

Theoretical and experimental studies on formation of diethylzinc-triphenylphosphine complex

Venkatesh Sadhana, Dhrujyoti Das, Chinduluri Sravania, Akella Sivaramakrishna, Kari Vijayakrishna & Hadley S. Clayton

To cite this article: Venkatesh Sadhana, Dhrujyoti Das, Chinduluri Sravania, Akella Sivaramakrishna, Kari Vijayakrishna & Hadley S. Clayton (2016) Theoretical and experimental studies on formation of diethylzinc-triphenylphosphine complex, Phosphorus, Sulfur, and Silicon and the Related Elements, 191:1, 35-40, DOI: [10.1080/10426507.2015.1085037](https://doi.org/10.1080/10426507.2015.1085037)

To link to this article: <http://dx.doi.org/10.1080/10426507.2015.1085037>



Published online: 15 Jan 2016.



Submit your article to this journal [↗](#)



Article views: 1



View related articles [↗](#)



View Crossmark data [↗](#)

Theoretical and experimental studies on formation of diethylzinc-triphenylphosphine complex

Venkatesh Sadhana^a, Dhruvdyoti Das^a, Chinduluri Sravania^a, Akella Sivaramakrishna^a, Kari Vijayakrishna^a, and Hadley S. Clayton^b

^aChemistry Division, School of Advanced Sciences, VIT University, Vellore 632 014, Tamil Nadu, India; ^bDepartment of Chemistry, UNISA, Pretoria, South Africa

ABSTRACT

This work is mainly focused on understanding the complex-forming behavior of diethylzinc with neutral phosphine ligands such as triphenylphosphine (PPh₃) to yield [Zn(PPh₃)₂Et₂]. The complex formation in solution is observed in the presence of a large excess of diethylzinc, but leaving an insoluble solid on aging. The product formed in solution was analyzed by spectroscopic data. ³¹P-NMR was also used as a tool to observe this behavior, i.e., the disappearance of the chemical shift of PPh₃ (δ -5.45) requires 14-fold excess of ZnEt₂ in solution. The alkyl chains reduce the Lewis acidity on Zn and thereby the formation of phosphine adducts is restricted. Results obtained from orbital analyses calculations reveal that the LUMO appears to be asymmetrically distributed, and localized on one of the PPh₃ ligands. The length of alkyl chains also influence the stability of [Zn(PPh₃)₂R₂] and the longer chains on Zn impart less stability.

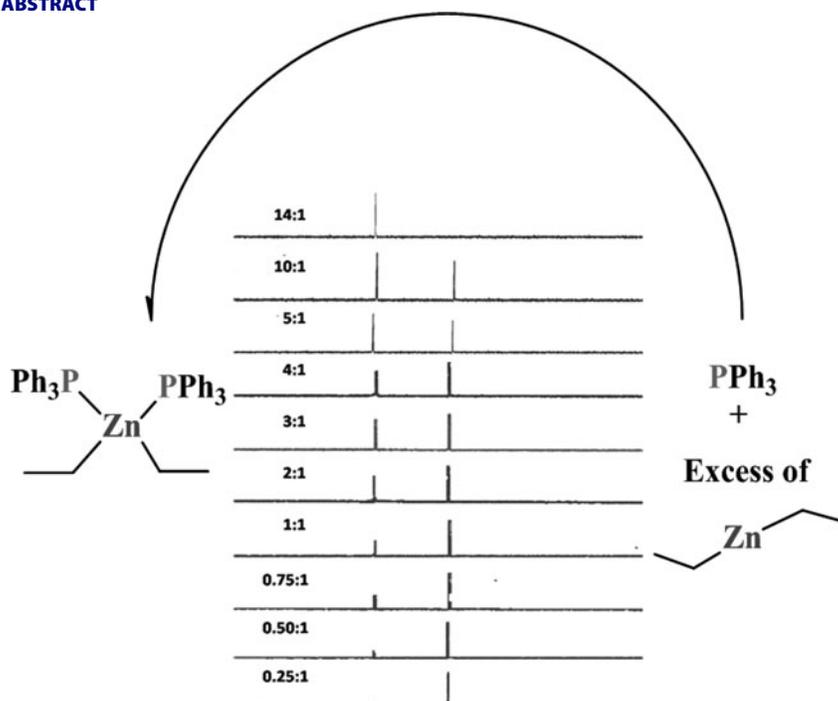
ARTICLE HISTORY

Received 3 March 2015
Accepted 5 August 2015

KEYWORDS

Organozinc complexes;
coordination behavior;
triphenylphosphine; DFT
calculation

GRAPHICAL ABSTRACT



Introduction

Metal-dialkyl species are an interesting class of compounds and known as key intermediates in many catalytic reactions including alkane functionalization reactions through the activation of carbon hydrogen bonds.¹ In general, the reactivity of dialkyl-metal complexes depends on the nature of

