Exploring the Structure, Energetic, and Magnetic Properties of Neutral Small Lithium Clusters Doped with Yttrium: Supermagnetic Atom Research

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Supporting Information

ABSTRACT: Density functional theory calculations based on magnetic and energetic stability criteria were performed to study a series of yttrium-doped lithium neutral clusters. A relativistic approximation was employed to properly describe the energy and multiplicity of the given clusters’ fundamental states. The interaction of the 4d-Y atomic orbitals with the sp-Li states had an important role in the magnetic and energetic behavior of the selected systems. The spin density was concentrated over the yttrium atom regardless of the size of the cluster. Li7Y is a new stable superatom due to its enhanced magnetic properties.

1. INTRODUCTION

Metallic clusters have been extensively researched both experimentally and theoretically due to their chemical, physical, electrical, optical, and magnetic properties. The study of clusters represents one of the fields of greatest growth in nanomaterials science.1−10 In recent years, the development of new clusters that mimic the chemical behavior of elements has been explored. The Jellium model predicts that certain electronic configurations confer greater stability to metallic clusters11,12 and, in analogy with the nuclear structure, the electronic levels are grouped into shells. This idea has led to Khanna and collaborators to suggest the concept of superatoms: metallic clusters that imitate the electronic and chemical behavior of atoms with which they share the same number of valence electrons.13−17 Lithium clusters have been studied intensively18−33 by different experimental methods such as electronic spin resonance,34−36 laser-induced fluorescence,37 optical resonance,38,39 and Raman spectroscopy.40−42 The structure identification of the clusters is difficult regardless of the technique used, especially when exploring beyond very small systems.44 At a computational level, the study of lithium clusters within the density functional framework and post Hartree–Fock methods has been carried out.45−52 An element that dopes a metal cluster leads to changes in its energy, structural properties, and the chemical nature of the bond.53 Lithium clusters doped with boron,54−56 aluminum,57 magnesium,58 germanium,59 carbon,60 and tin have been investigated.61−63 Aluminum- and boron-doped lithium clusters exhibiting covalence have also been reported54 and the study of highly ionic clusters of formula E5Li7 (E = C, Si, Ge, Sn, y Pb)63 has been carried out. The interaction between lithium and copper has also been analyzed through spectroscopic data from Russom and collaborators, who determined that this chemical union results in a σ bond.56 Previous work predicted high magnetic moments in a series of alkaline metal clusters doped with yttrium of formula M3Y, where M = Na, K, Rb, and Cs and n = 9−13. The stability of these systems was controlled by the combination of the yttrium 4d orbitals with the sp states of the alkaline metals. The YK12 and YRb12 clusters were determined to be superatoms of the icosahedral structure that mimic the atom of manganese.67 Currently, various methodologies like the gradient embedded genetic algorithm,68 and the Born–Oppenheimer molecular dynamics (BOMD) have been suggested to explore the potential energy surface (PES) for different types of systems.69 The advent of more accurate density functional theory methods such as the auxiliary density functional theory (ADFT) allows carrying out several hundred picosecond molecular dynamics using scarce computational wherewithal. This approximation has been very successful in...
the search for new alkaline and transition metal clusters. In a previous study, binary yttrium-alkali superatoms exhibiting outstanding energetic and magnetic properties in large systems were described. In this sense, it is interesting to look for superatom-like properties in smaller systems. For this reason, a study of the structural and energetic properties of yttrium-doped lithium clusters \( \text{Li}_nY, n = 1\text{−}8 \) was carried out in the present work. Minimal energy states were chosen from Born–Oppenheimer molecular dynamics trajectories considering an ambient temperature of 300 K, with different multiplicities of spin. The selected structures were subjected to local optimizations with the zero-order regular approximation. Parameters such as atomization energy (AE), gain energy, highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) energy gap, magnetic moment \((\mu_B)\), and exchange splitting were calculated.

