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Gas-phase ligand binding to Jacobsen's manganese salen catalyst: Functional group and steric effects

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ABSTRACT

Gas-phase equilibrium measurements have been used to determine the relative binding affinities of 18 ligands to Jacobsen's manganese salen catalyst. The group of ligands spans 5.7 kcal/mol and includes seven functional groups (alcohol, ketone, ester, acyclic ether, cyclic ether, epoxide, and amine). The data follow general trends seen in other gas-phase metal cation affinities, but are influenced to a much greater extent by steric effects. For example, a 2° amine is a stronger binder than a 1° amine (as typical for gas-phase cation binding), but a 3° amine is a much weaker binder due to excessive crowding with the bulky salen ligand. The impact of steric effects was also explored with computational modeling at the B3LYP/6-311+G(d,p)/B3LYP/6-31G(d) level. The study demonstrates the utility of using mass spectrometry to probe the ligand binding characteristics of sterically demanding, metal-centered catalysts.

1. Introduction

Jacobsen's manganese salen catalyst and subsequent variations have proven to be very valuable tools in enantioselective synthesis and the kinetic resolution of enantiomers [1–3]. Moreover, it is a model for an entire class of important enantioselective catalysts that incorporate a reactive metal center with a bulky, polydentate chiral ligand. Here, we report the first systematic gas-phase ligand binding affinities of any catalyst of this general type. An advantage of our gas-phase system is that it allows us to measure with good accuracy ligand binding affinities in the absence of competition with solvent or reaction processes, and recently several studies have established links between the characteristics of catalysts in the gas phase and solution [4–19]. Although there have been many careful studies of gas-phase binding with isolated metal centers, the approach generally has not been extended to real-world catalysts [20].

Previously, we have used mass spectrometric methods to show that derivatives of Jacobsen's catalyst preferentially bind to one enantiomer of 1-phenylethanol in the gas phase and this is the same enantiomer that it preferentially oxidizes in solution [21]. In the present study, the same gas-phase equilibrium methods are employed, but the target ligands span a range of functional groups. The goal is to probe general functional group preferences as well as steric effects in binding to the manganese. The results provide a general protocol for a relatively rapid method of screening the intrinsic binding abilities of potential ligands. The experiment is shown in Scheme 1.

2. Methods

The cationic catalyst is formed by electrospray ionization of the corresponding chloride salt of the R,R enantiomer of the Jacobsen manganese salen catalyst (referred to as Mn(salen)$^+$ in text). Using modified Finnigan LCQ or Deca quadrupole ion trap mass spectrometers, the manganese salen cation is isolated and then allowed to react with a mixture of the two ligands that had been added to the helium buffer gas of the ion trap [22]. The gas mixtures are prepared in a custom gas manifold and partial ligand pressures of 10^{-5}–10^{-8} Torr were used. In initial surveys, reaction times were systematically varied to determine when the systems had reached equilibrium. Generally 2–8 s were required to produce product distributions that did not change, beyond the experimental uncertainty, with additional reaction time. A typical plot of relative intensity versus time is given in Fig. 1. Equilibration rate was a limiting factor and species with affinities higher than those reported here had equilibration times beyond our instrument's limit of 10 s. All reagents and gases were obtained from commercial sources in the highest available purity and used without further purification.

The affinity ladder was developed from the consensus of a set of pair-wise equilibrium measurements that were employed in an over-determined, least-squares analysis. Using greater than the minimum number of pair-wise measurements to establish the ladder, it was possible to assess the reproducibility of the data and

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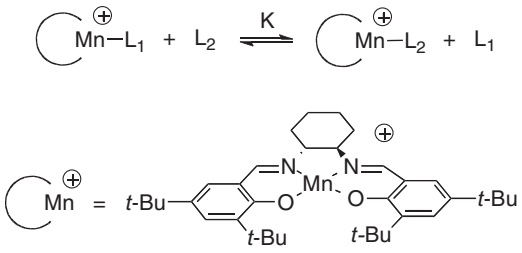

Scheme 1. Manganese salen reaction systems.

identify problem cases [23]. In the final analysis, errors were less than 0.1 kcal/mol in all cases where ligand affinities were linked by more than one set of measurements.

