Pergamon

Tetrahedron 58 (2002) 5357–5366

TETRAHEDRON

Non-symmetrical tetradentate vanadyl Schiff base complexes derived from 1,2-phenylene diamine and 1,3-naphthalene diamine as catalysts for the oxidation of cyclohexene

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Received 6 August 2001; revised 8 April 2002; accepted 2 May 2002

Abstract—Two series of the novel unsymmetrical diimino tetradentate Schiff bases derived from phenylenediamine and 1,3-naphthalene diamine and their vanadyl complexes were synthesized by template and non-template methods and characterized by ^{1}H, ^{13}C NMR, IR, UV–Vis and elemental analysis. These complexes are used as catalysts for the selective aerobic oxidation of cyclohexene. The catalytic activity increases as the number of electron-donor groups decreases, and the catalytic selectivity is varied by changing the substituents on the ligands. The catalytic system described here is an efficient and inexpensive method for the oxidation of olefins, with the advantages of high activity, selectivity, re-usability and short reaction times. Complexes containing the naphthylene bridged ligands had similiar redox potentials, however, their catalytic activities are quite varied. This difference in their activity is strongly dependent on fine structural data and ΔE_p. But in the complexes containing phenylene bridged ligands, comparing the GC, redox potential and ΔE_p measurements yields a good correlation between catalytic activity and redox potential and a slight corrolation to selectivity. In general, the conversion percentage decreases with the increase of ΔE_p and decrease of $E_{redox}^{0'}$. © 2002 Published by Elsevier Science Ltd.

1. Introduction

Particular attention has recently been paid to the synthesis and study of the diimino tetradentate Schiff bases and their complexes. This is due to a variety of reasons, not the least of which is their crucial role in some biological processes such as the biological functions of bacteriorhodopsin.[1] These complexes are used in some chemical processes[2,3] as catalysts and also as biological models in understanding the structure of biomolecules and biological processes.[4,5] Some of the important features of these compounds are their preparative accessibility, diversity and structural variability, which make them very attractive. There is extensive literature on their use as catalysts in some important industrial processes, particularly on the use of vanadyl-Schiff base complexes. All of these facts have convinced us that Schiff bases play a major role in coordination chemistry.[6] Although the magnetic, spectroscopic and catalytic properties of these Schiff base complexes are well-documented,[7] it still seems there could be new and specific applications for such a unique class of compounds. Due to the recent utilization of the *tert*-butyl alcohol co-product as an octane booster in gasoline (Halcon process)[8] the selective epoxidation of olefins catalyzed by d^o metal complexes of Mo(IV), V(V) and Ti(IV) have become the most important industrial process for the manufacture of propylene oxide. This process is also of importance in the production of fuels, commodity chemicals, and fine chemicals.[9] The use of molecular oxygen as an oxidant for such processes is particularly attractive from both economic and environmental perspectives.[10] With all of these and many other advantages in mind we have embarked upon a program aimed at developing catalysts that mimic perhalogenated metal porphyrins, but, which are more easily prepared. We chose Schiff base complexes for this investigation, as the ligand framework is similar to that of a porphyrin.[11,12]

In addition, the tunable electronic properties of Schiff bases make it possible to carry out systematic reactivity studies based on ancillary ligand modification.[13,14] In earlier works, we have synthesized some Schiff base complexes.[15–17] Here we report that novel vanadyl Schiff base complexes are moderately selective catalysts for aerobic olefin epoxidation. The ligands and complexes were characterized by ^{1}H, ^{13}C NMR, IR, UV–Vis spectroscopy and elemental analysis.

2. Results and discussion

Two series of unsymmetrical Schiff base ligands were prepared from commercially available starting materials, by the Schiff base condensation of 2,4-dihyroxyacetophenone; 2-hydroxyacetophenone or 2-hydroxysalicylaldehyde

Keywords: aerobic selective oxidation; selective epoxidation; catalytic oxidation of olefins; vanadyl tetradentate Schiff base; vanadyl Schiff base complexes; oxovanadium(IV) complexes.

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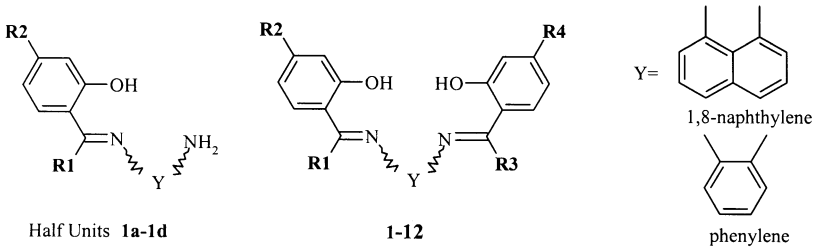
0040–4020/02/$ - see front matter © 2002 Published by Elsevier Science Ltd.
PII: S0040-4020(02)00481-7



Half Units **1a-1d** **1-12**

Compound	Y	R_1	R_2	R_3	R_4	%yield
1a	phenylene	H	H			
1b	phenylene	CH_3	H			
1c	naphthylene	H	H			
1d	naphthylene	CH_3	H			
1	phenylene	H	H	CH_3	H	71
2	phenylene	H	H	CH_3	OH	59
3	phenylene	CH_3	H	CH_3	OH	31
4	phenylene	H	H	H	H	93
5	phenylene	CH_3	H	CH_3	H	45
6	phenylene	CH_3	OH	CH_3	OH	25
7	naphthylene	H	H	CH_3	H	37
8	naphthylene	H	H	CH_3	OH	21
9	naphthylene	CH_3	H	CH_3	OH	18
10	naphthylene	H	H	H	H	46
11	naphthylene	CH_3	H	CH_3	H	28
12	naphthylene	CH_3	OH	CH_3	OH	15

Figure 1. General structure of precursors (half units) and tetradentate ligands.

and 1,2-diaminobenzene or 1,8-diaminonaphtalene in a simple molar ratio. In previous papers we have reported the synthesis of some new Schiff bases.[16–18] The recent interest in the chemistry of unsymmetrical diimino Schiff bases has prompted us to report some of our work concerning Schiff bases derived from *N*-salicylaldimino phenylenamine. The precursor **1a**=(2-[(2-2-amino-phenylimino)-methyl]-phenol) is prepared from salicylaldehyde and phenylenediamine[16,17] in a 1:1 molar ratio in an ethanolic solution, with subsequent removal of the excess diamine with extraction into benzene. The reaction of **1a** with 2-hydroxyacetophenone in degassed ethanol under argon gave yellow-orange needles of **1**. A similar condensation reaction with 2′,4′-dihydroxyacetophenone led to the isolation of red-brown crystals of **2**. The reaction of phenylendiamine with 2-hydroxyacetophenone followed by the condensation reaction with 2′,4′-dihydroxyacetophenone in degassed ethanol and under argon gave red-brown needles of **3** (Fig. 2). However, the reaction of these precursors (**1a** or **1b**) with 2-hydroxyacetophenone or 2,4-dihydroxyacetophenone was carried out in 1:1 molar ratio in ethanol, using highly dilute conditions (Fig. 1).

