Enantioselective Nitrogen Transfer to Sulfides from Nitridomanganese(V) Complexes

by **Craig S. Tomooka**[1]) and **Erick M. Carreira***

Laboratorium für Organische Chemie, ETH-Hönggerberg, CH-8093 Zürich

Dedicated to Professor *Dieter Seebach* on the occasion of his 65th birthday

We describe the facile preparation of novel, optically active nitridomanganese(V) complexes which serve as reagents for the electrophilic amination of sulfides. This amination method has several appealing features, including: *i*) the facile preparation of large quantities of the starting nitridomanganese reagent **3**, *ii*) the preparation of acylsulfilimines **2** in optically active form, and *iii*) the mild reaction conditions employed.

Introduction. – The discovery, study, and development of methods for the functionalization of substrates through the use of electrophilic N-transfer reagents is an important area of investigation in modern synthetic chemistry. A number of key features of research in this area are particularly exciting and timely: not only is understanding of the fundamental structure/reactivity requirements of reagents and catalysts that lead to successful N-transfer reagents and processes lacking, but also the development of practical preparative methods would find wide use and application in academic and industrial settings. The latter can be appreciated when one considers the paucity of preparatively useful processes for N-transfer when compared to the corresponding epoxidation reactions for which a myriad of reagents and catalysts are available. It is not surprising that, while much is known concerning O-atom transfer, by contrast, relatively little is known about the corresponding transformations involving N-atom transfer [1]. We have recently reported N-atom-transfer processes involving the use of manganese nitride reagents that are activated *in situ* to afford aziridines [2][3]. These reagents have also been the subject of investigation by *Komatsu* and co-workers on the aziridination of alkenes as well [4]. In the context of our studies aimed at developing and studying N-atom-transfer reactions that lead to amination reactions of wide scope, we have embarked on a program focused on the preparation of optically active sulfilimines from sulfides by means of manganese nitride reagents. Herein, we document our preliminary observations in this area in which optically active nitridomanganese complexes **3** undergo activation and N-transfer to sulfides **1** to afford optically active sulfilimines **2** (*Scheme 1*).

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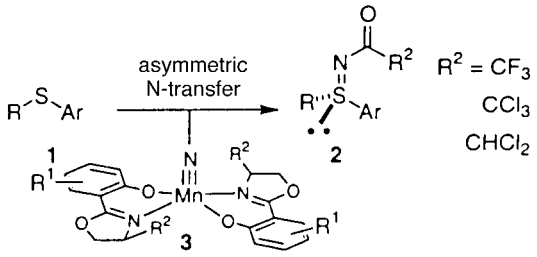
[1]) Part of the Ph.D. thesis of *C. S. T.*, California Institute of Technology, Pasadena, CA, USA.

Scheme 1



Chiral sulfilimines constitute an interesting class of compounds whose reactivity is largely untapped and have been used only sparingly[2][3][4][5][6]. Therefore, we decided to examine sulfides as potential substrates for N-atom transfer by chiral manganese nitride reagents. In this respect, we have documented novel methods that permit the synthesis of chiral nonracemic nitridomanganese complexes incorporating a variety of ligands. We thus embarked on an investigation involving such optically active complexes as sources of electrophilic N-atoms with which to convert sulfides to optically active *N*-acylsulfilimines. We speculated that the mechanistic aspects of such a transformation would likely be simpler when compared to the process involving olefins. Thus, the development of such a process could lead to a system that permits careful mechanistic studies of the atom-transfer step from the metal nitrides.

Results and Discussion. – Our investigations commenced with methyl *p*-tolyl sulfide (**4**) as a representative substrate with which we planned to identify optimal conditions for the atom-transfer reaction [10]. Initially we chose to carry out the reaction under conditions that we had developed in the context of alkene aziridination. Thus, treatment of a precooled solution of sulfide ($-78°$) in CH_2Cl_2 and nitrido complex **6** with trifluoroacetic anhydride ($(CF_3CO)_2O$; 5.0 equiv.) led to consumption of the starting material upon warming to 23° over *ca.* 4 h. The corresponding sulfilimine **5** was isolated in 68% yield and 72% enantiomeric excess (ee; *Scheme 2*). In an effort to follow up on this leading result, we subsequently decided to examine the use of *p*-toluenesulfonic anhydride (Ts_2O), as work by *Komatsu* and co-workers had demonstrated that this anhydride could function effectively as an activating group towards manganese nitride for enantioselective aziridination of styrene and related alkenes (*e.g.*, **7** + **8** → **9**; *Scheme 3*) [4].

The reaction was readily conducted as before except for the use of Ts_2O (*Scheme 4*). Following workup of the reaction mixture, we isolated not sulfilimine **10** but the corresponding sulfoxide **11**. We speculate that, although the *N*-tosylsulfilimine

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[2] For the preparation and physical and chemical properties of sulfilimines, see [5].