Computational data were obtained using the Spartan02 [24] and Gaussian03 [25] quantum mechanical suites. Initially, the PM3 force-field in Spartan02 was used to generate up to 100 lowest-energy structures from a Monte Carlo conformational search on the complexes of the Jacobsen catalysts with diethylamine and triethylamine. Each of these structures were then optimized at the B3LYP/6-31G(d) level in Gaussian03 and the most stable one was identified. Quintet states were used in the analysis [21], but data was also obtained for triplets and singlets (less stable at this level of theory [26]). Diethylamine and triethylamine were subjected to a similar conformational search/optimization strategy. Single-point calculations were completed at the B3LYP/6-311+G(d,p) level. Given the semi-quantitative nature of the theoretical level, no thermal or zero-point energy corrections were made.

3. Results and discussion

3.1. Factors affecting the Mn(salen)$^+$ affinities

Relative binding free energies are given in Table 1 and span approximately 6 kcal/mol from diethyl ether to diethylamine. In gas-phase work, affinities often have been associated with enthalpies of reaction and basicities with free energies of reaction (though basicity is an awkward term for metal binding). Here, all data refer to free energy changes, but will be referred to as affinities for the manganese system (basicity will be used with lithium for consistency with the original work). The values are from the best least-squares fit of a series of redundant pair-wise measurements (*i.e.*, a network of pair-wise measurements were used rather than a simple ladder scale). Errors in the least-squares fit were on the order of 0.1 kcal/mol. Three factors play a significant role in the trends in ligand affinity: functional group, polarizability, and steric effects. Each factor is discussed below.

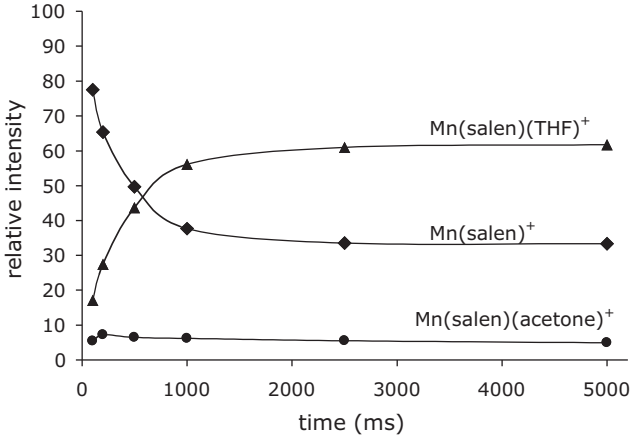

Fig. 1. Plot of relative ion intensities as a function of time in reaction of Mn(salen)$^+$ with acetone and THF in a 1:1 ratio. For greater accuracy in the measurements, a 10:1 ratio of acetone: THF was used in determining the equilibrium constant. Mixing ratios other than 1:1 were used in most cases for this reason.

Table 1
Relative binding affinities to Jacobsen's manganese catalyst, Mn(salen)$^+$, and corresponding gas phase basicities and lithium cation basicities of ligands in study.[a]

Ligand	Mn(salen)$^+$	H$^+$	Li$^+$
Diethylamine	5.7	28.7	−1.2[b]
Isopropylamine	4.5	21.5	−2.0[b]
2-MeTHF	4.1	3.0	1.0
3-Pentanone	4.1	2.0	3.4
THF	4.0	−1.1	−0.6
Ethyl acetate	3.4	1.3	2.7
Heptanol	3.1	−7.0[c]	NA
Dibutyl ether	3.1	4.6	3.2
(−) *Trans* 2,3-epoxybutane	3.1	−12.9[d]	NA
(+) *Trans* 2,3-epoxybutane	3.0	−12.9[d]	NA
3-Pentanol	2.9	NA	NA
Hexanol	2.8	−7.5[c]	NA
Acetone	2.5	−4.1	2.0
Isopropanol	1.2	−8.7	−1.0
Tert-butanol	1.1	−6.4	0.0
Triethylamine	0.8	36.0	−1.3[b]
Ethanol	0.3	−13.0	−2.9
Diethyl ether	0[e]	0	0

