.e.*, C_1-symmetrical molecules (as opposed to the more common C_2-symmetrical binaphthyls such as BINOL or BINAP). Thus we have reported new derivatives, such as NOBIN (**1**),[3] *iso*-NOBIN (**2**),[4] SOBIN (**3**),[5] MAP (**4**),[6] and others.

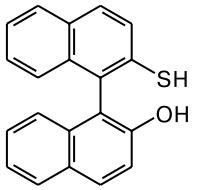
These molecules have found various applications in asymmetric catalysis. For instance, NOBIN (**1**) and its derivatives have been employed as ligands in the Et_2Zn addition to aromatic aldehydes,[7] and NOBIN (**1**), *iso*-NOBIN (**2**), and its amides have been used (by us in collaboration with Yu. N. Belokon′) as powerful chiral phase transfer catalysts for the alkylation of glycine-derived imines *via* Michael addition.[4,8,9] Several investigators used NOBIN (**1**) as a scaffold in the development of novel catalysts, *e.g.* Carreira for the Ti-catalyzed Mukaiyama-aldol reaction,[10] Zhang for Ru-catalyzed cyclopropanation,[11] Brunner in the Ru-catalyzed Meerwein—Ponndorf—Verley reduction of acetophenone,[12] Ding for the Ti-catalyzed Diels—Alder addition,[13] and Hoveyda in the Ru-catalyzed ring-closure metathesis.[14,15] Both enantiomeric forms of NOBIN are now commercially available.** Applications of SOBIN (**3**) for Ga-catalyzed hydroboration of ketones have been reported by Woodward.[16] We have shown (in collaboration with Lloyd-Jones) that MAP (**4**) exhibits a substantial memory effect in the asymmetric Pd-catalyzed allylic substitution[17] and is a very effective ligand in the Pd-catalyzed Hartwig—Buchwald coupling[6,17a,18] and the Suzuki—Miyaura coupling,[17a] in particular, in its asym-



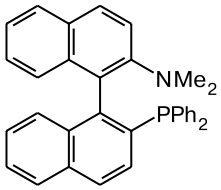
1 (NOBIN)



2 (*iso*-NOBIN)



3 (SOBIN)



4 (MAP)

* Dedicated to Prof. Belokon′ in appreciation of his achivements in asymmetric catalysis.

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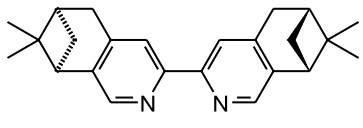
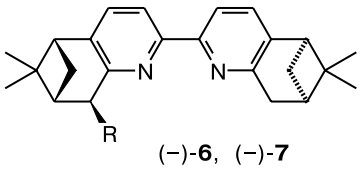
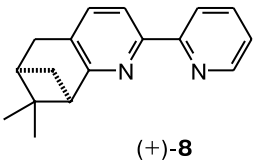


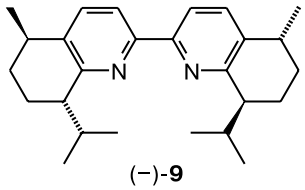
(−)-**5**



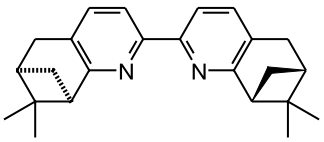
(−)-**6**, (−)-**7**



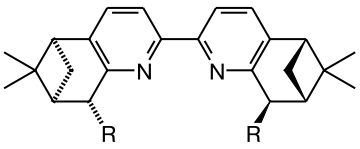
(+)-**8**



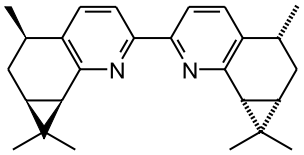
(−)-**9**



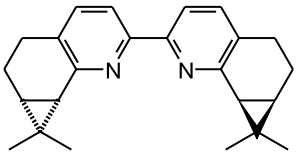
(+)-**10** (PINDY)



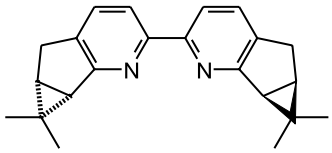
(−)-**11**, (−)-**12**, (−)-**13**, (−)-**14**
(*iso*-PINDY)



