

# Multibody effects in intermolecular interactions and reaction pathways for catalytic processes. Part I. Jean-Pierre Daudey's contributions to mexican science

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Recibido el 6 de febrero de 2009; aceptado el 24 de marzo de 2009

We review here a series of works by Jean-Pierre Daudey in the field of multibody expansions and non-additive effects in clusters ( $Ar_n$ ,  $Be_n$ ,  $Mg_n$ ,  $Ag_n$ ) and also for the structure-activity relation in homogeneous catalysts used for the hydrogenation of olefin and the production of heavy water. These works were developed during his constant visits to Mexico, in collaboration of one among various research groups here that benefited from his talent, expertise and generosity.

*Keywords:* Theoretical catalysis; multibody effects; nonadditivity; J.P. Daudey's contributions.

Revisamos aquí una serie de artículos con Jean-Pierre Daudey en los campos de desarrollo de multicuerpos y efectos no-adictivos en cúmulos ( $Ar_n$ ,  $Be_n$ ,  $Mg_n$ ,  $Ag_n$ ) y también de la relación estructura-actividad en catálisis homogénea para hidrogenación de olefina y producción de agua pesada. Estos artículos fueron desarrollados durante sus continuas visitas a México en colaboración con uno de varios grupos de investigación aquí que resultaron beneficiado por su experiencia, talento y generosidad.

*Descriptores:* Catálisis teórica; efectos de multicuerpos; noaditividad; contribución de J.P. Daudey.

PACS: 31.5.Ar; 31.25.-v; 31.50.-x

## 1. Introduction

Among several fields in theoretical physics which were influenced by Jean-Pierre Daudey's continuous visits to Mexico, two were of prime interest to our own research group. These two were respectively, multibody effects in finite clusters and the theoretical explanation of the quantum causes of the catalytic phenomenon. I refer to a couple of review papers on catalysis [1] and nonadditive effects [2]. The latter includes the adsorption of molecules on metal surfaces of elements like Li and Be, as a function of the size and geometry of these (and other) metal clusters [3,4]. Jean-Pierre joined us in studies on magnesium [5] and silver [6] clusters which will be reviewed here and also allowed us to extend our previous studies on noble gas clusters like  $He_n$  [7] and  $Ne_n$  [8], to heavier noble gases like argon through the use of pseudopotentials [9]. As concerns the catalytic phenomenon, he worked with us in the explanation of the quantum theory mechanisms [10,11] of the hydrogenation of olefin by palladium complexes, a problem previously studied experimentally by Germain et al. [12]. Also of invaluable help was his participation in our study of one of the catalysts utilized in heavy water production [13]. This, among other papers of our group on  $D_2O$  later caught the attention of the Heavy Water Division of the Bhabha Atomic Research Center in India and they invited me to co-write a book on this subject with two Indian colleagues [14]. In short, Daudey's most valuable help in these themes of research comes to my mind, mixed with the saddest feelings about his tragic and premature demise.

## 2. A personal introduction

When Jean-Pierre Daudey finished his PhD under the direction of Mme. Albèrte Pullman, they both decided that he should spend a Post-Doctoral stage in Mexico. Dr. Munguía, a closed personal friend of the Pullmans' was to receive him here, but became quite ill, so Jean-Pierre was redirected to Dr. Raúl Cetina at Instituto de Química of the National University (UNAM). He worked there for a year, then decided to extend his stay as a post-doc in Mexico for a second year. He, however, wanted to do so at Instituto de Física, UNAM where he had established a very close friendship both with Manuel Berrondo and myself. He was officially accepted as my postdoctoral student. Later he returned to France to help create the excellent CNRS Laboratory at Toulouse where he eventually became Director. He however willingly returned to Mexico often and we wrote joint papers as mentioned above, in one of which he became coauthor with the famous Polish scientist W. Kolos who stayed for a year in my group [5]. The two (Daudey and Kolos) had not met in person yet, so it was quite nice when in a later visit, Jean-Pierre finally met Wlodek in my office a happy coincidence. I received here post-doctoral students from Toulouse University and also sent over there a student to obtain his PhD under Daudey's direction. On his return I learned that Jean Pierre and his wife took him in as another member of the family. The warmth of Jean-Pierre Daudey when he greeted me in Toulouse, his open smile and his bright ideas, his love of Mexico and so many more positive memories; that is what

I cherish today, now that I cannot personally thank him for so many, many things. Adieu, cher ami.

