Inorganic Chemistry

Article

pubs.acs.org/IC

Dioxomolybdenum(VI) Complexes with Pyrazole Based Aryloxide Ligands: Synthesis, Characterization and Application in Epoxidation of Olefins

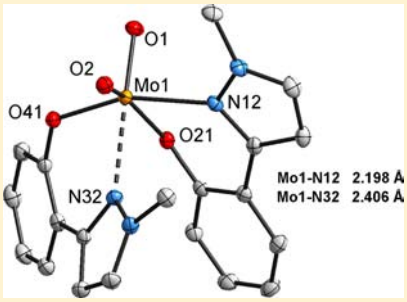
Jörg A. Schachner,[†] Pedro Traar,[†] Chris Sala,[†] Michaela Melcher,[†] Bastian N. Harum,[†] Alexander F. Sax,[‡] Manuel Volpe,[†] Ferdinand Belaj,[†] and Nadia C. Mösch-Zanetti*[,†]

[†]Institute of Chemistry, Karl-Franzens-University Graz, Stremayrgasse 16, 8010 Graz, Austria

[‡]Institute of Chemistry/Physical Chemistry, Karl-Franzens-University Graz, Heinrichstraße 28, 8010 Graz, Austria

Supporting Information

ABSTRACT: Synthesis, characterization, and epoxidation chemistry of four new dioxomolybdenum(VI) complexes $[MoO_2(L)_2]$ (**1**−**4**) with aryloxide-pyrazole ligands L = **L1**−**L4** is described. Catalysts **1**−**4** are air and moisture stable and easy to synthesize in only three steps in good yields. All four complexes are coordinated by the two bidentate ligands in an asymmetric fashion with one phenoxide and one pyrazole being trans to oxo atoms, respectively. This is in contrast to the structure found for the related aryloxide-oxazoline coordinated Mo(VI) dioxo complex **5**. This was confirmed by the determination of the molecular structures of complexes **1**−**3** by X-ray diffraction analyses. Compounds **1**−**4** show high catalytic activities in the epoxidation of various olefins. Cyclooctene (**S1**) is converted to its epoxide with high activity, whereas the epoxidation of styrene (**S2**) is unselective. Internal olefins (**S3** and **S4**) are also acceptable substrates, as well as the very challenging olefin 1-octene (**S5**). Catalyst loading can be reduced to 0.02 mol % and the catalyst can be recycled up to ten times without significant loss of activity. Supportive DFT calculations have been carried out in order to obtain deeper insights into the electronic situation around the Mo atom.



INTRODUCTION

Molybdenum catalyzed oxygen atom transfer (OAT) chemistry belongs to the very important chemical reaction both in biological systems as well as on industrial scale. In biology, molybdenum is found in a large family of enzymes that catalyze important OAT reactions in the living cell. Mechanistic details still remain unclear despite the determination of many crystal structures.[1−4] For this reason, several research groups, including ours, developed functional and structural model molybdenum complexes and investigated their OAT reactivity for a better understanding of this important reaction.[5−10] Industrial OAT reactions include the epoxidation of propylene with an estimated scale of 5 million metric tons annually,[11−13] which was patented more than 40 years ago and is now known as the Halcon/ARCO process.[14,15] The active heterogeneous catalyst contains mainly molybdenum in the oxidation state VI, formed in situ from the catalyst precursor $[Mo(CO)_6]$ and *alkyl*-hydroperoxides as oxygen source. Subsequently, many homogeneous molybdenum catalysts for epoxidation of olefins were developed.[16−22] However, significantly more attention received rhenium catalyzed homogeneous olefin epoxidation triggered by the discovery of the easy entry into the chemistry of the highly active methyltrioxorhenium (MTO) by Herrmann and co-workers.[23,24] Nevertheless the high oxidation state rhenium catalysts are hampered by their high Lewis acidity which results in destructive ring-opening of the formed epoxide.[25] The addition of various mono- and bidentate Lewis bases can prevent the acidic ring-opening but usually makes the adduct complexes more sensitive toward moisture rendering their handling more challenging.[25−27] Thus, it is still worthwhile to develop further homogeneous catalysts for epoxidation of olefins. A possible approach is the preparation of rhenium complexes in lower oxidation states, such as oxorhenium(V) compounds, or oxomolybdenum(VI) compounds as they tend to be more stable toward protic conditions. In this endeavor, we have developed and investigated as epoxidation catalysts several oxorhenium(V) complexes.[28−30] With one of them we were able to get an insight into the mechanism and found that the rhenium(V) precursor is stepwise oxidized to rhenium(VII) prior to the catalytic reaction which is again sensitive toward decomposition.[30] However, we have recently prepared oxorhenium(V) complexes equipped with aryloxide-pyrazole ligands and investigated their epoxidation chemistry.[29] Although we found them to be only moderately active catalysts in the epoxidation of cyclooctene, with yields ranging between 44 to 64% cyclooctane epoxide, their ease of preparation and handling prompted us to investigate the ligand system in molybdenum based epoxidation catalysis.

Here, we report air stable and easy to synthesize dioxomolybdenum(VI) complexes **1**−**4** equipped with the

Received: March 28, 2012
Published: June 29, 2012

   dx.doi.org/10.1021/ic300648p | *Inorg. Chem.* 2012, 51, 7642−7649

aryloxide-pyrazole ligand family together with their interesting catalytic behavior in epoxidation of various epoxides.

RESULTS AND DISCUSSION

Complex Synthesis. The pyrazole ligands were synthesized according to published literature procedures.[20,29,31] Synthesis involves a two step procedure by treating the respective methyl aryl ketone with sodium hydride and ethyl formate to give the aryl 3-oxopropanal intermediate product. The subsequent ring closure procedure of the aldehyde intermediates with methylhydrazine in refluxing ethanol yields the desired ligands **HL1**−**HL4** (Figure 1).