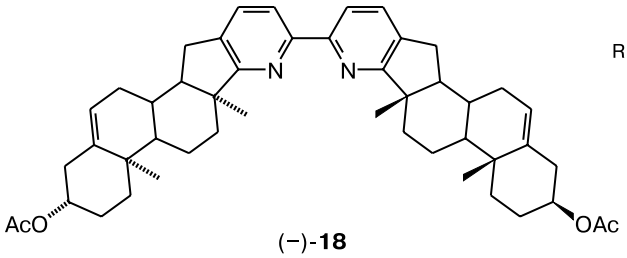
(−)-**15**



(−)-**16** (CANDY)



(+)-**17**



(−)-**18**

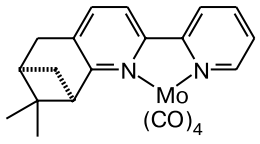
R = H (**6**, **11**), Me (**7**, **12**)
Bu (**13**), Pr^i (**14**)

metric version.[19] A series of papers reported MAP and its congeners as particularly effective ligands for the formation of C—N, C—O, and C—S bonds at the sp^2 carbon center.[2,20] A MAP-derived picolinic amide has been utilized by Zhang as a successful ligand in Cu-catalyzed 1,4-addition.[21]

2,2′-Bipyridine ligands

More recently, we became interested in the chemistry of chiral 2,2′-bipyridines, first of all, in their application as chiral ligands in metal-catalyzed asymmetric reactions.[22—25] A series of bipyridines were synthesized from various isoprenoids (α-pinene, β-pinene, 2-carene, 3-carene, menthol, pregnenolone, *etc.*) by annelation of the pyridine ring to the existing terpene or steroid skeleton. Those compounds that proved useful in catalysis were given acronyms (PINDY, *iso*-PINDY, CANDY, *etc.*).

Molybdenum complexes **19—22** were prepared from sterically less hindered ligands **5—8** and characterized by X-ray diffraction analysis. By contrast, more hindered ligands such as PINDY (**10**) did not give stable Mo complexes. However, Cu, Ni, and Pd complexes (**23—25**) were readily obtained even with this ligand (**10**). As shown by X-ray diffraction analysis, this became possible due to the distortion of their typical square-planar geometry, which removed the chlorides from clashing with the proxi-



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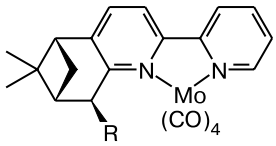
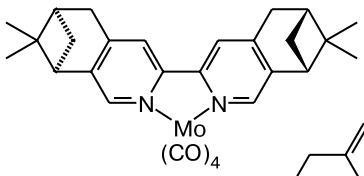
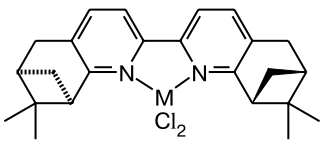


20: R = H
21: R = Me



22



23—25

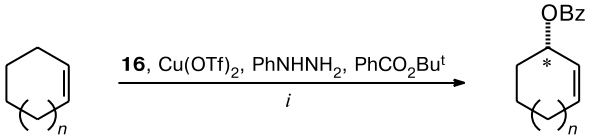
M = Cu (**23**), Ni (**24**), Pd (**25**)

mate CH groups.[22] Similar complexes have been reported by von Zelewsky.[26]

The Mo and Pd complexes exhibited low enantioselectivity as catalysts of the allylic substitution (≤22 and 26% *ee*, respectively).[22] More promising results were obtained in the cyclopropanation catalyzed by Cu complexes with ligand **12** (≤76% *ee*) and its congeners.[22,23]

The distortion of the square-planar geometry at Cu by ~60° in the Cu—PINDY complex (**23**) results in a stereochemistry more typical of Cu^{I} complexes. Therefore, we reasoned that this complex may exhibit interesting redox properties. Indeed, we were able to show that allylic oxidation (Scheme 1) catalyzed by complex **23** and related complexes proceeded much faster than that for copper complexes with bisoxazoline and other ligands, affording up to 82% *ee* with CANDY (**16**) as the ligand.[23]

Scheme 1

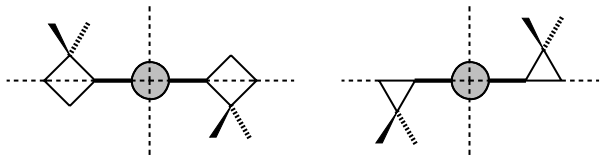


26 (*S*)-(−)-**27** (≤82% *ee*)

n = 0—2

i. Me_2CO, ~20 °C, 30 min or 0 °C, 2—5 h.