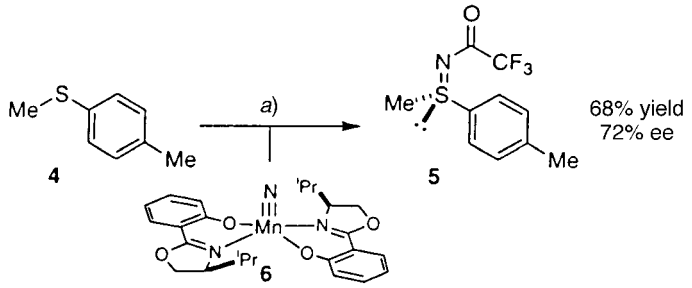
[3] *N*-Unsubstituted arylsulfilimines have been shown to react with acylating agents and activated halobenzenes, alkynes, and alkenes, see [6].

[4] *N*-Acylsulfilimines have been shown to react with ketenes to form dihydrooxazolones, see [7].

[5] Sulfilimines have been shown to react with chromium (*Fischer*) carbenes to form imidates, see [8].

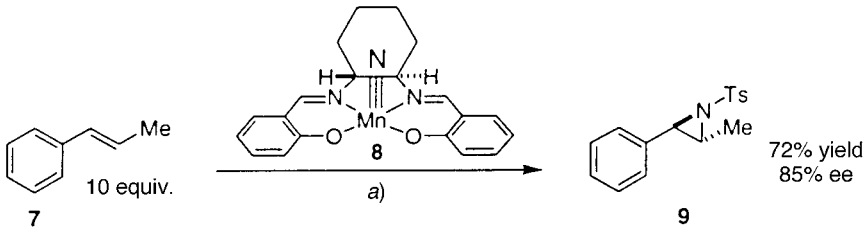
[6] Optically active 2-acylaziridines have been synthesized in one step by treating optically active sulfilimines with α,β-unsaturated ketones, see [9].

Scheme 2



a) MnN **6** (1.0 equiv.), $(CF_3CO)_2O$ (5.0 equiv.), CH_2Cl_2, −78 to 23° over *ca.* 4 h.

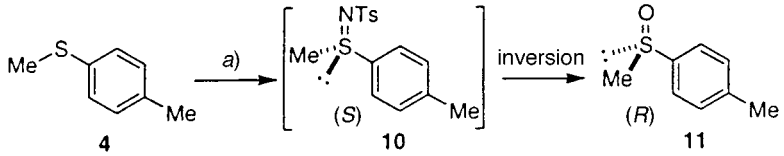
Scheme 3



a) MnN **8** (1.0 equiv.), pyridine (0.50 equiv.), Ts_2O (1.2 equiv.), pyridine *N*-oxide (1.2 equiv.), CH_2Cl_2, 3 h, 0°.

is the primary product, it undergoes hydrolysis to the corresponding sulfoxide. It should be noted that *Cram* and co-workers had shown that such sulfilimines undergo hydrolysis to the corresponding sulfoxide with inversion [10a]. The optical rotation of sulfoxide **11** was determined to be + 48.0. Given that the (*S*)-sulfoxide (> 99% ee) has been previously reported to possess an $[\alpha]_D$ of − 76 [11][7])[8])[9]), we concluded that the product from the N-transfer reaction was the (*R*)-sulfoxide **11**, which is consequently formed in at least 72% ee. This result, when compared to that observed with $(CF_3CO)_2O$, suggests that there is little dependence on the structure of the activating group on the enantioselectivity of the atom-transfer step.

Scheme 4

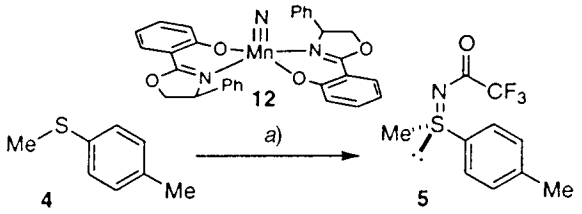


a) MnN **6** (1.0 equiv.), Ts_2O (5.0 equiv.), CH_2Cl_2, −78 to 23° over *ca.* 4 h.

[7]) For the facile conversion of sulfilimines to sulfoximines with dioxirans, see [10b].
[8]) For the highly enantioselective method to form sulfoxides, see [11b].
[9]) For examples of asymmetric synthesis with chiral sulfoxides, see [11c].

A series of investigations were then conducted to determine the effect of structural variations of the ligand structure associated with the nitridomanganese complex on the product enantioselectivity. As shown in *Scheme 5*, under otherwise identical N-transfer conditions, sulfilimine **5** was formed in slightly better ee when **12** was employed. This system was subsequently examined in some detail to determine whether the reaction displayed any significant sensitivity toward solvent effects. Unfortunately, reactions carried out in a variety of solvents failed to yield results that were significantly improved over the lead observation in CH_2Cl_2. Specifically, under otherwise identical conditions, the reaction in toluene[10]), tetrahydrofuran, and MeCN all resulted in lower enantiomer purity of the sulfilimine product (*Scheme 5*). Moreover, the addition of pyridine to the reaction mixture led to significant erosion in enantioselectivity of the process.