### 3. Non additivity in noble gas and metal clusters

The analysis of a multibody expansions of the energy of a cluster consisting of  $n$  atoms is the well-known expression [see Ref. 2]:

$$E(n) = E(2, n)[1 + \varepsilon(3, n) + \varepsilon(4, n) + \dots \varepsilon(n, n)] \quad (1)$$

Where  $E(2, n)$  is the purely additive energy contribution of all of the pairs of atoms contained in the  $n$ -body cluster. In turn the energy contribution of all of the triplets contained therein would be  $E(3, n)$  and  $\varepsilon(3, n) = E(3, n)/E(2, n)$  is therefore the percentual three-body contribution of the pairwise energy [and  $E(m, n)$  would consequentially be the total  $m$ -body contribution to the energy and  $\varepsilon(m, n)$  the percentual  $m$ -body contribution as the ratio of the purely additive energy  $E(2, n)$ ]. Thusly, the total energy of the  $n$ -body cluster would be given by Eq. (1), considering the diverse geometrical configurations of the  $n$ -body clusters. A key factor to consider in studying non-additivity is that beginning with three-body systems, different geometries like equilateral, isosceles or scalene triangular or linear, asymmetrical or symmetrical often lead to completely different non-additive corrections (*e.g.* in  $\text{He}_3$  [2] the linear structure gives moderate repulsive three-body corrections, but equilateral  $\text{He}_3$  has attractive ones that at very short range can be quite notable). Four-body forces may indeed have three dimensional configuration that, again, as for all larger clusters, may change magnitude considerably or even change sign; four-body attractions or repulsions. This may be studied elsewhere (see Ref. 2), we here shall simply add a label to distinguish three-body forces stemming from linear symmetrical, or from isosceles triangular configurations, and so on and so forth. Take the case of a trimer, there would be an  $E(3)$  (linear symmetrical) energy; an  $E(3)$  (equilateral) energy; an  $E(3)$  (isosceles) energy; etc., etc., each of them varying as a function of the internuclear separation (and as the case may be, the angular) parameters [2]. My first paper in this field was a collaboration with Richard Bader and Virgilio Beltrán [7] which produced a three-body potential energy surface which is still today the most complete and precise measure of the nonadditivity of helium and served to explain the anomalous crystallization of this element. Four-body effects in helium were also obtained by our group [15] and the case of Ne trimers was studied by us [16] for comparison.

The next step would mean studying heavier noble gas atoms as argon, but this was prohibitively costly in those days if one wanted to reach the Hartree-Fock limit precision achieved in helium. So when Jean-Pierre Daudey proposed, in one of his visits to Mexico, to send Jean-Claude Barthelat to do a postdoctoral stay with me, we started to plan an ambitious attack on argon clusters. Barthelat and coauthors [17]

has proposed a method that introduced a pseudo-potential operator for the inner shells at each atom of the form:

$$w^{PS} = \sum_{l=0}^{l_{\max}} W_l P_l,$$

where  $P_l$  is a projector, with associate component:

$$w^{PS} = \sum_{l=0}^{l_{\max}} c_l r^{nl} e^{-\alpha_l r^2},$$

where the parameters  $c$ ,  $\alpha$  and  $n$  are fitted to reproduce atomic orbital energies [18].

For argon trimers Daudey proposed we expand Slater-type orbitals into several Gaussians to find the best values for the  $\text{Ar}_2$  dimers as a starting basis set and when a satisfactory fit of the dimer was reached, we went for the argon trimer [9]. Several tests were made until the all-electron curves were quite indistinguishable from our pseudopotential calculations on the argon dimers [9]. Then the studies of the argon trimers and tetramers were done using the pseudopotential approach which led to results qualitatively similar to the very accurate  $\text{He}_3$  curves of Refs. 7 and 15. For instance we obtained that the tetrahedral  $\text{Ar}_4$  has a nonadditive contribution that more than doubles that of the square planar geometry. We also obtained that the perturbation theory calculations used for comparison in Ref. 9 reproduced the variational calculations using the pseudopotentials for the inner shell electrons of the argon atoms, and that the latter had great promise for the short-range interaction energies between closed-shell structures such as those of noble gas atoms, but more significant for the intermolecular interactions. After all, most molecules present closed shell configurations. Indeed these contributions of Daudey greatly helped us in our studies on nonadditivity in water [19], ammonia [20] and methane [21] oligomers.