Condensation reaction of 1,8-naphthalene diamine with salicylaldehyde or 2-hydroxyacetophenone produced the half units **1c** and **1d** in low yield. The condensation reaction of these precursors **1c** or **1d** with the desired carbonyl compounds was carried out in dilute solution. (Fig. 3). Although, the similar condensation reaction of precursors **1c** or **1d** (containing a 1,8-naphthylene group) was used in the synthesis of compounds **7**–**12**. Under the same synthetic conditions, the latter reaction takes place in lower yield than that of the phenylene bridged compounds. In addition, products yields are related to the polarity of the carbonyl groups. All compounds were characterized by ^1H, ^{13}C NMR, IR as well as elemental analysis.

We also attempted to prepare unsymmetrical Schiff bases **1** and **2** by using a template procedure.[18] Under a nitrogen atmosphere **1a** and cobalt(II) acetate were refluxed together for 20 min in a 2:1 molar ratio in ethanol followed by the addition of 2-hydroxyacetophenone or 2′,4′-dihydroxyacetophenone, in the correct molar proportion to the solution prior to refluxing for 3 h. The metal complexes were isolated on cooling as red-brown powders. We concluded that these complexes are planer as evidenced by comparing their electronic spectra with those of similar complexes containing the phenolic moiety.[19] Refluxing these complexes with dimethyl glyoxime in an ethanol solution for several hours gave yellow-orange powders. These products were characterized, by IR and ^1H NMR spectroscopy, and were found to be demetallated **1** and **2**, (yield 85–90%).

Also, Schiff base ligands with a naphthalene bridge (Fig. 1, Y=naphthylene) were synthesized without further purification of the half units and were directly used for preparation of their complexes.

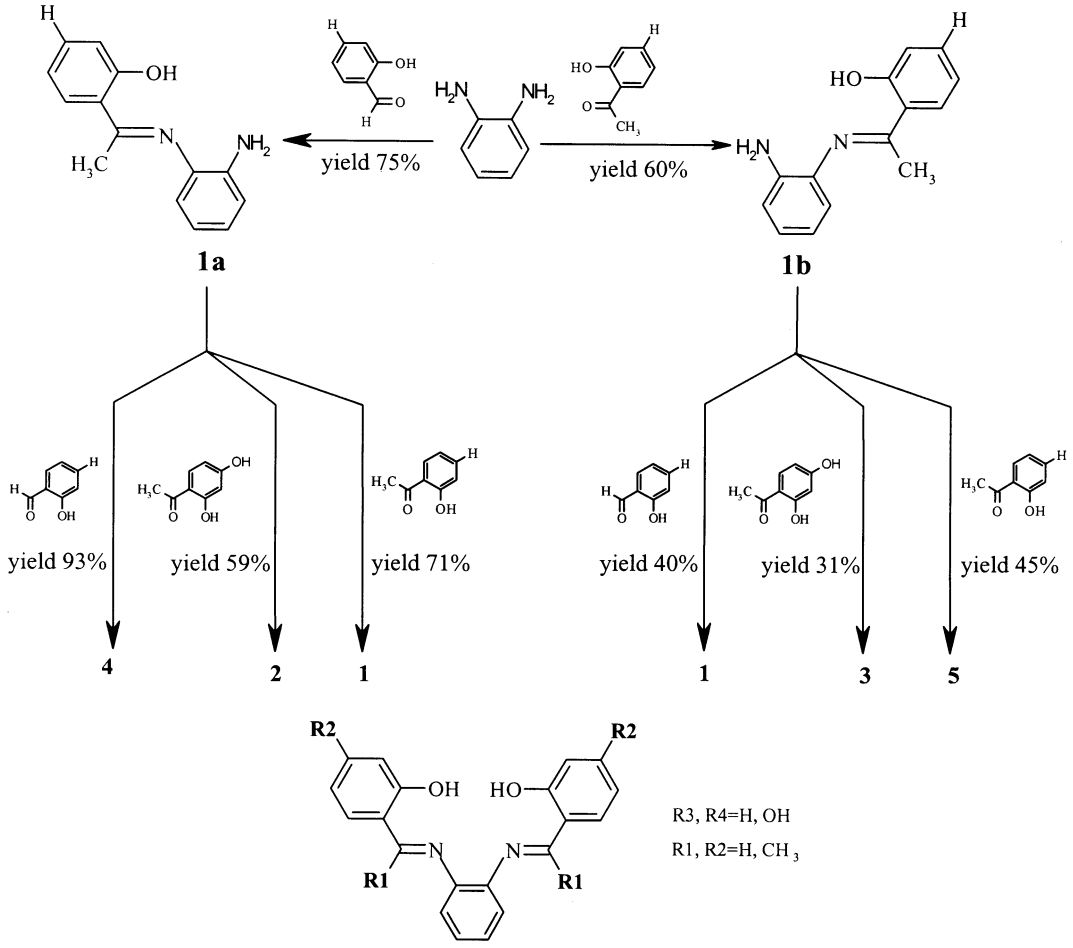


Figure 2. Overall synthesis path of tetradentate Schiff base ligands containing phenylene bridge.