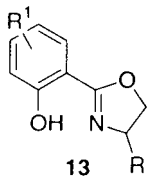
Scheme 5



Solvent	ee[%]
CH_2Cl_2	75
CH_2Cl_2 with 1.0 equiv. of pyridine	52
MeCN	68
toluene	38
tetrahydrofuran	16

a) MnN **12** (1.0 equiv.), $(CF_3CO)_2O$ (5.0 equiv.), solvent, −78 to 23° over *ca.* 4 h.

Further studies were focused on variation of the nitridomanganese structure by additional variation of its associated ligand[11]). In this regard, chiral ligand **13** was chosen for study as a ligand for nitridomanganese complexes because such ligands can be conveniently accessed from hydroxybenzonitriles; additionally, they permit ready access to a family of structural variants. Starting with perhaps one of the most simple of structural permutations, we investigated first the effect of alkyl substitution at the aromatic ring. Although 2-hydroxybenzonitrile (**16**; $R^1 = H$) is commercially available, an abundance of simple substituted derivatives are not. Consequently, we sought synthetic methodology for the formation of a family of 2-hydroxybenzonitriles.



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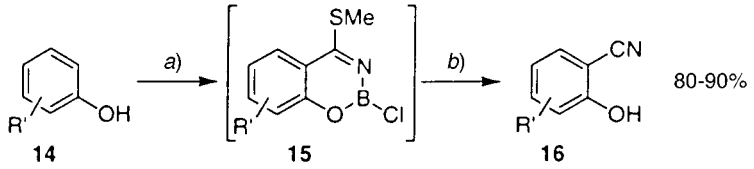
Although extensive precedence for the synthesis of 2-hydroxybenzonitriles from salicylaldehydes has been documented [12], the range of structurally varied phenols is larger. Given that a process for the selective *ortho*-cyanation of phenols in excellent yields had been reported, we decided to pursue a synthesis of the targeted ligands

[10]) Unlike all other solvent systems tested, nitride **12** is not completely soluble in toluene at −78°.

[11]) Variation of reaction conditions, such as the slow addition of various reagents and temperature control, did not lead to marked improvement of enantioselectivity.

commencing with hydroxybenzonitriles [13]. The preparation of hydroxybenzonitriles involves the addition of a stoichiometric amount of aluminium trichloride ($AlCl_3$), boron trichloride (BCl_3), and methyl thiocyanate (MeSCN) to a solution of a corresponding phenol. Heating the reaction mixture is suggested to lead to the formation of intermediate **15**, which, when subjected to alkaline hydrolysis followed by treatment with strong acid, affords the desired hydroxybenzonitriles **16** in consistently high yields (*Scheme 6*). Realizing the extensive commercial availability of phenols, this protocol seemed like an ideal approach to form a number of 2-hydroxybenzonitrile derivatives.

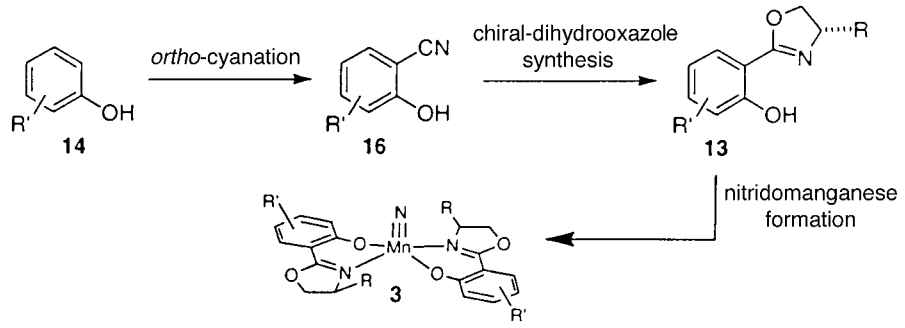
Scheme 6



a) BCl_3 (1.2 equiv.), MeSCN (1.2 equiv.), $AlCl_3$ (1.0 equiv.), dichloroethane, 80°, 3 h. *b*) 4N NaOH, 80°, 30 min, then 6N HCl, 23°.

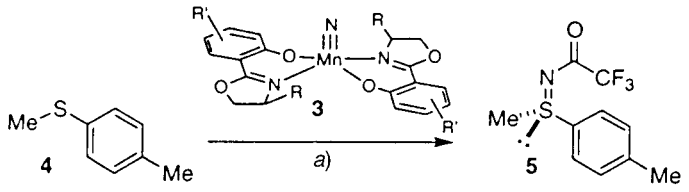
Several 2-hydroxybenzonitriles **16** were synthesized from the corresponding phenols **14** according to the procedure delineated above (*Scheme 7*). Conversion of each of the starting hydroxybenzonitriles to chiral dihydrooxazole ligands **13** followed by synthesis of the corresponding nitridomanganese complexes **3** was carried out in an efficient manner.

Scheme 7



The N-transfer process was then examined as a function of ligand structure (*Scheme 8*). As can be seen from the *Table*, product sulfilimines were prepared in 47–80% ee is the presence of various complexes **3**. Methyl groups positioned *ortho*, *meta*, and *para* relative to the phenolic OH group of **3** in general did not lead to significantly higher enantioselectivities than observed with nitrido complexes incorporating unsubstituted ligands (i.e., **6** and **12**; see above). For a given Me-substituted ligand, the nature of the R substituent at the dihydrooxazole moiety appeared not to exert a marked effect on the product enantioselectivity. In only one case was improved

Scheme 8



a) MnN **3** (1.0 equiv.), $(CF_3CO)_2O$ (5.0 equiv.), CH_2Cl_2, −78 to 23° over *ca.* 4 h.