ligand, metal, substituents on the alkyl chains.^{2,3} Metal-dialkyls [M(CH₂R)₂] decompose thermally by intermolecular attack on a C-H bond of an ancillary ligand *via* several modes such as α-, β-, or γ-hydrogen elimination, and also reductive elimination.⁴ For example, the metal dialkyls are ZnR₂, PtL₂R₂, and MoO₂L₂R₂, which have been studied in detail, have been

shown to undergo these types of reactions.⁵ Among them, the chemistry of organozinc is very well established⁶ and it is well known that zinc can form a variety of compounds with 6–8 coordination numbers, relatively little has been reported on the coordination behavior of diethylzinc. The Zn-alkyls, especially diethylzinc are important reagents for chemists to perform asymmetric organic transformations including cyclopropanation of alkenes with CH_2I_2 ,^{7–9} asymmetric additions to aldehydes and ketones^{10,11} and other addition reactions.¹² It has been found that organozinc compounds are capable of forming stable coordination complexes having well-defined stoichiometry with a variety of oxygen-, nitrogen-, phosphorus-, and arsenic-containing ligands.¹³ The present work reports an unexpected and unusual reactivity of ZnR_2 complex with phosphine ligands.

Results and discussion

Initially, the complex **1** was prepared by reacting anhydrous zinc chloride with PPh_3 at room temperature in CH_2Cl_2 .¹⁴ Upon addition of **1** to freshly prepared *n*-BuMgBr or *n*-octylMgBr at 0°C in dry ether, $^{31}\text{P}\{^1\text{H}\}$ -NMR chemical shift of the crude product mixture showed the free PPh_3 (a signal at δ -5.45) due to the dissociation of PPh_3 and subsequent formation of dialkylzinc (**3**) (Scheme 1). Also, the presence of **3** was confirmed by ^1H -NMR spectrum. This dissociation phenomenon can be accounted that the Zn center becomes electrophilic when it is bound to the electronegative Cl group. As a consequence Zn then prefers to accept the electron pair from PPh_3 and subsequently forms $[\text{Zn}(\text{PPh}_3)_2\text{Cl}_2]$. It is predicted that transmetalation of **1** with RMgX may lead to formation of the intermediates either **2a** or **2b** or both, where two electron donating alkyl groups donate electrons sufficiently to zinc to make electron rich leading to the formation of **3** by expelling PPh_3 .

Addition of PPh_3 to ZnEt_2 in solution: An exploratory analysis

This result prompted us to study further the coordination behavior of ZnR_2 , which is forced in the presence of a large excess of ligands. Different ratios of diethylzinc and triphenylphosphine were mixed in CDCl_3 and the ^{31}P NMR shifts were measured, which showed two distinct signals in $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra of the mixture and one signal is assigned to uncoordinated PPh_3

at δ -5.45. There is an additional signal which appears at δ 29.6 due to the formation of $[\text{Zn}(\text{PPh}_3)_2\text{Et}_2]$. The changes in the signal intensities at different ratios of PPh_3 and ZnEt_2 are given in Figure 1 (A and B). Initially the molar concentration of PPh_3 was kept constant and a molar concentration of ZnEt_2 was increased and then *vice versa*. The peak intensity of the product is found to increase with the increase of ZnEt_2 concentration and then decrease as the PPh_3 concentration is increased.

From $^{31}\text{P}\{^1\text{H}\}$ -NMR data, it was observed that the signal at δ 29.6 increases gradually with an increase in the concentration of ZnEt_2 . It is significant to note that one mole of PPh_3 requires 14 moles of ZnEt_2 to cause the free PPh_3 signal at complex δ -5.45 to disappear as shown in Figure 1.