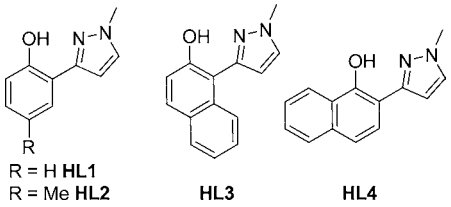
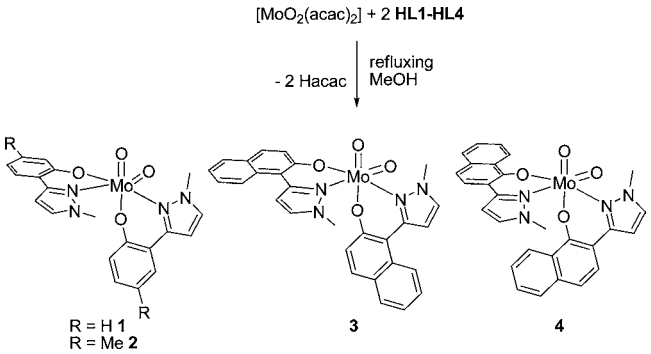


Figure 1. Aryloxide ligands used in this study with a pyrazol-3-yl bonded moiety.

The Mo complexes $[MoO_2(L)_2]$ (L = **L1**−**L4**) were synthesized by addition of the respective ligands **HL1**−**HL4** to $[MoO_2(acac)_2]$ dissolved in hot MeOH (Scheme 1). After

Scheme 1. Synthesis of Pyrazole Containing Mo(VI) Complexes 1−4



refluxing for 4−6 h complexes **1**−**4** precipitated and were isolated by filtration. After washing with cold MeOH the complexes were analytically pure in 65−76% isolated yield. To the best of our knowledge, complexes **1**−**4** represent the first examples of aryloxide-pyrazol-3-yl containing dioxomolybdenum(VI) complexes. A related complex, an isomeric pyrazol-1-yl-ligated complex, was published by Sorrell and co-workers, but was not tested in olefin epoxidation.[32]

Complexes **1**−**4** were isolated as yellow to orange powders. They are stable for month in air in the solid state, and in chloroform solution for approximately two weeks. They are insoluble in apolar (hexanes etc.) as well as medium polar solvents (Et_2O, toluene) and only sparingly soluble in strong polar solvents (MeOH, acetonitrile, $CHCl_3$). X-ray quality crystals of **1**−**3** were obtained by slow evaporation from solutions in MeOH at 8 °C. The ^{1}H NMR spectra of complexes **1**−**4** display two sets of proton signals for two inequivalent ligands. This is due to an unusual asymmetric coordination of the ligands, which was also revealed by X-ray crystallography (vide infra). Because of their low solubility in common organic solvents all ^{1}H NMR experiments were performed in d_4-methanol at 55 °C. For the same reason we could not obtain good quality ^{13}C NMR spectra due to the crystallization of the sample inside the NMR tube over the time of the experiment.

Because of the bidentate nature of ligands **L1**-**L4** a total of three geometric isomers are possible for bis substituted *cis* dioxo molybdenum(VI) complexes, depending on the coordinating atoms in trans position to the oxo groups: both N-donors trans to the terminal oxo ligands (N,N-isomer), both phenoxy groups trans to the terminal oxo ligands (O,O-isomer) or one N-donor and one phenoxy group trans to the terminal oxo ligands (N,O-isomer). The occurrence of two sets of ligand resonances in the proton spectrum evidence the exclusive formation of the N,O-isomer. Complexes **1**−**4** should be compared to the related aryloxide-oxazoline complexes $[MoO_2(hoz)_2]$ (Figure 4) featuring symmetric N,N-coordination. Several structurally related oxazoline containing Mo complexes have been previously published and tested in olefin epoxidation (vide infra).[18,19,21,22,33]

For complexes **1**−**3** the molecular structures were determined by single-crystal X-ray diffraction analysis. A molecular view of **1** is given in Figure 2. Molecular views of

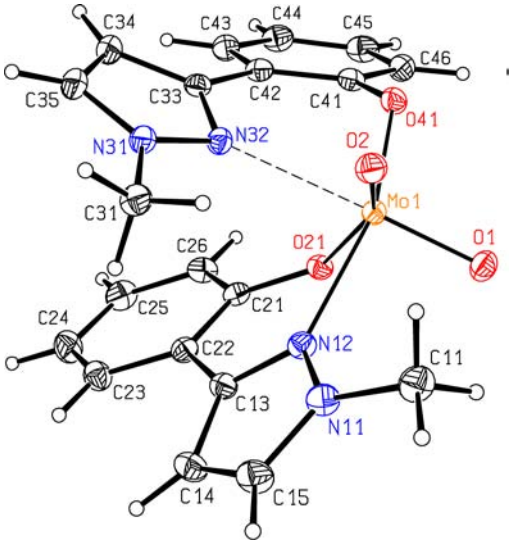


Figure 2. ORTEP plot of **1** at 50% probability with numbering scheme. H atoms drawn with arbitrary radii.

2 and **3** as well as selected bond lengths and angles and other crystallographic information of all three complexes can be found in the Supporting Information. All three complexes **1**−**3** display distorted octahedral coordination geometries around the Mo atom in the N,O-isomeric form consistent to the structure in solution.

As displayed in Figure 2, the nitrogen atom (N32) of one pyrazole moiety trans to terminal oxygen atom O1 is only weakly coordinated in the solid state, with a very long Mo1−N32 distance of 2.4060(17) Å. The second pyrazole moiety from the other ligand is bonded to the Mo atom with a Mo1−N12 distance of 2.1980(15) Å. Trans to the second terminal oxo ligand (O2) is a phenoxy moiety of one ligand (Mo1−O21 2.0178(13) Å) which is slightly longer than the corresponding molybdenum phenoxide distance trans to pyrazole (Mo1−O41 1.9302(11) Å). This asymmetric bonding situation around the Mo center is not reflected in the bond distances of the two

dx.doi.org/10.1021/ic300648p | Inorg. Chem. 2012, 51, 7642−7649

terminal oxo ligands to the Mo center in the solid state. They are virtually the same as Mo−O1 is 1.7084(15) Å and Mo−O2 is 1.7084(14) Å and fall within the expected range of other published dioxomolybdenum complexes.[34] A similar bonding situation can also be observed in complexes **2** and **3** (see Supporting Information). As mentioned above the related aryloxide-oxazoline Mo(VI) complex **5** was found to exhibit the symmetric N,N-isomeic structure.[19] Similar to **1**−**3** the Mo atom in **5** is coordinated in a distorted octahedral fashion by two terminal oxo ligands and two bidentate aryloxide-oxazoline ligands. Both terminal oxo ligands in **5** are at a distance of 1.7054(13) Å to the Mo atom and therefore reside at a very similar range as in complexes **1**−**3**. Trans to both oxo ligands of **5** the nitrogen atoms of the oxazoline moieties are located, resulting in the symmetric N,N-isomer. The nitrogen atoms are at a distance of 2.3024(14) Å to the Mo atom, which lies right between the distances for the two asymmetrically coordinated pyrazole ligands in **1** (vide supra).

