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On the modulation of N_2 activation from molecular orbitals viewpoint Triamidoamine-Mo complexes as case of study

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ABSTRACT

Simplified models (model A: $[(PhNCH_2CH_2)_3N]Mo$; model B: $[(PhNCH_2CH_2)_3N]Mo–N_2$) based on triamidoamine complexes were proposed to evaluate the electrostatic/orbital effects of the phenyl rings on complexation and reduction of N_2. The effect of systematic synchronized rotations (from 0° to 90°) of phenyl dihedral angles on the charge and/or orbital contribution of molybdenum to complex N_2 was studied by chemical descriptors like electrophilicity index (ω) and Mulliken charges. According with the results, there is a favorable modulation of the energy gap of interaction between $\text{HOMO/SOMO}_{\text{modelA}}$ and LUMO/LUMO+1_{N2} corresponding to π-back-donation interaction. It is confirmed that phenyl rings not only work as steric walls but also affect the orbital interactions. In accordance with ω values, Model A behaves as nucleophile with respect to N_2. This observation is in agreement with the suggestion that back-donation governs the complex-N_2 interaction. The rotation of dihedral angles of model B also has an effect on the electrophilicity index, allowing modulation in reductive processes. Inductive effects were also assessed by the substituents CN, Br and NH_2 in *para* position on the phenyl rings. The best scenario for N_2 complexation and activation was obtained with $[(p\text{-}NH_2PhenylNCH_2CH_2)_3N]Mo$. The Density Functional Theory was used as theoretical framework.

1. Introduction

Industrially, ammonia production from hydrogen and molecular nitrogen N_2 takes place at 550 °C and 150–350 atm of pressure through the Haber–Bosch process, to produce up to hundred millions of tons of NH_3 per year, even though such drastic conditions are involved [1]. Many systems using transition metals have been developed for N_2 activation [2,3]; however, some of them only coordinate N_2 or even weaken the N–N bond but non-catalytic process is involved and the reduction to NH_3 is not achieved. The most successful models to improve the catalytic reduction of N_2 by abiotic means have been those reported by Schrock et al. [4,5], based on molybdenum triamidoamine complexes with voluminous aryl ligands directly attached (Fig. 1).

The best results in terms of N_2 reduction were observed when the sterical hindrances were maximized via substituents, preventing the formation of bimetallic complexes, presumably unreactive toward the N_2 reduction, and improving the solubility [6,7]. The catalyst $[(ArNCH_2CH_2)_3N]Mo(III)$, where Ar = hexa-iso-propyl-terphenyl (HIPT) [8] (Fig. 1) was able to reduce N_2 at room temperature and 1 atm of pressure, with an efficiency around 63% [6].

After some experimental variations made on the Aryl part of the ligand, including more or less sterical hindrances, as well as different electronic environments, Schrock's group observed that such variations result in a significant decrease in the N_2 reduction efficiency (less than 9% of NH_3 in some cases), thus, the electronic and steric features of the HIPT seem to be "ideal" to carry out the N_2 reduction [4].

Since the publication of the catalytic cycle proposed by Schrock for the reduction of N_2, the thermodynamic evaluation to justify and even predict critical intermediates by the construction of energy profiles has been the most recurring issue theoretically addressed [9,10,11], taking advantage of the applicability of the Density Functional Theory (DFT) methodology [12]. Most of the approaches have made some kind of simplification on the $[(HIPTNCH_2CH_2)_3N]Mo$ molecule. The studies carried out by Reiher et al. have proved that in order to approximate the theoretical results to the experiment (N_2 and NH_3 coordination reactions) no simplification of the ligand should be done [12,13]. This idea is somewhat shared by the experimentalists [14].

Beyond the analysis of the whole catalytic cycle, in the present study we turn over the singular role of the aryl substituents on the

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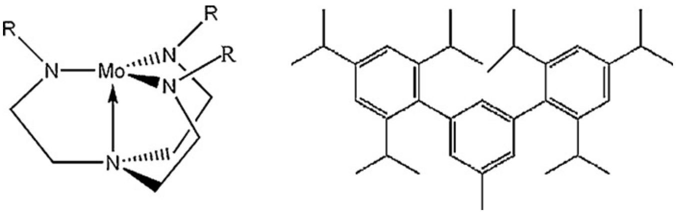

Fig. 1. Mo(III) complexes. R = aryl substituent.

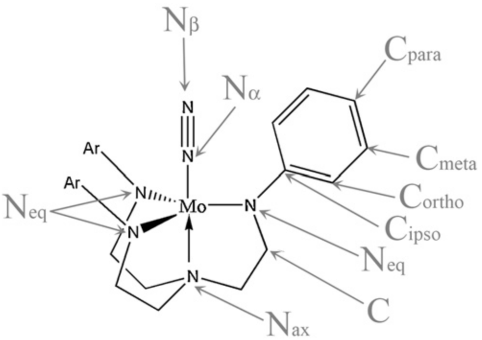

Fig. 2. Notation for triamidoamine ligands.