Several IR absorption bands in the 1250–1650 cm^{-1} region can be attributed to the C–O, C═O, C═N, C═C stretching vibrations of the compounds. The infrared spectra of the 'half units' show bands at 3338 and 3275 cm^{-1} that are assigned to the primary amine stretching. An intense sharp band at about 1600–1630 cm^{-1} in the spectra of **4**–**6**, **10**–**12** and a broad intense band at about 1600–1630 cm^{-1} in the spectra of **1**–**3**, **7**–**9** are assigned to the C–N (azomethine) vibrations. The lack of a band due to a free OH stretching vibration in the Schiff bases is consistent with the finding of Kovacic.[4] All new compounds were confirmed by ^{1}H and ^{13}C NMR.[17,†]

A new series of some oxovanadium(IV) complexes with tetradentate Schiff base ligands was prepared and characterized (Table 1) (Fig. 4).

Treatment of the Schiff base ligands with $VO(acac)_2$ under aerobic conditions gave the desired oxovanadium(IV) complexes.[20] Overall yields were reasonable (21–83%). The vanadyl compounds were identified by IR, UV–Vis spectroscopy and elemental analysis (Table 1), and are remarkably stable to air, water and heat. It was also possible to prepare those mentioned complexes by in situ reactions (template method). In our work, we used this method to synthesize some unsymmetrical Schiff base complexes.[15–17,21] All complexes show very strong and broad bands centered around 1553–1630 cm^{-1} corresponding to ν (C═N). These bands are probably broadened due to their overlap with the aromatic ring-carbon stretchings. IR spectra of these complexes show ν (V═O) in the region 884–1000 cm^{-1}. The IR data of these amorphous products show ν (V═O) at 938–1000 cm^{-1}, indicating monomeric structures. Only one of these oxovanadium(IV) tetradentate Schiff base complexes (**22**) shows ν (V═O) at 884 cm^{-1} corresponding to a polymeric form, the others have bonds around 970 cm^{-1} (938–1000 cm^{-1}) corresponding to monomeric forms.[22,23] Thus, **22** is assigned the polymeric structure and the others ones are assigned the monomeric five coordinate structure. The IR spectra of vanadyl(IV) complexes **14**, **15**, **18**, **20**, **21**, **24** show ν (O–H) bands in the region 3400 cm^{-1}.[24] In this study the electronic spectra of the major complexes in DMSO solution show d–d bands around 13,000 and 18,300 cm^{-1} and CT bands around 25,000 and 38,000 cm^{-1}, which are similar to those in the spectra of vanadyl(IV) complexes in polar solvents.[25] In the visible absorption spectra, the first band ($dxy \rightarrow dxz, dyz$) normally appears broad, approximately between 650 and 900 nm. In most cases there is a band at 560±50 nm. In **13** and **16** this band is not apparent. This shoulder probably corresponds to the second $dxy \rightarrow dx^2-y^2$ transition band.[26] The molar conductance values in DMF at a concentration

† In the ^{1}H NMR spectra of these compounds, signals at δ 3.0–4.2 ppm in the spectrum of half units assigned to the NH_2 group are based on the absence of these signal in the spectra of compounds **1**–**12**.[17]

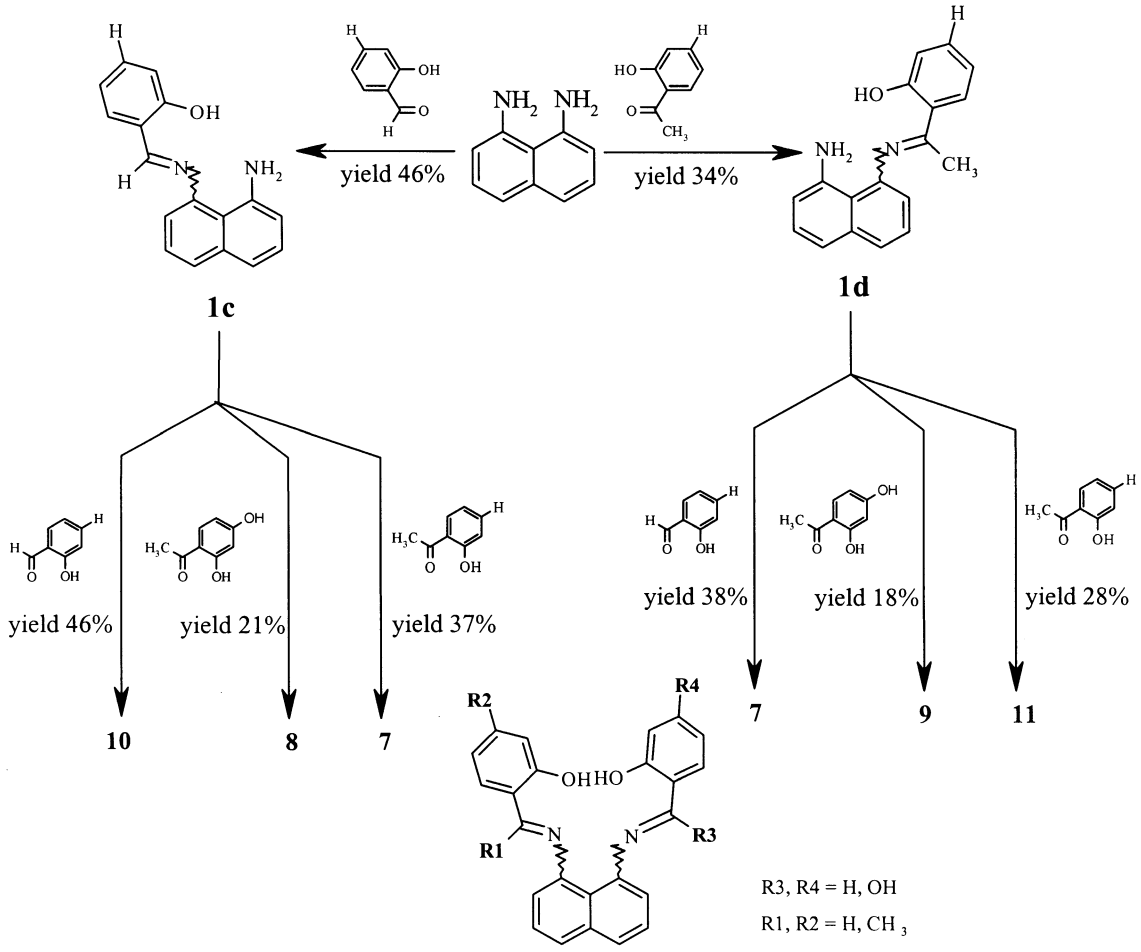


Figure 3. Overall synthesis path of tetradentate Schiff base ligands containing naphthylene bridge.

of 10^{-3} M are too low to account for any dissociation of the complexes. Also, the molar conductances of the complexes were measured in DMSO, indicating their non-electrolytic nature.