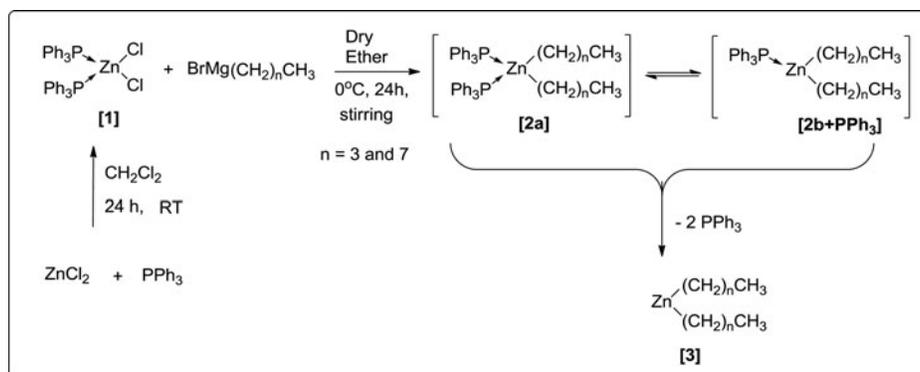
As expected, the ^1H -NMR spectrum of **2a** or **2b** was not much use in the structural analysis due to the presence of a large excess of diethylzinc as shown in Figure 2. In this context, the ^{31}P -NMR was a key tool for the investigations. On addition of 7 and 14 moles of PPh_3 to the 1:14 molar ratio of the mixture, a new peak was observed at δ -5.43 in ^{31}P spectrum, which indicates the presence of free ligand. When the molar concentration was increased up to 14 moles, the peak intensity of the free ligand also increases.

It is found that when the mixture containing the product, $[\text{Zn}(\text{PPh}_3)_2\text{Et}_2]$ and an excess of ZnEt_2 was subjected to a vacuum for long period, the product completely decomposed and this was evident from the ^1H -NMR spectrum of the decomposed crude (i.e., phenyl protons). On aging, this mixture turns to a turbid solution slowly and thus leading to a colorless product, which is insoluble in common solvents. It is predicted that this unknown product is a combination of zinc phosphide species.

UV/Vis absorption studies

The solutions of diethylzinc (0.01 g, 0.0823 mmol) in 100 mL of chloroform and triphenylphosphine (0.02 g, 0.0763 mmol) in 100 mL of chloroform were prepared. These solutions were used recording the absorption spectra. Solutions of diethylzinc (0.130 g, 1.07 mmol) and triphenylphosphine (0.02 g, 0.0763 mmol) were mixed in 100 mL of chloroform. This solution was used for recording the absorption spectrum.

The absorption spectrum of complex $[\text{Zn}(\text{PPh}_3)_2\text{Et}_2]$ shows two broad bands with maximum at 263 and 223 nm. The λ_{max} of the metal complex is significantly different from the free ligand



Scheme 1. Proposed mechanism for the formation of dialkylzinc.

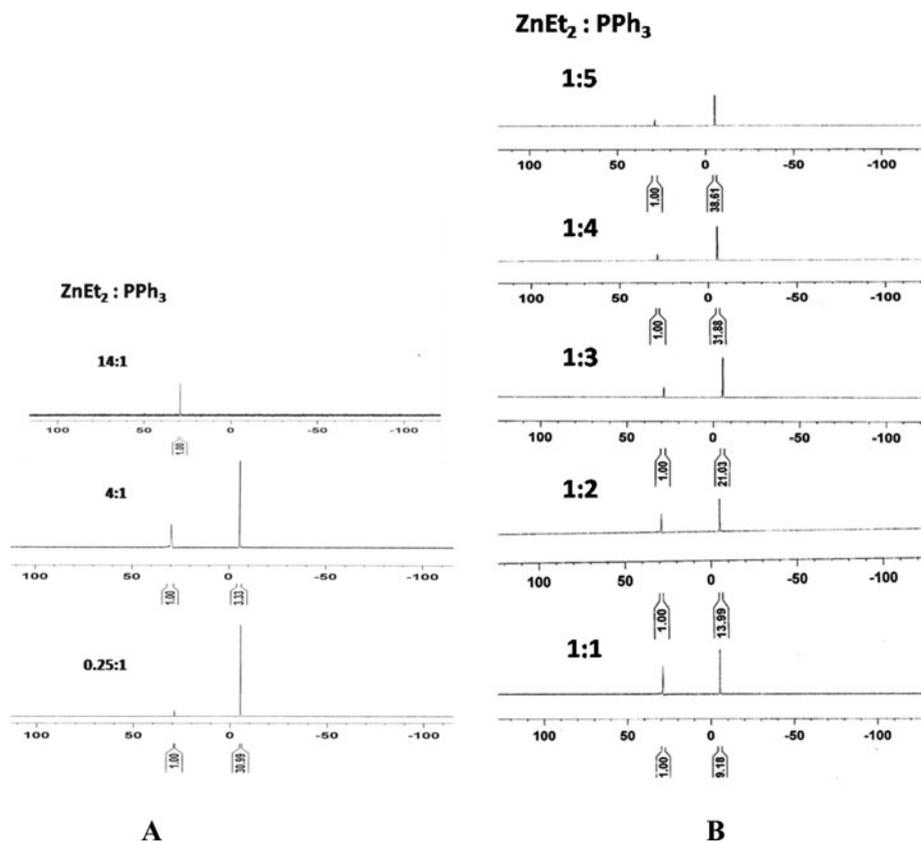


Figure 1. $^{31}\text{P}\{^1\text{H}\}$ -NMR spectral evidence for the formation of $[\text{Zn}(\text{PPh}_3)_2\text{Et}_2]$ in CDCl_3 solution at room temperature; **1A**: at constant PPh_3 concentration, **1B**: at constant ZnEt_2 concentration.