## 2. RESULTS AND DISCUSSION

Several initial geometries were used based on previously reported lithium clusters to obtain the low-lying isomers of the \( \text{Li}_nY, n = 1\text{−}8 \) systems. Permitted spin multiplicities were considered up to six, i.e., 1, 3, and 5 for clusters with an even number of electrons and 2, 4, and 6 for odd-numbered electron systems, while the charge remained at zero for every calculation. Born–Oppenheimer molecular dynamics trajectories were recorded at 300 K for each cluster. The BOMD simulation was 50 ps long, as shown in Figure 1. The linear and angular momenta was set to zero and maintained during the BOMD trajectory to ensure Galilei invariance. The average temperature was controlled by Nosé–Hoover three chains thermostat. This approach has been reported to be adequate for the study of alkali and transition metal clusters. Minima structures were extracted from each calculated trajectory and subjected to geometry optimizations without symmetry constraints within the DFT framework implemented in the ORCA code. Frequency analysis was carried out to verify the optimized minima on the potential energy surface (PES). Here, we report the structures and frequencies, relative energies without the zero-point energy correction, and the next electronic and magnetic properties: atomization energy, gain energy, HOMO–LUMO gap, exchange splitting, and magnetic moment.

### 2.1. Structures and Frequencies

The minimum energy state structures for \( \text{Li}_nY \) clusters are shown in Figures 2–5 \((n = 1\text{−}8) \). Lithium atoms are represented in pink while the yttrium is colored in yellow. The structures of the fundamental state of each cluster are represented on the left side of each figure. The relative energy of the third isomer of each family is found in the first table of the Supporting Information. The ground state structure of the \( \text{Li}Y \) cluster is a linear structure with a triplet potential energy surface (PES). As can be seen in Table 1, the

| cluster | bond | bond length | bond length |
|---------|------|-------------|-------------|
| \( \text{Li}_1 \) | 1–2 | 2.673 | 2.691 | \( \text{Li}Y \) | 1–2 | 3.106 |
| \( \text{Li}_1 \) | 3–1 | 2.730 | 2.741 | \( \text{Li}_2Y \) | 3–1 | 2.842 |
| | 1–2 | 3.200 | 3.209 | | 1–2 | 3.283 |
| \( \text{Li}_1 \) | 1–4 | 2.618 | \( \text{Li}Y \) | 1–4 | 2.776 |
| | 4–5 | 2.961 | 4–5 | 3.179 |
| | 1–5 | 2.961 | 1–5 | 3.174 |
| | 1–2 | 2.907 | 1–2 | 2.957 |
| | 1–3 | 2.908 | 1–3 | 2.956 |
| | 4–3 | 3.009 | 4–3 | 2.957 |
| | 5–2 | 3.010 | 5–2 | 3.234 |
| | 5–3 | 3.010 | 5–3 | 3.233 |
| | 4–2 | 3.009 | 4–2 | 2.958 |
| \( \text{Li}_1 \) | 1–2 | 2.978 | \( \text{Li}Y \) | 1–2 | 3.002 |
| 6–3 | 2.871 | 6–3 | 3.216 |
| 6–5 | 2.698 | 6–5 | 3.286 |

"The experimental results are from refs 78, 79."
Li–Y bond length is 3.106 Å, this distance is 0.433 Å greater than the reported experimental bond length for the Li₂ dimer \(^7\) \(^8\) and 0.415 Å greater than the theoretical bond length of the same dimer calculated at a DFT/SVWN level.\(^8\) The atomic radius reported in the literature for lithium is 1.67 Å, while for the atom of yttrium it is 2.12 Å,\(^8\) so that the sum of the atomic radius for the Li₂ dimer is 3.34 Å and the LiY system is 3.79 Å, compared to the bond distances presented, the Li–Y bond is weaker than that of the Li–Li bond. It was found that the energy needed to break the Li–Li bond is 0.86 eV, while to break the Li–Y bond is 0.57 eV. The next minimum of the cluster is found with a singlet PES with an energy of 0.088 eV greater than the ground state (Table 2). The third minimum corresponds to a quintet multiplicity with a stability of 0.908 eV (Table S2) greater than the triplet state on the potential energy surface.

### Table 2. Relative Energies for the Isomers of LiₙY, \(n = 1–8\) Clusters

| clusters | ground state | energy state nearest to the ground state | spin multiplicity | spin multiplicity | relative energy (eV) |
|----------|--------------|------------------------------------------|------------------|------------------|---------------------|
| LiY      | 3            | 1                                        | spin multiplicity | spin multiplicity | relative energy (eV) |
| Li₂Y     | 2            | 5                                        | 4                | 0.195            |
| Li₃Y     | 3            | 2                                        | 1                | 0.079            |
| Li₄Y     | 1            | 1                                        | 3                | 0.088            |
| Li₅Y     | 2            | 2                                        | 4                | 0.233            |
| Li₆Y     | 1            | 1                                        | 3                | 0.125            |
| Li₇Y     | 2            | 2                                        | 4                | 0.106            |
| Li₈Y     | 3            | 1                                        | 3                | 0.074            |