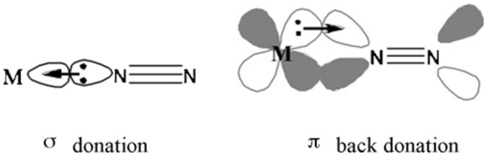

Fig. 3. Schematic representation of M–N electronic interaction.

reactivity of this kind of metal complexes towards the N_2 activation and reduction.

From the crystallographic data [15,16] summarized in Table 1 (see Fig. 2 for notation), among all the geometrical parameters, the dihedral angle Mo–N_{eq}–C_{ipso}–C_{ortho} of each intermediate in the catalytic cycle is one which exhibits marked variations along the cycle, indicating a relatively free rotation of the voluminous aryl substituents.

In the first step of the cycle (formation of [(HIPTNCH_2CH_2)$_3$N]Mo–N_2), simultaneous events of electron donation and back donation should take place, with the concomitant weakening of the N–N bond (Fig. 3).

Taking into account on the one hand the free-rotation of the aryl substituents and, on the other hand the electronic interactions involved in the first step to reduce N_2, the hypothesis to evaluate the contribution of aryl substituents was set forth as follows: If the manipulation of the aryl substituents (by systematic rotation of the dihedral angles Mo–N_{eq}–C_{ipso}–C_{ortho}) results in a favorable change in the interaction with N_2 from the electronic point of view, then sterical isolation is not their only role. The last consideration has been mentioned before by other authors [12,13,17] but it has not been systematically explored. Our hypothesis is that these aryl substituents might contribute to the electronic state of the Mo depending on the dihedral angle. If that is true, a favorable scenario of interaction could be found by systematic rotations of dihedral angles, which may be fixed by specific molecular templates (e.g. rigid dendritic scaffolds) to construct a nitrogen-reducer macromolecular catalyst.

In order to address the above hypothesis, restricted optimization calculations of simplified models of the [(HIPTNCH_2CH_2)$_3$N]Mo molecule were performed. The use of simplified models is necessary in the present study since some dihedral angles would not be accessible for sterical reasons.

It has been proposed that [(HIPTNCH_2CH_2)$_3$N]Mo is a highly delocalized system and population analysis to obtain localized charges does not describe properly any trend at all [17]. However, global descriptors of reactivity [18] such as electronic chemical potential (μ), chemical hardness (η) and the electrophilicity index (ω) defined by Parr et al. [19] consider the whole molecule. Particularly, relationships such as ω-dihedral angles, ω-energy profiles and ω-Diels-Alder reactions pairs have been estimated [20,21,22].

Thus, in this work μ, η and ω were calculated to rationalize the differences in the chemical environment when the aryl substituents are in different positions. Particularly the descriptor ω, as a measure of the energetic stabilization when a molecular system acquires additional electronic charge, would be useful to describe the interaction between N_2 and Mo-complex since electron transfer is entailed. A comparison between HIPT and phenyl as substituents was made in order to hint at the overall effect of the model simplification. Inductive effects due to some functional groups (NH_2, Br, CN) on reactivity were also analyzed. The DFT framework was used.

2. Computational details

2.1. Validation

In order to validate the method, full optimization of the crystallographic structure shown in Fig. 4 ([(HIPTNCH_2CH_2)$_3$N]Mo–N_2) was carried out at DFT level. The functionals BHandHLYP [23] and BP86 [24,25,26] with the restricted open shell formalism (RO) and the basis set LACVP* [27] with polarized functions on heavy atoms were used. Atomic sections were set, taking into account two fragments (differentiated by colors pink and blue in Fig. 4). All calculations were performed using the program Jaguar 6.5 [28].

The reproducibility of geometrical data was taken as a validation criterion [9,11,12], especially the N_α–N_β distance, directly related to the N_2 activation.

The functional BHandHLYP reproduced the N_α–N_β distance (difference of 0.05 Å) better than BP86 (difference 0.1 Å) with respect to the crystallographic structure. The discrepancy in the Mo–N_α distance was 0.1 Å in both cases. The functional BHandHLYP was

Table 1
Summary of crystallographic data of isolated intermediates from the Schrock catalytic cycle. Mo=[(HIPTNCH_2CH_2)$_3$N]Mo.

		–Mo–N_2	Mo–N=N–	Mo–N=NH	Mo–N=NH_2^+	Mo≡N	Mo=NH^+	Mo–NH_3^+	Mo–NH_3
Mo oxidation state		III	IV	IV	VI	VI	VI	IV	III
Distance (Å)	Mo–N_{ec}	1.978	2.030	2.010	1.954	2.003	1.944	1.948	2.003
	Mo–Na_x	2.188	2.241	2.228	2.236	2.395	2.286	2.147	2.205
	Mo–N_α	1.963	1.863	1.780	1.743	1.652	1.631	2.236	2.170
	N_α–N_β	1.061	1.156	1.302	1.304	–	–	–	–
Dihedral angle	67.38	–31.65	–32.23	69.11	34.06	67.88	74.02	64.26	
Mo–N_{ec}–C_{ipso}–C_{ortho}	69.14	–35.37	–33.47	71.54	34.81	70.77	74.77	69.02	
	70.83	–29.25	–39.47	73.20	35.29	72.07	82.07	72.95	