which indicates that the formation of complex. The free ligand PPh_3 show two broad bands with maximum at 261 and 215 nm, and the ZnEt_2 does not show any significant band under the concentrations taken as shown in Figure 3.

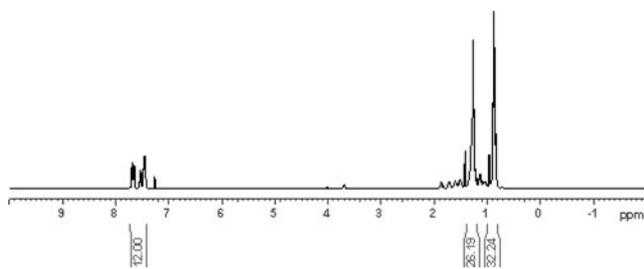


Figure 2. ^1H -NMR spectrum of the reaction mixture containing unreacted diethylzinc.

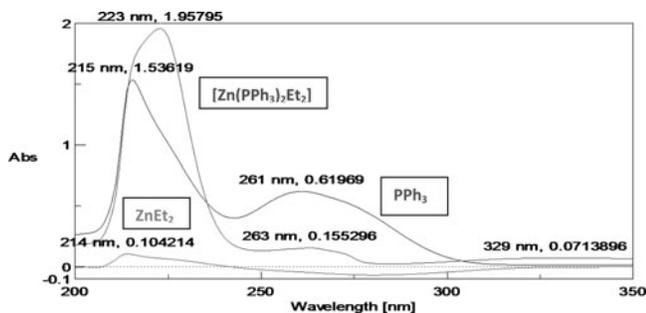


Figure 3. Comparison of absorption spectrum of the product, $[\text{Zn}(\text{PPh}_3)_2\text{Et}_2]$ formed with the precursors.

Effect of temperature on the formation of $[\text{Zn}(\text{PPh}_3)_2\text{Et}_2]$

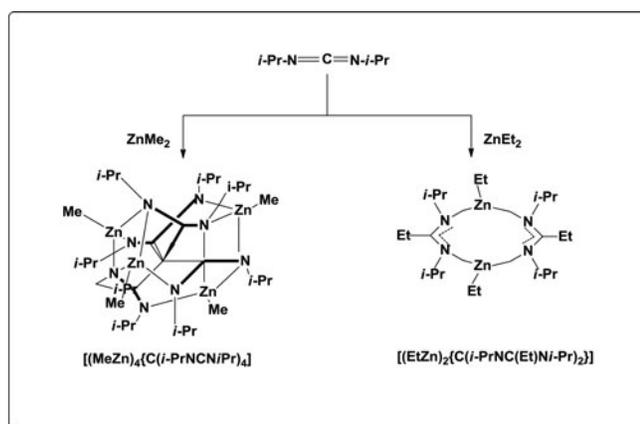
The mixtures of ZnEt_2 and PPh_3 with molar ratios of 1:1, 5:1, 10:1, and 14:1 in CDCl_3 were heated at 50°C for different time intervals (3h, 24 h and 72 h). No significant changes were observed in the peak intensities even after prolonged heating at 50°C and this suggests that the product(s) formation does not depend on the temperature.

Influence of other ligands

Addition of other ligands like 1,10-phenanthroline (1,10-Phen) to $[\text{Zn}(\text{PPh}_3)_2\text{Et}_2]$ formed by a 1:2 molar ratio of ZnEt_2 and PPh_3 increased the complexation from 6.6% to 13.4%. However, there is no significant change on addition of dppe to the complex. This experiment was performed to check whether the addition of other ligands may retard the complex formation completely due to competitive reactions.

Effect of dilution

The dilutions were performed with chloroform solutions of 5.0, 10.0, 15.0, and 20.0 mL containing mixtures of PPh_3 and ZnEt_2 where the ratio was maintained throughout as 1:14. No peak other than the one at 29 ppm was observed under these different dilution conditions. The dilution factor did not influence the dissociation of complex as evidenced by ^{31}P -NMR data. Attempts to isolate the product $[\text{Zn}(\text{PPh}_3)_2\text{Et}_2]$ from the mixture completely failed.