Daudey also became intrigued by a research paper we had done on the nonadditivity of copper trimers [22] so he decided to participate in a joint effort (see Ref. 6) to assess the importance of three-body nonadditive corrections to the energy and optimal geometry of silver trimers. The crucial importance of three-body effects to determine the stability of silver configuration [6] substantially different from those of other coinage metals, such as Cu [22] and Au [23,24] was remarked. Unlike  $\text{Cu}_3$  for instance, the linear trimer was not more stable than the equilateral for  $\text{Ag}_3$ . A Jahn-Teller stabilization was also obtained, showing that at the equilateral triangle a destabilizing effect came from the large three-body repulsions at this most symmetric configuration [6]. These results guided our group's studies on large gold clusters [25] where we followed Daudey's caveat: that the Jahn-Teller stabilization energies require very demanding efforts for obtaining the correlated description of the trimers of coinage metals. This of course requires substantial amounts of computer time [6]. Simpler metals like lithium [26] show very large nonadditive effects that even threaten the convergence of many-body expansions, thus exemplifying the dangers of

trying to explain catalytic effects by building finite cluster models of catalytic surfaces [27].

Daudey also helped establish that in the case of the alkaline earth metals, huge contrasts can exist. Earlier Novaro and Kolos [4] had shown that the schizophrenic behaviour of beryllium which, after  $\text{He}_2$ , has the hardest to detect dimer in the whole periodic table, with a Be-Be internuclear distance that almost doubles the internuclear distance of solid beryllium. This solid is metallic at room temperature however, contrasting with helium which refuses to solidify even at the lowest temperatures. Kolos and Novaro showed this to stem from the  $\text{Be}_3$  enormous three-body nonadditive attractions (comparably negligible in helium). The question whether other alkaline earths had a similar behaviour concerning non-additivity was answered by Daudey *et al.* [5] during another of his visits to Mexico. He opened a route by developing a decomposition of the SCF interactions (which before him had only been applied to the case of dimers) to the case of trimers and tetramers. Using his scheme we recalculated the  $\text{Be}_3$  and  $\text{Be}_4$  systems as well as the  $\text{Mg}_3$  and  $\text{Mg}_4$  clusters [5] for several geometrical configurations. Even though the non-additive effects showed the same general trends for magnesium as for beryllium, their relative weight compared to the purely additive contributions of the energy were substantially smaller for magnesium. Among other differences between Be and Mg, both have a weakly bound dimer but  $\text{Mg}_2$  has an internuclear distance very similar to the atomic separations in solid magnesium, while  $\text{Be}_2$  has an extremely long internuclear distance. Their ground-state dimers may both be considered a pure van der Waals pair and their excimer states are easy to explain using simple qualitative molecular orbital arguments, making the dimers highly polarizable. But for Be the situation is extreme since the equilibrium distance of the ground states differs as much as 4.5 bohrs from the excited states' minima, which in fact are closer to that of solid beryllium. This introduces a large resonance effect in Be, which is almost negligible for Mg. This explains the much smaller nonadditivity found for the latter [5].

Depicted in Fig. 1 we see the  $\epsilon(3,3)$  ratios for He, Ne and the Argon trimers as well as for  $\text{Be}_3$  and  $\text{Mg}_3$ . This figure contains Daudey's extension of the work of our group in noble gases by adding his calculations on  $\text{Ar}_3$  [9] which shows the similarities of this trimer to  $\text{He}_3$  and  $\text{Ne}_3$ . More telling are Daudey's results for  $\text{Mg}_3$  [5] which clearly contrasts with our (previous) results on  $\text{Be}_3$  which had a much deeper  $\epsilon(3,3)$  well and actually corrected the long distance predicted for the  $\text{Be}_2$  dimer, and already announces the Be solid.  $\text{Mg}_3$  has a much less marked well with a minimum that agrees both with the  $\text{Mg}_2$  well and the solid magnesium interatomic separation, as is evidenced in Fig. 1. Summarizing, the Daudey approach to Ar trimers using pseudopotential proves to be quite adequate and our three-body effects are practically identical to those of the lighter noble gases (He and Ne). The contrast between Be and Mg on the other hand is extreme as concerns their nonadditive effects. This may well be the cause of the fact that while their bulk structures seem to be similar, the Be