Catalytic Epoxidation. Complexes **1**−**4** were screened in the catalytic epoxidation of five different olefins using *tert*-butyl hydrogen peroxide (TBHP) as oxygen source (see Figure 3).

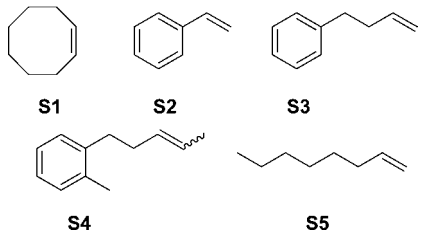


Figure 3. Substrates **S1**−**S5** used in epoxidation experiments with complexes **1**−**4**.

Under standard conditions experiments were performed in 3 mL of $CHCl_3$ with 2 mol % of catalyst and 3 equivalents of TBHP at 25 or 55 °C. Different conditions for **1** were also tested with substrate **S5** to allow for better comparison with previously published systems (vide infra). The five olefin substrates used were cyclooctene **S1**, styrene **S2**, 3-buten-1-ylbenzene **S3**, (E,Z)-1-methyl-2-(3-penten-1-yl)benzene **S4** and 1-octene **S5**.

At 55 °C, the epoxidation of cyclooctene **S1** was complete in less than two minutes with complexes **1**−**4**. At 25 °C the reaction reached completion (based on the detection limit of the GC-MS for **S1**) in less than 60 min (Table 1, Entries 1−4). This is in contrast to previously published, structurally related oxazoline Mo(VI) complexes $[MoO_2(hoz^*)_2]$ (Figure 4) which reached 41% conversion after 22 h in toluene under conditions

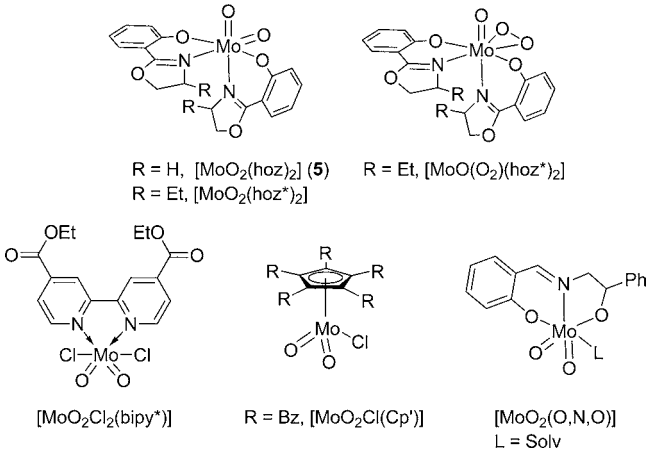


Figure 4. Selected literature examples of known Mo(VI) epoxidation catalysts.

as described in Table 1, entry 5.[21] When the peroxo complex $[MoO(O_2)(hoz^*)_2]$ was used, the yield increased to 83% (Table 1, entry 6).

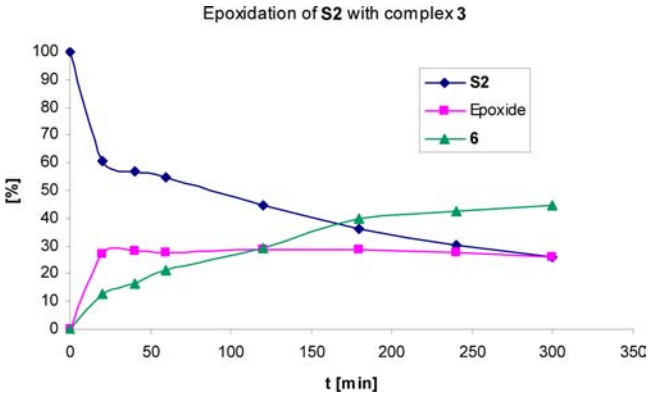


Figure 5. Epoxidation of styrene **S2** (♦) with complex **2** under formation of epoxide (■) and side product **6** (▲).

Bagherzadeh and co-workers published a comprehensive reactivity study on the parent oxazoline complex $[MoO_2(hoz)_2]$ **5** where they reported a very high conversion

Table 1. Epoxidation of Cyclooctene S1

entry	catalyst	mol %	equiv Ox.	solv.	T [°C]	t [min]	yield [%]	ref[a]
1	**1**	2	3	$CHCl_3$	25	40	>99	this work
2	**2**	2	3	$CHCl_3$	25	30	>99	this work
3	**3**	2	3	$CHCl_3$	25	30	>99	this work
4	**4**	2	3	$CHCl_3$	25	40	>99	this work
5	$[MoO_2(hoz^*)_2]$	2.5	1.5	toluene	25	1320	41	21
6	$[MoO(O_2)(hoz^*)_2]$	2.5	1.5	toluene	25	1320	83	21
7	$[MoO_2(hoz)_2]$ (**5**)	0.02	1	$C_2H_4Cl_2$	80	60	96	18
8	**1**	0.02	1	$C_2H_4Cl_2$	80	60	44	this work
9	$[MoO_2Cl_2(bipy^*)]$	1	1.5	neat	55	5	>99	17
10	$[MoO_2Cl(Cp')]$	1	2	neat	55	240	>99	16
11	$[MoO_2(O,N,O)]$	1	2	$C_2H_4Cl_2$	80	45	>99	35

[a]See reference section.

dx.doi.org/10.1021/ic300648p | *Inorg. Chem.* 2012, 51, 7642−7649

Table 2. Epoxidation of Styrene S2

entry	cat.	mol %	equiv Ox.	solv.	T [°C]	t [h]	yield [%]	ref[a]
1	**1**	2	3	$CHCl_3$	55	5	26	this work
2	**2**	2	3	$CHCl_3$	55	5	22	this work
3	**3**	2	3	$CHCl_3$	55	5	28	this work
4	**4**	2	3	$CHCl_3$	55	5	18	this work
5	$[MoO_2(acac)_2]$	2.5	1.5	toluene	35	18	2.8	33
6	$[MoO_2(hoz^*)_2]$	2.5	1.5	toluene	35	18	12.8	33
7	$[MoO_2(hoz)_2]$ (**5**)	0.02	1	$C_2H_4Cl_2$	80	5	45	18
8	$[MoO_2Cl(Cp')]$	1	2	neat	55	24	84	16

[a]See reference section.