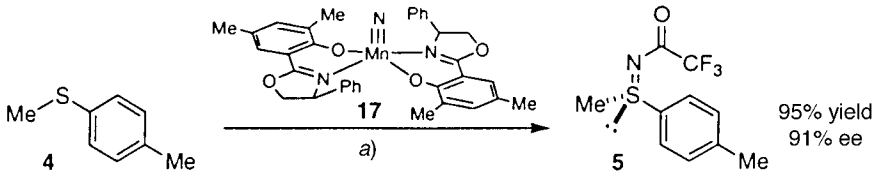
Table 1. *Enantiomer Excesses of Sulfilimines Obtained with a Variety of Mn≡N Complexes* **3**

Entry	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*	*12*
R	^{i}Pr	Ph	^{i}Pr	Ph	^{i}Pr	Ph	^{i}Pr	Ph	^{i}Pr	Ph	^{i}Pr	Ph
R′	H	H	6-Me	6-Me	5-Me	5-Me	4-Me	4-Me	4-Ph	4-Ph	4-^{t}Bu	4-^{t}Bu
ee [%]	72	75	59	47	60	70	80	73	66	72	73	76

enantioselectivity noted, namely, with the nitridomanganese complex derived from 2-hydroxy-4-methylbenzonitrile (R = ^{i}Pr) (*Table*, *Entry 7*, 80% ee).

Speculating that the use of ligands derived from hydroxybenzonitriles with added steric bulk at C(4) might lead to higher selectivities, we decided to prepare and examine two analogous nitridomanganese complexes substituted at C(4) with ^{t}Bu and Ph. N-Transfer from the corresponding activated nitridomanganese complexes to methyl *p*-tolyl sulfide (**4**) resulted in the corresponding sulfilimine **5** in only 73 and 76% ee for R = ^{i}Pr and Ph, respectively. These results suggested that the straightforward correlation of substituent size with product selectivity is difficult and that, therefore, the interplay of subtle steric effects may be significant. Consequently, we decided to examine ligands derived from dimethyl-substituted hydroxybenzonitriles. In this respect, nitrido complex **17** was prepared starting from 2,4-dimethylphenol. The structure of this nitrido complex was confirmed by X-ray crystal-structure analysis[12]). Under standard conditions, the use of **17** in an N-transfer reaction with methyl *p*-tolyl sulfide (**4**) furnished the corresponding sulfilimine **5** in 91% ee and 95% yield (*Scheme 9*)[13]).

Scheme 9



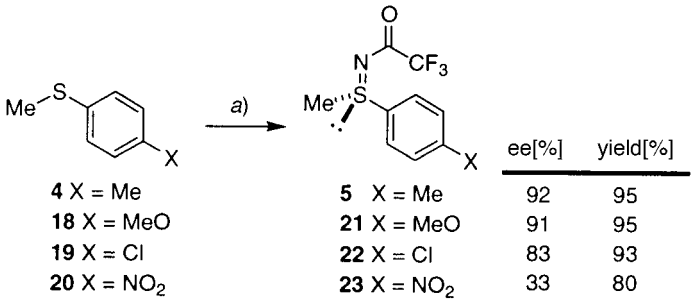
a) MnN **17** (1.0 equiv.), $(CF_3CO)_2O$ (5.0 equiv.), CH_2Cl_2, −78 to 23° over *ca.* 4 h.

12) The details of the structure will be reported in a full account of his work at a later time.

13) A slightly higher ee of sulfilimine **5** (94%) was realized when the reaction mixture was stirred at −78°, warmed to −61° for 15 h, and then quenched. We felt that the convenience of not having to strictly control temperature, however, adequately compensated for this additional enantioselectivity.

Having identified a process for the transfer of an N-atom to sulfides in high enantioselectivity, we proceeded to examine the reaction scope. As shown in *Scheme 10*, electron-donating or a Me substituent at the *para* position of the sulfide (see **18** and **4**) resulted in sulfilimine products **21** and **5**, respectively, with very high ee and yield. The use of aryl sulfides **19** and **20** possessing electronegative substituents (Cl, NO_2) led to products **22** and **23** being formed in lower enantioselectivity. However, the finding that each of the substrates furnished products in high yields underscores the wide substrate scope of the reaction. Following our preliminary observations employing aryl methyl sulfides, we proceeded to examine a wider range of sulfides in the N-transfer reaction. The conversion of ethyl phenyl sulfide (**24**) to the corresponding N-transfer product **25** was observed to proceed in 90% ee and 92% yield (*Scheme 11*).