The three most stable isomers found for the Li₃Y cluster have a molecular geometry of an isosceles triangle. The ground state structure is located on the doublet PES. The experimental bond lengths reported for a pure cluster of three lithium atoms correspond to an isosceles triangle structure with two sides of 3.200 Å and the remaining side of 2.730 Å, while the theoretical bond lengths are 3.209 and 2.741 Å, respectively.\(^8\) The bond lengths obtained for the Li₂Y cluster are 0.083 Å and 0.112 Å greater than the experimental bond lengths and 0.074 and 0.101 Å greater than the theoretical bond lengths reported for the Li, cluster. The following higher energy isomers were found on the potential energy surface at a multiplicity of 4 and 6 with relative energies of 0.079 and 1.264 eV, respectively. The minima structures found for the Li₄Y clusters are depicted in the first row of Figure 3. The ground state isomer is found with a spin multiplicity of three. The geometry of the system corresponds to a tetrahedron. The next lowest energy isomer of Li₄Y is characterized by quintet multiplicity conserving its tetrahedral geometry with the energy of 0.301 eV greater than the ground state. Next, the singlet state isomer is structured like a rhombus, differing from its lower energy counterparts. It has a relative energy of 0.349 eV. Previous theoretical works determined that the Li₄ cluster has a rhombic molecular geometry.\(^4\)\(^9\)\(^8\)\(^5\)\(^8\) This means that the yttrium atom heavily influences the geometry adopted by the metal cluster, such that the two lower energy structures are arranged like a tetrahedron. The results for the Li₄Y cluster showed that the most stable isomer is found on the doublet PES with a trigonal pyramidal geometry with bond lengths of 2.776 (1–4), 3.179 (4–5), 3.174 (1–5), 2.957 (1–2), 2.956 (1–3), 2.956 (1–3), 2.957 (4–3), 3.234 (5–2), 3.234 (5–2), 3.233 (5–3), and 2.958 (4–2) Å. These bond lengths can be seen along the calculated ones for the Li₅ cluster in Table 1.\(^8\)\(^8\)\(^2\)\(^3\) The 1–4, 4–5, 1–5, 1–2, 1–3, 2–5, and 3–5 bonds are longer for the yttrium-doped molecule, whereas the 3–4 and 2–4 bonds become shorter. The second least calculated energy isomer is found with a spin multiplicity of four with the energy of 0.279 eV greater than the ground state isomer (Table 2), while the highest energy isomer is located on the sextuplet potential energy surface with a relative energy of 0.517 eV (Table S2). Both isomers also shared the trigonal bipyramid structure of the ground state.

Once again, for the Li₅Y cluster there are geometry variations between multiplicity states. The singlet multiplicity structure is a rhomboidal bipyramid while the clusters of spin multiplicity of three and five have a triangular bipyramidal structure with an adjacent lithium atom, completing a third...
triangular pyramid (Figure 4). Alexandrova and co-workers (2005)\textsuperscript{84} found a minimum of Li\textsubscript{6} with molecular geometry of rhomboidal bipyramid geometry using genetic algorithms and using CCSD (T)/6-311+G\textsuperscript{*} to refine the molecular structure, similarly Brito and collaborators (2014)\textsuperscript{80} found a minimum for a Li\textsubscript{6} cluster at a DFT/SVWN level with the same molecular geometry. The relative energies for the clusters with spin multiplicities of three and five were 0.196 and 0.454 eV, respectively (Table 2 and Table S2).

The most stable isomers found for the Li\textsubscript{6}Y clusters are represented in the second row of Figure 4. The lowest energy isomer is found on the doublet potential energy surface with bond lengths of 3.002 (1\textendash{}2), 3.216 (6\textendash{}3), and 3.286 (6\textendash{}5) Å. These bond lengths are 0.024 (1\textendash{}2), 0.345 (6\textendash{}3), and 0.588 (6\textendash{}5) Å greater than the theoretical lengths reported for Li\textsubscript{7}.\textsuperscript{80} The molecular geometry of this system corresponds to a pentagonal bipyramid, this geometry has been previously reported for a pure Li\textsubscript{7} cluster.\textsuperscript{49,80,84} Shao and collaborators in 2012\textsuperscript{85} reported a lithium cluster of six atoms doped with a copper atom in which the resulting isomers corresponded to a pentagonal bipyramid geometry. Unlike the structure discussed in the present work, the doping atom is part of one of the vertices of the pentagon in the bipyramidal system. The next highest energy isomer is found with a spin multiplicity of four and with 0.233 eV greater than the ground state structure and the highest energy isomer is found with a spin multiplicity of six with a relative energy of 0.814 eV (Table S2).