The vanadyl salen complexes **13**–**24** were tested as catalysts for the aerobic oxidation of hydrocarbons. Our earlier work suggests that complexes with simple salen ligand systems should make efficient catalysts. In all experiments cyclohexene was used as a substrate. Typical catalytic reaction conditions involve acetonitrile or DMF solutions at elevated temperatures (78–81°C), stirred under 1 atm of O_2 which was continuously replenished, with periodic product sampling. Under these conditions, cyclohexene was oxidized to a mixture of cyclohexene oxide (**25**), 2-cyclohexene-1-ol (**26**) and 2-cyclohexene-1-one (**27**) (Fig. 5). The reactions were followed by quantitative GC determination of the oxygenated products using 1,2-dichlorobenzene as an internal standard. Samples were quenched by the addition of excess triphenylphosphine to destroy any remaining peroxide. The reaction products were identified by GC–MS coupling. The product distributions for cyclohexene oxidation are shown in Fig. 6. Some of the the vanadium complexes (**15**, **20**, **21**, **23**) perform the aerobic oxidation of cyclohexene with a moderate selectivity (up to 45% for epoxidation, Table 2).

Several control experiments were performed. Catalysis is not affected by the presence or absence of light. The salen catalysts are very stable to oxidative degradation under the reaction conditions. In the absence of the catalyst or in the presence of the ligand alone, little or no oxidation occurs. There is some correlation between the catalytic activity of vanadyl complexes containing phenylene bridged ligands and redox potential. In the case of the catalysts containing naphthylene bridged ligands, the catalytic activity of complexes with similar redox potential varies dependent on fine structural data. The catalytic activity of complex **20** is the most active, achieving approximately 333 turnovers in a 24 h period. The catalytic performance is shown as a function of redox potential in Fig. 7.

3. Conclusion

Cyclohexene oxidation by molecular oxygen using vanadyl Schiff base complexes as catalyst in acetonitrile, DMF and DMSO as solvents produced a mixture of cyclohexene oxide (**25**), 2-cyclohexene-1-ol (**26**) and 2-cyclohexene-1-one (**27**) which was observed for all complexes. The catalytic system described here is an efficient and inexpensive method for the oxidation of olefins, with the advantages of high activity, fair selectivity, re-usability and short reaction times. We have designed a family of

Table 1. Elemental analysis, vibrations parameters and some physical properties of vanadyl compexes **13–24**

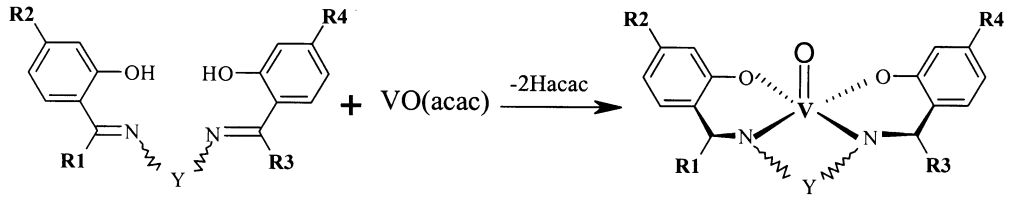
Compound (formula)	F. wt. (yield, %)	Color[a], (mp, °C)	Selective IR bands (cm^{-1})		Important abs. bands, nm (ε, M/cm)		Founded (calcd)			
			V=O	C=N	λ_{max}	Another	%C	%H	%N	%V
13 ($VC_{21}H_{16}N_2O_3$)	395.3 (1 83)	G (>400)	970	1607	–	415 (2560)	63.55 (63.81)	3.87 (4.08)	7.29 (7.09)	12.48 (12.89)
14·C_2H_5OH[b] ($VC_{21}H_{16}N_2O_4$)	411.32 (60)	DB (350)[c]	946	1607	520 (140)	534 (1336)	61.08 (61.32)	3.65 (3.92)	7.02 (6.81)	12.68 (12.38)
15 ($VC_{22}H_{18}N_2O_4$)	425.34 (43)	B (180)[c]	1000	1584	509 (134)	452 (2101)	61.91 (62.12)	4.04 (4.27)	6.88 (6.59)	12.20 (11.98)
16 ($VC_{20}H_{14}N_2O_3$)	381.28 (93)	G (340)[c]	984	1607	–	415 (3430)	62.71 (63.00)	3.67 (3.70)	7.40 (7.35)	13.41 (13.36)
17 ($VC_{22}H_{18}N_2O_3$)	409.34 (71)	DB (300)[c]	976	1584	512 (170)	373 (560)	64.47 (64.55)	4.38 (4.43)	6.95 (6.84)	12.13 (12.44)
20·C_2H_5OH ($VC_{22}H_{18}N_2O_5$)	441.34 (34)	B (>400)	1000	1584	528 (340)	440 (1045)	59.77 (59.87)	4.27 (4.11)	6.56 (6.35)	11.80 (11.54)
19 ($VC_{25}H_{18}N_2O_3$)	445.88 (32)	B (>400)	938	1600	614 (401)	413 (2850)	67.30 (67.34)	4.02 (4.07)	6.40 (6.28)	11.70 (11.42)
20 ($VC_{25}H_{18}N_2O_4$)	461.38 (28)	DG (260)[c]	938	1600	624 (246)	448 (778)	64.87 (65.08)	3.68 (3.93)	6.31 (6.07)	10.80 (11.04)
21 ($VC_{26}H_{20}N_2O_4$)	475.40 (21)	B (>400)	984	1600	534 (290)	408 (1290)	65.51 (65.69)	4.40 (4.24)	5.70 (5.89)	10.47 (10.72)
22 ($VC_{24}H_{16}N_2O_3$)	431.34 (38)	DB (300)[c]	884	1600, 1553	525 (380)	455 (3534)	66.99 (66.83)	3.58 (3.74)	6.76 (6.49)	11.98 (11.81)
23·C_2H_5OH[b] ($VC_{26}H_{20}N_2O_3$)	459.40 (33)	B (>400)	946	1600	620 (914)	480 (890)	67.72 (67.98)	4.35 (4.39)	6.35 (6.10)	11.26 (11.09)
24·C_2H_5OH ($VC_{26}H_{20}N_2O_5$)	141.40 (21)	B (>400)	1000	1600	522 (360)	457 (1100)	63.71 (63.55)	4.17 (4.10)	6.00 (5.70)	10.75 (10.37)

Infrared spectra measurement as KBr pellets.