[a] Values in kcal/mol and refer to relative free energies at approximately 300 K[27] for (R,R) enantiomer of Mn(salen)$^+$ catalyst. Uncertainties of less than 0.1 kcal/mol are expected based of the least squares fit of the equilibrium network. Gas phase basicities (298 K) from Ref. [28] and lithium cation basicities (373 K) from Ref. [29]. NA, not available.
[b] Values for methyl analogs (*i.e.*, Me_2NH, $MeNH_2$, and Me_3N).
[c] Values from Ref. [30].
[d] Values for oxirane.
[e] Absolute values can be determined, but have greater uncertainties. The free energy of Mn(salen)$^+$ binding to diethyl ether is estimated as 10.4 ± 0.5 kcal/mol from the association equilibrium. The absolute proton and lithium free binding energies of diethyl ether are 191.0 [28] and 33.3 kcal/mol [29].

3.1.1. Functional group

In this study, seven functional groups are investigated (ethers are viewed as three groups: acyclic, cyclic, and epoxide). In representative species with roughly similar sizes and steric bulk, the following trend emerges: amine (isopropyl amine) > cyclic ether (THF) ≈ ketone (3-pentanone) > ester (ethyl acetate) > epoxide (2,3-epoxybutane) > alcohol (1-hexanol) > acyclic ether (diethyl ether). This pattern generally parallels other ligand affinity scales, but there are several exceptions (see below). The trend with the ethers and alcohols suggests a balance between electron-donating ability and steric effects. The cyclic ethers benefit from both factors and are favored, whereas steric effects diminish the binding to acyclic ethers and weaker electron-donating ability diminishes binding to alcohols.

3.1.2. Polarizability

Size effects are very evident. The progressions from 2-propanol to 3-pentanol (2 added carbons), acetone to 3-pentanone (2 added carbons), and diethyl ether to dibutyl ether (4 added carbons) involve increases in ligand binding of 1.7, 1.6, and 3.1 kcal/mol, respectively. This trend is also seen in the subtle change from hexanol to heptanol, which leads to a 0.3 kcal/mol increase in ligand binding. The effect is more subtle in the smaller alcohols and there less than a 1 kcal/mol increase from ethanol to isopropanol and *tert*-butanol, which have similar affinities. Here, steric effects must be playing a role (see below). Polarizability is well known to be important in gas-phase binding to cations and similar trends are seen in gas phase basicities and lithium cation basicities (Table 1). As one might expect, the impact of ligand polarizability is greater in bond-

ing to protons because more charge will be transferred to the ligand than with Mn(salen)$^+$. For example, the preference for 3-pentanone over acetone is over 6 kcal/mol and the preference for dibutyl ether over diethyl ether is 4.6 kcal/mol on the gas phase basicity scale. The effect of polarizability is about the same in the Mn(salen)$^+$ and lithium cation scales.