The isomers found for the Li\textsubscript{7}Y clusters are depicted in the first row of Figure 5. The structures of the three isomers explored are very similar; they have a molecular geometry of a...
pentagonal bipyramid with an adjacent lithium atom. The ground state is found with five spin multiplicity and the following isomers are found with a spin multiplicity of one with a relative energy of 0.125 eV and the last for a spin multiplicity of three with a relative energy of 0.431 eV.

The results for the Li$_n$Y clusters are shown in the last row of Figure 5. Molecular structures have an icosahedral tendency. There are reports for yttrium-doped alkaline metal clusters of general formula M$_n$Y (M = Na, K, Rb, and Cs) where the same trend is observed. The isomers have a similar molecular structure, the state of minimal energy is found on the doublet potential energy surface. The second most stable isomer is found with a spin multiplicity of four with a relative energy of 0.106 eV and the isomer with the least energetic stability is found with a spin multiplicity of six with a relative energy of 0.720 eV.

In general, several metal clusters that have been studied present a semi-icosahedral structure (Li$_n$Y, Li$_2$Y, and Li$_3$Y). Quantum confinement in clusters can conduct to the grouping of electronic states into shells, and electronic orbitals disperse over multiple atoms, producing geometric effects. Another important aspect to consider is that in the geometrical optimizations carried out on the metal clusters of this work, it is observed that the atom of yttrium tends not to surround itself with lithium atoms; it occupies the position of the vertices of the structures. This leads to infer that the Li–Li interactions are favored over Li–Y. It was found that the energy needed to break the Li–Li bond is 0.86 eV, while to break the Li–Y bond is 0.57 eV. In this sense, less energy is needed to dissociate the Li–Y bond compared to the Li–Li bond. On the other hand, the sum of the atomic radius of Li–Li is 3.04 Å and of Li and yttrium is 3.92 Å, so it is corroborated again that the Li–Li bond is mostly favored. Meanwhile, in Table 3, the calculated harmonic vibrational frequencies are shown for each of the yttrium-doped lithium clusters. All the resulting values are positive, indicative of minimum energy states. Vibration modes were calculated using the zero-order regular approach. For the yttrium atom, it is important to include these relativistic effects since ZORA considers phenomena such as spin–orbit coupling. The vibrational frequency has been experimentally reported for the lithium dimer at 351.4 cm$^{-1}$. Computational calculations predict it at 341 cm$^{-1}$ with the B3LYP hybrid functional and 329.8 cm$^{-1}$ with the PW91 functional. In contrast, the present study found a shift to a band of 242 cm$^{-1}$ for the LiY system. The vibration modes for the Li$_n$ cluster have been calculated at B3LYP/6-311+G* and at CCSD (T)/6-311+G*, obtaining values of 348 and 329 cm$^{-1}$, respectively. In turn, a characteristic band of 362.2 cm$^{-1}$ was found for the Li$_4$Y cluster, as shown in Table 3. The Li$_6$ system presented bands at 352 and 326 cm$^{-1}$, calculated under the B3LYP/6-311+G* and at CCSD (T)/6-311+G* methods. These results are similar to the band found for the Li$_2$Y cluster at 326 cm$^{-1}$.

### 2.2. Energy Properties

With the purpose of analyzing the energetic stability of Li$_n$Y, $n = 1–8$ clusters, the atomization energy (AE) was calculated. This represents the energy needed to break-up the cluster into its atomic components

\[
AE = nE(Li) + E(Y) - E(Li_nY)
\]

here, $n E(Li)$, $E(Y)$, and $E(Li_nY)$ are the total energies of the lithium and yttrium atoms and of the Li$_n$Y cluster, respectively. The energy gained by the addition of a lithium atom to the preceding cluster of formula Li$_{n-1}$Y was calculated as

\[
\Delta E_{gain} = E(Li_{n-1}Y) + E(Li) - E(Li_nY)
\]

Table 4 shows calculated values of $\Delta E_{gain}$ and AE. Note that large atomization energy values along with low $\Delta E_{gain}$ values can be associated with molecular stability. These criteria single out the Li$_n$Y and Li$_2$Y systems—which tends towards an icosahedral structure—as stable clusters.