Scheme 2. Formation of Side Products Observed for Catalysts 1−4 during Epoxidation of Styrene S2

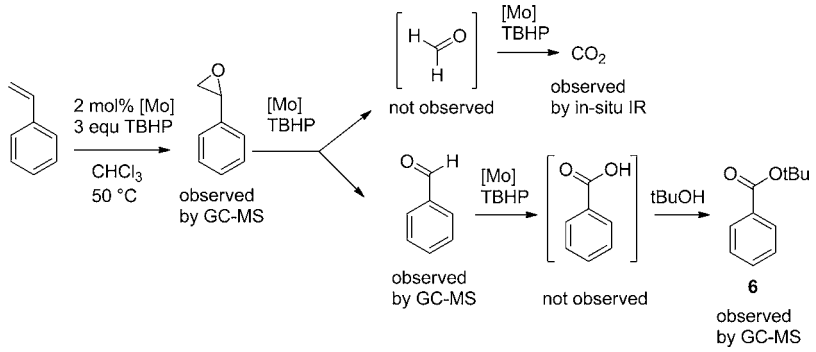


Table 3. Comparison of Epoxidation Yields of S3, (*E*,*Z*)-S4, and S5

entry	catalyst	substrate	equiv Ox	solv.	T [°C]	t [h]	yield [%]	ref[a]
1	**1**	**S3**	3	$CHCl_3$	55	24	86	this work
2	**2**	**S3**	3	$CHCl_3$	55	24	76	this work
3	**3**	**S3**	3	$CHCl_3$	55	24	84	this work
4	**4**	**S3**	3	$CHCl_3$	55	24	83	this work
5	**1**	(*E*,*Z*)-**S4**	3	$CHCl_3$	25	1(3)[b]	99(85)[c]	this work
6	**2**	(*E*,*Z*)-**S4**	3	$CHCl_3$	25	0.75(3)[b]	99(89)[c]	this work
7	**3**	(*E*,*Z*)-**S4**	3	$CHCl_3$	25	2(3)[b]	98(74)[c]	this work
8	**4**	(*E*,*Z*)-**S4**	3	$CHCl_3$	25	1(3)[b]	98(88)[c]	this work
9	**5**	**S5**	1	$C_2H_4Cl_2$	80	3	82	18
10	**1**	**S5**	1	$C_2H_4Cl_2$	80	3	0[d]	this work
11	$[MoO_2Cl(Cp')]$	**S5**	2	neat	50	24	15	16
12	**1**	**S5**	2	neat	50	24	25	this work

[a]See Reference section. [b]Numbers in brackets correspond to yield of second diastereomer. [c]Number in brackets corresponds to time for slower diastereomer. [d]After 24 h 8% conversion was observed.

of cyclooctene **S1** of 96% (Table 1, entry 7) within 1 h under optimized conditions (0.02 mol % **5**, 1 equiv TBHP, 80 °C, $C_2H_4Cl_2$).[18] Under these conditions **1** only yields 44% of epoxide after 1 h, and complete epoxidation is reached after 19 h (Table 1, entry 8). A similar activity to **1**−**4** was recently published for a series of bipyridine containing Mo(VI) complexes, the most active one reaching full conversion under neat conditions at 55 °C in less than 5 min (Table 1, entry 9).[17] A series of half-sandwich dioxo Mo(VI) complexes containing various cyclopentadienyl ligands (Cp) published by Romão, Kühn, and co-workers were all very active in epoxidation reactions (Table 1, entry 10), even surpassing the activity of MTO in one case.[16] Complexes **1**−**4** as well as the oxazoline complexes[18,21,33] can be obtained under standard laboratory conditions, whereas the bipyridine and Cp complexes are synthesized under exclusion of air and moisture. Furthermore, not only mono- and bidentate active ligand systems were published, but also tridentate systems, for example, a tridentate O,N,O-Schiff base complex (Table 1, entry 11).[35]

With the more challenging substrate styrene **S2** the selectivity of complexes **1**−**4** dropped significantly and is inferior to some previously published systems. At 55 °C and 5 h reaction time, the yield for styrene epoxide varied between 18 and 28% for complexes **1**−**4** (Table 2, entries 1−4). The low yield is caused by concomitant side reactions. One side product could be identified by GC-MS as benzaldehyd (<5%), the other one as 2-(*tert*-butoxy)-2-phenylethanol **6** (vide infra).

The problematic further reactivity of styrene oxide has also been observed in other published systems, with the main side product being identified as benzaldehyde.[18,33] In our case, we also observe a small amount of benzaldehyde by GC-MS (<5%). The other cleavage product from the styrene epoxide oxidation, formaldehyde,[36] was not observed. By in situ IR spectroscopy we could observe the formation of CO_2, which we attribute to a full oxidation of the initially formed formaldehyde.

dx.doi.org/10.1021/ic300648p | Inorg. Chem. 2012, 51, 7642−7649

The major side product (20−40%) was identified as *tert*-butyl benzoate **6** (Scheme 2), the product of *tert*-butanol (the end product from TBHP after oxygen transfer) and benzoic acid.[37] Benzoic acid is the final oxidation product from either styrene epoxide or styrene itself in a reaction series that starts with a C−C bond cleavage.

For **S3** good activities were observed for all four complexes, with conversions of 76−86% at 55 °C after 24 h (Table 3, entries 1−4) with high selectivity, since no side products were detected by GC-MS. We were also interested to test an unstrained internal olefin and screened the isomeric mixture of (*E*,*Z*)-**S4**. In this case complexes **1**−**4** also displayed good activity, converting all of (*E*,*Z*)-**S4** within 3 h at 55 °C (Table 3, Entries 5−8). For substrate (E,Z)-**S4** the formation of two different products corresponding to both diastereomers was observed (Figure 6). As displayed in the reaction profile in

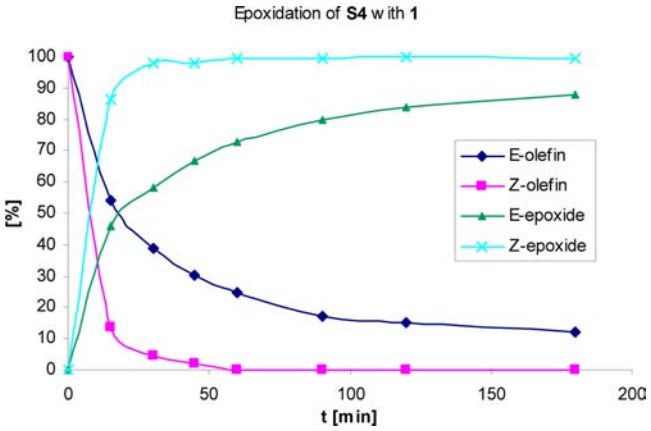


Figure 6. Epoxidation of (*E*,*Z*)-**S4** with complex **1**.