3.1.3. Steric effects

The most dramatic example of a steric effect is seen in the amines. The secondary amine, diethylamine, has the highest affinity in the set and is 1.2 kcal/mol stronger than the 1° amine, isopropylamine; however, the 3° amine, triethylamine, is one of the weakest in the set (4.9 kcal/mol weaker than diethylamine). This result clearly suggests that the 3° amine is too sterically demanding for the crowded salen ligand. When more crowded 3° amine bases are used, such as Hunig's base (N,N-diisopropylethylamine), we see no evidence of binding under our conditions. Molecular modeling on the diethylamine and triethylamine complexes of the catalyst was used to explore the nature of the steric problem with the 3° amine. The size of the systems limits computational options and we used PM3 in a Monte Carlo search to obtain up to 100 conformations of the complexes, which were then re-optimized at a modest level (B3LYP/6-31G(d)). The best conformation for each complex at this level is shown in Fig. 2 (see Section 2 for additional computational details). The structures show that the third group on the amine causes substantial steric crowding. In the diethylamine complex, the N–H bond of the diethylamine is directed toward the bulky *t*-butyl groups of the salen ligand, causing no steric crowding. In the triethylamine complex, this is not an option and the 3° amine folds its alkyl groups back to avoid the *t*-butyl groups of the salen. This causes crowding within the triethylamine group (added gauche interactions) and overall, interferes with the interaction of the amine with the manganese (increases Mn–N distance from 2.31 Å to 2.50 Å and leads to greater puckering of the Mn atom above the salen plane – compare (b) and (d)). The structures in Fig. 2 provide a clear rationale for the dramatic drop in affinity when the amine becomes tertiary. The calculations indicate a preference of about 10 kcal/mol at the B3LYP/6-311+G(d)//B3LYP/6-31G(d) level for the diethylamine complex (9 kcal/mol at the (BP86/6-311+G(d)//B3LYP/6-31G(d) level). This is nearly twice the preference observed in the experimental studies. The discrepancy is not surprising in that the B3LYP functional, as well as other DFT functionals, are known to overestimate steric effects because they underestimate the magnitude of mid-range van der Waals attractions [31]. Unfortunately, high-level, ab initio-based calculations that might accurately assess the steric interactions as well as characterize the bonding to manganese are not practical in a system of this size [26]. In any case, the computational data support the experimental result favoring the 2° amine, and the steric interactions in Fig. 2 point to the source of the problem with the 3° amine. As noted above, typical steric effects are also seen in the preference for THF over diethyl ether (4 kcal/mol). In addition, the enhanced affinity of 2-methyltetrahydrofuran over THF is only 0.1 kcal/mol, which suggests that steric effects mainly counter the advantages of the larger, more polarizable ether. A similar effect is seen with isopropanol and *tert*-butanol, where the larger, more polarizable alcohol has a slightly lower affinity. In addition, ethanol's affinity is less than 1 kcal/mol smaller than these larger, more bulky alcohols, indicating that steric effects are competing with polarizability effects. Overall, the data point to severe steric effects for a tertiary group coordinating to the manganese (*e.g.*, triethylamine) and modest ones when the alkyl substituent is separated from the coordinating atom by a carbon group (*e.g.*, 1°, 2°, and 3° alcohols). These data are consistent with scales of ligand steric effects, which suggest that ligand repulsion energies rise most sharply for an addition of an alkyl group at nitrogen than for an increase in the size of a particular alkyl group. Tabulated ligand repulsion energies for ethylamine, diethylamine, and triethylamine are 32, 73, and 111 kcal/mol, respectively, whereas the transition from ethylamine to *t*-butylamine causes only a small increase (from 32 to 50 kcal/mol) [32]. As noted above, the binding pocket in the Jacobsen catalyst is not symmetric so we see an even more dramatic effect in going to the 3° amine than the ligand repulsion energies suggest (they are based on a symmetric binding pocket).

This salen ligand is chiral so it potentially will differentially bond to the two enantiomers of a chiral ligand. In Table 1, the two enantiomers of *trans* 2,3-epoxybutane are included. These are interesting species because they are examples of the products from Mn(salen)$^+$ catalyzed epoxidations. There is a small, but reproducible difference between the enantiomers (in these experiments, a larger set of repeats were completed and a single, shared reference was used for both enantiomers, which greatly increased the precision of the relative measurement – with this approach, differences in binding as small as 0.05 kcal/mol can be identified). The lack of a significant preference though is not a surprise because the groups that define the chirality in the epoxide are small (methyl) and located outside the region that we have identified as sterically crowded (*i.e.*, they are two atoms away from the coordinating atom). In addition, we have previously shown that gas-phase stereoselectivity with Jacobsen's catalyst is limited when binding to small ligands such 2-butanol, but much larger with a bulkier ligand, 1-phenylethanol [21].

3.2. Comparisons to other cation/ligand scales

Comparisons to other affinity scales offer insights into the nature of the binding in the Mn(salen)$^+$ systems. In Table 1, data are also given for gas phase basicities and lithium cation basicities. At first glance, there is little correlation between the scales (Fig. 3); however, some patterns are evident. As has been observed previously, metal ion affinities span a more narrow range than gas phase basicities. For these ligands, the basicity scale spans over 35 kcal/mol whereas the Mn(salen)$^+$ and Li$^+$ scales span only 5–6 kcal/mol.