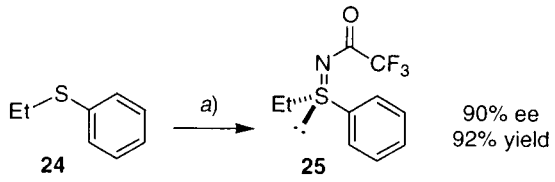
Scheme 10



		ee[%]	yield[%]
4 X = Me	**5** X = Me	92	95
18 X = MeO	**21** X = MeO	91	95
19 X = Cl	**22** X = Cl	83	93
20 X = NO_2	**23** X = NO_2	33	80

a) MnN **17** (1.0 equiv.), $(CF_3CO)_2O$ (5.0 equiv.), CH_2Cl_2, −78 to 23° over *ca.* 4 h.

Scheme 11

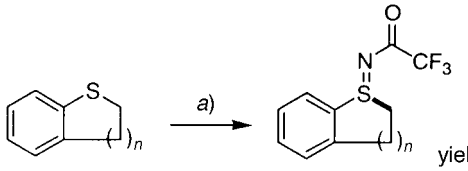


24 **25**

a) MnN **17** (1.0 equiv.), $(CF_3CO)_2O$ (5.0 equiv.), CH_2Cl_2, −78 to 23° over *ca.* 4 h.

The use of cyclic alkyl aryl sulfides such as **26** [14] and **27** [15] was subsequently investigated. The corresponding sulfilimine products **28** and **29** could be isolated in high yields following activation of **17** with $(CF_3CO)_2O$ under standard conditions, albeit with the products possessing significantly lower enantioselectivity (*Scheme 12*). We speculate that the reason behind the diminished levels of selectivity observed with cyclic substrates stems from the rigidity of the system. In this respect, the aryl group being constrained to a conformation that renders it roughly coplanar with the saturated ring leads to a sulfide substrate that displays two substituents of effectively similar size.

Scheme 12

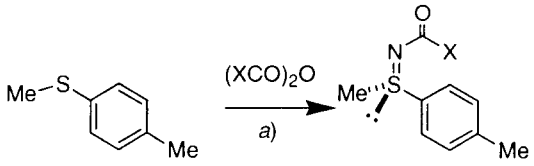


		yield[%]	ee[%]
26 $n = 1$	**28** $n = 1$	87	46
27 $n = 2$	**29** $n = 2$	91	50

a) MnN **17** (1.0 equiv.), $(CF_3CO)_2O$ (5.0 equiv.), CH_2Cl_2, −78 to 23° over *ca.* 4 h.

To date, activation of manganese nitrides for the transfer of an N-atom to organic substrates has been reported to proceed with Ts_2O, $(CF_3CO)_2O$, and $BF_3 \cdot Et_2O$ [16]. In the context of our studies involving sulfides, we examined the acylation/activation reaction of the manganese nitride and N-transfer with additional agents. Towards this end, $(CCl_3CO)_2O$ and $(CHCl_2CO)_2O$ both successfully activated nitrido complex **17**, yielding the corresponding trichloroacetylated and dichloroacetylated sulfilimines **30** and **31**, respectively, in similarly high yields and ee (*Scheme 13*)[14]). The expansion of the range of activating groups for N-transfer and thus the protecting group of the resulting product without significant loss of reaction efficiency is a key feature of the dihydrooxazole-derived complexes. This feature of the process can be exploited in synthetic planning wherein the nature of the protecting groups employed at the N-atom can be customized.

Scheme 13



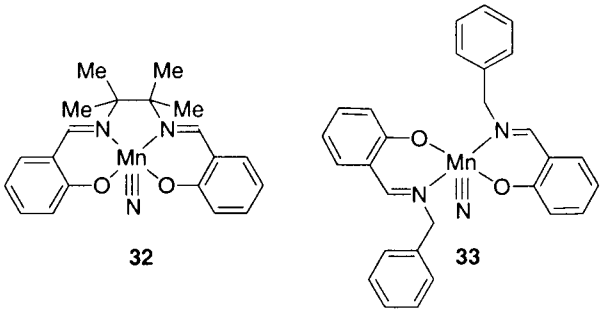
	X	yield[%]	ee[%]
5	CF_3	95	92
30	CCl_3	91	86
31	$CHCl_2$	90	83

a) MnN **17** (1.0 equiv.), $(XCO)_2O$ (5.0 equiv.), CH_2Cl_2, −78 to 23° over *ca.* 4 h.

In the course of the studies described above, we have noted some interesting qualitative reactivity differences between the N-transfer process from the chiral oxazole-derived nitridomanganese and the salen-derived nitridomanganese as well as *Schiff* base derived nitridomanganese complexes we have previously documented. In this respect, for nitrido complexes **32** and **33**, room temperature is essential for the activation of the nitrido complex and subsequent N-transfer to sulfides. For nitrido complex **17**, however, the starting material is consumed at temperatures well below 0°. Our observations made by monitoring the course of the reaction by IR spectroscopy suggest that the nitridomanganese complex undergoes acylation/activation by $(CF_3CO)_2O$ at −78°; the subsequent transfer of the $NCOCF_3$ moiety to the sulfide can be carried out at −25° [17]. Thus, on the basis of these observations, the activated

[14]) Acylating agents weaker than $(CHCl_2CO)_2O$, such as $(CH_2ClCO)_2O$, Ac_2O, and ClCOOEt, however, failed to activate the nitrido complex and N-transfer to methyl *p*-tolyl sulfide.

oxazole-derived nitridomanganese complex **17** appears to have increased reactivity over both *Groves*' nitrido(porphyrinato)manganese and nitridomanganese complexes **32** and **33** we have previously described. The observations highlighted above suggest that the chiral oxazole-derived nitrido complexes are inherently more reactive towards N-transfer. Our current ongoing investigations are aimed at confirming this conclusion quantitatively. Although a rigorous explanation is not yet possible, it is interesting to note, however, that all previous nitridomanganese complexes that have shown the ability, once activated, to transfer the N-atom to anorganic substrates, display structures that can be described as square pyramidal; by contrast, the chiral oxazole-derived nitrido complexes are best described as trigonal bipyramid complexes[15]).