### 2.3. Exchange Splitting

The magnetic robustness of the clusters was analyzed by calculating the relative energy between the calculated ground state and the next low-lying isomer. Li$_4$Y presents the largest relative energy among the series at 0.301 eV.
eV, as shown in Figure 6. In this sense, the Li\textsubscript{7}Y system presented large energetic stability to the change of spin multiplicity. This makes it a system of interest for further studies. For example, Khanna’s group in Virginia Commonwealth University (VCU) has worked on the research of magnetic superatoms’ assemblies could be ideal for molecular electronic devices.\textsuperscript{9}

It is known that the HOMO–LUMO gap is a useful criterion to determine the stability of small clusters. Table 4 presents that the system that has the highest HOMO–LUMO gap with a value of 0.810 eV corresponds to the structure of Li\textsubscript{7}Y. This system’s spin electromers share a similar molecular geometry with a magnetic moment of 1 \( \mu_\text{B} \) for the lowest energy isomer. In the case of systems with a greater number of atoms, the HOMO–LUMO energy gap was 0.715, 0.446, 0.474, and 0.451 eV for Li\textsubscript{5}Y, Li\textsubscript{6}Y, Li\textsubscript{7}Y, and Li\textsubscript{8}Y, respectively. There are theoretical studies of pure lithium clusters from five to twenty atoms, where the reported values for the HOMO–LUMO gap are 0.81–1.36 eV for the Li\textsubscript{4}Y system and 0.23–0.50 eV for Li\textsubscript{n}\textsuperscript{88}

2.3. Magnetic Robustness and Exchange Splitting. An important parameter indicates the increase in the magnetic moment if the cluster is to obtain high values of exchange splitting from the external levels. Therefore, in Li\textsubscript{7}Y structures, the exchange splitting of the one-dimensional (1D) orbitals is calculated, as the difference of the energies of the orbitals with the highest occupied energy \( \alpha \) and \( \beta \). Figure 7 depicts the variation of the exchange splitting with respect to the size of the Li\textsubscript{7}Y cluster and Figure 8 shows the variation of exchange splitting and magnetic moment versus the size of the Li\textsubscript{7}Y cluster. As can be seen, the Li\textsubscript{7}Y system has the highest exchange splitting with a value of 0.3571 eV and a magnetic moment of 4 \( \mu_\text{B} \). Clearly, there is a correlation between the magnetic moment and the exchange splitting, the higher values of each parameter are corresponding, the higher the magnetic moment the higher the exchange splitting.

In the literature there are reports on the effect of transition metal doping on alkaline clusters, Guo and co-workers, 2014,\textsuperscript{89} found an exchange splitting of 0.5 eV in a Na\textsubscript{8}Y system. González-Ramírez and co-workers, 2013,\textsuperscript{67} found maximum exchange splitting values compared to exchange splitting values of the yttrium atom in yttrium-doped alkaline potassium and rubidium metal clusters with an icosahedral structure. Values calculated for the Na\textsubscript{8}Y system from density functional theory at a PW91/ZORA/TZP level report a magnetic moment value of 1 \( \mu_\text{B} \).\textsuperscript{67} On the other hand, for example, a cluster with another transition metal, Na\textsubscript{8}Ti, was found to have a magnetic momentum value of 3 \( \mu_\text{B} \)\textsuperscript{90} and in other systems such as the same number of atoms as Li\textsubscript{7}Y, values of 3 \( \mu_\text{B} \) were obtained.\textsuperscript{2} The Li\textsubscript{7}Y cluster is reported as the system with the highest magnetic yield has a magnetic moment 4 times greater than an yttrium atom.

2.4. Molecular Orbital Description. The electronic energy levels and the angular momentum of the superatomic molecular orbitals were analyzed. Starting with the Li\textsubscript{7}Y cluster that has four valence electrons, two of these in a S super quantum state and the remaining in a P state and the other in a D\textsubscript{s} state, such that the superorbital configuration is 1S\textsuperscript{2}1P\textsuperscript{4}1D\textsubscript{g}.\textsuperscript{1} The next cluster is Li\textsubscript{8}Y with a superorbital configuration of 1S\textsuperscript{2}1P\textsuperscript{4}1P\textsuperscript{3}1P\textsuperscript{1} it is important to highlight that it is unique that the D super quantum state is less energetic that the P super quantum state. The Li\textsubscript{7}Y has a fill of six valence electrons, three of them of lithium and other three of yttrium, the superorbital configuration is 1S\textsuperscript{2}1P\textsuperscript{4}3P\textsuperscript{3}1P\textsuperscript{1}. It is important to note that it has the same number of valence electrons as the chalcogen group in the periodic table. The cluster has a value of 0.076 eV and a magnetic moment of 2 \( \mu_\text{B} \) (Figure 9). The Li\textsubscript{8}Y cluster possesses seven valence electrons, two of these fill the 1S\textsuperscript{2} and five the 1P\textsuperscript{3} superorbitals. This cluster presents an exchange splitting of 0.010 eV and a magnetic moment of 1 \( \mu_\text{B} \). Li\textsubscript{7}Y is the unique closed shell species with a 1S\textsuperscript{2}1P\textsuperscript{6} configuration with zero magnetic moment and without exchange splitting, i.e., 1P\textsubscript{d} Bareal and 1P\textsubscript{β} orbitals have the same