Figure 6, one isomer of **S4** reacts faster (■) than the other isomer (◆). Although not proven, we believe, from a steric point of view it is feasible that the Z-isomer of **S4** can approach the active Mo catalyst more easily than the E-isomer and is therefore converted faster. Comparing both isomers of **S4** to **S3** shows the internal, more electron-rich, olefin **S4** to be more reactive.

Lastly, we chose the very challenging substrate 1-octene **S5**, since terminal olefins are good model substrates for the important industrial epoxidation of propylene.[11] Epoxidation of **S5** with catalyst **1** leads to 25% selective conversion under neat conditions at 50 °C (Table 3, entry 12). In comparison, complex [$MoO_2Cl(Cp')$] reaches 15% yield of epoxide after 24 h in the same neat conditions (Table 3, entry 11).[16] Significantly better is complex [$MoO_2(hoz)_2$] (**5**) which converts 82% of **S5** to the epoxide within 3 h in $C_2H_4Cl_2$ at 80 °C (Table 3, entry 9).[18] Complex **1** shows no conversion under the latter conditions (Table 3, entry 10).

After the initial round of screening and testing it was apparent that out of the four complexes **1**−**4** catalyst **1** was displaying the best performance. Therefore we used catalyst **1** to further explore the catalytic performance by decreasing the catalyst loading from 2 mol % to 0.02 mol % (Table 4) in the epoxidation of model substrate cyclooctene **S1**. Experiments were performed at 55 °C in $CHCl_3$ or 80 °C in $C_2H_4Cl_2$ to study the influence of temperature. Interestingly, we found that our catalyst **1** does not perform as well as under the optimal conditions for [$MoO_2(hoz)_2$] (**5**).[18] At 80 °C in $C_2H_4Cl_2$ with 0.02 mol % catalyst loading and 1 equiv of TBHP the

Table 4. Epoxidation Results of Catalyst 1 with Substrate S1 at Different Catalyst Loadings[a]

mol %	yield [%]	*t* [h]	TON[b]	TOF [h^{-1}][c]
2	>99	0.03	50	1666
0.2	>99	0.5	500	3125
0.02	>99	4	5000	5000

[a]Conditions: $CHCl_3$, 55 °C, 3 equiv TBHP. [b]mol product/mol catalyst. [c]TON/time; at the time interval of highest conversion.

epoxidation of cyclooctene **S1** with catalyst **1** is slower than with **5** and does not reach completion within 5 h. However under our optimal conditions ($CHCl_3$, 55 °C, 3 equiv TBHP) **S1** gets fully converted by **1** within 4 h.

The catalyst stability of **1** was tested by ten repeated additions of aliquots of **S1** and TBHP (2 mol % **1**, $CHCl_3$, 55 °C, 1.5 equiv TBHP). In contrast to our above-described standard conditions, the repeated addition experiments were performed with 1.5 equiv of TBHP as initial tests with repeated additions of 3 equiv of TBHP increased the amount of side products, mainly the ring-opened diole. This was probably due to the increasing excess of TBHP that remained in the reaction after each new addition of substrate and TBHP. Therefore the amount of TBHP was reduced to 1.5 equiv of TBHP which resulted in higher selectivity. To counter the concomitant loss in catalyst activity with 1.5 equiv TBHP the temperature was raised from 25 to 55 °C in these experiments. Under these conditions conversion of cyclooctene **S1** took ∼90 min in the first six cycles and ∼120 min for the last 4 cycles to reach complete conversion. Cycles 9 and 10 were done after the reaction vial had been standing over the weekend at room temperature with no apparent loss in activity compared to cycles 7 and 8, which further demonstrates the stability of **1**. It seems that catalysts **1**−**4** have their optimal activity at 55 °C and 3 equiv of TBHP. Reducing the amount of TBHP to 1.5 equiv significantly increases the reaction times for all substrates under investigation. It also seems that $CHCl_3$ is the optimal solvent for epoxidation, also compared to the higher boiling solvent $C_2H_4Cl_2$. We also investigated the use of H_2O_2 as oxidant in different solvents but all attempts were unsuccessful.

Theoretical Calculations. For a better understanding of the influence of the two found isomeric forms in complexes **1** and **5** on the catalytic properties the different bonding situations of the two isolated and two hypothetical isomers shown in Figure 7 were investigated by DFT calculations employing the popular hybrid density functional B3-LYP.

Aryloxide-pyrazole ligands, as demonstrated in this manuscript, coordinate in an asymmetric way to form the N,O-isomer (Figure 7, **1**(N,O)) whereas the oxazoline derivative was found to form the symmetric N,N-isomer (Figure 7, **5**(N,N)).[18,19] The results of these calculations showed that the *hypothetical* symmetric complex ***1****(N,N)* and the isolated complex **5**(N,N) feature two almost identical oxo groups in *trans* position to the nitrogen atom whereas the asymmetric isolated complex **1**(N,O) and the *hypothetical* complex ***5****(N,O)* exhibit two electronically different oxo groups.