32 **33**

Conclusions. – We documented the use of chiral nitridomanganese complexes bearing chiral phenolic/dihydrooxazole ligands in N-transfer to sulfides, affording optically active sulfilimines. In the context of this study, we carried out an investigation of complexes with variable electronic and steric demands. In general, sulfilimines possessing high ee were obtained in a process that necessitates the use of a single equiv. of both the reagent and the substrate. We also noted that the increased reactivity of the nitridomanganese complexes permits the use of additional activating agents ($(CCl_3CO)_2O$ and $(CHCl_2CO)_2O$) in the process. Our investigations not only expand the scope of nitridomanganese reagents to include sulfide substrates, but also provide data regarding reactivity and structure of manganese nitrides. These will be useful in our ongoing investigations of N-atom-transfer processes.

Experimental Part

General. Toluene, MeCN, THF, and CH_2Cl_2 were purified by passage through a column of activated alumina prior to use. Air- and moisture-sensitive liquids were transferred *via* syringe. Org. solns. were evaporated in a rotary evaporator below 50°. Chromatographic purification: forced-flow chromatography on *Fluka* silica gel *60* (230–400 mesh). TLC: *Merck* 0.25-mm silica-gel *60F* plates (230–400 mesh); visualization with UV light or by staining with phosphomolybdic acid or anisaldehyde. GC Analyses: *Varian 3400-GC* system with a *Supelco SPB-5* capillary column. M.p.: *Büchi 510* melting-point apparatus; uncorrected. $[\alpha]_D$ temp. [°]: *Jasco DIP-1000* digital polarimeter operating at 589 nm; concentration in g/100 ml. IR Spectra: *Perkin-Elmer Spectrum-RXI-FT-IR* spectrometer; either KBr pellets or thin films on NaCl salt plates; $\tilde{\nu}$ in cm^{-1}. NMR

[15]) This information can be observed by comparison of the crystal-structure data of the nitrido complexes.

Spectra: *Varian Mercury 300*, at 300 MHz for ^{1}H and 75 MHz for ^{13}C; internally referenced to residual δ(H) of solvent; δ in ppm, J in Hz. Combustion analysis was performed by the analytical laboratory at ETH-Zentrum.

2-[(4S)-4,5-Dihydro-4-phenyloxazol-2-yl]-3,5-dimethylphenol. TLC (hexanes/AcOEt 20:1): R_f 0.26. M.p. 63–64°. IR (film): 2909 (br.), 1635, 1602, 1477, 1369, 1272, 1195, 1126, 1020, 959, 777, 758, 698. ^{1}H-NMR ($CDCl_3$, 400 MHz): 1215 (br. *s*, 1 H); 7.38–7.33 (*m*, 3 H); 7.31–7.25 (*m*, 3 H); 7.09 (*s*, 1 H); 5.46 (*t*, J = 9.0, 1 H); 4.77 (*tm*, J = 9.0, 1 H); 4.21 (*td*, J = 8.4, 1.1, 1 H); 2.27 (*s*, 6 H). ^{13}C-NMR ((D$_6$)acetone, 75 MHz): 166.2; 156.0; 141.8; 135.2; 128.4; 127.4; 126.8; 126.2; 125.2; 125.0; 109.0; 73.7; 68.3; 19.3; 14.8. Anal. calc. for $C_{17}H_{17}NO_2$: C 76.18, H 6.41, N 5.24; found: C 76.18, H 6.60, N 5.26.

Bis[2-[(4S)-4,5-dihydro-4-phenyloxazol-2-yl-κN^3]phenolato-κO]nitridomanganese (**17**). TLC (hexanes/AcOEt 8:1): R_f 0.35 (slight dec.) M.p. 205–206°. IR (film): 1625, 1601, 1562, 1469, 1435, 1317, 1262, 1249, 1210, 1145, 1046, 1020, 961, 844, 779, 749, 697. ^{1}H-NMR ((D$_6$)DMSO, 400 MHz, 19°): 7.50–7.38 (*m*, minor); 7.35–7.23 (*m*, 4 H); 7.13–7.07 (*m*, 3 H); 6.97 (*s*, minor); 5.45 (*s*, *dd*, J = 9.3, 3.5, 1 H); 5.35 (*d*, minor); 4.81 (*s*, J = 9.2, 1 H); 4.74 (*m*, minor); 4.44 (*dd*, J = 8.9, 3.5, 1 H); 2.20 (*s*, 3 H); 2.14 (*s*, 3 H); 2.07 (*s*, minor); 1.90 (*s*, minor). ^{1}H-NMR ((D$_6$)DMSO, 400 MHz, 100°): 7.37–7.23 (*m*, 4 H); 7.17–7.07 (*m*, 3 H); 5.46 (*dd*, J = 1.8, 0.9, 1 H); 4.78 (*t*, J = 9.0, 1 H); 4.44 (*dd*, J = 9.0, 3.9, 1 H); 2.20 (*s*, 3 H); 2.15 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 165.6; 164.5; 140.2; 136.9; 128.8; 128.7; 127.9; 126.9; 125.7; 124.2.