[a] Y: yellow; G: green; O: orange; B: brown; D: dark.

[b] Including solvent molecule.

[c] Decomposed.



Compound	Y	R_1	R_2	R_3	R_4	%yield
13	phenylene	H	H	CH_3	H	83
14	phenylene	H	H	CH_3	OH	60
15	phenylene	CH_3	H	CH_3	OH	43
16	phenylene	H	H	H	H	93
17	phenylene	CH_3	H	CH_3	H	71
18	phenylene	CH_3	OH	CH_3	OH	34
19	naphthylene	H	H	CH_3	H	32
20	naphthylene	H	H	CH_3	OH	28
21	naphthylene	CH_3	H	CH_3	OH	21
22	naphthylene	H	H	H	H	38
23	naphthylene	CH_3	H	CH_3	H	33
24	naphthylene	CH_3	OH	CH_3	OH	21

Figure 4. General structure of oxovanadium(IV) complexes.

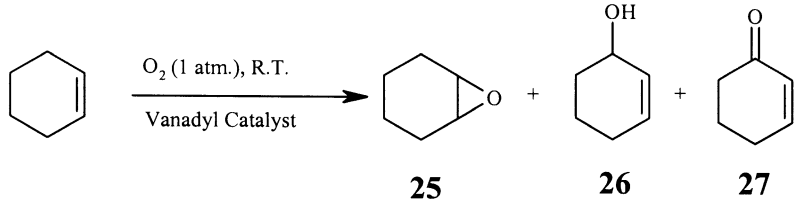
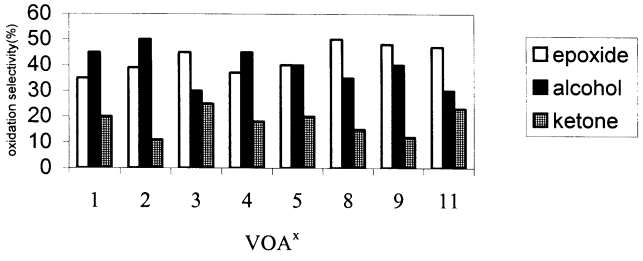


Figure 5. Oxidation of cyclohexene by O_2 using vanadyl Schiff base complexes as catalyst at room temperature.



Figuer 6. Product selectivity for the aerobic oxidation of cyclohexene catalyzed by vanadyl complexes **12**–**24**.

catalysts for olefin oxidation by dioxygen under mild conditions using inexpensive and readily available salen ligands. Further, if the complexes were completely unsymmetrical, it should be possible to increase the selectivity of catalytic oxidation. The process could be repeated many times without any evident chemical degradation. A striking feature of each series of these catalysts is the correlation of their catalytic activity with redox potential, ΔE_p and fine structural data. In addition to redox potential, the fine structural details of the complexes play an important role. Ligand distortions caused by substitution may strongly influence the reorganization energy of the ground state

Table 2. Catalytic oxidation of cyclohexene by O_2 and formal potentials for redox couples of vanadium (V/IV)

Compound[a]	$E^{0'}$ (V^{5+}/V^{4+}) (mV) vs AgCl/Ag, (ΔE_p (mV))[b]	Turnover (% conversion)	Products, relative ratio		
			25	**26**	**27**
13	587 (86)	75 (18)	35	45	20
14	870 (86)	196 (47)	39	50	11
15	905 (90)	242 (58)	45	30	25
16	620 (101)	75 (18)	37	45	18
17	515 (70)	96 (23)	40	40	20
20	903.5 (67)	333 (80)	50	35	15
21	890 (73)	312.5 (75)	48	40	12
23	900.5 (89)	150 (24)	47	30	23

[a] The complexes **18**, **19**, **22**, **24** are insoluble.

[b] Electrochemical measurements made in anhydrous acetonitril (**13**–**17**) or DMF (**20**, **21**, **23**) containing 0.1 M tetrabutyl ammonium hexafluorophosphate (TBAH). In the case of complexes that were soluble in both solvents (**13**, **14**, **16**), redox potential changes were negligible. Irreversible reduction was observed for the complexes at potentials less than −1550 mV accompanied by decomposition of the complexes.

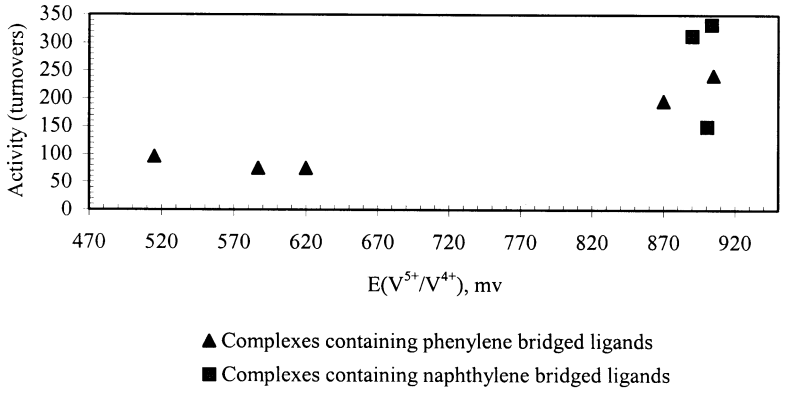


Figure 7. Plot of activity for catalytic cyclohexene oxidation vs V^{5+}/V^{4+} potential (mV) for vanadyl complexes **13**–**17**, **20**, **21**, **23**.

towards that of the transition state in redox reactions and thus lower the overall activation energy. As we showed in the complexes containing naphthylene bridged ligand, in spite of the similarity of their V(V/IV) redox potentials, their activities are very different, but their selectivities are similar. But in the complexes containing phenylene bridged ligands, comparing GC, ΔE_p and $E_{redox}^{0'}$ results shows some correlation between redox potential and activity. In general, the percentage conversion decreases on increasing ΔE_p and decreasing $E_{redox}^{0'}$. Maximum percentage conversion and activity is seen for **20** and **21** which have the minimum ΔE_p and maximum $E_{redox}^{0'}$.