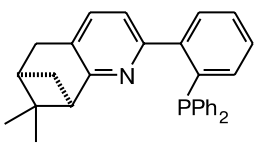
The enhanced enantioselectivity attained with CANDY (**16**) as compared to PINDY (**10**) has been rationalized by the improved contrast in the steric congestion in the individual octants (compare **A** for PINDY and **B** for CANDY).



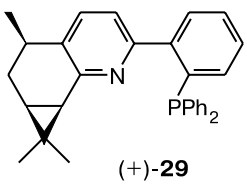
A (**10**) **B** (**16**)

Pyridine-phosphine ligands

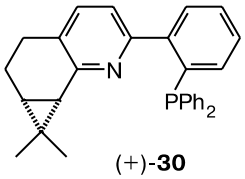
In order to extend the realm of pyridine-based ligands, we have also prepared pyridine-phosphines **28—31** as representatives of heterobidentate *P,N*-ligands.



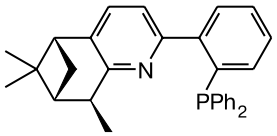
(+)-**28**



(+)-**29**



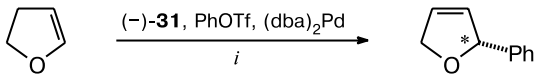
(+)-**30**



(−)-**31**

These ligands provide efficient catalysis of the asymmetric Heck reaction (≤88% *ee* with **31**)[24] (Scheme 2) and allylic substitution (≤85% *ee* with **30**).[27] *

Scheme 2



(*R*), ≤88% *ee*

i. Pr^{i}_2NEt, THF, 60 °C, 48 h.

Pyridine *N*-oxides

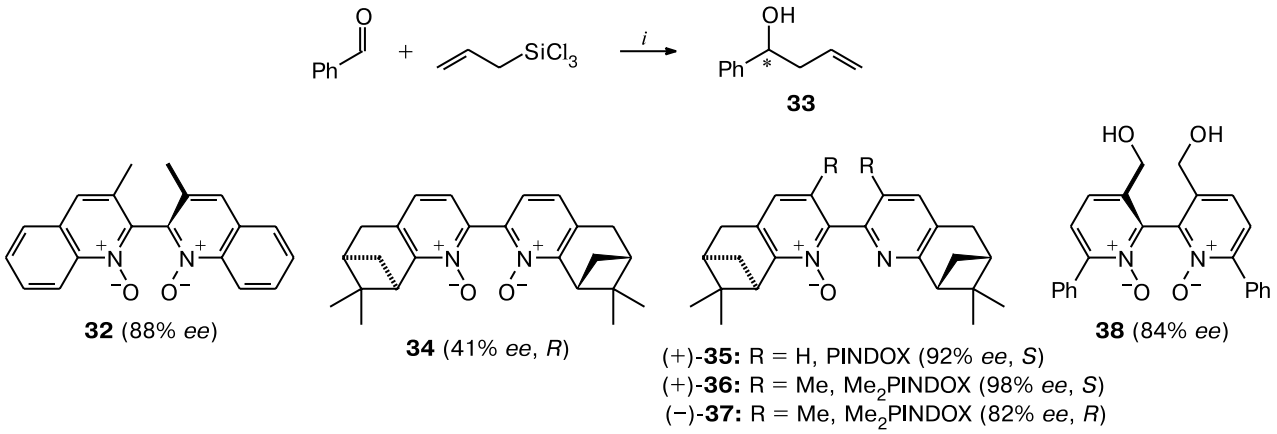
The oxygen atom of pyridine *N*-oxides posseses Lewis basicity and, hence, it should potentially be capable of activating nucleophilic reagents having a Lewis acidic moiety. Thus the C_2-symmetrical bipyridine-type *N,N*-bisoxide **32** has been shown to catalyze allylation of benzaldehyde and other aromatic aldehydes with allyltrichlorosilane to give the corresponding homoallylic alcohols **33** in 88% *ee* (Scheme 3).[28] The analogous PINDY-derived *N,N*-bisoxide **34** provided only 41% *ee*, whereas the corresponding *N*-monoxide **35**, which we prepared by controlled oxidation of compound **10** with 1 equivalent of MCPBA at 0 °C, produced the opposite enantiomer in 92% *ee*.[29] Further enhancement (to 98% *ee*) was attained by using the dimethyl analog **36** with the R_a-configured chiral axis; the (S_a)-atropoisomer (−)-**37** furnished the opposite enantiomer of **33** with a slightly reduced enantiocontrol (82% *ee*), demonstrating that the chiral 2,2′-axis plays the decisive role in this asymmetric induction.[29] Subsequently, Hayashi reported that *N,N*-bisoxide **38** is also an effective catalyst for the allylation of aromatic aldehydes (84% *ee* in the case of benzaldehyde).[30]