Nitrogen Transfer to Sulfides: General Procedure. A soln. of sulfide (1.0 equiv.) and nitridomanganese **17** (1.0 equiv.) in CH_2Cl_2 (0.05M) was cooled to −78°. $(CF_3CO)_2O$ (5.0 equiv.) was then added dropwise to the dark purple soln. The soln. was allowed to warm slowly from −78° to 23° within 4–5 h. During this time, the mixture turned dark brown. Silica gel (2 g/mmol) and $NaHCO_3$ (20 equiv.) were added, along with hexanes (10 ml/mmol). The dark brown slurry was stirred vigorously at 23° for 5 min before being filtered through a plug of silica gel (20 g/mmol) with Et_2O as eluent. Evaporation of the filtrate afforded a pale yellow residue, which was purified by chromatography (silica gel).

S-*Methyl*-S-*(4-methylphenyl)*-N-*(trifluoroacetyl)sulfilimine* (**5**). M.p. 70–72°. TLC (hexanes/AcOEt 1:2). IR (film): 1633, 1179, 1141, 978, 876, 810, 773. ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.69 (*dm*, J = 8.4, 2 H); 7.38 (*d*, J = 8.1, 2 H); 2.93 (*s*, 3 H); 2.43 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$, 100 MHz): 166.7 (*q*, J = 37); 144.3; 131.0; 129.7; 127.1; 117.0 (*q*, J = 286); 34.7; 21.5. ^{19}F-NMR ($CDCl_3$, 400 MHz): −73.4. Anal. calc. for $C_{10}H_{10}F_3NOS$: C 48.19, H 4.04, N 5.62; found: C 47.93, H 3.92, N 5.90.

S-*(4-Methoxyphenyl)*-S-*methyl*-N-*(trifluoroacetyl)sulfilimine* (**21**). M.p. 80–82°. TLC (hexanes/AcOEt 1:2): R_f 0.28. IR (film): 1634, 1594, 1498, 1307, 1263, 1182, 1140, 1086, 1025, 977, 876, 832, 799, 773. ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.80 (*d*, J = 8.7, 2 H); 7.11 (*d*, J = 8.7, 2 H); 3.92 (*s*, 3 H); 2.98 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 166.3 (*q*, J = 38); 163.3; 129.1; 122.9; 116.7 (*q*, J = 286); 115.6; 55.5; 34.5. ^{19}F-NMR ($CDCl_3$, 400 MHz): −73.5. Anal. calc. for $C_{10}H_{10}F_3NO_2S$: C 45.28, H 3.80, N 5.28; found: C 45.28, H 3.88, N 5.22.

S-*(4-Chlorophenyl)*-S-*methyl*-N-*(trifluoroacetyl)sulfilimine* (**22**). M.p. 82–84°. TLC (hexanes/AcOEt 1:2): R_f 0.32. IR (film): 1631, 1183, 1140, 978, 824, 773. ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.76 (*dm*, J = 8.7, 2 H); 7.58 (*dm*, J = 8.7, 2 H); 2.96 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$, 100 MHz): 167.9 (*q*, J = 35); 139.9; 131.7; 130.7; 128.6; 116.9 (*q*, J = 286); 34.8. ^{19}F-NMR ($CDCl_3$, 400 MHz): −73.5. Anal. calc. for $C_9H_7ClF_3NOS$: C 40.09, H 2.77, N 5.19; found: C 39.94, H 2.77, N 5.17.

S-*Methyl*-S-*(4-nitrophenyl)*-N-*(trifluoroacetyl)sulfilimine* (**23**). M.p. 137–139°. TLC (hexanes/AcOEt 1:2): R_f 0.42. IR (film): 1633, 1530, 1347, 1182, 1141, 978, 854, 804, 772, 744, 726, 680. ^{1}H-NMR ($CDCl_3$, 300 MHz): 8.46 (*d*, J = 9.0, 2 H); 8.03 (*d*, J = 9.0, 2 H); 3.04 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$, 100 MHz): 166.7 (*q*, J = 35); 150.6; 140.2; 128.3; 125.2; 116.9 (*q*, J = 286); 34.6. ^{19}F-NMR: ($CDCl_3$, 400 MHz): −73.5. Anal. calc. for $C_{10}H_7F_3N_2O_3S$: C 38.57, H 2.52, N 10.00; found: C 38.63, H 2.46, N 9.89.