Figure 6. Variation of the relative energy (E\textsubscript{rel}) and the energy gain (\( \Delta E_{\text{gain}} \)) of yttrium-doped lithium clusters, Li\textsubscript{n}Y\textsubscript{n} = 2–8. The blue strip represents the cluster where the maximum value of relative energy is found.

Figure 7. Variation in exchange splitting with respect to the number of lithium atoms in Li\textsubscript{7}Y clusters, n = 1–8. The exchange splitting of the Y atom is given as ref 67.

Figure 8. Exchange splitting and variation of the magnetic moments of spin (\( \mu_\text{B} \)) of yttrium-doped lithium clusters, Li\textsubscript{n}Y\textsubscript{n} = 2–8. The blue strip represents the cluster where the maximum value of exchange splitting and magnetic moment is found.
energy. The Li6Y cluster with a superorbital configuration of 1S^21P^61D^1 presents a magnetic moment of 1 \( \mu_B \) with an exchange splitting of 0.269 eV. The next cluster under analysis is Li7Y (Figure 10) with a superorbital configuration of 1S^21P^31P^21D^2 \( \alpha \), in other words it has 10 valence electrons with a magnetic moment of 4 \( \mu_B \). The 1D states have a contribution of roughly 30% from the atomic orbital 4d-Y. These reports have previously been identified as the origin of the magnetism of similar clusters. The Li7Y cluster stands out with a magnetic moment of 4 \( \mu_B \), which is 4 times more than a single Y atom. This unusually high magnetic moment is the product of the presence of the most stable isomer on the quintuplet's potential energy surface and the delocalized superorbitals it presents.

3. CONCLUSIONS

First principle calculations including Born–Oppenheimer molecular dynamics were employed to predict several yttrium-doped lithium clusters based on established energetic and magnetic principles of stability. The stabilities of the clusters are governed by the electronic configurations. These clusters presented an orbital combination of the 4d-Y levels with the sp-Li states, which enhances the systems’ exchange splitting. This is determined for the position of the delocalized orbitals presented on the clusters. The Li7Y cluster stands out with a magnetic moment of 4 \( \mu_B \), which is 4 times more than a single Y atom. This unusually high magnetic moment is the product of the presence of the most stable isomer on the quintuplet’s potential energy surface and the delocalized superorbitals it presents.

4. COMPUTATIONAL DETAILS

Born–Oppenheimer molecular dynamics calculations were carried out using ADFT as implemented in the deMon2k package. For the exchange and correlation functional, the PW86 functional was employed. The exchange–correlation potential was numerically integrated on a fixed fine grid. A variational fitting procedure was used to estimate the Coulomb energy. The DZVP basis set was employed for the lithium species while the yttrium atom was described using a relativistic model core potential. The GEN-A2* auxiliary function set was utilized for all calculations. Geometry optimizations were effected by the ORCA software using the exchange–correlation functional proposed by Becke and Perdew (BP86). This functional helps to obtain accuracy in the geometry of metallic and organometallic systems. The def2-TZVP basis set was used to describe all electrons in the system. The ZORA approximation was employed to include the scalar relativistic effects. The electronic and magnetic properties for the final structures were calculated under the same parameters.

The figures concerning the systems under study were obtained with the molecular visualizer Chemcraft.
coordinates (Å) of the Li6Y, n = 1–8 clusters are given in the Supporting Information.

**ASSOCIATED CONTENT**

* Supporting Information
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J.P.M.-S., K.P.-U., R.F.-M., and Z.G.-S. contributed and helped in writing this manuscript. J.P.M.-S., R.F.-M., and Z.G.-S. performed and analyzed the deMon2k and ORCA calculations. All authors approved of the final manuscript.

**Supporting Information**

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