Table 5 summarizes the calculated Shared Electron Numbers (SENs) for molybdenum-oxo functionalities O_1 and O_2 and the coordinating aryloxide ligands L as well as the natural charges of all three of these coordinating moieties around Mo in both systems **1** and **5**, respectively. The calculations reveal that the synthetically accessed oxazoline based complex **5**(N,N) features two electronically equivalent oxo groups whereas its asym-

dx.doi.org/10.1021/ic300648p | *Inorg. Chem.* 2012, 51, 7642−7649

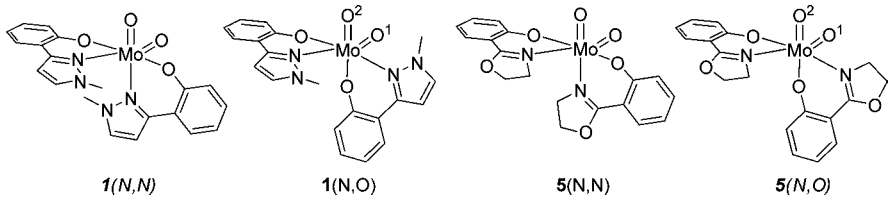


Figure 7. N,N- and N,O- isomers of *cis*-dioxo molybdenum(VI) complexes **1** and **5**. Hypothetical isomer labels are in *italic*. Terminal oxygen ligands for isolated complexes of **1** and **5** are labeled (see Table 5).

Table 5. Electronic Properties of N,N- and N,O-Isomers of *cis*-Dioxomolybdenum(VI) Complexes 1 and 5 at the B3-LYP def2-TZVP Level of Theory

	SEN[a]		natural charge				
complex	Mo•••O2[b]	Mo•••O1	Mo	O2[b]	O1	L2[c]	L1[c]
1(N,N)	1.085	1.084	1.834	−0.523	−0.524	−0.394	−0.397
1(N,O)	0.858	1.029	1.815	−0.632	−0.543	−0.303	−0.337
5(N,N)	1.061	1.061	1.805	−0.522	−0.522	−0.380	−0.380
5(N,O)	0.931	1.072	1.780	−0.589	−0.511	−0.335	−0.346

[a]Two center shared electron number (SEN) and atomic charges with multicenter corrections as calculated by population analysis based on molecular orbitals. [b]For the asymmetric complexes **1**(N,O) and *5(N,O)* O2 represents the oxo group in trans position to a phenolate oxygen. [c]Natural charges summed up over one ligand. For the asymmetric complexes **1**(N,O) and **5**(N,O) L2 represents the ligand with the phenolate oxygen in trans position to the oxo group.

metric pyrazole analog **1**(N,O) exhibits two different oxo groups. The SEN in both oxo groups of **5**(N,N) is with 1.061 significantly higher in comparison to the oxo groups in asymmetric complex **1**(N,O) (O1 SEN = 1.029; O2 SEN = 0.858) pointing to generally weaker bonds in the latter. This is remarkable since this is not reflected in the experimentally determined Mo−O bond lengths in **1**(N,O) as they are identical. Natural population analysis further indicates a shift of electron density from the Mo═O1 bond to the O2 atom leading to a more nucleophilic oxo group. Thereby, molybdenum becomes slightly more positive and, hence, more electrophilic. Furthermore, in the *hypothetic* asymmetric oxazoline complex *5(N,O)* the Mo═O1 bond is significantly stronger in comparison to the pyrazole complex **1**(N,O) (SEN 1.084 vs 1.029). In summary, compound **5**(N,N) exhibits less polar and stronger molybdenum oxo bonds compared to those in **1**(N,O). The natural charge on molybdenum is lower in **5**(N,N) compared to **1**(N,O) and is even lower in the hypothetical *5(N,O)* consistent with a decreasing electrophilic nature of the molybdenum atom. The catalytic activity under similar conditions is higher with **5**(N,N) compared **1**(N,O). Possibly, the lower electrophilic character of the molybdenum atom in **5**(N,N) is beneficial for the oxygen atom transfer to the olefin. Thus, the hypothetical *5(N,O)* compound would potentially be more reactive.

Consequently, DFT calculations suggest that the activity of the investigated catalysts depends not only on the electronic properties of the ligands, but also on the isomeric form of the complexes. Therefore, in designing new ligands for catalysts the rationale should also include the control of the appropriate isomer. The preference for one isomer over the other with regard to the ligand system used can not be answered by these calculations and remains a topic for future investigations.

CONCLUSIONS

Within this paper we present aryloxide-pyrazole ligated dioxo Mo(VI) complexes **1**−**4**. Complexes **1**−**4** are easy to synthesize, air- and moisture stable, and display good activity in the epoxidation of olefins. Terminal (**S3**) as well as internal (**S4**) olefins are cleanly converted to the respective epoxides. Challenging substrates like 1-octene do also show some conversion under neat conditions, although an improved activity would be desirable. With catalyst **1** and the benchmark substrate cyclooctene **S1** high activity reflected by a TOF of ∼5000 h^{-1} can be achieved. Only with styrene **S2** all four catalysts displayed poor selectivity similar to many other published systems. When compared to the closely related aryloxide-oxazoline complex **5**, complexes **1**−**4** display lower reactivity in olefin epoxidation. We attribute this to the higher electrophilic nature of molybdenum in complexes **1**−**4** as demonstrated by DFT calculations for **1** which is shown by the analysis of partial charges. Possibly, the lower electrophilic character of the molybdenum atom in **5**(N,N) is beneficial for the oxygen atom transfer to the olefin. This suggests that asymmetric coordination of ligands like in **1**(N,O) could increase the overall activity if the electrophilicity on molybdenum is lower as calculated for *5(N,O)*. However these initial DFT results do not explain which isomer is formed preferably.

EXPERIMENTAL SECTION

General. The metal precursor $[MoO_2(acac)_2]$ was purchased from Sigma Aldrich and used as received. Ligands **HL1**−**HL4** were prepared according to literature.[20,31] Chemicals were purchased from commercial sources and were used without further purification. NMR spectra were recorded with a Bruker (300 MHz) instrument. Chemical shifts are given in ppm and are referenced to residual protons in the solvent. Signals are described as s (singlet), bs (broad singlet), d (doublet), dd (doublet of doublet), t (triplet), m (multiplet) and coupling constants (J) are given in Hertz (Hz). Elemental analyses were carried out using a Heraeus Vario Elementar automatic analyzer. Mass spectra were recorded with an Agilent 5973 MSD − Direct Probe using the EI ionization technique. Samples for infrared spectroscopy were directly measured on a Bruker Optics ALPHA FT-IR Spectrometer equipped with an ATR diamond probe head. GC-MS measurements were performed on an Agilent 7890 A with an Agilent 19091J−433 column coupled to a mass spectrometer type Agilent 5975 C. Crystallographic data (excluding structure factors) for **1**−**3** were deposited with the Cambridge Crystallographic

dx.doi.org/10.1021/ic300648p | Inorg. Chem. 2012, 51, 7642−7649

Data Center as supplementary publication no. CCDC-851222 (**1**), CCDC-851223 (**2**), CCDC-850224 (**3**).