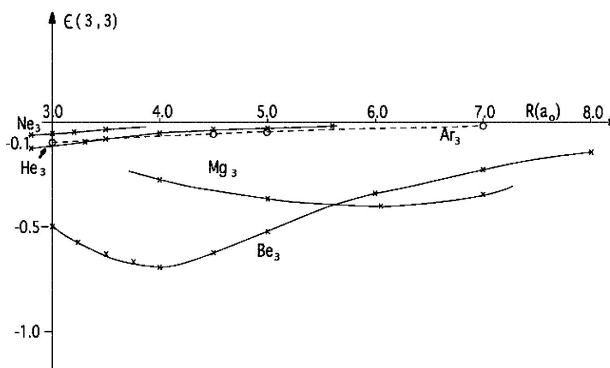


FIGURE 1. Plot of the three-body nonadditive ratios for the  $\text{He}_3$ ,  $\text{Ne}_3$ ,  $\text{Ar}_3$ ,  $\text{Mg}_3$  and  $\text{Be}_3$  trimers, all in equilateral triangular configuration of increasing sides  $R$ . Notice the perfect similarities between the noble gases, even though the  $\text{He}_3$  and  $\text{Ne}_3$  systems were studied at an all-electron ab-initio level, while for  $\text{Ar}_3$  the pseudopotential method of Jean-Pierre Daudey was utilized. A large contrast with the alkaline earth trimers is evident, but the three-body effect in beryllium in turn also contrast with the  $\text{Mg}_3$  case. While both show three-body potential energy wells with energies various times deeper than for the noble gases, the magnesium equilateral-triangle cluster has a shallow well whose minimum lies at a separation of around  $6a_0$  well in accord both with the equilibrium distance of the  $\text{Mg}_2$  dimer and also with the interatomic separations in solid Mg. The case of Be is quite different; the very deep well for the equilateral  $\text{Be}_3$  triangle has its minimum around  $4a_0$ , similar to the solid Be separations, but substantially shorter than the minimum for the pairwise energies of about  $8a_0$  (see text and Ref. 13).

semimetal volatilizes in a way that is well known (and feared) by chemists which have to manipulate it in their laboratories.

#### 4. Quantum mechanical description of catalyst structure and activity

In his visits to Mexico, J.P. Daudey became interested in our work on catalytic processes, where we had been able to establish the first ab-initio reaction coordinate of a real catalytic process. Said process was the Ziegler-Natta polymerization, where we had the invaluable support of Enrico Clementi and his group [28]. Daudey's interest was patent when he invited me [29] to a Congress in Pau, France where he mixed wisely theoreticians and catalysis experts including Prof. Germain. So when we met in Mexico again we decided to do a theoretical study on one of Germain *et al.* [12] most interesting discoveries, the hydrogenation of olefin with palladium chloride complexes. Jean-Pierre was sure that his pseudopotential approach was vastly superior to semiempirical methods previously used for such systems and in fact we carefully optimized the electronic structure of the palladium tetrachloride ion to show that our results corrected the inconsistencies of semiempirical studies, and allowed us to obtain new identifications which correlate perfectly with the experimental data and show the same trends as similar ab-initio studies [10].

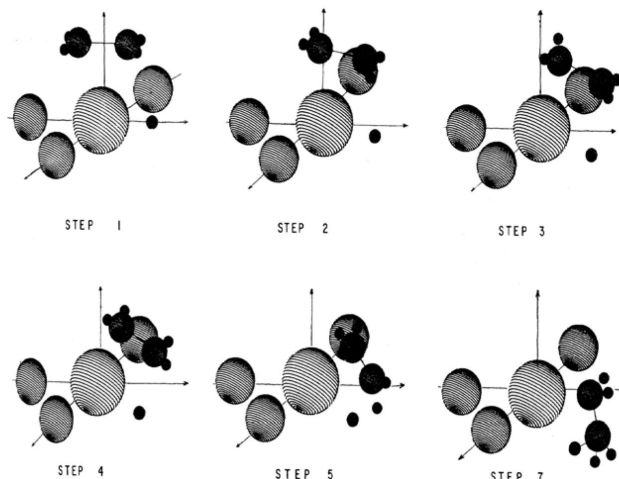


FIGURE 2. Three-dimensional model, in the  $x$ - $z$  plane, for the collapse mechanism of the hydrogenation of olefin by palladium catalysts (see text). Here the first five steps of this mechanism and the final configuration of the complex  $[\text{PdCl}_3\text{C}_2\text{H}_5]^{-2}$ , are depicted.