Scheme 2. Complexes resulting from insertion reactions of $C(Ni-Pr)_2$ with $ZnMe_2$ and $ZnEt_2$ reported by Schulz et al.¹⁵

Theoretical calculations

Schulz and coworkers¹⁵ have recently reported on a cluster formation from the insertion reactions of carbodiimide, $C(NPr^i)_2$, with $ZnMe_2$ and $ZnEt_2$. Surprisingly, different cluster morphologies were obtained depending on the alkyl chain length (see Scheme 2). It is assumed that the chelate structure of tetra-coordinated zinc for the 1:1 complexes with bidentate ligands is possible along with the planar complexes by a monodentate ligand. By increasing the electronegative character of the organic group R on zinc, the polar character of the zinc-carbon bond will be enhanced. The negative charge is being pulled away from the zinc atom causing the electron affinity of the vacant orbitals of zinc and, consequently, the tendency to form donor-acceptor complexes to be increased.¹² The influence of the organic substituent (R) on the acceptor properties of the zinc atom has been investigated by suitable variation of R . It is the fact that phenyl groups are more electron attracting than butyl groups and subsequently diphenylzinc forms coordination complexes more readily than does dibutylzinc. This phenomenon is further supported by DFT calculations.

The intriguing behavior exhibited by the diethylzinc complexes in solution with PPh_3 led us to investigate the nature of these species computationally in order to obtain evidence, which supports, or refutes, cluster formation. While calculations on the proposed clusters complexes were not computationally feasible due to their size of fluxional behavior, we examined possible key intermediates involved in the clustering mechanism.

The electronic structures and properties of five Zn species were calculated using density functional theory (DFT). The DFT global chemical reactivity descriptors (chemical hardness (η), electronic chemical potential (μ), and electrophilicity (ω)) were calculated for the compounds and used to predict their relative stability and reactivity. In addition, the activation energy for PPh_3 addition to diethylzinc, a key step in the formation of the cluster, has been determined. The possible formation mechanism of zinc clusters is discussed on the basis of these theoretical results.

The energies of HOMO and LUMO are popular quantum mechanical descriptors as these orbitals have been shown to play a major role in governing many chemical reactions. The HOMO and LUMO orbital energies are related to gas phase ionization

energies (I) and electron affinities (A) according to the Koopmans' theorem as given in Eqs. 1 and 2.^{16,17} Diagrams and energies of the calculated HOMO and LUMO orbitals are given in Table 1. The calculated reactivity indices are given in Table 2.

$$A = -\varepsilon_{LUMO} \quad (1)$$

$$I = -\varepsilon_{HOMO} \quad (2)$$

Chemical hardness (η) is associated with the stability and reactivity of a chemical system. In a molecule, it measures the resistance to change in the electron distribution or charge transfer. On the basis of frontier molecular orbitals, chemical hardness corresponds to the HOMO-LUMO energy gap and is approximated using Eq. 3. The larger the HOMO-LUMO energy gap, the more stable/less reactive the molecule.

$$\eta = (\varepsilon_{LUMO} - \varepsilon_{HOMO})/2. \quad (3)$$

The electronic chemical potential (μ) is defined as the negative of electronegativity of a molecule and determined using Eq. 4. Physically, μ describes the escaping tendency of electrons from an equilibrium system. The greater the electronic chemical potential the less stable or more reactive the molecule.¹⁸

$$\mu = (\varepsilon_{HOMO} + \varepsilon_{LUMO})/2. \quad (4)$$

The electrophilicity index (ω), introduced by Parr, is calculated using the electronic chemical potential and chemical hardness as shown in Eq. 5. ω measures the capacity of a species to accept electrons. Accordingly, it is a measure of the stabilization in energy after a system accepts additional electronic charge from the environment.

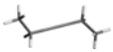
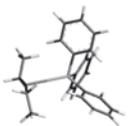
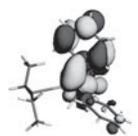
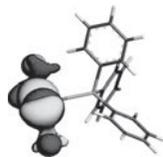
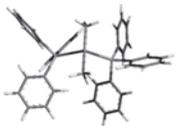
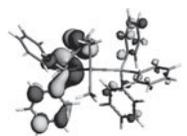
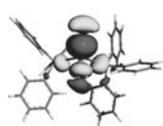
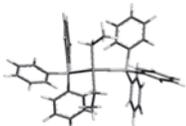
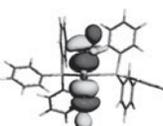
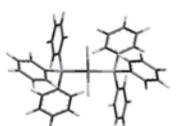
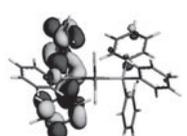
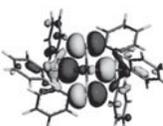
$$\omega = \mu^2/2\eta. \quad (5)$$