Synthesis of complex **1**: $[MoO_2(acac)_2]$ (486 mg, 1.43 mmol) was dissolved in a minimum amount of methanol with gentle heating. To this, a solution of 500 mg (2.87 mmol) **HL1** in methanol (10 mL) was added at room temperature and stirred for 16 h. The yellow precipitate was filtered and washed with cold methanol to give 440 mg (0.927 mmol, 65%) of analytical pure complex **1**. ^{1}H NMR (d_4-MeOH, 300 MHz, 55 °C) δ: 7.62 (m, 4H), 7.16 (m, 2H), 6.88 (m, 4H), 6.71 (m, 2H), 4.03 (bs, 6H). IR (ATR, cm^{-1}): 1238.54, 916.40, 886.60, 854.85, 787.94, 756.58, 412.08. EI-MS: m/z 476.04 [M^+]. Anal. Calcd. for $C_{20}H_{18}MoN_4O_4$ (474.34): C 50.64, H 3.82, N 11.81; found: C 50.23, H 3.73, N 11.73.

Synthesis of complex **2**: $[MoO_2(acac)_2]$ (433 mg, 1.33 mmol) was dissolved in a minimum amount of methanol with gentle heating. To this a solution of 500 mg (2.66 mmol) **HL2** in methanol (10 mL) was added at room temperature and stirred for 16 h. The orange precipitate was filtered and washed with cold methanol to give 517 mg (1.03 mmol, 72%) of analytical pure complex **2**. ^{1}H NMR (d_4-MeOH, 300 MHz, 55 °C) δ: 7.63 (m, 2H), 7.42 (m, 2H), 6.99 (m, 2H), 6.80 (m, 2H), 6.70 (m, 2H), 2.28 (s, 6H), 2.10 (s, 6H). IR (ATR, cm^{-1}): 1510.08, 1245.48, 867.58, 809.06, 771.82, 549.67. EI-MS: m/z 504.07 [M^+]. Anal. Calcd. for $C_{22}H_{22}MoN_4O_4$ (502.39): C 52.60, H 4.41, N 11.15; found: C 52.33, H 4.40, N 11.13.

Synthesis of complex **3**: $[MoO_2(acac)_2]$ (364 mg, 1.12 mmol) was dissolved in a minimum amount of methanol with gentle heating. To this a solution of 500 mg (2.23 mmol) **HL3** in methanol (10 mL) was added at room temperature and stirred for 16 h. The brownish precipitate was filtered and washed with cold methanol to give 464 mg (0.806 mmol, 72%) of analytical pure complex **3**. ^{1}H NMR (d_4-MeOH, 300 MHz, 55 °C) δ: 8.40 (m, 2H), 7.73 (m, 7H), 7.40 (m, 7H), 7.08 (m, 2H), 6.79 (m, 2H), 4.38 (s, 3H), 3.97 (s, 3H). IR (ATR, cm^{-1}): 1372.29, 1341.59, 909.30, 886.30, 821.50, 771.43, 733.74, 671.5, 403.13. EI-MS: m/z 576.07 [M^+]. Anal. Calcd. for $C_{28}H_{22}MoN_4O_4$ (574.46): C 58.54, H 3.86, N 9.75; found: C 58.34, H 3.93, N 9.39.

Synthesis of complex **4**: $[MoO_2(acac)_2]$ (364 mg, 1.12 mmol) was dissolved in a minimum amount of methanol with gentle heating. To this a solution of 500 mg (2.23 mmol) **HL4** in methanol (10 mL) was added at room temperature and stirred for 16 h. The red-brown precipitate was filtered and washed with cold methanol to give 489 mg (0.851 mmol, 76%) of analytical pure complex **4**. ^{1}H NMR (d_4-MeOH, 300 MHz, 55 °C) δ: 8.09 (bs, 2H), 7.75 (m, 6H), 7.40 (t, 2H), 7.28 (t, 2H), 7.18 (d, 2H), 6.68 (bs, 2H), 4.10 (s, 6H). IR (ATR, cm^{-1}): 1235.52, 913.93, 874.76, 815.14, 791.97, 742.46, 592.56, 552.71. EI-MS: m/z 574.46 [M^+]. Anal. Calcd. for $C_{28}H_{22}MoN_4O_4$ (574.46): C 58.54, H 3.86, N 9.75; found: C 58.25, H 3.85, N 9.72.

Epoxidation: In a typical epoxidation experiment the respective catalyst was stirred in 3 mL of $CHCl_3$ and substrate was added. After the respective experiment temperature was reached TBHP was added to start the reaction and samples for GC-MS were withdrawn. GC samples were diluted with ethyl acetate and mesitylene was used as internal standard.

Computational Details. The geometries of two isomers (N,N- and N,O-isomer) of complexes **1** and **5** were optimized in the gas phase using the hybrid density functional B3LYP[38−40] as implemented in the TURBOMOLE program. First geometry optimizations were performed with the standard double-ζ quality basis def2-SVP.[41,42] The geometries were then reoptimized with the larger def2-TZVP basis.[42,43] Input geometries were obtained from crystal structures if available. The stationary points were confirmed as minima by calculation of analytical harmonic frequencies. Natural Population Analysis (NPA)[44] as well as calculations of the shared electron number (SEN)[45] were performed with the larger def2-TZVP basis.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Selected bond distances and angles for **1**, **2**, and **3**, crystal data for **1**, **2**, and **3**, and ORTEP plots of **1**, **2**, and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: nadia.moesch@uni-graz.at.

Notes

The authors declare no competing financial interest.