Although Me_2PINDOX (+)-**36** proved to be the most efficient catalyst (see above), its further development was held up by the difficulties associated with its synthesis, which were not encountered in the synthesis of PINDOX (**35**). Therefore, we prepared the isomeric catalysts *iso*-PINDOX (**39** and **40**) and showed them to perform with the same efficiency as **36** (97% *ee*).[29b]

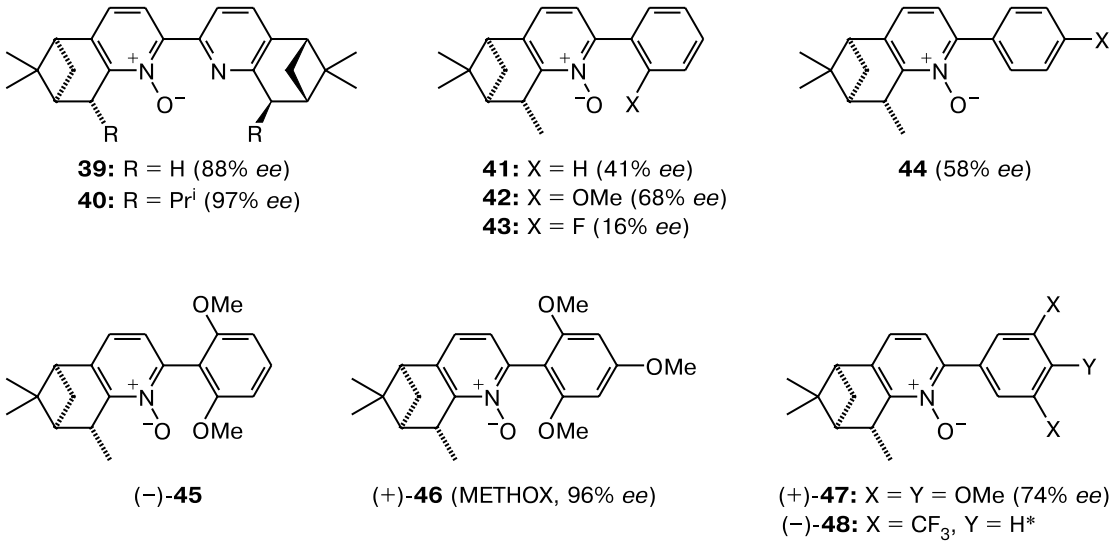
The *N,N*′-bisoxides **32**, **34**, and **38** are believed to chelate the silicon atom of the reagent to give a seven-

* A. V. Malkov, M. Bell, F. Castelluzzo, and P. Kočovský, unpublished results.

Scheme 3



i. Catalyst, CH_2Cl_2, −78 °C.



* The reaction does not proceed.

membered ring.[28,30] We have proposed an analogous *O,N*-chelation in the case of bipyridine-type *N*-monoxides **35—37**, **39**, and **40** to give a six-membered ring.[29] However, the phenyl derivative **41** proved also to induce appreciable enantioselectivity (41% *ee*); its 2-methoxy derivative **42** exhibited a much higher asymmetric induction (68% *ee*), whereas the corresponding 2-fluoro derivative **43** gave an almost racemic product (16% *ee*).[31] Since the 4-methoxy isomer **44** afforded 58% *ee* in the allylation reaction, the chelation of silicon by the N—O and OMe groups can be excluded as the major effect in the case of **42**.* On the other hand, comparison of the catalysts **41—44** suggests that electronic effects may play an important role. Therefore, electron-rich di- and tri-methoxy analogs **45** and **46** were synthesized and shown to exhibit much higher enantioselection (80 and 96% *ee*, respectively).* The enhanced enantioselectivity in the case of the 3,4,5-isomer **47** (74%) indicates that the chelation, if any, is rather unimportant. On the other hand, the electron-deficient derivative **48** proved inert, which clearly demonstrates the key role of the electronic factors.* Therefore, arene—arene interactions between the catalyst and the incoming aldehyde can be considered.