Further work directed towards the development of an efficient homogeneous catalyst for asymmetric oxidation of olefins to their corresponding epoxy compounds is in progress.

4. Experimental

4.1. Physical measurements

Infrared spectra were recorded as KBr pellets using Unicam Matson 1000 FT-IR, ^1H and ^{13}C NMR spectra by a Bruker FT-NMR AC-80 (80 MHz) and 500 (500 MHz) spectrometer using $CDCl_3$ and $(CD_3)_2SO$ as solvents. Elemental analyses (C, H, N) were performed using a Heraeus Elemental Analyzer CHN–O-Rapid (Elemental-Analysesnysteme KBr pellets, Gmbh-West Germany). Melting points were determined on a BUCHI Melting point B-540. The products were identified by GC with a CHROMPACK CP 9001 gas chromatograph, and their retention times compared to authentic samples. Hyphenated GC-MS systems consist of a GC HP 6890 series and a MS HP 5973 MSD. Cyclic Voltammetry was performed using a Bioanalytical systems apparatus. The working, auxiliary, and reference electrodes were glassy carbon, platinium wire, and AgCl/Ag, respectively. An EG and G potantiostat/galvanostat 273 A was empolyed to evaluate electrochemical measurements at room temperature (25°C) under argon with 0.1 M tetrabutylammonium hexafluorophosphate (TBAH) as the supporting electrolyte.

4.2. Materials

Oxygen gas was passed through a calcium chloride drying tube before admission to the reaction system. Cyclohexene was distilled under argon and stored in a refrigerator. Salicylaldehyde, 2-hydroxyacetophenone, *o*-phenylenediamine, 1,8-naphthalenediamine, dimethyl glyoxime, cobalt(II) acetate tetrahydrate, vanadyl acetylacetonate were used as received from commercial (Merck and Aldrich). Solvents (ethanol, ether, methanol, and acetonitrile) were dried and distilled before use by standard methods. DMF and DMSO were used without any further purification as received. Reference samples of cyclohexene oxides, 2-cyclohexene-1-ol and 2-cyclohexene-1-one (Aldrich) were distilled and stored in a refrigerator.

4.3. Synthesis of ligands

Synthesis of half units, ***1a–1d***. The precursors were prepared according to the modified method described earlier[16,17] by mono condensation of the appropriate diamines, with aldehyde or ketones. To the vigorously stirred and cool dilute solution (T=5–10°C) of the diamine (20 mmol) in 100 mL anhydrous ethanol, was added dropwise a cooled solution of salicylaldehyde or 2′-hydroxyacetophenone or 2′,4′-dihydroxyacetophenone (15 mmol) in 80 mL anhydrous ethanol. After the addition was complete, the mixture was stirred for 15–30 min and then refluxed for 15–60 min. The resulting solution was evaporated under vacuum to remove the solvent and the excess diamine was extracted by benzene and was used for the next step without further purification.

Synthesis of compounds ***1–12***. The unsymmetrical Schiff bases were obtained by condensation of the half units and the appropriate aldehyde or ketones. To the stirred solution of the precursor (half units, **1a**–**1d**) (10 mmol) in 60 mL anhydrous ethanol was added a solution of salicylaldehyde or 2′-hydroxyacetophenone or 2′,4′-dihydroxyacetophenone (10 mmol) in 20–30 mL anhydrous ethanol. In some cases (compounds **2**, **3**, **6**, **8**, **9**, **12**), a few drops of piperidine were added to the reaction mixture and refluxed for 30–180 min. The mixture was concentrated in vacuum by evaporation of the solvent until a colored solid precipitated. The product was filtered, washed with cold solvent and recrystallized from the appropriate solvents (compounds **5**–**12** ethanol; **1**, **3** acetonitrile; **4**, **10** MeOH) to give colored crystals. Yields ranged from 18 to 93% based on the diamine used (in stiochiometric molar ratio). Physical

properties, spectral data and other characterization data are given below.

4.3.1. Compound 1. F.W.=330.39, yield 71%, color yellow-orange, mp=148.1–149.7°C. Selective IR bands (cm^{-1}), KBr pellets (O–H, C=N, C–O), 3400, 1623 (w), 1246. Anal. calcd for $C_{21}H_{18}N_2O_2$: C, 76.23; H, 5.49; N, 8.48. Found: C, 76.17; H, 5.65; N, 8.58. ^{1}H NMR (500 MHz) chemical shift (δ ppm), 13.65 (br, 2H, O–*H*), 8.16 (s, 1H, C*H*=N), 6.48–7.61 (m, 12H, *H*-aryl), 2.21 (s, 3H, C$H_{3(azomethine)}$). ^{13}C NMR (500 MHz) chemical shift (δ ppm) 18, 118, 119, 120 (3), 122, 125, 127, 128, 132 (3), 140, 142, 161, 162, 163, 172.

4.3.2. Compound 2. F.W.=346.39, yield 59%, color red-brown. mp=125°C (decomposed). Selective IR bands (cm^{-1}), KBr pellets (O–H, C=N, C–O), 3330, 3180, 1623 (w), 1276. Anal. calcd for $C_{21}H_{18}N_2O_3$: C, 72.82; H5.24; N, 8.09. Found: C, 72.93; H, 5.29; N, 8.17. ^{1}H NMR (500 MHz) chemical shift (δ ppm), 12.65 (br, 2H, O–*H*), 6.1 (br, 1H, O–*H*), 8.68 (s, 1H, C*H*=N), 2.12 (s, 3H, C$H_{3(azomethine)}$), 6.50–7.53 (m, 11H, *H*-aryl). ^{13}C NMR (500 MHz) chemical shift (δ ppm) 19, 103 (2), 107, 108, 113, 115 (2), 117 (3), 120, 122, 125, 127 (3), 132, 134 (2), 141, 142, 161, 164, 165, 173.