■ REFERENCES

(1) Hille, R. *Eur. J. Inorg. Chem.* **2006**, 1913−1926.
(2) Romao, M. J. *Dalton Trans.* **2009**, 4053−4068.
(3) Romao, M. J.; Archer, M.; Moura, I.; Moura, J. J. G.; LeGall, J.; Engh, R.; Schneider, M.; Hof, P.; Huber, R. *Science* **1995**, *270*, 1170−1176.
(4) Hille, R. *Arch. Biochem. Biophys.* **2005**, *433*, 107−116.
(5) Enemark, J. H.; Cooney, J. J. A.; Wang, J.-J.; Holm, R. H. *Chem. Rev.* **2004**, *104*, 1175−1200.
(6) Sugimoto, H.; Tsukube, H. *Chem. Soc. Rev.* **2008**, *37*, 2609−2619.
(7) Schulzke, C. *Eur. J. Inorg. Chem.* **2011**, 1189−1199.
(8) Hine, F. J.; Taylor, A. J.; Garner, C. D. *Coord. Chem. Rev.* **2010**, *254*, 1570−1579.
(9) Lyashenko, G.; Saischek, G.; Judmaier, M. E.; Volpe, M.; Baumgartner, J.; Belaj, F.; Jancik, V.; Herbst-Irmer, R.; Mösch-Zanetti, N. C. *Dalton Trans.* **2009**, 5655−5665.
(10) Judmaier, M. E.; Wallner, A.; Stipicic, G. N.; Kirchner, K.; Baumgartner, J.; Belaj, F.; Mösch-Zanetti, N. C. *Inorg. Chem.* **2009**, *48*, 10211−10221.
(11) Bregeault, J.-M. *Dalton Trans.* **2003**, 3289−3302.
(12) Deubel, D. V.; Frenking, G.; Gisdakis, P.; Herrmann, W. A.; Roesch, N.; Sundermeyer, J. *Acc. Chem. Res.* **2004**, *37*, 645−652.
(13) Kühn, F. E.; Santos, A. M.; Herrmann, W. A. *Dalton Trans.* **2005**, 2483−2491.
(14) Sheng, M. N.; Zajacek, G. J. Method for production of epoxides. GB Patent 1136923, 1968.
(15) Kollar, J. Catalytic epoxidation of an olefinically unsaturated compound using an organic hydroperoxide as an epoxidizing agent. U.S. Patent 3,350,422, 1967.
(16) Abrantes, M.; Santos, A. M.; Mink, J.; Kühn, F. E.; Romao, C. C. *Organometallics* **2003**, *22*, 2112−2118.
(17) Günyar, A.; Betz, D.; Drees, M.; Herdtweck, E.; Kühn, F. E. *J. Mol. Catal. A: Chem.* **2010**, *331*, 117−124.
(18) Bagherzadeh, M.; Tahsini, L.; Latifi, R.; Woo, L. K. *Inorg. Chim. Acta* **2009**, *362*, 3698−3702.
(19) Bagherzadeh, M.; Tahsini, L.; Latifi, R.; Ellern, A.; Woo, L. K. *Inorg. Chim. Acta* **2008**, *361*, 2019−2024.
(20) Catalan, J.; Fabero, F.; Claramunt, R. M.; Santa Maria, M. D.; Foces-Foces, M. d. l. C.; Hernandez Cano, F.; Martinez-Ripoll, M.; Elguero, J.; Sastre, R. *J. Am. Chem. Soc.* **1992**, *114*, 5039−5048.
(21) Brito, José A.; Gómez, M.; Muller, G.; Teruel, H.; Clinet, J.-C.; Duñach, E.; Maestro, Miguel A. *Eur. J. Inorg. Chem.* **2004**, 4278−4285.
(22) Kandasamy, K.; Singh, H. B.; Butcher, R. J.; Jasinski, J. P. *Inorg. Chem.* **2004**, *43*, 5704−5713.
(23) Herrmann, W. A.; Fischer, R. W.; Marz, D. W. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1638−1641.
(24) Herrmann, W. A.; Wang, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1641−1643.
(25) Rudolph, J.; Reddy, K. L.; Chiang, J. P.; Sharpless, K. B. *J. Am. Chem. Soc.* **1997**, *119*, 6189−6190.
(26) Ferreira, P.; Xue, W.-M.; Bencze, E.; Herdtweck, E.; Kühn, F. E. *Inorg. Chem.* **2001**, *40*, 5834−5841.
(27) Qiu, C.-J.; Zhang, Y.-C.; Gao, Y.; Zhao, J.-Q. *J. Organomet. Chem.* **2009**, *694*, 3418−3424.

(28) Schröckeneder, A.; Traar, P.; Raber, G.; Baumgartner, J.; Belaj, F.; Mösch-Zanetti, N. C. *Inorg. Chem.* **2009**, *48*, 11608−11614.
(29) Traar, P.; Schachner, J. A.; Steiner, L.; Sachse, A.; Volpe, M.; Mösch-Zanetti, N. C. *Inorg. Chem.* **2011**, *50*, 1983−1990.
(30) Grünwald, K. R.; Saischek, G.; Volpe, M.; Mösch-Zanetti, N. C. *Inorg. Chem.* **2011**, *50*, 7162−7171.
(31) Catalan, J.; Del Valle, J. C.; Claramunt, R. M.; Maria, M. D. S.; Bobosik, V.; Mocelo, R.; Elguero, J. *J. Org. Chem.* **1995**, *60*, 3427−3439.
(32) Sorrell, T. N.; Ellis, D. J.; Cheesman, E. H. *Inorg. Chim. Acta* **1986**, *113*, 1−7.
(33) Gómez, M.; Jansat, S.; Muller, G.; Noguera, G.; Teruel, H.; Moliner, V.; Cerrada, E.; Hursthouse, M. *Eur. J. Inorg. Chem.* **2001**, 1071−1076.
(34) Wong, Y.-L.; Tong, L. H.; Dilworth, J. R.; Ng, D. K. P.; Lee, H. K. *Dalton Trans.* **2010**, *39*, 4602−4611.
(35) Rezaeifard, A.; Sheikhshoaie, I.; Monadi, N.; Stoeckli-Evans, H. *Eur. J. Inorg. Chem.* **2010**, 799−806.
(36) Spyroudis, S.; Varvoglis, A. *J. Org. Chem.* **1981**, *46*, 5231−5233.
(37) Thiel, W. R.; Angstl, M.; Hansen, N. *J. Mol. Catal. A: Chem.* **1995**, *103*, 5−10.
(38) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372−1377.
(39) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652.
(40) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−789.
(41) Schäfer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571.
(42) Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297−3305.
(43) Weigend, F.; Häsler, M.; Patzelt, H.; Ahlrichs, R. *Chem. Phys. Lett.* **1998**, *294*, 143−152.
(44) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735−746.
(45) Ehrhardt, C.; Ahlrichs, R. *Theor. Chim. Acta* **1985**, *68*, 231−245.