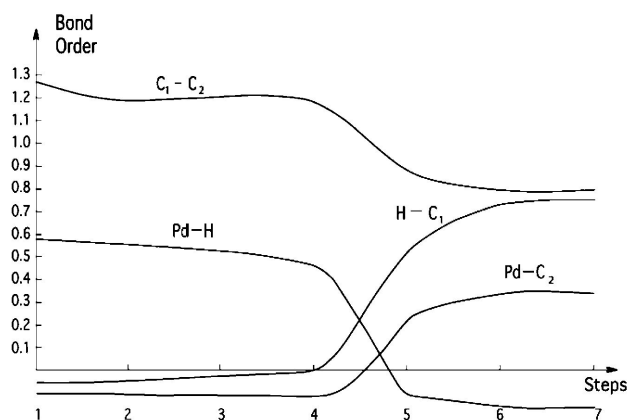


FIGURE 3. Evolution of the bond orders during the seven steps of the "collapse mechanism" depicted in Fig. 2. These bond orders, obtained by the traditional Mulliken population analysis of the wave-functions obtained at each step, leads us to understand the bond formation during the collapse and the concomitant disappearance of the original Pd-H bond in the catalyst as well as the weakening of the ethylene's double bond.

Only then we proceeded to face the tricky business of proposing the catalytic action of this palladium complex, which in fact was somewhat different from Germain's assumptions in his original paper [12]. Figure 2 shows the mechanism proposed by Daudey and coworkers [11], showing the capture of ethylene by the  $\text{PdCl}_3\text{H}$  catalytic complex and its activation by a "collapse" mechanism that leads to the hydrogenation of the olefin. The large central sphere represents the palladium metal atom, surrounded by three medium-size chlorides and a small H atom while the olefin approaches it in the vertical axis. Through the collapse, the olefin replaces the H-atom which hydrogenates it. This reaction is clear in Fig. 3 where the bond breaking and formation is evident. The formation of the C1-H and Pd-C2 bonds is shown by their growing bond

order, while the Pd-H bond disappears and the olefin's double bond clearly becomes a single bond, thus summarizing the meaning of our proposed collapse mechanism.

Years later, in a Mexico-France meeting on Catalysis in Mexico [30] Prof. Germain generously recognized that our quantum theory results led him to revise his own conclusions. Our quantum mechanical results proved to him that the catalyst regeneration indeed was an integral part of the original palladium-complex+olefin reaction.

On an earlier visit to Mexico, Daudey had also provided his invaluable help to our study on the catalytic exchange, in sodium amide catalysts, between hydrogen and deuterium molecules. This work [13] utilized ab-initio MO-SCF calculations to study the reaction pathway of the catalytic exchange between the  $\text{NaNH}_2$  catalyst and HD molecules. This process is crucial in the production of Heavy Water, specially useful in ammonia plants which were then very important for a national program in Mexico to buy a CANDU nuclear reactor which depended on local production of Heavy Water. In any case Jean-Pierre Daudey enthusiastically joined our project and helped us to establish beyond a doubt, that the amide was quite capable of lowering the activation barrier for the HD scission. His main interest once again was to show that the pseudopotential method developed in his Laboratory in Toulouse produced results basically adequate to reproduce our fully ab-initio results. These consisted in showing that the prevalent idea that the interaction of the Na-N bond of the amide with the H-D bond could bring a polarization and weakening of the latter was unfounded, which lies in contrast with other catalysts such as ruthenium-chloride which do work that way. In Fig. 4 the evolution of the energy is depicted as the HD molecule approaches the sodium amide catalyst (the phase labeled "reactants" in Fig. 4), followed by the catalysts activation that abstracts the D moiety (the "reaction steps" part of the reaction pathway) and finally the