3.2.1. Comparison to gas phase basicities

Aside from the compression of the Mn(salen)$^+$ scale, there are significant shifts linked to functional groups. First, alcohols are systematically preferred over ethers in the manganese scale. For example, hexanol is favored by 2.8 kcal/mol over diethyl ether on the manganese scale, but disfavored by 7 kcal/mol on the proton scale. This is likely a steric issue and in the Mn(salen)$^+$ scale, the advantage of two polarizable groups at the coordination center (ether) is outweighed by the steric disadvantage of more bulk at this center. Second, epoxides are preferred over acyclic ethers in the Mn(salen)$^+$ scale. Again steric effects are outweighing effects related to the intrinsic basicity of the ligand (strain/rehybridization reduces the proton basicity of the epoxide oxygen). Third, there is an advantage to bonding to carbonyl species in the Mn(salen)$^+$ system. For example, acetone is favored over diethyl ether by 2.5 kcal/mol in binding to manganese and disfavored by 4.1 in binding to a proton. A combination of steric effects disfavoring ethers in the Mn(salen)$^+$ system and π-binding effects favoring ketones are likely here.

3.2.2. Comparisons to lithium cation basicities

First, the Li$^+$ scale appears to be slightly more compressed than the Mn(salen)$^+$ scale. Second, the steric effects seen in the manganese scale are absent in the lithium scale, presumably because they are only realized in crowded metal systems. For example there is no prejudice against 3° amines and all the amines seem to have about the same affinity on the Li$^+$ scale. There is no advantage

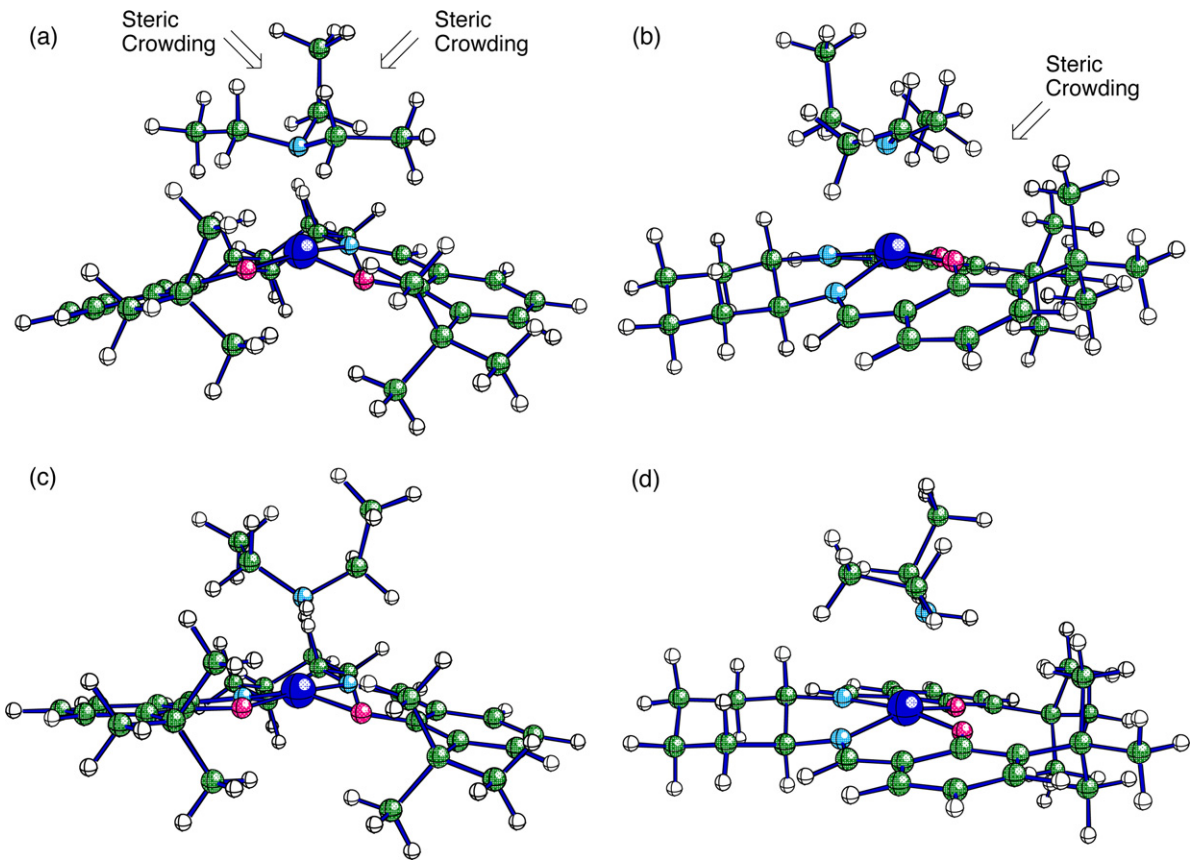

Fig. 2. Best B3LYP/6-31G(d) conformations for Mn(salen)$^+$ complexes of triethylamine and diethylamine. Projections (a) and (b) are front and side views of triethylamine complex, whereas (c) and (d) are front and side views of diethylamine complex. Amine ligand is above dark blue manganese atom. Carbon is green, oxygen is red, nitrogen is light blue, manganese is dark blue, and hydrogen is white. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