4.3.3. Compound 3. F.W.=360.41, yield 31%, color red-brown. mp=113°C (decomposed). Selective IR bands (cm^{-1}) KBr pellets, (O–H, C=N, C–O), 3359, 1623 (w), 1253. Anal. calcd for $C_{22}H_{20}N_2O_3$: C, 73.32; H, 5.59; N, 7.77. Found: C, 73.06; H, 5.65; N, 7.97. ^{1}H NMR (500 MHz) chemical shift (δ ppm), 14.35 (br, 1H, O–*H*), 12.7 (br, 1H, O–*H*), 6.42–7.71 (m, 11H, *H*-aryl), 6.1 (br, 1H, O–*H*), 2.45 (s, 3H, C$H_{3(azomethine)}$), 2.25 (s, 3H, C$H_{3(azomethine)}$). ^{13}C NMR (500 MHz) chemical shift (δ ppm), 18, 19, 103 (2), 107, 108, 113, 115 (2), 118 (2), 120, 122, 126, 132 (3), 134, 140, 141, 162, 164, 172, 174.

4.3.4. Compound 4. F.W.=316.36, yield 93%, color orange, mp=162.5–164.1°C. Selective IR bands (cm^{-1}), KBr pellets (O–H, C=N, C–O), 3415, 1615 (s), 1276. Anal. calcd for $C_{20}H_{16}N_2O_2$: C, 75.93; H, 5.10; N, 8.85. Found: C, 75.71; H, 5.01; N, 8.98. ^{1}H NMR (500 MHz) chemical shift (δ ppm), 12.95 (s, 2H, O–*H*), 8.49 (s, 2H, C*H*=N), 6.60–7.33 (m, 12H, *H*-aryl).

4.3.5. Compound 5. F.W.=344.414, yield 45%, color yellow-orange, mp=81.9–83.5°C. Selective IR bands (cm^{-1}), KBr pellets (O–H, C=N, C–O), 3607, 1615 (s), 1276. Anal. calcd for $C_{22}H_{20}N_2O_2$: C, 76.72; H, 5.85; N, 8.13. Found: C, 76.54; H, 5.57; N, 8.32. ^{1}H NMR (500 MHz) chemical shift (δ ppm), 14.85 (s, 2H, O–*H*), 6.31–7.83 (m, 12H, *H*-aryl), 2.25 (s, 6H, C$H_{3(azomethine)}$). ^{13}C NMR (500 MHz) chemical shift (δ ppm) 18, 115 (2), 117, 118 (3), 120, 122, 126, 130, 132, 133, 135, 140, 162, 174.

4.3.6. Compound 6. F.W.=376.41, yield 25%, color brown, mp=100°C (decomposed). Selective IR bands (cm^{-1}), KBr pellets(O–H, C=N, C–O), 3450, 3600, 1630 (s), 1276, 1207. Anal. calcd for $C_{22}H_{20}N_2O_4$: C, 70.20; H, 5.36; N, 7.44. Found: C, 70.01; H, 5.30; N, 7.64. ^{1}H NMR (500 MHz) chemical shift (δ ppm), 12.56 (s, 2H, O–*H*), 10.67 (s, 2H, O–*H*), 6.25–7.59 (m, 10H, *H*-aryl), 2.33 (s, 6H, C$H_{3(azomethine)}$). ^{13}C NMR (500 MHz) chemical shift (δ ppm) 19, 103 (2), 107, 108, 113, 115 (2), 118 (2), 122, 126, 133 (3), 141, 162, 173.

4.3.7. Compound 7. F.W.=380.96, yield 37%, color red-brown, mp=160°C (decomposed). Selective IR bands (cm^{-1}), KBr pellets (O–H, C=N, C–O), 3330, 1605 (w), 1223, 1240. Anal. calcd for $C_{25}H_{20}N_2O_2$: C, 78.82; H, 5.29; N, 7.35. Found: C, 78.57; H, 5.01; N, 7.53. ^{1}H NMR (500 MHz) chemical shift (δ ppm), 14.47 (s, 1H, O–*H*), 12.83 (s, 1H, O–*H*), 8.57 (s, 1H, C*H*=N), 6.50–7.45 (m, 14H, *H*-aromatic), 2.25 (s, 3H, C$H_{3(azomethine)}$). ^{13}C NMR (500 MHz) chemical shift (δ ppm) 57, 113 (2), 116 (2), 118, 119, 127 (2), 129 (2), 132, 133, 135, 136, 143, 144, 153, 155, 162, 164.

4.3.8. Compound 8. F.W.=396.45, yield 21%, color red-brown, mp=160°C (decomposed), Selective IR bands (cm^{-1}), KBr pellets (O–H, C=N, C–O), 3365, 3315, 1600 (w), 1246. Anal. calcd for $C_{25}H_{20}N_2O_3$: C, 75.74; H, 5.08; N, 7.07. Found: C, 75.60; H, 4.96; N, 7.26. ^{1}H NMR (500 MHz) chemical shift (δ ppm), 14.73 (s, 1H, O–*H*), 12.68 (s, 1H, O–*H*), 9.71 (s, 1H, C*H*=N), 6.51–7.55 (m, 13H, *H*-aromatic), 5.74 (s, 1H, O–*H*), 2.61 (s, 3H, C$H_{3(azomethine)}$). ^{13}C NMR (500 MHz) chemical shift (δ ppm) 61, 105, 108 (2), 113 (2), 116 (2), 127 (2), 129 (2), 132, 135, 136, 144, 153, 156, 163, 165.

4.3.9. Compound 9. F.W.=410.47, yield 18%, color dark brown, mp=170°C (decomposed). Selective IR bands (cm^{-1}), KBr pellets (O–H, C=N, C–O), 2976, 3373, 1607 (w), 1276. Anal. calcd for $C_{26}H_{22}N_2O_3$: C, 76.08; H, 5.40; N, 6.82. Found: C, 75.79; H, 5.11; N, 6.99. ^{1}H NMR (500 MHz) chemical shift (δ ppm), 12.74 (s, 2H, O–*H*), 6.55–7.28 (m, 13H, *H*-aromatic), 5.82 (s, 1H, O–*H*), 2.58 (s, 3H, C$H_{3(azomethine)}$), 2.21 (s, 3H, C$H_{3(azomethine)}$). ^{13}C NMR (500 MHz) chemical shift (δ ppm) 58, 61, 105, 108 (2), 113 (2), 116 (2), 119, 127 (2), 129 (2), 132, 135, 136, 144, 147, 154, 156, 163, 165.