All calculated structures indicate the HOMO orbital contain significant contribution from the Zn center. This strongly suggests that the metal center is directly involved in the reactivity of cluster formation. In addition, in the $ZnEt_2$ complex, the LUMO is nearly completely positioned on the Zn metal, indicating the metal center is susceptible to nucleophilic attack. There is a noteworthy difference in the HOMO energies of $ZnMe_2(PPh_3)_2$ and $ZnEt_2(PPh_3)_2$ which influences the reactivity indices of the compounds and suggests that these might not react to form clusters in the same way. The reactivity indices indicate that relative to $ZnEt_2$, its phosphine adduct $ZnEt_2(PPh_3)$ is significantly more reactive.

Conclusion

The addition of large excess of diethylzinc to PPh_3 yields the corresponding zinc complex in solution. It was not possible to isolate the product from solution and subsequently the product in solution was identified by UV-Vis, IR and ³¹P-NMR spectral data. The transformation requires 14 times excess of $ZnEt_2$ in solution for the disappearance of chemical shift of PPh_3 to form $[(PPh_3)_2ZnEt_2]$ complex. The longer alkyl

Table 1. Optimized structures and calculated frontier orbitals.

Optimized structure	LUMO orbital	HOMO orbital
 ZnEt ₂	 $E = -0.343\text{eV}$	 $E = -5.419\text{eV}$
 ZnEt ₂ (PPh ₃)	 $E = -1.850\text{eV}$	 $E = -4.957\text{eV}$
 ZnMe ₂ (PPh ₃) ₂	 $E = -1.783\text{ eV}$	 $E = -5.015\text{ eV}$
 ZnEt ₂ (PPh ₃) ₂	 $E = -1.788\text{eV}$	 $E = -4.588\text{eV}$
 ZnCl ₂ (PPh ₃) ₂	 $E = -2.027\text{eV}$	 $E = -5.521\text{eV}$

chains reduces the Lewis acidity on Zn and thereby the formation of phosphine adducts is restricted. Results obtained from orbital analyses calculations reveal that the LUMO appears to be asymmetrically distributed, and localized on one of the PPh₃ ligands.

Experimental

All the reactions were carried out under dry nitrogen using Schlenk techniques. Solvents were dried and purified by standard methods. Reagents like diethylzinc (in hexane) and triphenylphosphine were purchased from Sigma-Aldrich. Grignard reagents were prepared as described from the literature reports.¹⁹ NMR spectra were recorded on a Bruker Avance DMX-400 spectrometer and operating frequencies were 400.13 MHz (¹H), 100.61 MHz (¹³C), and 161.92 MHz (³¹P). All the spectra were recorded in CDCl₃ solvent. Spectra are reported in δ (ppm) relative to TMS, as determined from standard residual solvent-proton (or carbon) signals for ¹H and ¹³C. All ³¹P chemical shifts were ¹H decoupled and referenced to an 85%

phosphoric acid external peak at 0 ppm. Electronic spectra were recorded by JASCO-V-550 UV/Vis Spectrophotometer. Varian Inc, USA (410 Prostar Binary LC with 500 MS IT PDA Detectors) Direct Infusion Mass with ESI & APCI Negative & Positive mode ionization Mass spectrometer was used to record the spectrum.

The precursor complex [Zn(PPh₃)₂Cl₂] (1) was prepared by reacting ZnCl₂ (2.014 g, 14.78 mmol) with PPh₃ (8.14 g, 31.04 mmol) in 20 mL of CH₂Cl₂ for 2 h as per the literature.¹⁴ The obtained solid product (9.2 g, 94%) was filtered and washed with 2 × 5 mL of petroleum ether and dried under high vacuum pump for 2 h.

Procedure for the preparation of [Zn(PPh₃)₂Et₂] (2): Diethylzinc [3.28 g (26.7 mmol)] was added to a clean 25 mL RB flask, and evaporated the hexane at RT by rotavap. To this, PPh₃ [0.5 g (1.91 mmol)] was added followed by CHCl₃ (10.0 mL). The reaction was monitored by ³¹P-NMR to make sure that there is no free triphenylphosphine left. As the product was not possible to isolate from the mixture in the presence of excess diethylzinc even under high vacuum.

Table 2. Global chemical reactivity indices for ZnR₂ compounds.