S-*Ethyl*-S-*phenyl*-N-*(trifluoroacetyl)sulfilimine* (**25**). M.p. 62–64°. TLC (hexanes/AcOEt 1:2): R_f 0.40. IR (film): 1634, 1180, 1140, 882, 802, 775, 748, 688. ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.80–7.75 (*m*, 2 H); 7.64–7.57 (*m*, 3 H); 3.32–3.18 (*m*, 2 H); 1.26 (*t*, J = 7.5, 3 H). ^{13}C-NMR ($CDCl_3$, 75 MHz): 166.7 (*q*, J = 37); 132.9; 130.5; 129.9; 127.3; 116.8 (*q*, J = 285); 43.8; 7.2. ^{19}F-NMR ($CDCl_3$, 400 MHz): −73.4. Anal. calc. for $C_{10}H_{10}F_3NOS$: C 48.19, H 4.04, N 5.62; found: C 47.86, H 4.20, N 5.58.

N-*(2,3-Dihydro-1H-1λ^4-benzothien-1-ylidene)trifluoroacetamide* (**28**). M.p. 96–97°. TLC (hexanes/AcOEt 1:2): R_f 0.32. IR (film): 1622, 1185, 1133, 884, 796, 764. ^{1}H-NMR ($CDCl_3$, 400 MHz): 8.01 (*d*, J = 8.0, 1 H); 7.56 (*t*, J = 7.5, 1 H); 7.56–7.42 (*m*, 2 H); 3.92 (*dt*, J = 16.1, 8.4, 1 H); 3.73–3.61 (*m*, 2 H); 3.44 (*ddd*, J = 16.1, 7.3, 3.3, 1 H). ^{13}C-NMR ((D$_6$)acetone, 100 MHz): 171.4 (*q*, J = 34); 150.2; 140.4; 138.4; 133.8; 133.7; 131.8; 122.6 (*q*, J = 358); 50.2; 37.3. ^{19}F-NMR ($CDCl_3$, 400 MHz): −73.4. Anal. calc. for $C_{10}H_{18}F_3NOS$: C 48.58, H 3.26, N 5.67; found: C 48.48, H 3.07, N 5.48.

N-*(3,4-Dihydro-1λ^4-1-benzothiopyran-1(2H)-ylidene)* (**29**). M.p. 100–102°. TLC (hexanes/AcOEt 1:2): R_f 0.34. IR (film): 1633, 1179, 1139, 880, 760. ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.89 (*dd*, J = 7.8, 1.2, 1 H); 7.51

(*td*, *J* = 7.5, 1.4, 1 H); 7.39 (*tm*, *J* = 4.4, 1 H); 7.31 (*dm*, *J* = 7.5, 1 H); 3.55 (*ddd*, *J* = 13.5, 5.7, 2.4, 1 H); 3.25 (*ddd*, *J* = 14.4, 11.4, 3.0, 1 H); 3.16 (*td*, *J* = 17.6, 4.9, 1 H); 2.95 (*ddd*, *J* = 17.6, 10.8, 5.4, 1 H); 2.76–2.61 (*m*, 1 H); 2.28–2.17 (*m*, 1 H). ^{13}C-NMR ($CDCl_3$, 100 MHz): 167.3 (*q*, *J* = 34); 137.1; 132.8; 132.7; 131.3; 128.0; 126.5; 117.1 (*q*, *J* = 286); 39.2; 27.6; 15.6. ^{19}F-NMR ($CDCl_3$, 400 MHz): −73.4. Anal. calc. for $C_{11}H_{10}F_3NOS$: C 50.57, H 3.86, N 5.36; found: C 50.30, H 4.01, N 5.37.

S-*Methyl*-S-*(4-methylphenyl)*-N-*(trichloroacetyl)sulfilimine* (**30**). M.p. 103–105°. TLC (hexanes/AcOEt 1:2): R_f 0.42. IR (film): 1633, 1279, 978, 949, 845, 819, 796, 678. ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.71 (*dm*, *J* = 8.4, 2 H); 7.38 (*d*, *J* = 8.2, 2 H); 2.94 (*s*, 3 H); 2.44 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$, 100 MHz): 171.8; 144.1; 131.0; 130.3; 127.0; 95.2; 34.9; 21.6. Anal. calc. for $C_{10}H_{10}Cl_3NOS$: C 40.22, H 3.38, N 4.69; found: C 40.32, H 3.34, N 4.70.

N-*(Dichloroacetyl)*-S-*methyl*-S-*(4-methylphenyl)sulfilimine* (**31**). M.p. 82–84°. TLC (hexanes/AcOEt 1:2): R_f 0.28. IR (film): 1614, 1312, 1178, 976, 945, 802, 668. ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.67 (*dm*, *J* = 8.1, 2 H); 7.37 (*d*, *J* = 8.1, 2 H); 6.06 (br. *s*, 1 H); 2.89 (*s*, 3 H); 2.43 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$, 100 MHz): 174.2; 143.9; 130.9; 130.6; 127.0; 68.8; 34.9; 21.6. Anal. calc. for $C_{10}H_{11}Cl_2NOS$: C 45.47, H 4.20, N 5.30; found: C 45.32, H 3.93, N 5.23.

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