The arene—arene interactions are of two kinds, namely, edge-to-face and face-to-face interactions (Fig. 1). The former are known to be most pronounced for electron-rich π-donor systems and practically independent of the electronic effects of the "edge" compo-

* A. V. Malkov, M. Bell, F. Castelluzzo, and P. Kočovský, unpublished results.

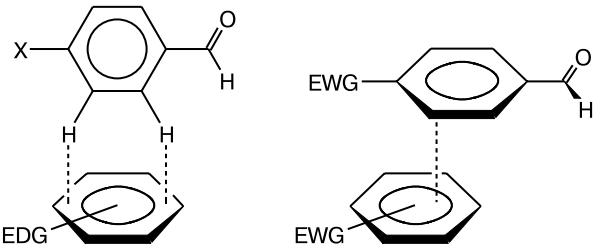
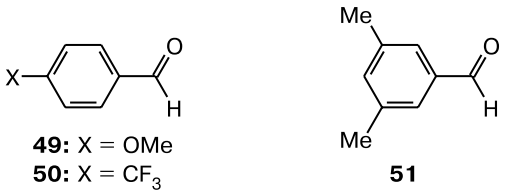
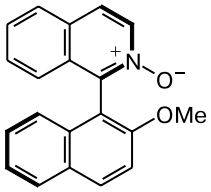


Fig. 1. Arene—arene interactions. EDG is the electron-donating group, EWG is the electron-withdrawing group.

nent, while the latter type of interaction is typical of two electron-deficient partners.[32] *

The reactivity of benzaldehyde and its electron-rich and electron-deficient congeners **49** and **50** in the presence of METHOX (**46**) as the catalyst showed very little dependence of the enantioselectivity and/or the reaction rate on the electronic properties of the *para*-substituents (96% *ee* for **49** and 93% *ee* for **50**), suggesting the edge-to-face (rather than face-to-face) arene—arene interaction. This hypothesis is further supported by the lack of reactivity of 3,5-dimethylbenzaldehyde (**51**) whose edge face is blocked.**





(*R*)-(+)-**52** (QUINOX)

By contrast, the reactivity and enantioselectivity of allylation in the presence of QUINOX (**52**) were shown to be crucially dependent on the electronic properties of the aldehyde, giving 87% *ee* with benzaldehyde, 12% *ee* with **49**, and 96% *ee* with **50**.[33] Furthermore, unlike METHOX (**46**), QUINOX (**52**) did catalyze the allylation of aldehyde **51**, which rules out the edge-to-face mechanism. Hence, in the case of QUINOX (**52**), face-to-face arene—arene interaction can be suggested.*

* * *

For 15 years (1989—2004), we have been interested in a number of areas of catalytic asymmetric chemistry and have developed series of both transition metal catalysts with chiral ligands and metal-free organocatalysis. The metal-catalyzed reactions include the addition of diethylzinc to aldehydes, allylic substitution (Pd and Mo), the Heck reaction (Pd), cyclopropanation (Cu), and allylic oxidation (Cu). The organocatalytic reactions include the asymmetric alkylation of enolates and allylation of aromatic and heteroaromatic aldehydes with allyltrichlorosilane. Further extension of the latter approach, such as asymmetric imine reduction (using a different Lewis-basic catalyst)[34] is on the way. We believe that our mechanistic and structural studies have contributed to the wealth of knowledge of the fascinating behavior of transition metal-based catalysis and organocatalysts.

We are particularly indebted to our external collaborators, Prof. Y. N. Belokon´ (Moscow), Prof. Guy Lloyd-Jones (Bristol),[35] Dr. Vratislav Langer (Göteborg), and Dr. Ivana Císařová (Prague), to our coworkers and students,** and to Dr. Alfred Bader.

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* In solutions, strong π—π-interactions typically occur between electron-deficient partners (for example, aromatic molecules with electron-withdrawing groups) or between molecules with very different polarity (donor/acceptor).[32a,b] Chloroform has been shown[32c,d] to be the solvent of choice to promote the arene—arene interactions.

** A. V. Malkov, M. Bell, F. Castelluzzo, and P. Kočovský, unpublished results.

* A. V. Malkov, M. Bell, F. Castelluzzo, and P. Kočovský, unpublished results.

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