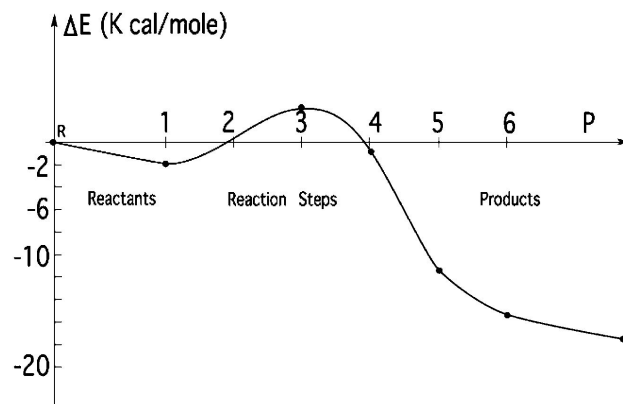


FIGURE 4. Evolution of the total energy of the sodium-amide catalyst and HD during their reaction leading from these reactants, to the intermediate complex and finally to the reaction products. Notice that the activation barrier for the N-D bond breaking is quite small (of the order of 3 kcal/mol). This shows the powerful role played by the catalyst (the bond breaking of an H-D bond in vacuum requires about 20 times this energy).

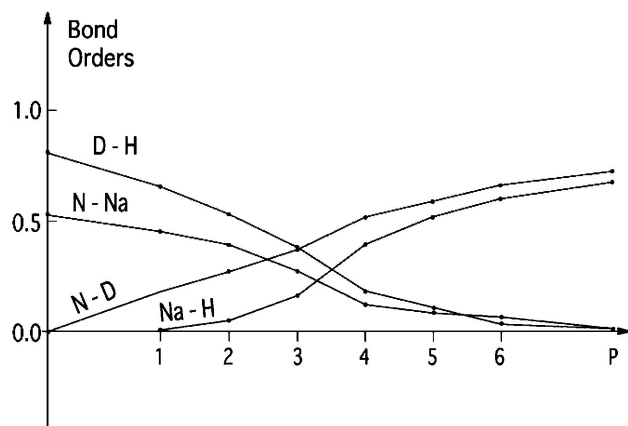


FIGURE 5. Evolution of the bond orders along the reaction coordinate of Fig. 4. Notice the H-D bond breaking and the formation of new Na-H and N-D bonds which allows the liberation of D that will allow heavy water enrichment (see text).

liberation of the products. Thus the energy evolution is fully depicted. Figure 5 in turn clearly represents the H-D scission with a concomitant weakening of the Na-N bond of the catalyst shown by the diminishing of the corresponding bond orders. Then a simultaneous creation of the new bonds appear: N-D and Na-H. Thus we see the complete [13] explanation of the heavy water enrichment process that drew the attention of the heavy Water Department of the Bhabha Atomic Research Center in India [14]. This led to experiments and patents at Instituto Mexicano del Petróleo and visits by the experts of Canadian nuclear company CANDU to Mexico. The reason is that the mechanism we proposed was quite promising and furthermore the IMP Director of the Catalysis Department, Ferreira, devised a combination of this and another process

involving platinum catalysts. Perhaps not-so-coincidentally, India announced their success at heavy water production precisely at this period of time.

Our main discovery is that the mechanism we proposed is substantially unique, implying a linear approach of HD towards the nitrogen-atom lone pair electrons in the catalyst. The line of approach of the HD molecule in fact forms an ammonia-like angle of  $107^\circ$  with the original N-H bonds and leads to an intermediate complex  $\text{NaNH}_2\text{-HD}$  which allows for the admixing of the ground state of the D-H pair with the nitrogen p-orbitals. The new bond thus created leads to an intermediate complex which activates H-D by surmounting a very small activation barrier of  $\sim 3\text{kcal/mol}$  [13]. Thus the very strong H-D bond of the isolated molecule becomes labile and scission is achieved. The nature of the transient intermediate complex, so hard to study experimentally, is then understood at a quantum mechanical level, giving a quantitative justification of the experimental assumptions. This study also helped the Toulouse group to reassess their pseudopotentials.

## 5. Conclusion

Jean-Pierre Daudey's work in Toulouse provided us with useful techniques that allowed for a strong theoretical-experimental collaboration between our group in Mexico and the Lash Miller Laboratory headed by Geoffrey Ozin in Toronto. We exchanged students and published joint or complementary papers. (see Refs. 31 to 36). This never would have become possible without Daudey's generosity towards us and Mexican science in general.

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