	ZnEt ₂	ZnEt ₂ (PPh ₃)	ZnMe ₂ (PPh ₃) ₂	ZnEt ₂ (PPh ₃) ₂	ZnCl ₂ (PPh ₃) ₂
LUMO (eV)	-0.343	-1.850	-1.783	-1.788	-2.027
HOMO (eV)	-5.419	-4.957	-5.015	-4.588	-5.521
η (eV)	2.538	1.554	1.616	1.400	1.747
μ (eV)	-2.881	-3.404	-3.399	-3.188	-3.774
ω (eV)	1.635	3.728	3.575	3.630	4.076

Computational analysis

All calculations were carried out using the DMol³ density functional theory (DFT) code as implemented in the Accelrys Material Studio 6.0 software package.²⁰ The nonlocal generalized gradient approximation (GGA) using the PW91 exchange-correlation functional was used for geometry optimizations in all cases.²¹ A double numeric, polarized split valence (DNP) basis set was used in this study with a DFT semicore pseudopotential to account for the core electrons of P. The size of the DNP basis set is comparable to Gaussian 6–31 G**, but the DNP is more accurate than the Gaussian basis set of the same size.²² Geometry optimizations were performed without any symmetry constraints. The convergence criteria for these optimizations consisted of the following threshold values: 1×10^{-5} Ha for energy; $0.002 \text{ Ha}\text{\AA}^{-1}$ for gradient and 0.005\AA for displacement convergence, while a self-consistent field density convergence threshold of 1×10^{-6} Ha was specified. All optimized geometries were subjected to a full frequency analysis at the same level of theory (GGA/PW91/DNP) to verify the nature of the stationary points. Optimized geometries were characterized by the absence of imaginary frequencies.

Funding

Dr. ASRK is highly grateful to Council of Scientific and Industrial Research (CSIR, New Delhi, India) (Ref. No. 01(2541)/11/EMR-II) for the financial support. Our sincere thanks are due to DST-VIT-FIST for NMR and SIF-VIT for GC-MS facilities. Mr. Venkatesh Sadhana is thankful to CSIR for the Junior Research Fellowship.