to the cyclic ethers in the lithium scale (diethyl ether and THF are about the same), and there is a significant preference for 2-methyltetrahydrofuran over THF, as expected based on its higher polarizability. With alcohols and ethers, the lithium system shows a preference for ethers, presumably due to their greater electron-donating ability, but this is reversed in the Mn(salen)$^+$ system due to the previously noted steric effects. The lack of direct comparisons in the amine data (see footnotes in Table 1) limits the depth of the analysis, but the results suggest manganese has a higher affinity for nitrogen-centered ligands (relative to oxygen-centered) than lithium does. This is consistent with expectations based on hard/soft acid/base theory.

4. Summary

This is the first broad survey of the gas-phase, ligand-binding preferences of a metal cation bearing a fixed, polydentate ligand. The data indicate that general metal/ligand bonding trends persist

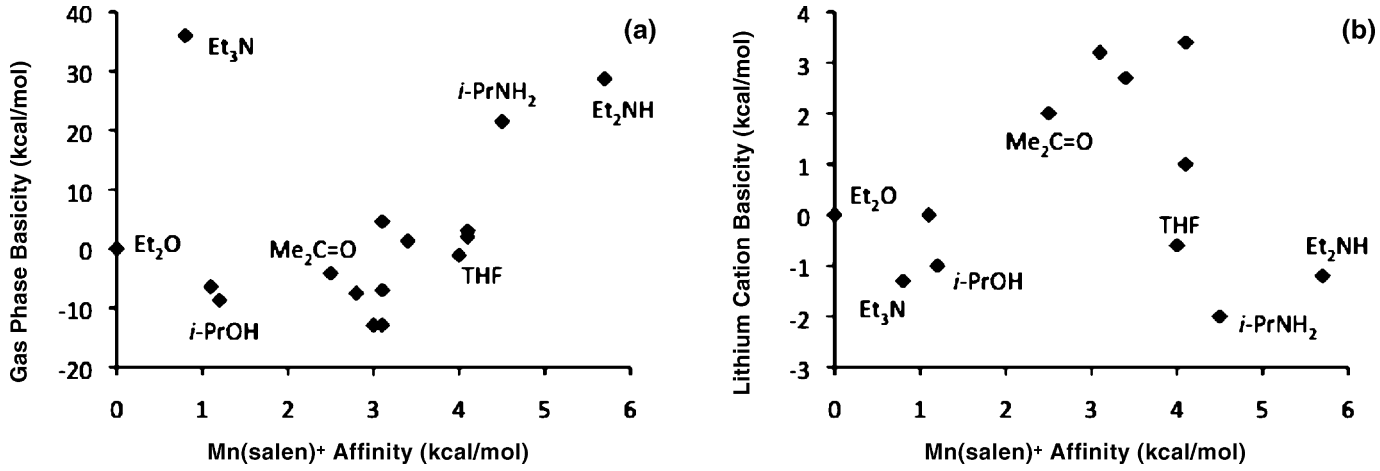

Fig. 3. Plots of (a) gas phase basicity and (b) lithium cation basicity vs. Mn(salen)$^+$ affinity. In each case, the scales are referenced to diethyl ether with an affinity of 0 kcal/mol. Selected species are labeled.

in these species, but that typical enantioselective catalysts of this general type can have significant steric demands that greatly alter the binding patterns in ligand affinities. The data also indicate that mass spectrometry is a useful alternative for studying ligand affinities in common catalysts bearing large, polydentate ligands and can give clear insights into the steric demands of these catalysts. Overall, the study suggests opportunities for using gas-phase studies to survey the utility of potential catalyst ligands.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ijms.2011.05.008.

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