4.3.10. Compound 10. F.W.=366.42, yield 46%, color green, mp=160°C (decomposed). Selective IR bands (cm^{-1}), KBr pellets, (O–H, C=N, C–O), 3361, 1600 (s), 1246. Anal. calcd for $C_{24}H_{18}N_2O_2$: C, 78.67; H, 4.95; N, 7.64. Found: C, 78.48; H, 4.89; N, 7.91. ^{1}H NMR (500 MHz) chemical shift (δ ppm), 14.82 (s, 2H, O–*H*), 9.58 (s, 2H, C*H*=N), 6.48–8.15 (m, 14H, *H*-aromatic). ^{13}C NMR (500 MHz) chemical shift (δ ppm) 113 (2), 116 (2), 118 (2), 121, 127 (2), 128, 129 (2), 135 (3), 144, 162, 155.

4.3.11. Compound 11. F.W.=394.47, yield 28%, color red-brown, mp=180°C (decomposed). Selective IR bands (cm^{-1}), KBr pellets, 3338, 1605 (s), 1223. Anal. Calcd for $C_{26}H_{22}N_2O_2$: C, 79.17; H, 5.62; N, 7.10. Found: C, 78.84; H, 5.55; N, 7.23. ^{1}H NMR (500 MHz) chemical shift (δ ppm), 12.75 (s, 2H, O–*H*), 6.48–7.62 (m, 14H, *H*-aromatic), 2.27 (s, 6H, C$H_{3(azomethine)}$). ^{13}C NMR (500 MHz) chemical shift (δ ppm) 57, 113 (2), 116 (2), 127 (2), 129 (2), 135, 136, 143, 144, 153, 163.

4.3.12. Compound 12. F.W.=426.47, yield 15%, color

red-brown, mp=160°C (decomposed). Selective IR bands (cm^{-1}), KBr pellets (O–H, C=N, C–O), 3380, 3300, 1600 (s), 1246. Anal. calcd for $C_{26}H_{22}N_2O_4$: C, 73.23; H, 5.20; N, 6.57. Found: C, 73.01; H, 5.24; N, 6.65. ^{1}H NMR (500 MHz) chemical shift (δ ppm), 9.8 (s, 2H, O–*H*), 6.54–7.23 (m, 12H, *H*-aromatic), 5.68 (s, 2H, O–*H*), 2.21 (s, 6H, $CH_{3(azomethine)}$). ^{13}C NMR (500 MHz) chemical shift (δ ppm) 62, 105, 108 (2), 113 (2), 116 (2), 127 (2), 129 (2), 135 (3), 143, 147, 156, 164.

4.4. Preparation of vanadyl complexes, 13–24

The vanadyl complexes were prepared under ambient conditions. To a hot solution of **1**–**12** (1.7 mmol) in a mixed solvent (for **1**, **3**, **5**; CH_3Cl 10 ml/EtOH 15 ml/MeOH 10 ml and **2**, **4**, **6**; EtOH 10 ml/MeOH 20 ml/DMSO 50 ml and **7**–**12**; DMSO 80 ml) a hot solution of VO(acac) (1.7 mmol) in methanol (10 ml) was added. The mixture was heated and a few drops of triethylenamine were added. The reaction mixture was refluxed for 30–90 min. The colored solution was concentrated and cooled to yield colored powders or crystals. In some cases products were oily. A small amount of cooled ether was added until a solid product precipitated. Recrystallization from EtOH; EtOH/$CHCl_3$; DMSO/EtOH; DMSO/MeOH mixtures in a 1:1 ratio for compounds **16**, **22**; **12**, **17**, **23**; **14**, **15**, **18**; **19**, **21**, **24**; **20** respectively, gave analytically pure products (21–93% yield). Analytical data and some physical properties for complexes are listed in Table 1.

4.5. Template method

To a solution of half unit, **1a** or **1b**, (1 mmol) in ethanol and a methanolic solution of the $Co(OAc)_2$ (1 mmol), was added the appropriate acetophenone (1 mmol) in methanol. This mixture was refluxed and was then cooled and left to allow the complex precipitate. This precipitate was filtered and washed with solvent. The cobalt complexes were synthesized under an argon atmosphere. Refluxing these complexes with 1.1 mmol of dimethyl glyoxime in 60 ml ethanolic solution for several hours gave yellow-orange powders (yields 85–90%). These products were characterized, by IR and NMR spectroscopy, and data were in accordance with **1** and **2**. Anal. calcd for $CoC_{21}H_{16}N_2O_2\cdot C_2H_5OH$: C, 63.74; H, 5.12; N, 6.46; Co, 13.87. Found: C, 63.58; H, 4.94; N, 6.53; Co, 13.60. Selective IR band (cm^{-1}), KBr pellets (C=N), 1607. Anal. calcd for $CoC_{21}H_{16}N_2O_3\cdot C_2H_5OH$: C, 61.47; H, 4.93; N, 6.23; Co, 13.11. Found: C, 61.29; H, 4.84; N, 6.44; Co, 13.33. Selective IR band (cm^{-1}), KBr pellets (C=N), 1607.

4.6. Catalytic oxidations

Catalytic oxidation was performed in stirred flasks. All glassware was oven-dried prior to use. In a typical experiment 10 μmol of the vanadyl complexes were dissolved in freshly distilled acetonitrile (15 ml) or DMF (10 ml) at 40°C, the system evacuated and purged with argon gas. After saturation of the solution with dioxygen, 50 mmol of freshly distilled cyclohexene was injected. The reactions were carried out at 79–81°C for 24 h under 1 atm of O_2 that was continually replenished. The reaction products were monitored at periodic time intervals using gas chromatography. The oxidation products were identified by comparison with authentic samples (retention times in GC) and GC–MS coupling.

Acknowledgements

We thank Dr F. Gobal and Dr A. Salimi for their help in obtaining CV curvs and Dr H. Bagheri and Dr M. Sarajy for the GC–MS and gas chromatograms.

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