References

- Hager, E. B.; Sivaramakrishna, A.; Clayton, H.; Mogorosi, M. M.; Moss, J. R. *Coord. Chem. Rev.* **2008**, 252, 1668-1688.
- (a) Wilkinson, G.; Stone, F. G. A. (Eds.), *Comprehensive Organometallic Chemistry*, 5th ed.; Pergamon Press: Oxford, 1995; (b) Yamamoto, A. *J. Organomet. Chem.* **1995**, 500, 337-348; (c) Yamamoto, A. *J. Organomet. Chem.* **2002**, 653, 54-57; (d) Yamamoto, A. *J. Organomet. Chem.* **2004**, 689, 4499-4510; (e) Komiya, S.; Ozaki, S.; Endo, I.; Inoue, K.; Kasuga, N.; Ishikazi, Y. *J. Organomet. Chem.* **1992**, 433, 337-351; (f) Shapley, P. A.; Schwab, J. J.; Wilson, S. R. *J. Organomet. Chem.* **1994**, 32, 213-222; (g) Thoonen, S. H. L.; Lutz, M.; Spek, A. L.; Deelman, B. J.; van Koten, G. *Organometallics*. **2003**, 22, 1156-1159; (h) Soderberg, B. C. G. *Coord. Chem. Rev.* **2006**, 250, 2411-2490; (i) Cross, R. J. *The Chemistry of Metal-Carbon Bond*, 2nd ed.; Wiley: New York, 1985; (j) Green, M. L. H.; Nagy, P. L. *J. Organomet. Chem.* **1963**, 1, 58-69.
- (a) James, B. R. In: G. Wilkinson, F. G. A. Stone, E. W. Abel (Eds.), *Comprehensive Organometallic Chemistry*; 8th ed.; Pergamon: Oxford, **1982**, 285; (b) Takacs, J. M. In: E. W. Abel; F. G. A. Stone; G. Wilkinson (Eds.), *Comprehensive Organometallic Chemistry* 2, 12th ed.; Elsevier, **1995**, 785; (c) Crabtree, R. H.; Mingos, D. M. P. (Eds.), *Comprehensive Organometallic Chemistry* 3, Elsevier, **2007**, 10-11; (d) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed., John Wiley and Sons: New York, **1999**, 1194; (e) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, 250, 395; (f) Brookhart, M.; Green, M. L. H.; Wong, L. L. *Prog. Inorg. Chem.* **1988**, 36, 1; (g) Friedrich, H. B.; Moss, J. R. *Adv. Organomet. Chem.* **1991**, 33, 235; (h) Ferretti, O. A.; Casella, M. L. *Latin Am. Appl. Res.* **1995**, 25, 125.
- (a) Rothwell, I. P. *Polyhedron* **1985**, 4, 177-200; (b) Bulls, A. R.; Schaefer, W. P.; Serfas, M.; Bercaw, J. E. *Organometallics* **1987**, 6, 1219-1226; (c) Komiya, S.; Morimoto, Y.; Yamamoto, A.; Yamamoto, T. *Organometallics* **1982**, 1, 1528-1536; (d) Bruno, J. M.; Smith, G. M.; Marks, T. J.; Fairs, C. K.; Schultz, A. J.; Williams, J. M. *J. Am. Chem. Soc.* **1986**, 108, 40-56; (e) Chanberlain, L. R.; Rothwell, A. P.; Rothwell, I. P. *J. Am. Chem. Soc.* **1984**, 106, 1847-1848.
- Halpern, J. *Inorg. Chim. Acta.* **1985**, 100, 41-48;
- (a) Bollermann, T.; Gemel, C.; Fischer, R. A. *Coord. Chem. Rev.* **2012**, 256, 537-555; (b) Drewry, J. A.; Gunning, P. T. *Coord. Chem. Rev.* **2011**, 255, 459-472; (c) Kozłowski, H.; Janicka-Klos, A.; Brasun, J.; Gaggelli, E.; Valensin, D.; Valensin, G. *Coord. Chem. Rev.* **2009**, 253, 2665-2685; (d) Zhai, T.; Fang, X.; Zeng, H.; Xu, X.; Bando, Y.; Goldberg, D. *Pure Appl. Chem.* **2010**, 82, 2027-2053; (e) Van der Kerk, G. J. M. *Pure Appl. Chem.* **1972**, 30, 389-408; (f) D'Souza, F.; Ito, O. *Coord. Chem. Rev.* **2005**, 249, 1410-1422; (g) Carmona, E.; Galindo, A. *Angew. Chem. Int. Ed.* **2008**, 47, 6526-6536; (i) Grirrane, A.; Resa, I.; Rodriguez, A.; Carmona, E. *Coord. Chem. Rev.* **2008**, 252, 1532-1539.
- Smith, M. B.; March, J. *March's Advanced Organic Chemistry*, 5th ed., Wiley: New York, **2001**, Ch. 15 and references therein.
- Nishimura, J.; Kawabata, N.; Furukawa, J. *Tetrahedron*, **1969**, 25, 2647-2659.
- Bertinato, P.; Sorensen, E. J.; Meng, D.; Danishefsky, S. J. *J. Org. Chem.* **1996**, 61, 8000-8001.
- Jeon, S.-J.; Li, H.; Garcia, C.; LaRochelle, L. K.; Walsh, P. J. *J. Org. Chem.* **2005**, 70, 448-455.
- Jeon, S.-J.; Walsh, P. J. *J. Am. Chem. Soc.* **2003**, 125, 9544-9545.
- (a) Chen, Y. K.; Walsh, P. J. *J. Am. Chem. Soc.* **2004**, 126, 3702-3703; (b) Lurain, A. E.; Carroll, P. J.; Walsh, P. J. *J. Org. Chem.* **2005**, 70, 1262-1268.
- Vaughan, B. A.; Arsenault, E. M.; Chan, S. M.; Waterman, R. J. *Organomet. Chem.* **2012**, 696, 4327-4331.
- Chauhan, A. K. S.; Singh, N.; Srivastava, R. C. *Appl. Organomet. Chem.* **2003**, 17, 856-859.
- Schmidt, S.; Gondzik, S.; Schulz, S.; Bläser, D.; Boese, R. *Organometallics*. **2009**, 28, 4371-4376.
- Parr, P. G.; Pearson, R. G. *J. Am. Chem. Soc.* **1983**, 105, 7512-7516.
- Parr, R. G.; Szentpaly, L.; Liu, S. *J. Am. Chem. Soc.* **1999**, 121, 1922-1924.
- Chattaraj, P. K.; Maiti, B. *J. Am. Chem. Soc.* **2003**, 125, 2705-2710.
- McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.*, **1976**, 98, 6521-6528.
- (a) Delley, B. *J. Chem. Phys.* **2000**, 113, 7756; (b) Delley, B. *J. Chem. Phys.* **1990**, 92, 508.
- Perdew, J. P.; Wang, Y. *Phys. Rev.* **1992**, B45, 13244-13249.
- Benedek, N. A.; Snook, I. K.; Latham, K.; Yarovsky, I. *J. Chem. Phys.* **2005**, 122, 144102.